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Standards in Laser Diffraction

1. Introduction

The technology of laser diffraction for determining particle size distributions has undergone a vigorous development during the past two decades. At the beginning of the 1970's, efforts with the method, which was quite novel at the time, were intended for reproducing the results of established techniques, such as sedimentation or sieve analysis. The analytical methods were frequently oriented with respect to given distribution types, to which the values measured for the particle size distribution were adapted.

With the development of improved algorithms, which were referred solely to the physics of Fraunhofer diffraction and which reproduce arbitrary distribution forms in a parameter-free manner, Heuer and Leschonski [1] published the principles allowing for the establishment of laser diffraction as an independent method.

Since laser diffraction detects an agglomerate of particles as a single large particle, the agglomerate must be decomposed into individual particles before passage through the measuring zone. The development of efficient dispersing systems was therefore of decisive importance.

After the development of dry dispersion by Leschonski, Röthele, and Menzel [2], the limitation on application to particles in suspension was thereby removed.

Two decades after introduction on the market, laser diffraction provides for the first time a method which is capable of determining particle size distributions in the range from 0.1 µm to about 3000 µm without changing the measuring principle; the method is fast and independent of material and medium. The dynamic performance rate, u, introduced by Röthele and Kesten [3] demonstrates the superiority of this technology in comparison with classical methods. It explains why laser diffraction is in the process of becoming the dominant technique for determining particle size distributions.

2. Present situation

At present, several renowned manufacturers of particle measuring equipment offer laser diffraction instruments. A feature common to all is the use of the Fraunhofer diffraction theory as basis for the range of particle diameters x above 1 µm.

For $x \leq 1$ µm, this common feature is abolished: Parameter-free solutions exist within the scope of a generalized Fraunhofer diffraction theory [4] in parallel with Mie solutions which require the additional specification of optical constants for the material under investigation for the evaluation of its particle size distribution.

As a rule, the latter are unknown and must be determined empirically, since the constants for small particles in the practical application usually deviate from the tabulated macroscopic constants. A standardization which is independent of manufacturer is thus rendered difficult.

An additional step further is represented by the socalled full range analyzers, which determine particle size distributions from about 0.1 µm to values of about 1000 µm within a single measuring range by combination of laser diffraction with other measuring methods. The composition of such methods differs

widely from manufacturer to manufacturer. The recognizable development of laser diffraction equipment during the interim toward a certain standardization of the optical system, the data acquisition, and the algorithm for evaluation is thus a futile attempt.

To an increasing extent, manufacturers are limiting their assortment to instruments with a broader measuring range, a larger number of classes, and a wider data path in the associated computer system. As a rule, no information is available on the accuracy of the results of measurements or the resolution of the instrument.

The situation is similar in the case of dispersing systems, especially as far as concerns dry dispersion. Such systems are now available in addition to wet dispersion from several manufacturers. In the most favourable case, instruments with insufficient dispersive effectivity are designated as dry feeders.

The trend currently extends to automated laser diffraction systems, in which the manual operations are restricted to filling with sample. The latter operation is then assumed by a robot in the course of laboratory automation or, in the case of on-line applications, by a sample coupler [5].

Laser diffraction is thus becoming capable of being integrated into production processes. The possibility of comparing results for all manufacturers, as well as simple subsequent checking of the measuring accuracy are of paramount importance. For this purpose, standards are useful and renouncable in the long term at least.

3. Present standards

Laser diffraction yields the diameter of spheres equivalent with respect to diffraction as particle size, x. In the case of perfect spheres, this value corresponds to the geometrical

diameter. Ideally, reference materials for laser diffraction should be spherical; moreover, their surface should exhibit total absorption of light for avoiding reflection and refraction. The latter requirement can no longer be satisfied as the wavelength of the laser employed is approached.

For wet dispersing systems, in addition, a value for the particle density near to the density of the dispersion fluid is required, in order to avoid sedimentation in the suspension. In dry dispersing systems, comminution or electrostatic charging of the particles must be avoided. Attention must thereby be paid to the fact that dry dispersion permits much larger quantities (typically greater 10 g) than wet dispersion.

Certified materials with these properties are currently not available commercially.

