INTERNATIONAL STANDARD

ISO 13320

First edition
2009-10-01

Corrected version
2009-12-01

Particle size analysis — Laser diffraction methods

Analyse granulométrique — Méthodes par diffraction laser

Reference number
ISO 13320:2009(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 13320 was prepared by Technical Committee ISO/TC 24, *Particle characterization including sieving*, Subcommittee SC 4, *Particle characterization*.

This first edition of ISO 13320 cancels and replaces ISO 13320-1:1999.

This corrected version of ISO 13320:2009 incorporates the following correction:

— in Figure A.2, lower graph, the symbols for datapoints corresponding to "1,39 – 0,0i" and "2,19 – 0,0i" have been changed to match the plots to which they refer.

Introduction

The laser diffraction technique has evolved such that it is now a dominant method for determination of particle size distributions (PSDs). The success of the technique is based on the fact that it can be applied to various kinds of particulate systems, is fast and can be automated, and that a variety of commercial instruments is available. Nevertheless, the proper use of the instrument and the interpretation of the results require the necessary caution.

Since the publication of ISO 13320-1:1999, the understanding of light scattering by different materials and the design of instruments have advanced considerably. This is especially marked in the ability to measure very fine particles. Therefore, this International Standard has been prepared to incorporate the most recent advances in understanding.

Particle size analysis — Laser diffraction methods

1 Scope

This International Standard provides guidance on instrument qualification and size distribution measurement of particles in many two-phase systems (e.g. powders, sprays, aerosols, suspensions, emulsions and gas bubbles in liquids) through the analysis of their light-scattering properties. It does not address the specific requirements of particle size measurement of specific materials.

This International Standard is applicable to particle sizes ranging from approximately 0,1 µm to 3 mm. With special instrumentation and conditions, the applicable size range can be extended above 3 mm and below 0,1 µm.

For non-spherical particles, a size distribution is reported, where the predicted scattering pattern for the volumetric sum of spherical particles matches the measured scattering pattern. This is because the technique assumes a spherical particle shape in its optical model. The resulting particle size distribution is different from that obtained by methods based on other physical principles (e.g. sedimentation, sieving).

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 9276-1, *Representation of results of particle size analysis — Part 1: Graphical representation*

ISO 9276-2, *Representation of results of particle size analysis — Part 2: Calculation of average particle sizes/diameters and moments from particle size distributions*

ISO 9276-4, *Representation of results of particle size analysis — Part 4: Characterization of a classification process*

ISO 14488, *Particulate materials — Sampling and sample splitting for the determination of particulate properties*

ISO 14887, *Sample preparation — Dispersing procedures for powders in liquids*

3 Terms, definitions and symbols

3.1 Terms and definitions

3.1.1
absorption
reduction of intensity of a light beam not due to scattering

3.1.2
coefficient of variation

CV

relative standard deviation (deprecated)

⟨positive random variable⟩ standard deviation divided by the mean

NOTE 1 The coefficient of variation is commonly reported as a percentage.

NOTE 2 Adapted from ISO 3534-1:2006[24], 2.38.

3.1.3
complex refractive index

$\underline{n}_\mathrm{p}$

refractive index of a particle, consisting of a real and an imaginary (absorption) part

NOTE The complex refractive index of a particle can be expressed mathematically as

$$\underline{n}_\mathrm{p} = n_\mathrm{p} - \mathrm{i}k_\mathrm{p}$$

where

i is the square root of -1;

k_p is the positive imaginary (absorption) part of the refractive index of a particle;

n_p is the positive real part of the refractive index of a particle.

In contrast to ISO 80000-7:2008[27], item 7-5, this International Standard follows the convention of adding a minus sign to the imaginary part of the refractive index.

3.1.4
relative refractive index

m_rel

ratio of the complex refractive index of a particle to the real part of the dispersion medium

NOTE 1 Adapted from ISO 24235:2007[26].

NOTE 2 In most applications, the medium is transparent and, thus, its refractive index has a negligible imaginary part.

NOTE 3 The relative refractive index can be expressed mathematically as

$$m_\mathrm{rel} = \underline{n}_\mathrm{p}/n_\mathrm{m}$$

where

n_m is the real part of the refractive index of the medium;

$\underline{n}_\mathrm{p}$ is the complex refractive index of a particle.

3.1.5
deconvolution

⟨particle size analysis⟩ mathematical procedure whereby the size distribution of an ensemble of particles is inferred from measurements of their scattering pattern

3.1.6
diffraction

⟨particle size analysis⟩ scattering of light around the contour of a particle, observed at a substantial distance (in the 'far field')

3.1.7
extinction

⟨particle size analysis⟩ attenuation of a light beam traversing a medium through absorption and scattering

3.1.8
model matrix

matrix containing vectors of the scattered light signals for unit volumes of different size classes, scaled to the detector's geometry, as derived from model computation

3.1.9
multiple scattering

consecutive scattering of light by more than one particle, causing a scattering pattern that is no longer the sum of the patterns from all individual particles

NOTE See **single scattering** (3.1.20).

3.1.10
obscuration

optical concentration

fraction of incident light that is attenuated due to extinction (scattering and/or absorption) by particles

NOTE 1 Adapted from ISO 8130-14:2004[25], 2.21.

NOTE 2 Obscuration can be expressed as a percentage.

NOTE 3 When expressed as fractions, obscuration plus **transmission** (3.1.22) equal unity.

3.1.11
optical model

theoretical model used for computing the model matrix for optically homogeneous and isotropic spheres with, if necessary, a specified complex refractive index

EXAMPLES Fraunhofer diffraction model, Mie scattering model.

3.1.12
reflection

⟨particle size analysis⟩ change of direction of a light wave at a surface without a change in wavelength or frequency

3.1.13
refraction

process by which the direction of a radiation is changed as a result of changes in its velocity of propagation in passing through an optically non-homogeneous medium, or in crossing a surface separating different media

[IEC 60050-845:1987[28]]

NOTE The process occurs in accordance with Snell's law:

$$n_\mathrm{m} \sin \theta_\mathrm{m} = n_\mathrm{p} \sin \theta_\mathrm{p}$$

See 3.2 for symbol definitions.

3.1.14
repeatability (instrument)

⟨particle size analysis⟩ closeness of agreement between multiple measurement results of a given property in the same dispersed sample aliquot, executed by the same operator in the same instrument under identical conditions within a short period of time

NOTE This type of repeatability does not include variability due to sampling and dispersion.

3.1.15
repeatability (method)

⟨particle size analysis⟩ closeness of agreement between multiple measurement results of a given property in different aliquots of a sample, executed by the same operator in the same instrument under identical conditions within a short period of time

NOTE This type of repeatability includes variability due to sampling and dispersion.

3.1.16
reproducibility (method)

⟨particle size analysis⟩ closeness of agreement between multiple measurement results of a given property in different aliquots of a sample, prepared and executed by different operators in similar instruments according to the same method

3.1.17
scattering

⟨particle size analysis⟩ change in propagation of light at the interface of two media having different optical properties

3.1.18
scattering angle

⟨particle size analysis⟩ angle between the principal axis of the incident light beam and the scattered light

3.1.19
scattering pattern

angular pattern of light intensity, $I(\theta)$, or spatial pattern of light intensity, $I(r)$, originating from scattering, or the related energy values taking into account the sensitivity and the geometry of the detector elements

3.1.20
single scattering

scattering whereby the contribution of a single member of a particle population to the total scattering pattern remains independent of the other members of the population

3.1.21
single shot analysis

analysis, for which the entire content of a sample container is used

3.1.22
transmission

⟨particle size analysis⟩ fraction of incident light that remains unattenuated by the particles

NOTE 1 Transmission can be expressed as a percentage.

NOTE 2 When expressed as fractions, **obscuration** (3.1.10) plus transmission equal unity.

3.1.23
width of size distribution

the width of the particle size distribution (PSD), expressed as the x_{90}/x_{10} ratio

NOTE For normal (Gaussian) size distributions, often the standard deviation (absolute value), σ, or the coefficient of variation (CV) is used. Then, about 95 % of the population of particles falls within $\pm 2\sigma$ from the mean value and about 99,7 % within $\pm 3\sigma$ from the mean value. The difference $x_{90} - x_{10}$ corresponds to $2{,}6\sigma$.

3.2 Symbols

A_i	extinction efficiency of size class i
C	particulate concentration, volume fraction
CV	coefficient of variation
f	focal length of lens
i	square root of −1
i_n	photocurrent of detector element, n
$I(\theta)$	angular intensity distribution of light scattered by particles (scattering pattern)
I_h	intensity of horizontally polarized light at a given angle
$I(r)$	spatial intensity distribution of light scattered by particles on the detector elements (measured scattering pattern by detector)
I_v	intensity of vertically polarized light at a given angle
J_i	first order Bessel Function
k	wavenumber in medium: $2\pi n_\mathrm{m}/\lambda$
k_p	imaginary (absorption) part of the refractive index of a particle
l_a	distance from scattering object to detector
l_b	illuminated pathlength containing particles
$\boldsymbol{L}_n$	vector of photocurrents (i_1, i_2 ... i_n)
m_rel	relative, complex refractive index of particle to medium
$\boldsymbol{M}$	model matrix, containing calculated detector signals per unit volume of particles in all size classes
n_m	real part of refractive index of medium
n_p	real part of refractive index of particle
$\underline{n}_\mathrm{p}$	complex refractive index of particle
O	obscuration (1 − transmission); only true for single scattering
r	radial distance from focal point in focal plane
$\boldsymbol{V}$	vector of volume content in size classes (V_1, V_2 ... V_i)
V_i	volume content of size class i
v	velocity of particles in dry disperser
x	particle diameter
x_i	geometric mean particle size of size class i
x_{50}	median particle diameter; here used on a volumetric basis, i.e. 50 % by volume of the particles are smaller than this diameter and 50 % are larger
x_{10}	particle diameter corresponding to 10 % of the cumulative undersize distribution (here by volume)
x_{90}	particle diameter corresponding to 90 % of the cumulative undersize distribution (here by volume)
α	dimensionless size parameter: $\pi x n_\mathrm{m}/\lambda$
$\Delta Q_{3,i}$	volume fraction within size class i

θ	scattering angle with respect to forward direction
θ_m	angle with respect to perpendicular at boundary for a light beam in medium (as used in Snell's law; see 3.1.13, Note)
θ_p	angle with respect to perpendicular at boundary for a light beam in particle (as used in Snell's law; see 3.1.13, Note)
λ	wavelength of illuminating light source in vacuum
σ	standard deviation
ω	angular frequency

4 Principle

A sample, dispersed at an adequate concentration in a suitable liquid or gas, is passed through the beam of a monochromatic light source, usually a laser. The light scattered by the particles, at various angles, is measured by multi-element detectors, and numerical values relating to the scattering pattern are recorded for subsequent analysis. These numerical scattering values are then transformed, using an appropriate optical model and mathematical procedure, to yield the proportion of the total volume of particles to a discrete number of size classes forming a volumetric particle size distribution (PSD).

The laser diffraction technique for the determination of PSDs is based on the phenomenon that particles scatter light in all directions with an intensity pattern that is dependent on particle size. Figure 1 illustrates this dependency in the scattering patterns for two sizes of spherical particles. In addition to particle size, particle shape and the optical properties of the particulate material influence the scattering pattern.