3.1 Latex samples

A number of latex samples consisting of nearly transparent spheres with a very narrow size distribution are available, the following types for instances from the Community Bureau of Reference (BCR) [6]:

	x_{geom}
CRM 165	2.223 µm ± 0.013 µm
CRM 166	4.821 µm ± 0.019 µm
CRM 167	9.475 µm ± 0.018 µm

Table 1 : BCR Latices

These materials were originally developed for use with red blood cell counters for example. In addition latices supplied by instrument makers are available. Because of the transparency of the latex samples, they are only conditionally suited for laser diffraction instruments with wet dispersion.

From figure 1, it can be seen that the average particle sizes, x_{50}, are represented quite precisely by laser diffraction instruments (refer to [1]), but deviations are evident with the fine fraction resulting of fine particles sticking to surface of the coarse ones.

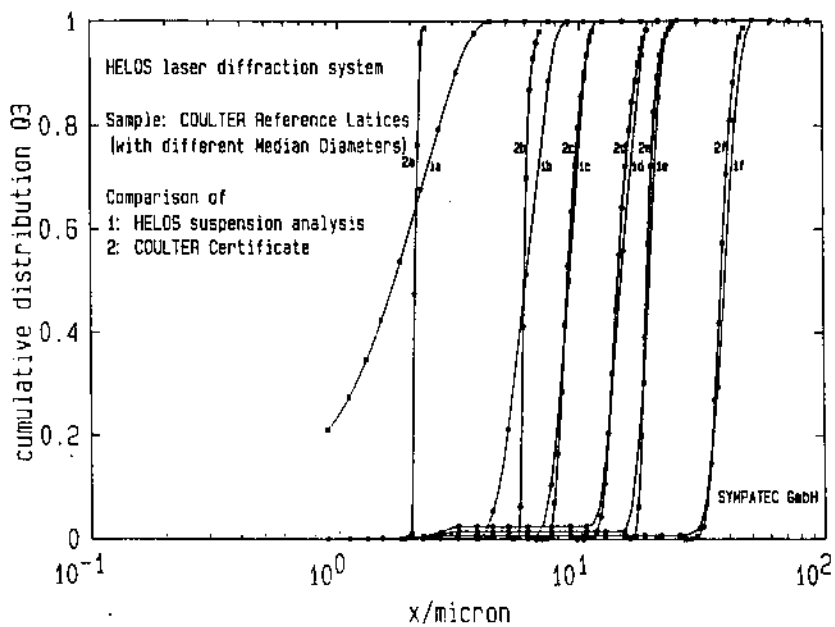

Figure 1: Results of measurements on latex samples

3.2 BCR quartz samples

An international standard for the determination of particle size distributions was created for the first time by BCR. For this purpose, large quantities of quartz sand were subjected to careful sample splitting and measured in various institutes by sedimentation or, for coarse particles, by sieve analysis. The following BCR standards are available:

Designation				Particle size/µm
CRM 066	: Stokes	diameter	:	0.35 - 3.5
CRM 067	: Stokes	diameter	:	2.4 - 32.0
CRM 068	: Volume	diameter	:	160 - 630
CRM 069	: Stokes	diameter	:	14 - 90
CRM 070	: Stokes	diameter	:	1.2 - 20
CRM 130	: Volume	diameter	:	50 - 220
CRM 131	: Volume	diameter	:	480 - 1800
CRM 132	: Volume	diameter	:	1400 - 5000

Table 2 : BCR quartz reference materials

The selection of the material was oriented especially with respect to the requirements of the measuring instruments established or investigated at that time. It was not possible to take the requirements of the still novel laser diffraction method into account.

On the basis of the materials, CRM 66, 67, 69, and 70, Allen and Davies [7] performed in 1990 a broadbased comparison among 24 measuring systems from various manufacturers. Nine laser diffraction instruments equipped exclusively with wet dispersion systems were thereby included for the first time. The results differed strongly among the individual instruments. The maximum deviations of the measured particle size, x, with respect to the BCR standard, x_S, is indicated in table 3:

Product	Particle size / µm	Var. manufacturers $(x - x_S) / x_S$ / %	HELOS $(x - x_S) / x_S$ / %
CRM 066	0.35 - 3.5	- 31 .. + 43	-
CRM 070	1.2 - 20	- 64 .. + 24	- 13 .. + 25
CRM 067	2.4 - 32	- 66 .. + 56	- 66 .. + 32
CRM 069	14 - 90	- 35 .. + 20	- 28 .. + 26

Table 3 : Deviations of the particle size, x, from the BCR standard, x_S, according to [7] and [8]

The deviation cannot be explained solely by the difference in equivalent diameter between sedimentation and laser diffraction; it also reflects the differences in optics, data acquisition, and algorithms. The authors' own measurements on the HELOS system have confirmed similar deviations. However, they indicate that the large standard deviations presented are probably due to sampling errors. From figure 2 , it is evident that the standard deviation of BCR 70 standard for eight different samples measured, can be considerably decreased by sample splitting.

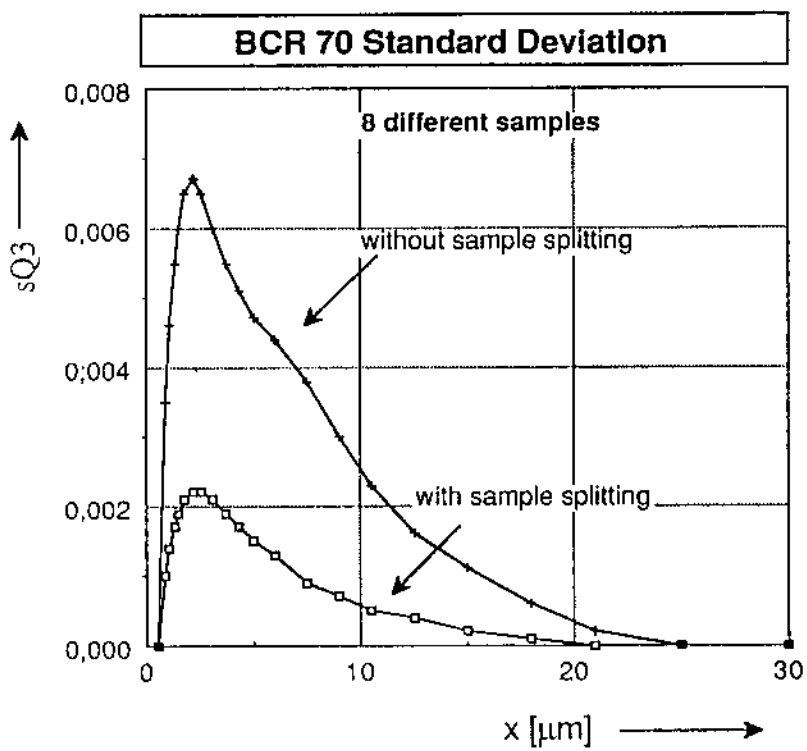

Figure 2: Results of measurements on BCR material, CRM 070 according to [8]

In the case of CRM 067, in fact, a value of 0.0012 was obtained for sQ_{3max}; this value demonstrates the excellent reproducibility of our laser diffraction instruments.

3.3 JFCC-Project

In a new study by JFCC [9], which is hitherto available only in Japanese, 45 particle measuring instruments from various manufacturers and with different sample-split materials have been compared. The laser diffraction range encompasses nine manufacturers. The results are compiled in table 4.

Material	$x_{10}/\mu m$	$x_{50}/\mu m$	$x_{90}/\mu m$	Decades	$\Delta lg\ x_{50}$
Boron nitride	2.6 -5.0	7.1 -12	13 -27	0.70	0.23
Silicon nitride	2.5 -6.0	7.6 -13	16 -34	0.78	0.23
Barium titanate	0.22-1.3	1.2 - 1.7	21 -36	0.92	0.29
Alumina	0.35-1.5	1.4 - 2.7	2.6- 5.5	0.92	0.29
Silicon carbide	>0.1 -0.36	0.42- 0.9	1.2- 4.5	0.96	0.67
Zirconia	>0.1 -0.8	1.3 - 9.5	8.5-26	1.65	0.86

Table 4 : Comparability of laser diffraction equipment from various manufacturers

The shapes of the distributions are very similar for the different instruments, although the absolute values still vary. The comparability of the values is quite good for narrow distributions. Differences occur especially in the submicron range.