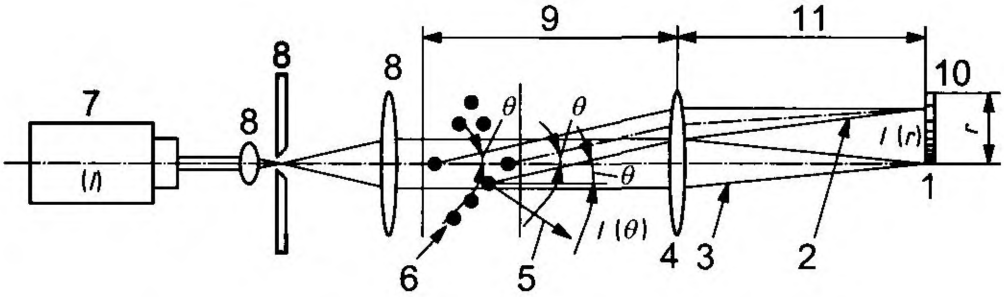
a) b)

Figure 1 — Scattering pattern for two spherical particles: the particle generating pattern a) is twice as large as the one generating pattern b) (simulated images for clarity)

5 Laser diffraction instrument

A set-up for a laser diffraction instrument is given in Figure 2.

In this Fourier set-up, a light source (typically a laser or other narrow-wavelength source) is used to generate a monochromatic, coherent, parallel beam. This is followed by a beam processing unit, usually a beam expander with integrated filter, producing an extended and nearly ideal beam to illuminate the dispersed particles.



Key

1	obscuration/optical concentration detector
2	scattered beam
3	direct beam
4	fourier lens
5	scattered light not collected by lens 4
6	ensemble of dispersed particles
7	light source (e.g. laser)
8	beam processing unit
9	working distance of lens 4
10	multi-element detector
11	focal distance of lens 4

NOTE For explanations of symbols, see 3.2.

Figure 2 — Fourier set-up of a laser diffraction instrument

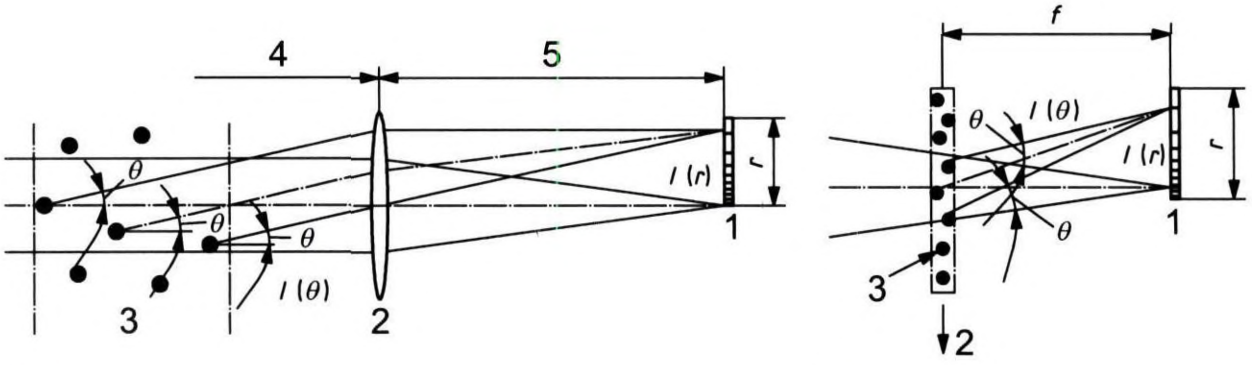
A sample of particles, dispersed at an adequate concentration, is passed through the light beam in a measuring zone by a transporting medium (gas or liquid). This measuring zone should be within the working distance of the lens used. Sometimes, the particle stream in a process passes directly through the laser beam for measurement. This is the case in the measurement of sprays and aerosols. In other cases (e.g. when measuring emulsions, pastes and powders), samples can be dispersed in fluids and caused to flow through the measurement zone. Often dispersants (wetting agents; stabilizers) and/or mechanical forces (agitation; sonication) are applied for deagglomeration of particles and for stabilization of the dispersion. For these liquid dispersions, a recirculation system is most commonly used, consisting of an optical measuring cell, a dispersion bath usually equipped with stirrer and ultrasonic elements, a pump and tubing.

Dry powders can also be converted into aerosols through application of dry powder dispersers, which apply mechanical forces for deagglomeration. Here, a dosing device feeds the disperser with, ideally, a near-constant mass flow of sample. The disperser uses the energy of a compressed gas or the differential pressure to a vacuum to disperse the particles. It outputs an aerosol that is blown through the measuring zone, usually into the inlet of a vacuum pipe that collects the particles. Coarse, non-agglomerated powders can be transported through the measurement zone by gravity.

There are two positions in which the particles can enter the laser beam. In the Fourier optics case, the particles enter the parallel beam before and within the working distance of the collecting lens [see Figure 3a)]. This allows for the measurement of spatially extended particle systems. In the reverse Fourier optics case, the particles enter behind the lens and, thus, in a converging beam [see Figure 3b)].

The advantage of the Fourier set-up is that a reasonable pathlength for the sample is allowed within the working distance of the lens. The reverse Fourier set-up demands small pathlengths but provides one solution that enables the measurement of scattered light at larger angles.

The interaction of the incident light beam and the ensemble of dispersed particles results in a scattering pattern with different light intensities scattered at various angles (see Annex A for the theoretical background of laser diffraction). The total angular intensity distribution $I(\theta)$, consisting of both direct and scattered light, is then focused by a positive lens or an ensemble of lenses onto a multi-element detector. The lens(es) provide(s) for a scattering pattern which, within limits, is not dependent upon the location of the particles in the light beam. The continuous angular intensity distribution $I(\theta)$ is converted into a discrete spatial intensity distribution $I(r)$ on a set of detector elements.



Key

1	detector
2	fourier lens
3	ensemble of dispersed particles
4	working distance
5	focal distance

Key

1	detector
2	flow through cuvette for dispersed particles
3	particle

NOTE For explanations of symbols, see 3.2.

a) Fourier set-up: particles are in parallel beam before and within working distance of lens

b) Reverse Fourier set-up: particles are in converging beam between lens and detector

Figure 3 — Illustrations of optical arrangements used in laser diffraction instruments

Some instruments contain extra features to improve particle size analysis:

a) an extra light source at the same optical axis having a different wavelength;

b) one or more off-axis light sources, either at less or at more than 90° with respect to the optical axis;

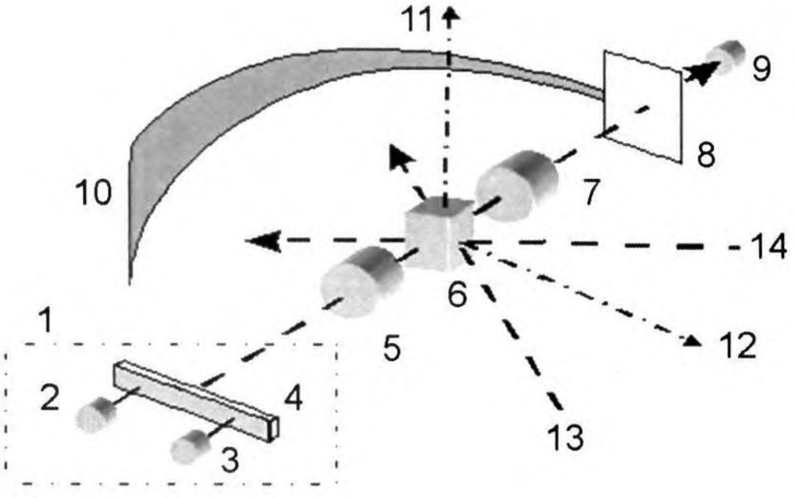
c) polarization filters for light source and detectors;

d) scattered light detectors at angles smaller than 90° but larger than the conventional angular range (forward scattering);

e) scattered light detectors at around 90° for measurement of intensities in different polarization directions;

f) scattered light detectors at angles larger than 90° (backscattering).

These possibilities are illustrated in Figure 4.



Key

1	light source assembly including beam expansion and/or collimation
2	light source wavelength 1
3	light source wavelength 2
4	beam switching arrangement
5	reverse Fourier lens(es) position
6	measurement cell or general measurement zone
7	Fourier lens(es) position
8	low angle detector(s), either bespoke design or pixel array
9	transmission or obscuration detector
10	high angle detector array
11	horizontally polarized light detector
12	vertically polarized light detector
13	alternative entry point for light source
14	alternative entry point for light source

Figure 4 — Possibilities for optical arrangements in laser diffraction instrument

It is assumed that the recorded scattering pattern of the particle ensemble is identical to the sum of the patterns from all individual particles (single scattering). Furthermore, the scattering pattern is assumed to come from spherical particles.

Detection of the scattering pattern is done by a number of silicon detectors or photodiodes and/or a pixel array detector. These detectors convert the spatial intensity distribution $I(r)$ into a series of photocurrents, i_n. Subsequent electronics then convert and digitize the photocurrents into a set of energies, L_n, representing the scattering pattern. A central element measures the intensity of the scattered and non-scattered light and, thus, with a calculation, provides a measure of optical concentration or obscuration. Some instruments provide special geometries of the central element in order to automatically re-centre or re-focus the detector by moving the detector or the lens. It is desirable that the detector elements are positioned so as to prevent the light reflected from internal surfaces from re-traversing the optical system.

A computer controls the measurement and is used for storage and manipulation of the detected signals, for storage and/or calculation of a proper form of the optical model (usually as a model matrix containing light-scattering vectors per unit of volume per size class, scaled to the detector's geometry and sensitivity) and for calculation of the PSD (see Annex A for the theoretical background of laser diffraction). Also, it may provide automated instrument operation.

Significant differences exist, both in hardware and software, not only between instruments from different manufacturers but also between different types from one company. The instrument specifications should give adequate information for proper judgement of these differences. Annex B contains recommendations for the specifications of laser diffraction instruments.

6 Operational procedures

6.1 Requirements

6.1.1 Instrument location

The instrument should be located in a clean environment that is free from excessive electrical noise, mechanical vibration and temperature fluctuations, and out of direct sunlight and airflows. The operating area should conform to local health and safety requirements. The instrument should either contain a rigid internal optical bench or be installed on a rigid table or bench to avoid realignment of the optical system at frequent intervals.

WARNING — The radiation of instruments equipped with a laser can cause permanent eye damage. Never look into the direct path of the laser beam or its reflections. Avoid blocking the laser beam with reflecting surfaces. Observe relevant local laser radiation safety regulations.

6.1.2 Dispersion liquids

Any suitable, optically transparent liquid of known refractive index may be used. Thus, a variety of liquids is available for the preparation of liquid dispersions of powders. Annex C provides information on the dispersion liquids.

Observe local health and safety regulations if an organic liquid is used for dispersion. Use a cover for the ultrasonic bath when using liquids with a high vapour pressure to prevent the formation of hazardous vapour concentrations. Evaporation of volatile organic liquids may cause sufficient cooling as to induce fluctuating refractive index values in the liquid medium, which in turn may induce artefacts in the particle size results.

6.1.3 Dispersion gases

For dry dispersion and spray applications, a compressed gas can be used. If used, it is essential that it is free from oil, water and particles. To achieve this, a dryer with a filter is required. In spray applications, it is essential that evaporation of the liquid does not cause artefacts in the particle size results. Any vacuum unit should be located well away from the measurement zone, so that the output of the hot air does not disturb the measuring zone. Draught should be avoided in order to avoid unstable particulate streams.

6.2 Sample inspection, preparation, dispersion and concentration

6.2.1 Sample inspection

Inspect the material to be analysed, visually or with the aid of a microscope, in order to: a) estimate the size range and particle shape; and b) check whether the particles have been dispersed adequately.

The size distribution measured in a sample is only valid for a batch of material if the sample is representative for that batch and has been dispersed adequately.

6.2.2 Preparation

Prepare a representative sample of suitable volume for the measurement by using an adequate sample splitting technique, e.g. a rotating riffler (ISO 14488).

Very small samples can be taken out of a well-mixed paste of particles in liquid. The consistency of the paste then minimizes segregation errors. The pastes are formed by adding dispersant to the sample drop by drop while mixing it with a spatula. A good consistency for the paste is one like honey or toothpaste. If, by mistake, the paste becomes too fluid, it shall not be used, and a new preparation shall be initiated.

If the maximum size exceeds the measuring range, remove the material that is too coarse, e.g. by pre-sieving. In this case, determine and report the amount/percentage removed.

Sprays, aerosols and gas bubbles in liquid are usually measured directly, provided that their concentration is at an adequate level (see 6.2.3 and 6.2.4), since sampling or dilution is generally very difficult without altering the PSD. If droplets are sprayed into still air, then the small droplets decelerate faster than the large ones, leading to a potential velocity bias. Therefore, it is preferable to spray into a suitable moving air stream matched to that of the spray. Consideration should also be given to the prospect of droplet evaporation, which may cause significant errors, especially for droplets in the (sub-)micrometer range. Firstly, the fast evaporation of such droplets reduces their size or even makes them disappear. Moreover, artefacts in the size distribution may appear due to a changing refractive index around the droplets, resulting from the evolving vapour and the temperature decrease during evaporation.

6.2.3 Dispersion

6.2.3.1 General

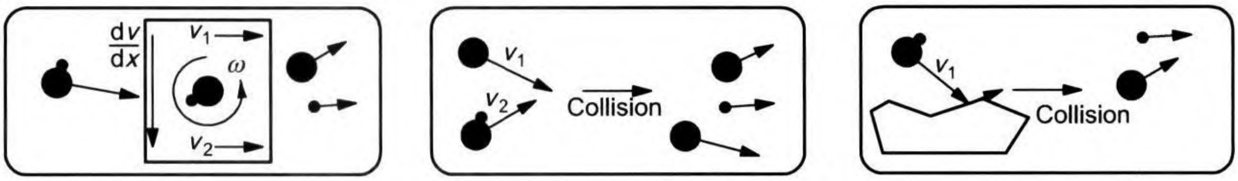
Dry powders can be dispersed either in air or in a liquid. The dispersion procedure should be adjusted to the purpose of the measurement, e.g. it has to be decided whether agglomerates should be detected or dispersed to primary particles.

The transport conditions for the particles through the measurement zone should also be considered. Adequate flow should be applied to ensure that particles of all sizes pass the measurement zone at similar velocity in order to avoid velocity bias in the result. Particles having a high aspect ratio have a tendency to show preferred orientations at the flow conditions existing in the measurement cell. Even at turbulent conditions their orientation may not be fully random. Annex A discusses the fact that different orientations of non-spherical particles lead to different scattering patterns and, thus, different sizing results.

6.2.3.2 Dispersion in gas

For dispersion in gas, an adequate dry disperser should be applied. For coarse, free-flowing particles, free fall by gravity is usually sufficient for dispersion. For agglomerated particles, compressed gas or vacuum is generally required for dispersion by shear stress with the assistance of mechanical deagglomeration by particle-particle or particle-wall collisions (see Figure 5). The complete fractional sample shall be used for the measurement. All particles should ideally have the same approximate velocity in the measurement zone. Often, large sample quantities are used for dry dispersion, which can assist the representation of coarse particles in a wide size distribution. Check that comminution of the particles does not occur and conversely that a good dispersion has been achieved. This is often done by direct comparison of a dry with a liquid dispersion: ideally, the results should be the same. Another means for checking the degree of dispersion or comminution is by changing the dispersing energy (e.g. the primary air pressure) and monitoring the change of the size distribution. Usually, upon increasing the dispersing energy, the amount of fines is increased at first, due to improved dispersion. Then, sometimes, a point is reached, where the size distribution is nearly constant with increasing energy. At still higher energies, the amount of fines may rise again as a result of comminution. If such a plateau is reached, its centre defines the optimum dispersing energy.

NOTE A plateau is not usually found, e.g. in case of highly aggregated or fragile particles.



a) Velocity gradients caused by shear stress **b) Particle-to-particle collisions** **c) Particle-to-wall collisions**

NOTE For explanations of symbols, see 3.2.

Figure 5 — Processes involved in dry dispersion of powders

6.2.3.3 Dispersion in liquid media

For the preparation of liquid dispersions, refer to ISO 14887. A variety of liquids is available. Annex C contains guidelines on the selection of an appropriate liquid for wet dispersion. Generally, pasting, stirring and sonication can be used to facilitate proper dispersion of particles in the liquid. A preliminary check on the dispersion quality can be made by visual/microscopic inspection of the suspension. Also, it is possible to perform some measurements of the suspension in the laser diffraction instrument, with intermediate sonication: the measured size distribution should not change significantly if the sample is well dispersed and the particles are neither fragile nor soluble.

The minimum volume of sample required for repeatable measurement increases as the width of the size distribution becomes greater in order to allow a sufficient number of large particles to be present (see ISO 14488). The volume of the dispersion fluid required to suspend these samples increases accordingly if the limits of optical concentration are to be observed.

For example, ISO 14488 demands for a powder containing particles in the broad size range of 2 µm to 200 µm, a true sample volume of at least 0,3 ml for a precision of 3 % for the x_{90}. This requires at least 500 ml of suspension fluid to ensure single scattering. The measurement time (or the number of detector readings that are averaged for a measurement) should be sufficient to ensure that an adequate representation of all particle sizes is reached. Appropriate conditions should be established experimentally, in relation to the desired precision.

6.2.4 Concentration

The particle concentration in the measurement zone should be high enough to produce an adequate signal (or in other words to reach an acceptable signal-to-noise ratio with respect to precision), yet low enough to ensure multiple scattering to be insignificant to the particle size result.

The effect of multiple scattering is generally to increase the angle of scattering and, thus, to shift the size distribution results to lower sizes. An exact concentration range cannot be given, as it is a function of particle size, PSD width, laser beam width and pathlength of the dispersed particles in the measurement zone. As an indication, it can be said that the typical volumetric concentration for analysis of 1 µm particles is about 0,002 % — for measurement in a cell with 2 mm pathlength — whereas the concentration for 100 µm particles could be about 0,2 %. Check the instrument documentation for additional information. Some guidance can be taken from the measured obscuration or transmission value, which is for the above examples about 5 % and 25 %, respectively. In general, the proportion of small particles in a size distribution dominates in the upper concentration limit. If all the particles are larger than 100 µm, then an obscuration of up to 30 % may not cause multiple scattering. To ensure appropriate obscuration limits, perform particle size measurements at different concentration levels for the material of interest, and monitor shifts in the distribution. Clause A.9 provides some information on the relation between particulate concentration, particle size and obscuration.

6.3 Measurement

6.3.1 Procedure

6.3.1.1 General

A typical measurement of a PSD by laser diffraction comprises the following steps:

6.3.1.2 Setting up instrument and blank measurement

After selection of the appropriate particle size range and proper optical alignment, perform a blank measurement immediately prior to the sample measurement in which a particle-free dispersion medium is used under the same instrument conditions to be employed for the sample measurement. These background signals are used: 1) to check the proper functioning of the instrument; and 2) to be subtracted later from the detector signals coming from the measurement of the material of interest.

6.3.1.3 Sample preparation

Prepare and disperse a sample according to 6.2. Ensure that the sample is representative for the batch of product within a stated confidence interval. The amount of test sample should correspond to at least the minimum required for precision. The dispersion conditions should lead to complete deagglomeration without comminution and to a sufficiently low concentration to ensure single scattering.

6.3.1.4 Data collection of the scattering pattern

Allow a measuring time for data collection sufficient for statistically adequate representation of the sample. Check therefore the effect of the elapsed measurement duration on the sizing result. For each detector element, an average signal is calculated, sometimes together with its standard deviation. Net signals may be calculated by subtraction of the background signals. The magnitude of the signal from each detector element depends upon the detection area, the light intensity and the quantum efficiency. The co-ordinates (size and position) of the detector elements together with the focal distance of the lens determine the region of scattering angles for each element. Generally, all these factors are factory determined and stored in the computer.

Most instruments also measure the power of the central laser beam. The fractional difference between a dispersed sample and a blank experiment is given as a value of obscuration or transmission, which is indicative of the total amount of scattered light and the particle concentration.

6.3.1.5 Selection of an appropriate optical model

Most often either the Mie theory or the Fraunhofer approximation is used for calculation of a scattering matrix, which represents the signal at each detector element per unit volume of particles in given size classes. The choice depends upon the size range of the particles to be measured, their optical properties and the application (see Annex A). Other light-scattering theories may be applied for the calculation of this scattering matrix; however, such occurrences are uncommon.

When using the Mie theory, the refractive indices of particulate and medium, or their ratio, should be established and entered into the instrument in order to allow calculation of the model matrix (see Annex D for refractive index values of liquids and solids). For practical reasons, values of the imaginary part of the refractive index (about 0,01i to 0,03i) are required to accommodate surface roughness of particles, where some light is randomly scattered.

Good understanding of the influence of the complex refractive index in the light scattering from particles is strongly advised in order to apply the Mie theory or the Fraunhofer approximation correctly. Inappropriate choice of the optical model or of the values of the refractive index may result in significant bias of the resulting PSD. This bias often manifests itself as inappropriate quantities of material being ascribed to the size classes at the lower end of the size distribution.

To obtain traceable results it is essential that the refractive index values are used as reported.

6.3.1.6 Conversion of scattering pattern into PSD

This deconvolution step is the inverse of the calculation of a scattering pattern for a given PSD. Several mathematical algorithms have been developed for this purpose (References [5], [7], [8], [11], [14], [17]). They contain some weighting of deviations between measured and calculated scattering patterns (e.g. least squares) and some constraints of the size distribution curve. These constraints restrict the final particle size result to values for the quantity in each size class that are either positive or zero and limit the differences between the quantities in subsequent size classes. A procedure (Reference [6]) uses the observed fluctuations of the detector signals to introduce proper weighting of these data and to calculate confidence intervals for the PSD.

6.3.2 Precautions

6.3.2.1 Before starting, and during any measurement, follow the instructions given in the instrument manual. Take the precautions in 6.3.2.2 to 6.3.2.10.

6.3.2.2 Before switching on the power to the instrument, make sure that all components of the system are properly earthed (grounded). All the particle dispersing and transporting devices, such as the ultrasonic bath, the dry disperser, the vacuum inlets and vacuum hoses, shall be earthed to prevent ignition of organic solvents or dust explosions caused by electrostatic discharges.

6.3.2.3 After switching the power on, allow sufficient time for the instrument to stabilize. Gas lasers such as the He-Ne laser require adequate warm-up time (usually more than 30 min).

6.3.2.4 Check the instrument status and, if necessary, set up the required measuring range and lens. In manually aligned systems, ensure, by watching the signals of the detector elements, that the detector is properly centred and positioned in the focal plane of the lens. Without particles, the background signal should be below the specified thresholds for that instrument set-up and dispersing device. If this is not the case, inspect and, if necessary, clean the optical components to ensure proper performance.