3.4 Silicon carbide

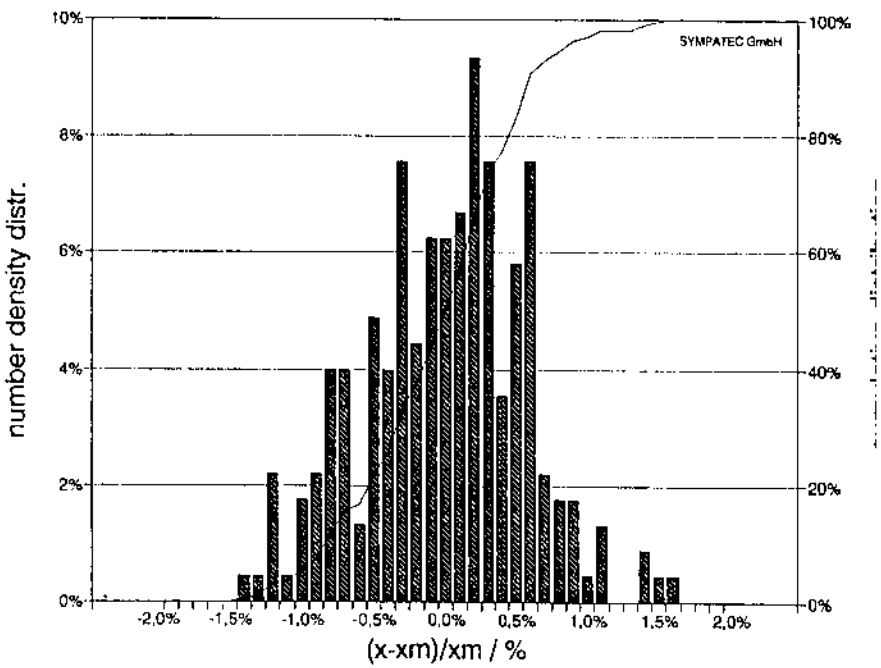

Figure 3: Comparability of measured results for a manufacturer Measurements on SiC (FEPA: P 1200)

Silicon carbide (SiC) possesses excellent longterm stability, is easy to disperse, and is available in many grain bands according to FEPA standards [10]. Consequently, it is employed by some manufacturers as an internal company standard for quality assurance.

In figure 3, the values measured on split SiC samples are presented for laser diffraction instruments, type HELOS, of different configurations and measuring ranges taken out of the routine production of the SYMPATEC Company. The frequency of the relative deviations of the x_{10}, x_{50}, and x_{90} values are plotted with reference to the respective average value for dry

dispersion with RODOS. The deviations are typically less than 1 per cent independent of the selected dispersion medium.

With broad distributions, the dispersing device exerts a decisive influence on the results. From figure 4 it can be seen that dry dispersion of such distributions is feasible to somewhere distinctly below 1 µm. The wear which thereby occurs on the dispersing path can cause changes in the results; however, this is mastered, as is documented in figure 5 by 16000 measurements on Portland cement.