6.3.2.5 Make sure that the particles are only introduced into the laser beam within the specified working distance of the lens, so that all relevant scattering radiation leaving the particles strikes within the clear aperture of the lens that focuses it on the detector.

6.3.2.6 Qualify the instrument performance with respect to both precision and accuracy at regular time intervals by measuring a reference material of known size distribution (see 6.4 and 6.5.2) and record the date and results.

6.3.2.7 In the case of wet dispersion, check that air bubbles are absent from the dispersion liquid. Bubbles are usually readily visible at the surface of the liquid dispersion or can be detected as random signal fluctuations of the low-angle detectors (if a live display is available) or by strong fluctuations of the obscuration output. Avoid foaming agents where possible (e.g. as a surfactant).

6.3.2.8 In the case of dry dispersion, check, visually or by inspection of subsequent obscuration values, that the dosing unit for the disperser generates a steady mass flow.

6.3.2.9 For aerosols and sprays, ensure that no bright daylight is allowed to illuminate the detector, either directly or via scattering by particles. Ensure that the flow of particles/droplets is even. If possible, use some form of extraction for the particulate stream at the exit of the measurement zone to assist the particles in maintaining the same velocity and to ensure the safety of the operator.

6.3.2.10 Investigate, if possible, the influence of the optical model (relative refractive index) on the resulting PSD.

6.4 Precision

6.4.1 Reference materials

In all cases, the CV is used to express precision. For testing, reference materials with an x_{90}/x_{10} ratio of 1,5 to 10 should be used. These materials should possess sufficient background data and a robust, written sampling/dispersion/measurement protocol suitable for laser diffraction analysis. Further, they should have documented results given to the precision and the stability. Recommendations for development of such protocols are given in Annex E.

6.4.2 Repeatability

Set up the instrument adequately, select the proper settings for operating conditions and allow all parts sufficient warm-up time.

Follow the measurement protocol given for the reference material.

Perform at least three consecutive measurements with the same dispersed test portion or dispersed single shot samples at an adequate sample concentration and signal integration period to allow a sufficient number of particles to be analysed (see ISO 14488). Calculate the mean and CV for the x_{10}, x_{50}, x_{90}, and other eventual percentile size values of interest in the range x_{10} to x_{90}. Report all details of the operation and its results properly.

An instrument is considered to comply with this International Standard if the CV for the distribution, e.g. the median size, x_{50}, does not exceed 3 %. Values at the sides of the distribution, e.g. x_{10} and x_{90}, should have a CV not exceeding 5 %. Below 10 µm, these maximum values should be doubled.

For well-functioning instruments, well-trained operators, well-behaved samples and good procedures, a better precision can be met, viz. better than about 0,5 % and 1 %, for characteristic sizes above and below 1 µm respectively.

If a larger CV value is obtained, check all potential error sources (see 6.6) and/or seek expert advice.

6.4.3 Reproducibility

Reproducibility tests shall follow the same procedures and protocol as repeatability. Even then, a CV larger than that of repeatability may be expected due to differences in procedures for sampling or dispersion or between analysts or instruments. The certification for the reference material contains information about the acceptable error for that material.

6.5 Accuracy

6.5.1 General

Laser diffraction systems are based on first principles, though with idealized particle properties (cf. Annex A). Thus, calibration by the user is not required (see 6.5.2).

Confirm the correct operation of the instrument by a qualification procedure (6.5.2. to 6.5.5).

6.5.2 Reference materials

For certification for accuracy, use traceable spherical certified reference materials (CRMs), e.g. particles that are traceable and certified to or by national standards institutions. This ensures that the instrument is correctly functioning as an analytical platform. Should any modifications or major maintenance be required, again use traceable CRMs to ensure the accuracy of the instruments.

For accuracy, traceable spherical CRMs are required, which are declared suitable for the laser diffraction technique and consist of a known distribution having a range of spherical particles with an x_{90}/x_{10} ratio of at least 1,5 and also having common density and optical properties. They should be certified by or under the auspices of an (inter)national standards institution to percentage mass fraction or percentage volume fraction by an absolute and traceable technique. The real and imaginary parts of the complex refractive index should be specified for the material if the Mie theory is to be applied in data analysis. It is essential that a robust procedure is available that describes sub-sampling, sample dispersion and laser diffraction measurement in full detail. This procedure shall be followed in its entirety and the title and version number reported.

Once the instrument performance has been compared to CRMs and accuracy has been demonstrated to be within acceptable limits, or if it has been deemed that the accuracy test is not mandated, instrument qualification can then be demonstrated with reference materials that do not have traceability to an (inter)national standards institution(s). Additionally, they do not have to be spherical. Reference materials containing non-spherical particles, which are declared suitable for the laser diffraction technique, may also be used. The particle distribution should consist of a known range of particles with an x_{90}/x_{10} ratio of at least 2. For non-spherical materials, the aspect ratio shall be restricted to 1:3. The PSD shall consist of documented values coming from laser diffraction analyses in one or more instrument types according to an agreed, detailed operational procedure which has been shown to yield adequate and stable results over time. If the reference values come from other methods than laser diffraction, a significant bias may result, for reasons previously stated.

For single shot analysis, use the full contents of the container. If sub-sampling is necessary, exercise due care while using a method that has been proven to yield adequate results (see ISO 14488).

If a protocol for sampling, dispersion or measurement is not available, the procedure that is used shall be reported with the final results (see also Annex E).

6.5.3 Instrument preparation

Follow the instructions and advice given in the instrument manual for preparation of the instrument. The functionality of the unit shall have passed the supplying manufacturer's operational qualification (OQ) test or equivalent, with the date and result of the test recorded. The appropriate lens system and cell assembly shall be installed. The instrument should be clean. Particle-free dispersion gas or liquid should be used during measurement.

The analysis mode, if selectable, shall be suitable for this class of measurement. Set sufficient measurement duration and gas rate or pumping speed for transport of particles. The blank (background) measurement shall give results within the required range of values (refer to the manufacturer's specifications), in order to ensure absence of air bubbles and contamination.

A well-trained operator shall prepare the instrument and perform the qualification test.

The result presentation software shall preferably be set so as to produce an output of the cumulative undersize distribution in accordance with ISO 9276-1.

6.5.4 Qualification test

The test protocol of the CRM shall be followed during the measurement.

Single shot analysis may be applied. If sub-sampling is necessary, analysis of a single sample is only allowed if the procedure for sub-sampling has proven to give good repeatability. Otherwise, analysis of at least three test portions is preferred, for which the average results shall be used.

The sample loading shall achieve obscuration/transmission values specified in the operational procedure.

The measurement period shall be sufficiently long to obtain statistically representative results for the particulate sample.

It is preferred that a live display of light-scattering pattern or obscuration values be made available. All values should be without significant fluctuation or sudden changes.

6.5.5 Qualification acceptance

The 95 % tolerance limits stated for each size value of the CRM specification form a set of maximum and minimum values that define the stated parameter.

The qualification test shall be accepted as fulfilling the requirements of this International Standard if the resulting measured particle size distribution achieves the following criteria:

a) the reported values of the cumulative undersize distribution between the 10th and 30th percentiles do not exceed the quoted maximum or minimum values for the reference material over this percentile range by more than 3 % relative;

b) the reported values of the cumulative undersize distribution between the 30th and 70th percentiles do not exceed the quoted maximum or minimum values for the reference material over this percentile range by more than 2,5 % relative;

c) the reported values of the cumulative undersize distribution between the 70th and 90th percentiles do not exceed the quoted maximum or minimum values for the reference material over this percentile range by more than 4 % relative.

If a larger deviation is obtained, check all potential error sources (see 6.6) and/or seek expert advice.

If a higher standard of accuracy is required for any reason, then a CRM should be chosen with a narrow confidence interval, and a total protocol for sampling, dispersion and measurement should be used that guarantees minimum deviations.

For non-CRMs (both spherical and non-spherical), acceptance criteria shall be provided by the supplier and shall meet the above criteria with respect to documentation, stability, and reproducibility.

6.6 Error sources and diagnosis

6.6.1 Systematic measurement errors (bias) may arise from improper sample preparation, departure from the theoretical assumptions for the particulate material, improper operation or functioning of the instrument and/or data uncertainties.

6.6.2 Errors made in sample preparation are often the largest contributor to the total error and can be attributed to the following causes.

- *Improper sampling technique*, leading to a non-representative sample in the measurement zone. This type of error is especially significant when using an inadequate sample splitting technique in the case of a large batch of free flowing material having a wide size distribution. Errors can also be due to selective transport within the instrument. For example, application of too low a pumping speed may lead to sedimentation of the larger particles in the pumping circuit. In a dry measurement, inappropriate use of a flow system may lead to loss of large particles from the system prior to measurement.
- *Incomplete deagglomeration of particles*, due to an improper dispersion procedure (liquid, dispersant, sonication).
- *Comminution of particles* by mechanical forces during dispersion (e.g. sonication in a wet measurement or excessive differential pressure and/or collisions with walls in a dry measurement). These effects are always more obvious for high-aspect-ratio and fragile/friable particles.
- Swelling, re-agglomeration, dissolution or evaporation of particles/droplets before or during measurement.
- *Inclusion of air bubbles* due to foaming dispersants and/or vigorous stirring.
- *Scattering from differences in refractive index in the dispersing liquid or gas* due to temperature fluctuations, generated, for example, by evaporation of the dispersing liquid or presence of an external heat source.

6.6.3 Another main source for bias arises from departure from the theoretical assumptions for the particulate material. Again, the errors can come from different sources.

- *Asphericity.* Most particles in real life do not fulfil the assumption of sphericity. The scattering cross-sections of non-spherical particles are influenced by the orientation of the particles with respect to the light source. It is assumed that the particles are presented to the incident light in all possible orientations, which is not always true, especially in the case of particles having a large aspect ratio. Often, such particles have a preferred orientation.

- *Surface roughness*. The particle surface may be rough instead of smooth. This causes diffuse light scattering at the boundary and loss of light due to random scattering, which often has an influence similar to absorption of light within the particle.
- *Optical heterogeneity*. The particles may be optically heterogeneous, as is the case for agglomerated or porous particles, or mixtures of different compositions. Crystalline materials can exhibit different refractive indices depending upon the axis of observation. Mie theory may have been used for mixtures of materials with different refractive indices. Only one refractive index is used in the model.
- *Fluorescence*. For some materials, absorbed light can be re-emitted as fluorescence. The angular spectrum of this fluorescent radiation is not related to particle size and, thus, disturbs the size distribution determination.
- *Inappropriate optical model or parameters*. Last but not least, an inappropriate optical model or parameters may have been chosen. For instance, if the Fraunhofer approximation is applied to samples containing an appreciable amount of small, transparent particles, a significant error in the quantity of particles ascribed to the smaller size classes can be reported (see Annex A). Generally, the choice of an incorrect model or its refractive index parameters also results in a (large) difference between the particulate concentrations as calculated by the instrument and from the known mass of sample and the volume of dispersion medium (see also 6.6.6).