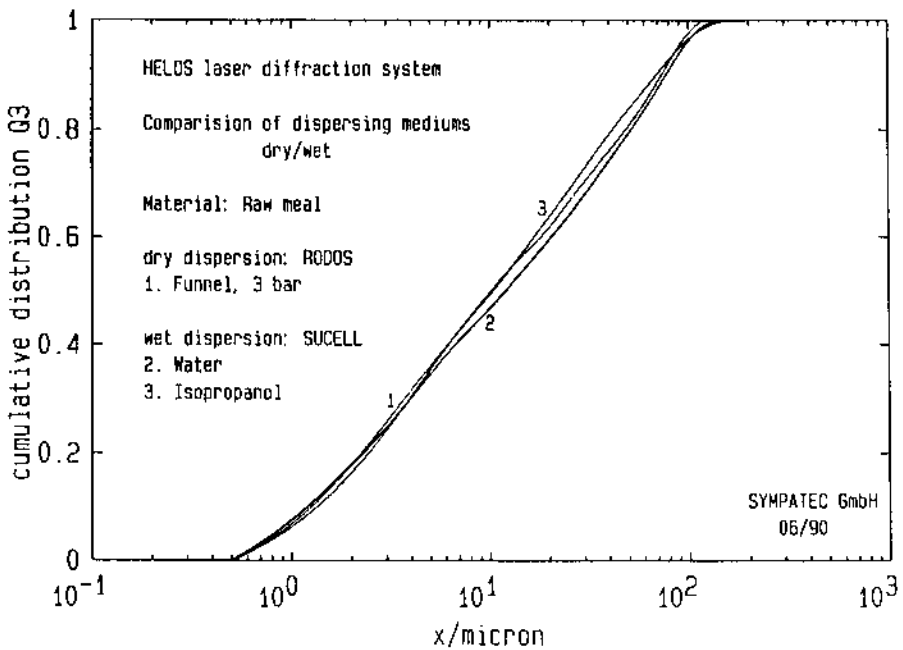

Figure 4: Dispersion of very broad distributions

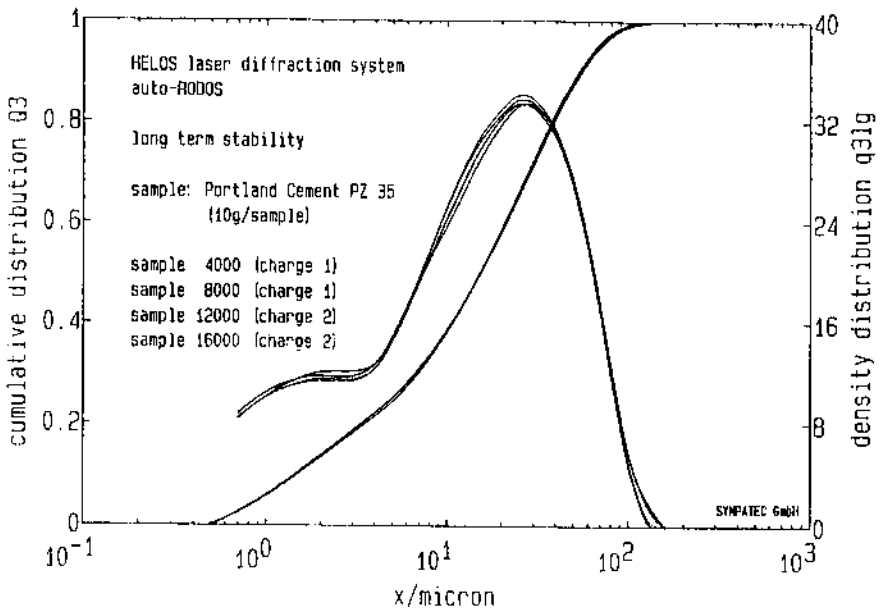

Figure 5: Effect of wear in the dispersion path on the results of measurement

4. Future standards

The indication of the measuring accuracy with laser diffraction instruments is far more difficult than with spectral analyzers, for instance, which likewise yield distributions. The reason for this is the fact that steep filters normally exclude any influence of adjacent values on the particular point being measured. In the case of laser diffraction, however, the results of measurements in all intensity classes of the diffraction pattern contribute to the value of each individual particle size class indicated. Hence, the successive measurement of numerous monomodal distributions is not sufficient. Instead, appropriate mixtures must be generated therefrom in arbitrary linear combination, in order to appraise limits of detection, resolution, and mutual interaction.

A further problem involves the Q_3 distribution. In figure 4, $Q_3(x)$ behaves almost linearly over more than two decades. Particles of sizes between 1 µm and 100 µm are present at approximately equal mass fractions; as far as concerns the absolute numbers, however, only a single 100 µm particle occurs for one million 1 µm particles. This imposes exacting demands on the dynamics of data acquisition as well as on the dispersing system. This explains the fact that broad distributions in table 4 are determined with much larger errors than narrow distributions.

4.1 Standard materials

Future standard materials for laser diffraction instruments should exhibit the properties described in section 3. Besides a finely graduated number of certified, narrow distributions, A_i, certified mixtures, M_i, of these A_i should be available, too.

The mixtures may be selected in such a way, for example, that in the usual plot $Q_3(\lg(x))$ increases linearly in analogy with figure 4:

Mixture	Range/µm	x_{10}/µm	x_{50}/µm	x_{90}/µm
M1	0.1 - 10	0.126	1.00	7.94
M2	1 - 100	1.26	10.00	79.4
M3	10 - 1000	12.6	100.00	794

With the usual logarithmically graduated class averages, x_{mi}, this corresponds to equal mass fractions per class, i. With these mixtures, the user can check the proper operation of his instrument, <u>including</u> the dispersion unit, with a high level of certainty.