6.6.4 Possible errors in the operational procedure or in the functioning of the instrument are:

a) presence of particles with diameters beyond the measuring range — in this case, adapt the measuring range (change the lens) and/or remove the coarse material, e.g. by pre-sieving;

b) introduction of the sample into the laser beam outside the working distance of the lens;

c) dirty lens(es) or windows of the measurement cell, which, thus, should be cleaned;

d) measurements conducted with excessive levels of background, due to reflections of laser light inside the instrument, too large a spread of the focused laser beam, overlap of a focused laser beam and scattered light detectors at small angles (misalignment), large temperature fluctuations in measurement volume or by intrusion of ambient lighting;

e) an improperly aligned optical system;

f) too high a particle concentration, causing multiple scattering;

g) too low a particle concentration, leading to too low a signal-to-noise ratio;

h) an inappropriate mathematical procedure for deconvolution of light intensity values to PSD for the elected measurement (check with the instrument manufacturer).

6.6.5 Failure to maintain good control on the points listed in 6.6.4 may also lead to errors of a random nature. Moreover, errors may result from:

a) insufficient measurement time or number of readouts of each detector output;

b) working at significantly different obscuration;

c) instrument imperfections, e.g. fluctuating laser intensity or noisy detector elements.

6.6.6 Errors of specific parts of the procedure may be diagnosed by the following operations.

- *Measurement of the intensity of the laser beam for at least 1 h during a blank experiment*. It should be stable within the limits given in the instruction manual.

- *Observation of the signals from all detector elements during a blank measurement* (provided that a live display of the signals is available). The background signal should show a smooth behaviour with only small positive or zero values. Negative or overload (100 %) readings may indicate faulty detector elements, defects in the electronics or dirty or scratched cell windows or lenses. Significant intensities on only localized detector elements are often caused by reflections at damaged optical surfaces of the lens, the cuvette or other parts illuminated by the laser beam.

  Excessive detector signal fluctuation in background measurement is often observed when using volatile solvents, whose evaporation causes thermal fluctuations that steer the laser beam onto the inner detector rings. The resultant effect is to produce a 'ghost' peak at the top of the measurement range of the instrument. Allowing the thermal fluctuations to die out by waiting a sufficient period of time is recommended for these cases. Application of ultrasound energy to a volatile liquid system produces a similar effect and again time must elapse to allow the fluctuations to die down.

- *Observation of the detector signals from repeated sample measurements*, calculating both mean values for each element and their standard deviations. A systematic comparison of the measured signals for all detector elements with previously measured ones can ensure consistency. Thus, an impression is gained of the precision and accuracy of these signals: large systematic differences or zero values for the signals may indicate a faulty detector element, a defect in the electronics, dirty windows or lenses, bad alignment, presence of air bubbles or a problem in the sampling and/or dispersion procedure.

- *Comparison of known particulate concentration with theoretical value.* For particle systems where all the particles have an aspect ratio of less than about 4:1 (see Reference [12]), a comparison of the known particulate concentration of the sample presented for measurement with that of the concentration value determined using the equation shown in Clause A.9 may provide guidance as to the appropriate choice of optical model and refractive index values.

For particle systems of low aspect ratio, small differences in the two concentration values can provide justification for the choice of optical model and the values of refractive index employed.

Investigate large differences between the known and predicted concentration values further.

- *Comparison for all detector elements of the measured light energy signals with the calculated values*, created after a best "fit" is obtained for the PSD. Large systematic differences indicate a faulty element, contamination or an inappropriate choice of optical model.

6.7 Resolution and sensitivity

The resolution of the PSD, i.e. the capability to differentiate between different particle sizes, and the sensitivity for small changes in the amounts of particles in a given size class are restricted by:

a) number, position and geometry of the detector elements;

b) signal-to-noise ratio;

c) fine structure in the measured scattering pattern;

d) detectable difference in scattering pattern between adjacent size classes;

e) actual size range of the particulate material;

f) adequacy of the optical model;

g) smoothing applied in the deconvolution procedure.

These factors prevent the laser diffraction technique in its usual form from being a high-resolution technique: the minimum width of each size class is usually about 1,1 to 2,0 (ratio of upper to lower limit of the size class). In specific cases a better resolution may be possible.

Moreover, the sensitivity to small amounts of large particles at the upper end of the size distribution is fairly low in the normal deconvolution procedure, which uses averaged detector signals.

Actual values for resolution and/or sensitivity for quality control reasons may be determined by using mixtures of known composition.

7 Reporting of results

Report results in accordance with ISO 9276-1, ISO 9276-2, and ISO 9276-4. Moreover, the information listed in this clause should be available in the form of a written protocol or reported so that the measurements can be readily repeated by different operators in different laboratories.

Characteristic size values below x_5 and above x_{95} are likely to be vulnerable to additional uncertainty and systematic error, as a result of sampling problems as well as by limitations of laser diffraction. Quotation of an x_{100} value by laser diffraction is specifically deprecated by this International Standard.

The report of results shall contain at least the following information:

a) sample:

   1) complete sample identification, such as chemical type, batch number and/or location, date and time of sampling, etc.,

   2) sampling procedure, i.e. sampling method and sample splitting procedure,

   3) sample pre-treatment (optional), e.g. pre-sieving, type and conditions,

   4) amount of sample,

   5) date of analysis;

b) dispersion:

   1) for dry dispersion:

      i) specific details of dispersing device, e.g. diameter of delivery tube, primary pressure,

      ii) type of dosing/feeding device,

      iii) dosing rate,

      iv) dispersion pressure;

   2) for wet dispersion:

      i) dispersion liquid: identification, volume and, if necessary, temperature,

      ii) dispersant(s): type and concentration,

      iii) sonication: type of unit, frequency (energy), duration and pause before starting measurement,

      iv) pump speed,

      v) optical pathlength;

c) laser diffraction measurement:

   1) instrument type and number,

2) software version,

3) volume of dispersion unit,

4) optical arrangement applied (e.g. focal length of lens),

5) date and time of last alignment,

6) date of last qualification test,

7) date and time of measurement,

8) optical concentration/obscuration,

9) trigger thresholds for start/stop conditions (if applied),

10) threshold for acquisition of valid data (if applied),

11) type of light-scattering model applied,

12) real and imaginary part of complex refractive index, if the Mie theory is applied,

13) real part of the refractive index of the fluid employed,

14) (optional) fit parameter resulting from deconvolution (e.g. log difference, chi-squared, percent residual);

d) analyst identification:

   1) name and address of laboratory,

   2) operator's name or initials.

Annex A
(informative)

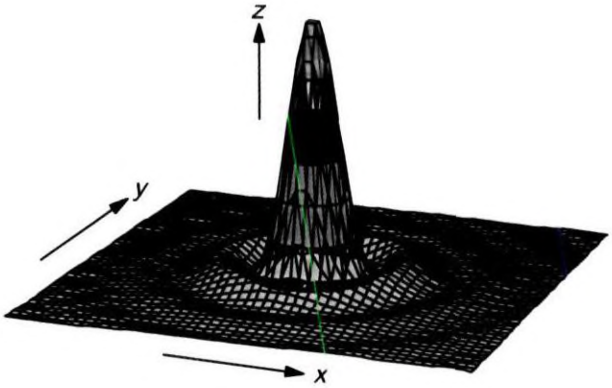
Theoretical background of laser diffraction

A.1 Introduction

Four types of interaction between light and a particle influence laser diffraction measurements (References [2] to [8], [11], [17]):

- diffraction at the contour of the particle (Fraunhofer diffraction);
- reflection at the boundary of a particle, both outside and inside the particle;
- refraction at the boundary of a particle coming from medium to particle and vice versa;
- absorption inside the particle.

These interactions lead to interference phenomena, which cause a characteristic pattern of scattered light intensities versus scattering angle (scattering pattern) as well as reduction of the incident light intensity (extinction). Both scattering pattern and extinction are dependent on the size, shape and optical properties (refractive index) of the particle. Thus, they form the basis for particle size analysis by laser diffraction.



Key

x detector, x-axis

y detector, y-axis

z relative intensity

Refractive index of the medium, n_{H_2O} = 1,33; wavelength, λ = 633 nm.

The particle refractive index is given by $\underline{n}_p$ = 1,59 − 0,0 i.

Figure A.1 — Light scattering pattern for a 5 µm sphere

As an example, Figure A.1 gives the scattering pattern of a 5 µm sphere. It clearly shows the characteristics of the scattering pattern of single particles:

a) the highest intensity is in the forward direction and the intensity gradually decreases towards larger scattering angles;

b) there are large differences in light intensities, with characteristic maxima and minima at different angles in relation to particle size;

c) there is circular symmetry in the scattering pattern of spherical particles — such symmetry is not present in the patterns of irregular particles at a single orientation;

d) the characteristic scattering patterns form the basis for application of the laser diffraction technique for measurement of particle size. In laser diffraction, a PSD is formed for an ensemble of particles passing through a measurement zone. Thus, the light scattered by a single spherical particle has to be extended to an ensemble of particles. This is possible provided that

    1) each particle scatters as an independent entity, i.e. there is no significant multiple scattering, which means that particle concentration should be low, and

    2) there is no optical interference between the scattered radiation from different particles; this is satisfied if all particles move randomly with respect to each other and if the overall scattering pattern is sampled many times.

A.2 Extinction

For particles that are very large compared with the illuminating wavelength, the quantity of light extinguished from the incident beam is equal to twice the quantity of light that is incident on the geometrical cross-section of the particle. This is the case when the extinction is measured at a significant distance from the particle, in the so-called "far field".

Reference [11] gives an explanation for the apparent paradox of the factor two. Reference [11] reasons that one unit of light is removed from the incident beam by the geometric cross-section by absorption or reflection and that an equal quantity is removed from it by diffraction, provided that the observation is made at great distance (in the 'far field'). This means that the scattering efficiency, expressed as the ratio of scattering cross-section and geometric cross-section, equals 2 for these large particles.

When the wavelength of illumination can no longer be considered as small in comparison to the size of the particle, the quantity of light extinguished is no longer equal to twice the geometrical cross-section of the particle, as illustrated in Figure A.2.

In general, the quantity of light extinguished by a particle in a beam of light depends upon:

a) particle size (scattering cross-section);

b) refractive index relative to the medium in which the particle is embedded;

c) wavelength of the illuminating source;

d) particle shape;

e) aperture angle.

The refractive index value of particles ($\underline{n}_p = n_p - k_p i$) is a complex number with a real, n_p, and imaginary term, $k_p i$.

EXAMPLE Polystyrene 'latex' particles have $\underline{n}_p = 1{,}59 - 0{,}0\,i$. The zero imaginary part indicates that they are non-absorbing. The white, milky appearance of concentrated suspensions is due to a degree of multiple scattering at all visible wavelengths.

The absorption coefficient, k_p, is usually provided as a positive number, the negative sign is included in the definition of $\underline{n}_\text{p}$. The refractive index of non-absorbing dispersion media contains only a real part. Some information on refractive index values is given in Annex D. The real part can be established by direct measurement using one of several techniques (Reference [21]). The determination of the imaginary part is more problematic.

The imaginary part might be considered as apparent absorption where light energy is dissipated as heat. In addition, at irregular particle boundaries some light may well be lost due to total internal reflection. This too may be included in the imaginary part of the refractive index by an apparent value of k_p of approximately 0,01 to 0,03.

The simplification that k_p relates exclusively to absorption may be misleading for some materials. Check the validity of assuming a small value of k_p to explain an apparent absorption for the relevant material system; the use of an apparent k_p has to be clearly stated in the measurement report.

A.3 Scattering

The quantity of scattered light emanates at refractive index boundaries or gradients. Therefore, the relative refractive index, m_rel, of particle and dispersion medium is decisive in determining the quantity of light scattering that occurs. If the particle and the medium have the same refractive index, they are said to be index-matched and no scattering occurs.