The developer can demonstrate the accuracy, resolution, an limits of detection by selectively adding specific A_i to th mixture.

4.2 Reticles

The problems involved in the creation of the referenc materials described can be partially avoided if the effect o the dispersing system is neglected and attention is limite exclusively to the function of the sensor itself (optics, dat acquisition, algorithm for evaluation). For this purpose, th introduction of particle size distributions, for instance, o lantern slides, into the beam path is sufficient.

Distributions of this kind can be transferred from a high precision photographic original to an optically inactiv support plate by a photochemical process. The advantage o these arrangements, which are designated as reticles, is th possibility of realizing every distribution type and simpl preparing identical, arbitrarily reusable copies therefrom.

For obtaining a standard which can be applied independently o manufacturer as far as possible, however, the followin requirements must be satisfied:

a) The statistical spatial distribution of the particles i weighted with the Gaussian distribution of the lase radiation (see figure 6). Since the beam radius, R differs from manufacturer to manufacturer, this effec must be eliminated. This can be best accomplished if th particles are limited to the radius R_{min}, the <u>shortes</u> beam radius available! From table 5, it can be seen tha the weighting error, Δ, is only -1.5 per cent for a equal-area distribution of only 13 particles on a squar lattice with an edge length of a//2.

Particle n(r/R)	n_{tot}	Δ/%
1(0)	1	+ 27.07
1(0) + 4(1)	5	- 12.42
1(0) + 4(1) + 4(1/$\sqrt{2}$)	9	- 7.64
1(0) + 4(1) + 4(1/$\sqrt{2}$) + 4(1/$\sqrt{2}$)	13	- 1.55
1(0) + 4(1) + 4(1/$\sqrt{2}$) + 4(1/$\sqrt{2}$) + 4(0.5/$\sqrt{2}$)	25	+ 0.04

Table 5 : Weighting error, Δ, for a Gaussian distribution of laser intensity: $I = I_0 \cdot \exp(-x^2/(2R^2))$

For a given surface density, C_A, with respect to a spatial distribution of infinite extent, the optical concentration, C_{opt}, decreases by a factor of 2.5 to

$$C_{opt} = 2 \cdot (1-\exp(-0.5)) \cdot C_n \approx 79\% \; C_A$$

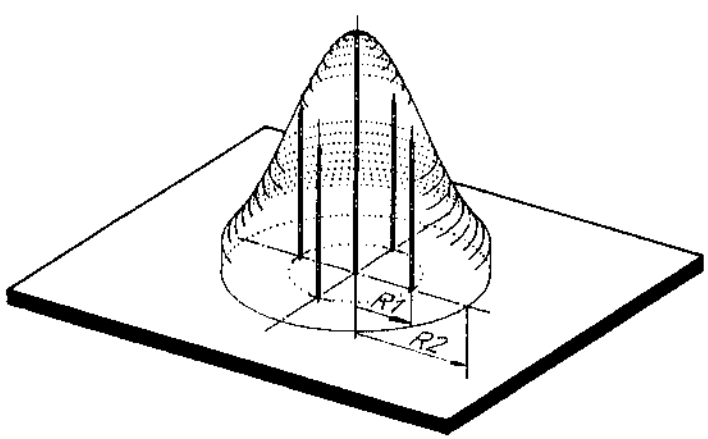

Figure 6: Gaussian distribution of the laser radiation

b) Not all manufacturers have detectors which integrate the angular distribution over 180°. These instruments impose more stringent demands on the quality of the statistical

distribution, since any remaining symmetry results in measuring errors. This is due especially to the diffraction generated among the particles themselves because of their stationary distribution. A possible remedial measure is the rotation of the reticle; however, displacement of the beam by refraction on the supporting material must be avoided.

c) The particle distribution is limited from above by the weighting error, Δ, and from below by the accuracy of the manufacturing process. Progress in semiconductor technology is shifting this limit downward. The accuracy is currently about 0.3 µm, which corresponds to ±3 per cent at a particle diameter of 10 µm.