In laser diffraction, the understanding of how light is scattered by particles is decisive for the determination of particle size and quantity. Use is made of:

a) angular dependence;

b) amplitude dependence;

c) wavelength dependence;

d) polarization influence.

These properties are sometimes taken in isolation and sometimes in combination with the effect equipment has on them.

The quantity of light scattered by large spherical particles is proportional to their geometric cross-section.

The use of precise scattering from ensembles of irregular particles has yet to be fully implemented and some simplification is called for.

The property of the sphere is utilized as being a shape that can be fully characterized by a single value, namely its diameter. Present laser diffraction instruments report their size distributions based upon scattering patterns deduced for spheres. The equivalent sphere values for irregular particles are *not* comparable to those of other techniques. Each irregular particle may present itself in different orientations and, hence, with different cross-sections having different scattering features. Consequently, the measurement result is a distribution of spherical particles that 'fit' with the light scattered from the irregular shaped objects. ISO 9276-1 adopts the convention that the diameter of the equivalent sphere is described as x.

For large particles, the scattered light increases in proportion to x^2. For particles very much smaller than the wavelength (typically $x < \lambda/10$; the Rayleigh region), the light scattered is proportional to x^6.

A.4 Light-scattering theories (References [2], [4], [5], [11])

The interpretation of laser diffraction "spectra" to PSDs depends on two major operations. The first requires that mathematical models be created on how homogeneous particles scatter light. The second involves the deconvolution of the measured scattering pattern into a PSD.

The angular intensity distribution of unpolarized light scattered by a single, optically homogeneous spherical particle, $I(\theta)$ can be written as

$$I(\theta)=\frac{I_0}{2\,k^2\,l_a^2}\left\{\left[S_1(\theta)\right]^2+\left[S_2(\theta)\right]^2\right\} \tag{A.1}$$

where

k is the wavenumber in the medium;

l_a is the distance from scattering object to detector;

I_0 is the intensity of the incident unpolarized light;

$S_1(\theta)$, $S_2(\theta)$ are dimensionless, complex functions defined in general scattering theory, describing the change of amplitude in the perpendicular and the parallel polarized light respectively, as a function of angle θ with respect to the forward direction.

In 1908 Gustav Mie described the light-scattering properties of homogeneous spheres of known optical properties, when illuminated by an infinite plane wave of known wavelength, by solving Maxwell's equations for defined boundary conditions. In this way, he solved the complex functions $S_1(\theta)$ and $S_2(\theta)$. This Mie theory provides a rigorous solution that is valid for all sizes of spheres (References [5], [11]). When using this theory, it is assumed that:

a) all particles are optically homogeneous, isotropic, and spherical (although some special or regular shapes can be considered as well, i.e. coated spheres);

b) the particle is illuminated by a plane wave of known wavelength;

c) the refractive index of the particle, both real and imaginary, and that of the medium it is dispersed in are known;

d) the particles have no surface charges and no surface currents.

The scattering pattern of particles can be predicted over the full 360°, together with the amplitude, wavelength and polarization dependence of scattering. Computer algorithms have been developed (Reference [4]) in order to allow computation of these functions and, thus, of $I(\theta)$.

To exploit this theory to its full capacity, the optical properties of the system must be known, i.e. the complex refractive index (including both the real and the imaginary part) of the particle and the (real) refractive index of the dispersion medium. It should be noted that this knowledge may not be readily available: especially the imaginary (absorptive) part. This imaginary part is often strongly dependent on the wavelength of the light and is often given a finite value in order to account for specific surface structure of the particles, e.g. surface roughness. Annex D lists refractive index values for a large variety of liquids and solids (without the surface structure effects).

The Fraunhofer approximation was the first optical model employed for particle size measurement. It was formulated by considering the fraction of a plane wave of known wavelength that passed through an aperture in a thin metal plate. Using Babinet's principle, it can be shown that the same scattering signature is obtained from a totally opaque disk of the same diameter. In its present application, it is assumed that:

1) the particle absorbs the light completely — only diffraction at the contour of the particle is considered;

2) all particles have a circular cross-section (although other, regular shapes can also be taken into account);

3) the particle is illuminated by a plane wave of known wavelength;

4) only diffraction in the near-forward direction is considered (i.e. θ is small);

5) $x \gg \lambda$.

For small particles, e.g. beyond the Fraunhofer approximation, an accurate knowledge of the optical properties of the material is essential to avoid errors in calculating the PSD.

The Fraunhofer approximation does not predict polarization influence or account for light transmission through the particle. It does not require knowledge of particle refractive index.

For these approximations:

$$S_1^2 = S_2^2 = \alpha^4 \left[\frac{J_1(\alpha \sin \theta)}{\alpha \sin \theta} \right]^2$$

Thus, the general Equation (A.1) simplifies to:

$$I(\theta) = \frac{I_0}{k^2 l_a^2} \alpha^4 \left[\frac{J_1(\alpha \sin \theta)}{\alpha \sin \theta} \right]^2 \qquad \text{(A.2)}$$

where

α is a dimensionless size parameter, $\alpha = \pi x n_m / \lambda$;

J_1 is the Bessel function of the first kind of order unity.

NOTE An extra factor, $(1 + \cos^2\theta)/2$, is often added to the right-hand side of Equation (A.2) in order to extend it to larger angles (Reference [12]).

The advantage of Equation (A.2) is that it is relatively simple. It does not require any knowledge of the optical properties of the material. Therefore, it is often applied to products for which the optical properties are unknown or variable or which are mixtures of different materials. In practice, the Fraunhofer approximation is valid for large particles (diameter much larger than the wavelength of the light, or $\alpha \gg 1$). For small particles, (i.e. beyond the Fraunhofer approximation) an understanding of the optical properties of the material is essential to avoid errors in predicting particle size.

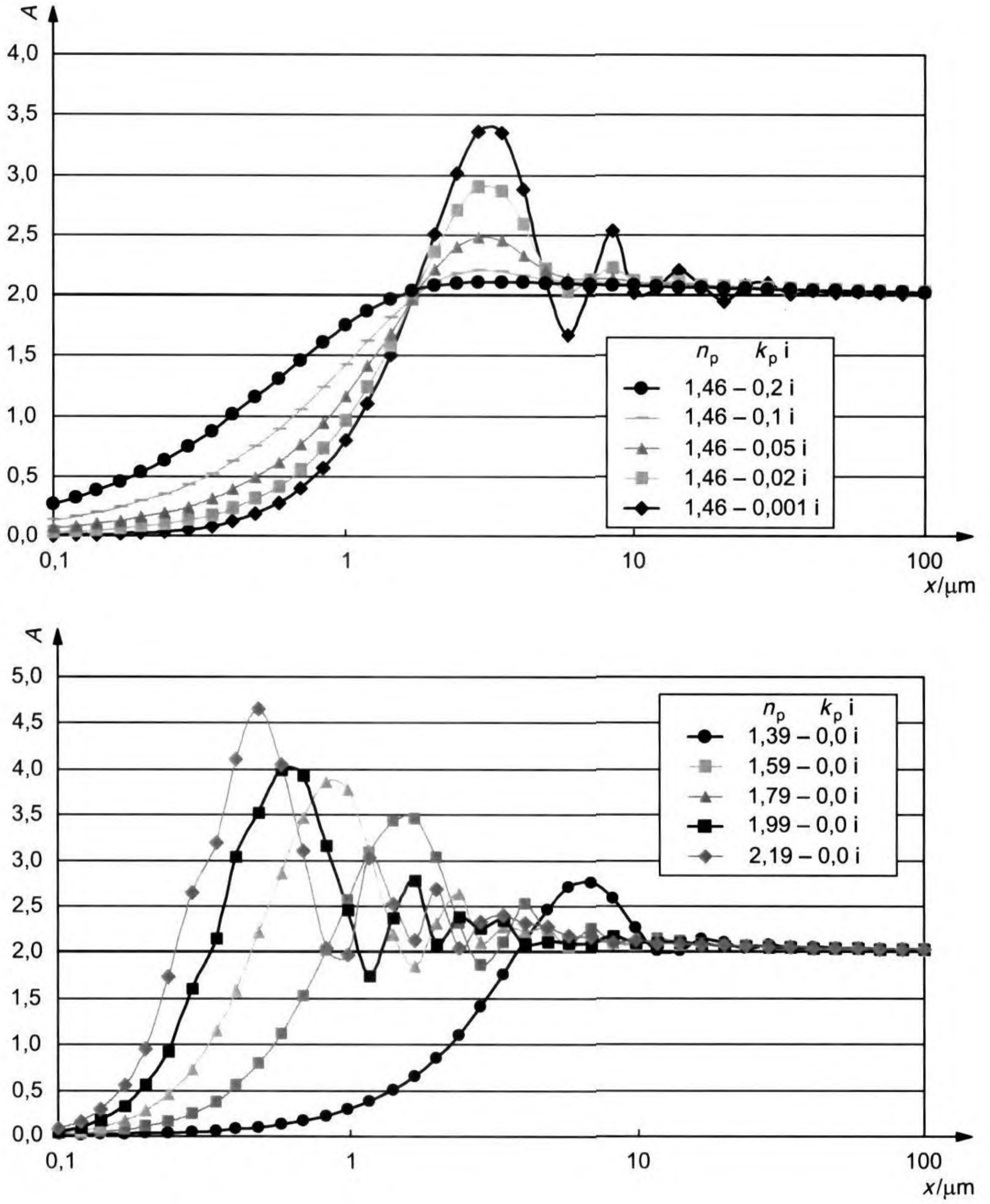
A.5 Model selection

In modern instruments, either the Mie or Fraunhofer models can be used (instrument dependent) by the operator to calculate the size of spherical particles. As indicated above, the two theories differ principally for medium and small particles. Knowledge of the optical properties of the material to be measured is needed to allow for the selection of an appropriate optical model. For most particles larger than about 50 µm with relative refractive index greater than 1,2, such knowledge may not be necessary, as the Mie theory and Fraunhofer approximation give similar results.

Mie theory provides a rigorous solution for the complete scattering pattern that is valid for all sizes of spheres, provided that they are homogeneous and isotropic, and their optical properties are known. Also, amplitude, wavelength and polarization dependence of scattering can be calculated.

The Fraunhofer approximation requires that particles are large in comparison to the wavelength of light and/or opaque. It does not make use of any knowledge of the optical properties of the material. Its application is limited to the near-forward direction (small scattering angles). Moreover, it does not predict polarization nor account for light transmission through the particle.

Figure A.2 compares the extinction efficiencies according to Mie and Fraunhofer models for both transparent and absorbing particles.



Key

A	extinction efficiency
k_p	coefficient of the imaginary part of the refractive index
n_p	real part of the refractive index
x	particle size

Refractive index of the medium, $n_{H_2O} = 1{,}33$; wavelength, $\lambda = 633$ nm (Fraunhofer assumes an extinction efficiency of 2 for all particle sizes).