For the measuring range of about 0.1 µm to 3 mm available at present for laser diffraction analysers, the calculated numbers of particles are compiled in table 6 for monomodal distributions.

lg (x/µm)	x/µm	n	
- 0.5	0.316	$5.204 \cdot 10^7$	
- 0.25	0.562	$1.646 \cdot 10^7$	
0	1.00	$5.204 \cdot 10^6$	↑
0.25	1.78	$1.646 \cdot 10^6$	present
0.5	3.16	$5.204 \cdot 10^5$	technological
0.75	5.62	$1.646 \cdot 10^5$	limit
1	10.0	$5.204 \cdot 10^4$	↑
1.25	17.8	$1.646 \cdot 10^4$	upper limit for
1.5	31.6	$5.200 \cdot 10^3$	3% accuracy
1.75	52.2	$1.646 \cdot 10^3$	
2	100	$5.204 \cdot 10^2$	
2.25	178	$1.646 \cdot 10^2$	lower limit for
2.5	316	$5.204 \cdot 10^1$	weighting error Δ
2.75	562	$1.646 \cdot 10^1$	↓
3	1000	$5.204 \cdot 10^0$	
3.25	1780	$1.646 \cdot 10^0$	
3.5	3160	$5.204 \cdot 10^{-1}$	

Table 6 : Numbers of particles for monomodal distributions at R = 3.2 mm and C_{opt} = 10%

The range, $x \leq 1$ µm, cannot at present be attained with the use of reticles. In this case, reference materials must be employed.

The range, 1 µm < x < 10 µm, is attainable with limited accuracy; however, the extreme particle numbers result in enormous costs. A decrease in optical concentration or impairment of the statistics (by copying of segments) is probably inevitable.

The range, 10 µm < x < 1000 µm, in contrast, is accessible with high precision.

Particle numbers less than 10 are present in the range, x > 1000 µm, and these result in large weighting errors.

Besides the monomodal distributions, the mixtures described in section 4 can be generated with linear $Q_3(lg(x))$. However, distributions of this type, which extend over two decades, cannot be realized without additional effort, since the number of 100 µm particles is less than 10 in the range from 1 µm to 100 µm and at a value of 10 per cent for C_{opt}, for example. This also applies to a reticle with RRSB distribution already available in the range from 5 to 93 µm.

Reticles with linear $Q_3(lg(x))$, which extend over one decade each, have been announced for May 1992.

5. Conclusions

Existing standard materials do not satisfy the requirements described for laser diffraction.

Comparisons of instruments on BCR and various other materials independently of manufacturers have indicated large deviations among the different manufacturers of laser diffraction analysers, especially in the submicron range and with broad distributions. These deviations have to be approximated to the one percent limit which has been demonstrated among different SYMPATEC instruments, by the creation of appropriate standards.

Above the submicron range, special reticles can be employed as standards; however, the efficiency of the dispersing system thereby remains unevaluated. Linear $Q_3(lg(x))$ distributions, as well as monomodal distributions, can be generated precisely and reproduced simply. The distribution width is limited from above by the number of particles, which decreases in proportion with x^6. For periodic checking of the sensor for correct function, they are ideally suited by virtue of the reusability.

Future reference materials to be made available for laser diffraction instruments should consist of spherical, nonabsorbent particles. For conclusive tests, especially wide distributions are necessary, since special demands are thereby imposed on the dispersing system, the data acquisition, and the algorithms for evaluation. The generation of three distributions in decadic succession with linear $Q_3(lg(x))$ by mixing is a desirable objective; each should extend over two decades.

7. Nomenclature

C_A	total particle surface area per unit of area
C_{opt}	optical concentration
I	intensity of the laser radiation
I_o	intensity of the laser radiation on the optical axis
n	number of particles
n_{tot}	total number of particles
Q_3	cumulative volume distribution
R	width of the Gaussian distribution
r	distance of the particle from the optical axis

x	particle diameter (equivalent diameter)
x_{geom}	particle diameter (geometrical)
x_{mi}	particle size of class average for i^{th} class
x_S	particle diameter as specified on BCR certificate
x_{10}	particle diameter at Q_3 = 10 %
x_{50}	particle diameter at Q_3 = 50 %
x_{90}	particle diameter at Q_3 = 90 %
Δ	weighting error associated with intensity distribution of the laser
Δlgx_{50}	difference between logarithms of smallest and largest x_{50} values
η	performance rate

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