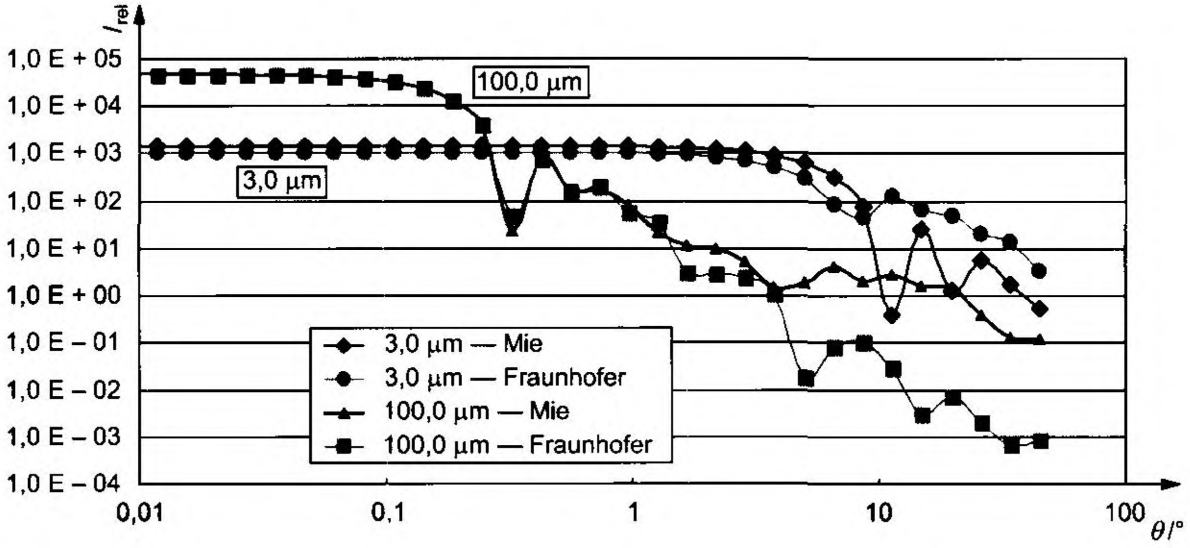
The complex refractive index is given by $\underline{n}_p = n_p - k_p$ i.

Figure A.2 — Extinction efficiencies in relation to particle size and refractive index (Mie model)

These figures show good agreement between the Mie and Fraunhofer theories for transparent particles larger than about 50 µm and for opaque particles ($k_p > 0,2$) larger than about 2 µm. In the range 2 µm to 50 µm, agreement depends on the relative real part and imaginary part of the refractive index. Where both theories do not agree, Mie theory shows the strong fluctuations that exist in the extinction efficiency in the size range below about 50 µm (size depending on complex refractive index). Both figures also indicate a rapid fall of the extinction efficiency in the sub-micrometre region.

Figure A.2 illustrates that for particles smaller than approx. 50 µm, the error in the quantity of particles predicted depends upon the optical properties of the material being measured.

The scattering patterns show similar regions of agreement and disagreement between the two theories with respect to particle size and refractive index. Figure A.3 compares the Mie and Fraunhofer predictions for the scattering patterns for 3 µm and 100 µm transparent particles.



Key

θ scattering angle

I_{rel} relative intensity

Refractive index of the medium, $n_{H_2O} = 1,33$; wavelength, $\lambda = 633$ nm.

The particle refractive index, $\underline{n}_p = 1,59 - 0,0$ i.

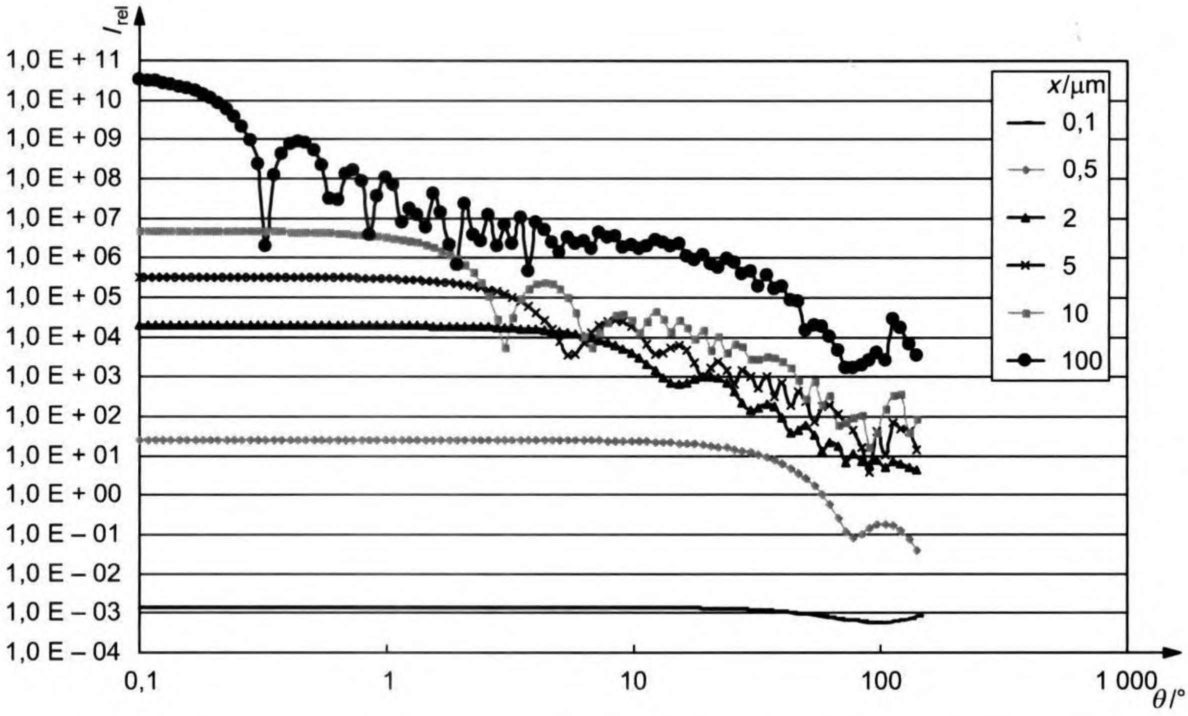
Figure A.3 — Comparison of scattering patterns of non-absorbing particles according to the Fraunhofer and Mie models

The choice between the two models may be guided by considering particle size, real refractive index, and absorption (imaginary part of refractive index). If all particles in the size distribution are larger than about 50 µm, then the Fraunhofer approximation and Mie theory usually provide very similar results. For particles in the size range of 2 µm to 50 µm, the degree of agreement between the two theories strongly depends on the values for the complex refractive index. Good agreement is usually obtained for opaque particles, dissimilar results for transparent particles. For smaller particles, the Mie theory offers a good general solution. In all cases where Mie theory is used, good values for the optical properties of the material in question need to be provided. Some study or further measurements may be required.

Guidance as to which theoretical model is the more realistic together with confirmation of the optical properties employed can be given through comparison of the computed concentration from the size distribution data with the true concentration. Large deviation indicates that either the optical model or the applied refractive index is incorrect. Moreover, other techniques (e.g. microscopy or sedimentation) can be employed to check for the existence of a significant proportion of small particles. Note, however, that a very large number of small particles is required to yield a significant volume in comparison to a single large particle and vice versa.

A.6 Scattered light detection

The intensity of scattered light with respect to the angle of observation for various single particle sizes is shown in Figure A.4.



Key

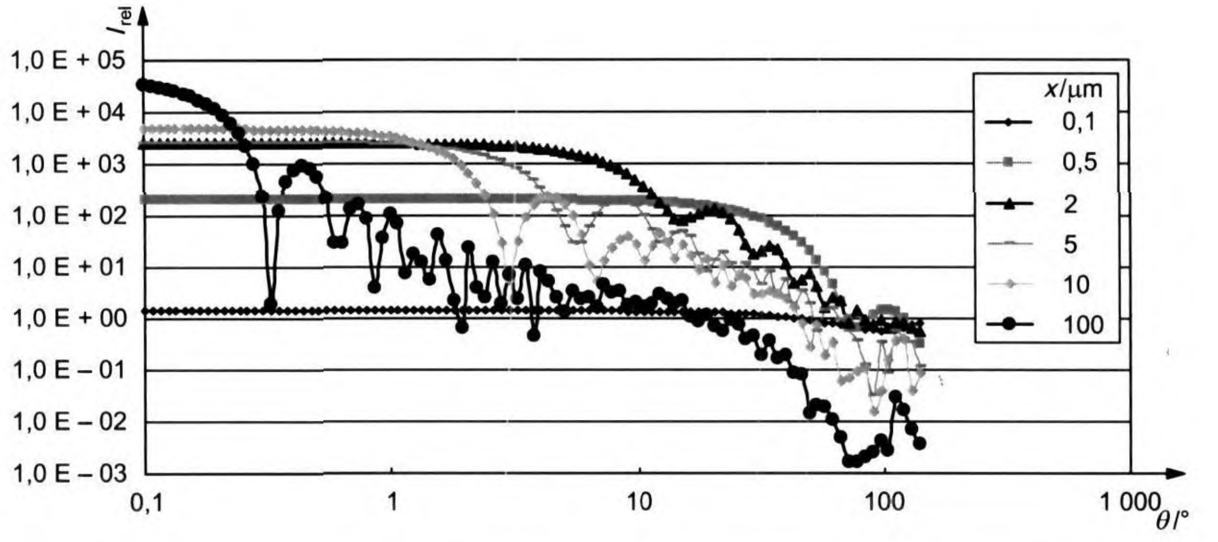
θ	scattering angle
I_{rel}	relative intensity
x	particle size

Refractive index of the medium, $n_m = 1{,}33$; wavelength, $\lambda = 633$ nm.

The particle refractive index, $\underline{n}_p = 1{,}59 - 0{,}0$ i.

Figure A.4 — Scattering intensity pattern for single particles in relation to size (Mie model)

The dynamic range of scattering amplitude between a single 0,1 µm particle and a single 100 µm particle is approximately 10^{13}. This dynamic range is too great for the detectors currently employed. It can be reduced by weighting particles by their volume, which is related to x^3. Thus, laser diffraction units are designed to respond to the volume of particles that have these sizes, as shown in Figure A.5.



Key

θ scattering angle

I_{rel} relative intensity

x particle size

Refractive index of the medium, $n_m = 1{,}33$; wavelength, $\lambda = 633$ nm.

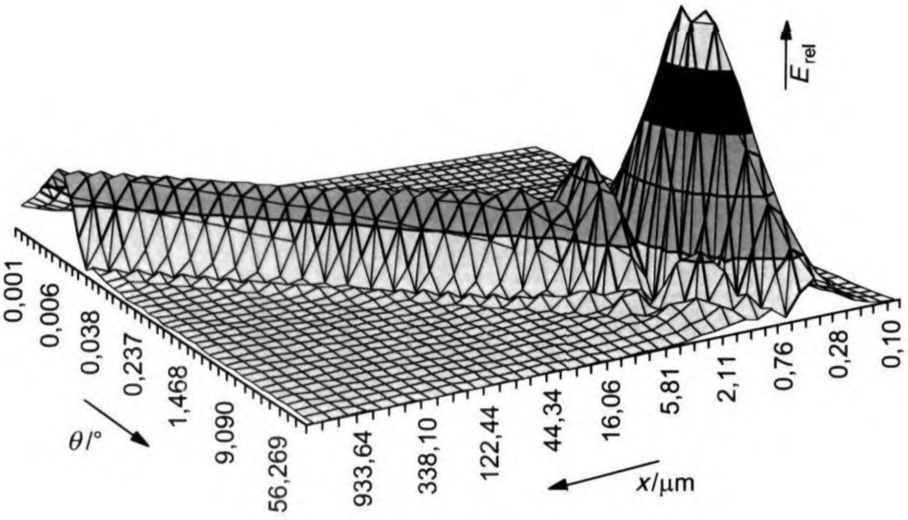
The particle refractive index, $\underline{n}_p = 1{,}59 - 0{,}0$ i.

Figure A.5 — Light intensity scattering patterns for equal particle volumes in relation to size (Mie model)

By using equal volumes of each size of particle, the dynamic range of scattering amplitudes is reduced to approximately 10^4 over the size range from 0,1 µm to 100 µm. This dynamic range may be further reduced by rigorous and careful detector design.

In view of the characteristic features of the scattering patterns, it is advantageous to sample the light intensities over the widest range of angles and, for fairly narrow size distributions, to employ an adequate number of detectors with respect to angle. On the other hand, the signal of each detector element is the product of the intensity of scattered light, the geometric area of the element, and its sensitivity. Consequently, any decrease of the geometric area leads to smaller signals and, thus, a lower signal-to-noise ratio. This is especially important at higher scattering angles, where the intensity of the scattered light is usually very low. In practice, this leads to some optimum situation for the number of detector elements, their size, and the angular range that they cover. Different designs have been implemented by instrument manufacturers.

The current output of a silicon light-sensitive detector is proportional to the intensity multiplied by the detector area. By arranging small detectors at low angles and higher relative area detectors at higher angles, a further reduction in dynamic range of detection can be achieved. For the larger scattering angles, the number of detectors per unit angle can be reduced substantially in comparison to the smaller angles, in relation to the information content for particle size. The current signal output of an optimum detector, which has a flat, horizontal response when plotted against angle for larger particles, is shown in Figure A.6.



Key

θ	scattering angle
E_{rel}	relative energy
x	particle size

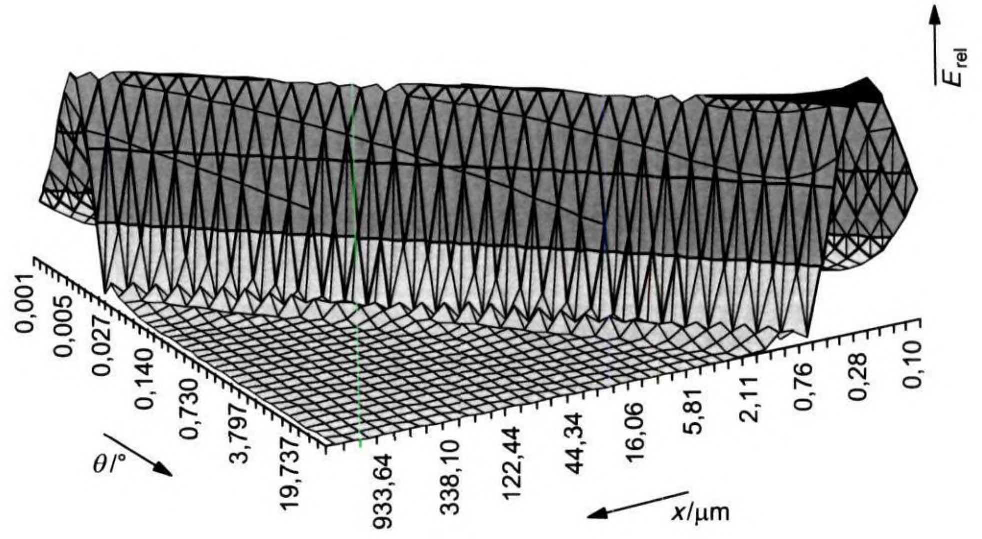
Refractive index of the medium, n_m = 1,33; wavelength, λ = 633 nm.

The particle refractive index, $\underline{n}_p$ = 1,59 – 0,0 i.

Figure A.6 — Scattering patterns for an optimum detector configuration against particle size for equal volumes of particles (Mie model)

For large particles, where the scattering cross-section remains in proportion to the geometric cross-section, equal energy values for equal volumes of particles are achieved. However, for the small particles, where the scattering cross-section becomes dependent upon the refractive index of the particles and their size, the constant values cannot be maintained. It can also be seen that the scattering power from sub-micrometre particles falls rapidly.

A graph of the light energy predicted by the Fraunhofer model for the same conditions, with the range of angles reduced to 30°, is shown in Figure A.7.



Key

θ scattering angle

E_{rel} relative energy

x particle size

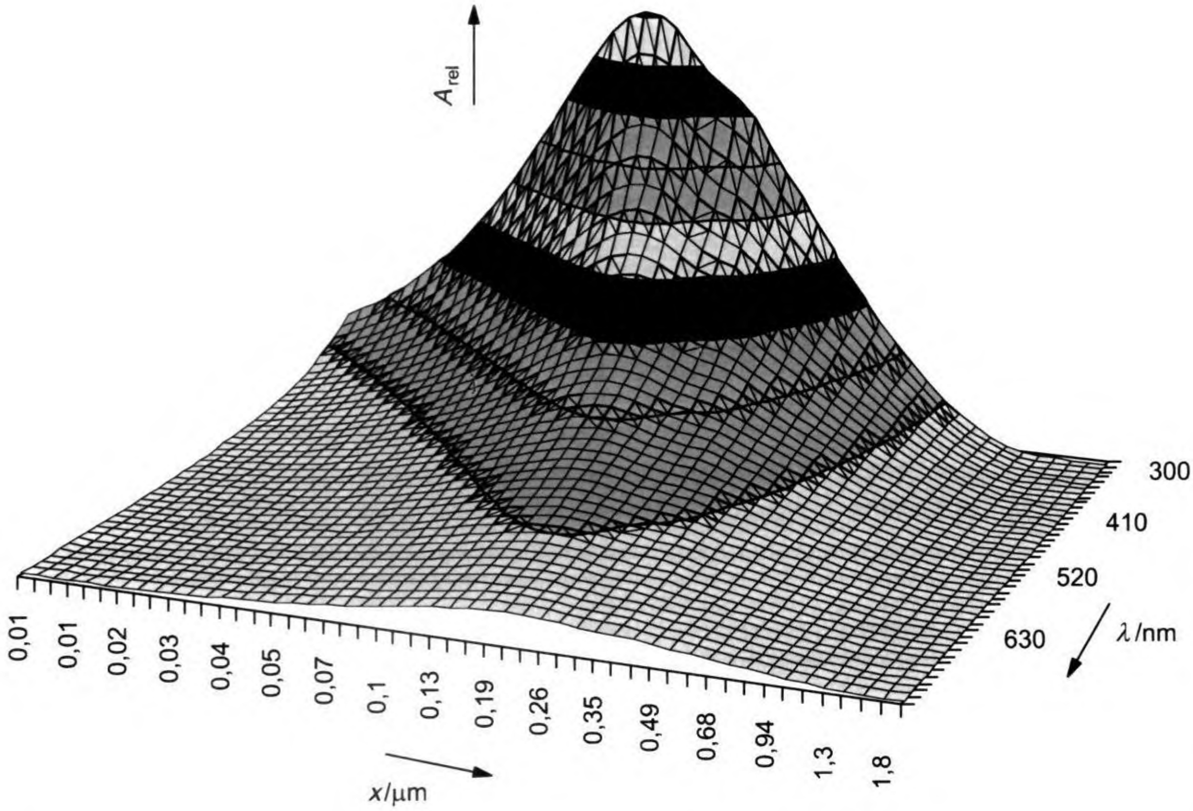
Figure A.7 — Scattering patterns for an optimum detector configuration against particle size for equal volumes of particles (Fraunhofer model)

Figures A.6 and A.7 illustrate regions of agreement and differences between Mie and Fraunhofer theory for large and small particles, respectively.

A.7 Wavelength dependence and polarization difference

Examination of the predicted light scattering from sub-micrometre particles shows that the angular dependence is weak below about 0,3 µm. In order to provide more data about these very small particles, additional information is desirable. This can be achieved by using additional light sources having another wavelength and/or by measuring differences of polarization and wavelength.

The light scattered from very small particles exhibits a strong dependence upon wavelength. Such scattering is inversely proportional to the fourth power of the wavelength, $1/\lambda^4$. Some implementations of laser diffraction make use of this phenomenon. An illustration of wavelength dependence (Mie derived) is illustrated in Figure A.8.



Key

λ wavelength

A_{rel} relative extinction

x particle size

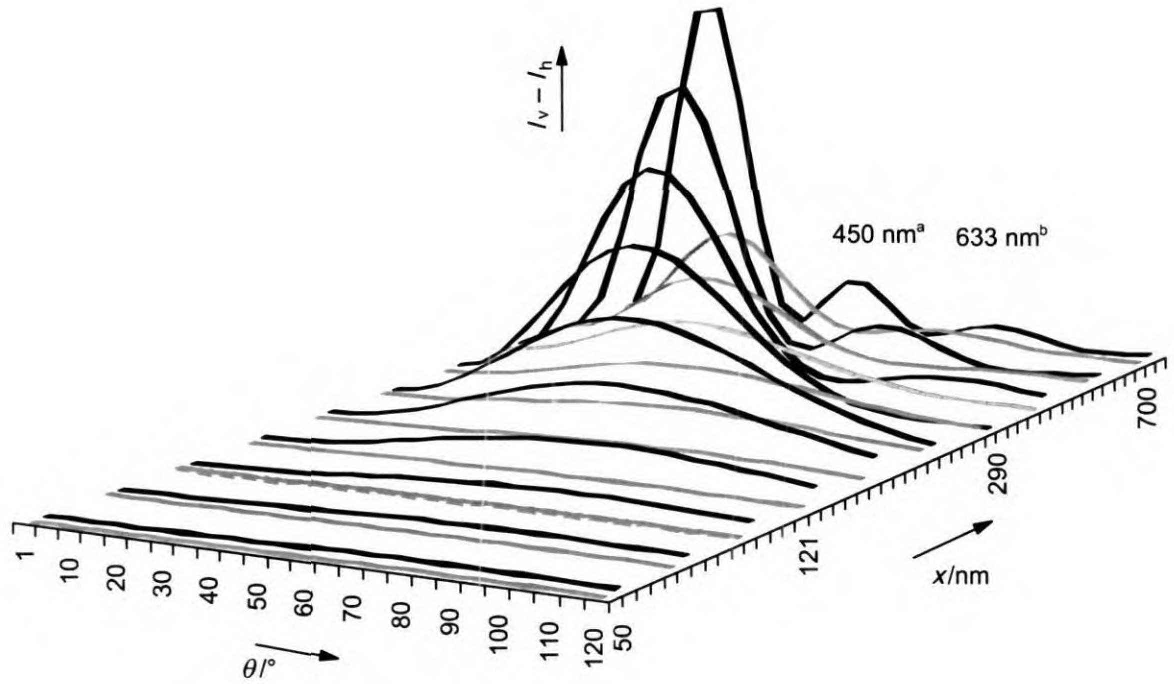
Refractive index of the medium, n_m = 1,33.

The particle refractive index, $\underline{n}_p$ = 1,59 – 0,0 i.

Figure A.8 — Wavelength dependence of extinction for equal volumes of different particle sizes in water

For sub-micrometre particles, the polarization of the scattered light in the parallel and perpendicular direction varies strongly with size. Also, there is a wavelength dependence of scattered light for small particles. The combined influence of polarization difference and wavelength is illustrated in Figure A.9.

This illustrates that observation angles of around 90° are the most significant and have strong wavelength dependence. However, the light scattered by such small particles remains very weak.



Key

θ	scattering angle
$I_v - I_h$	relative polarization intensity difference
x	particle size

[a] Black line.

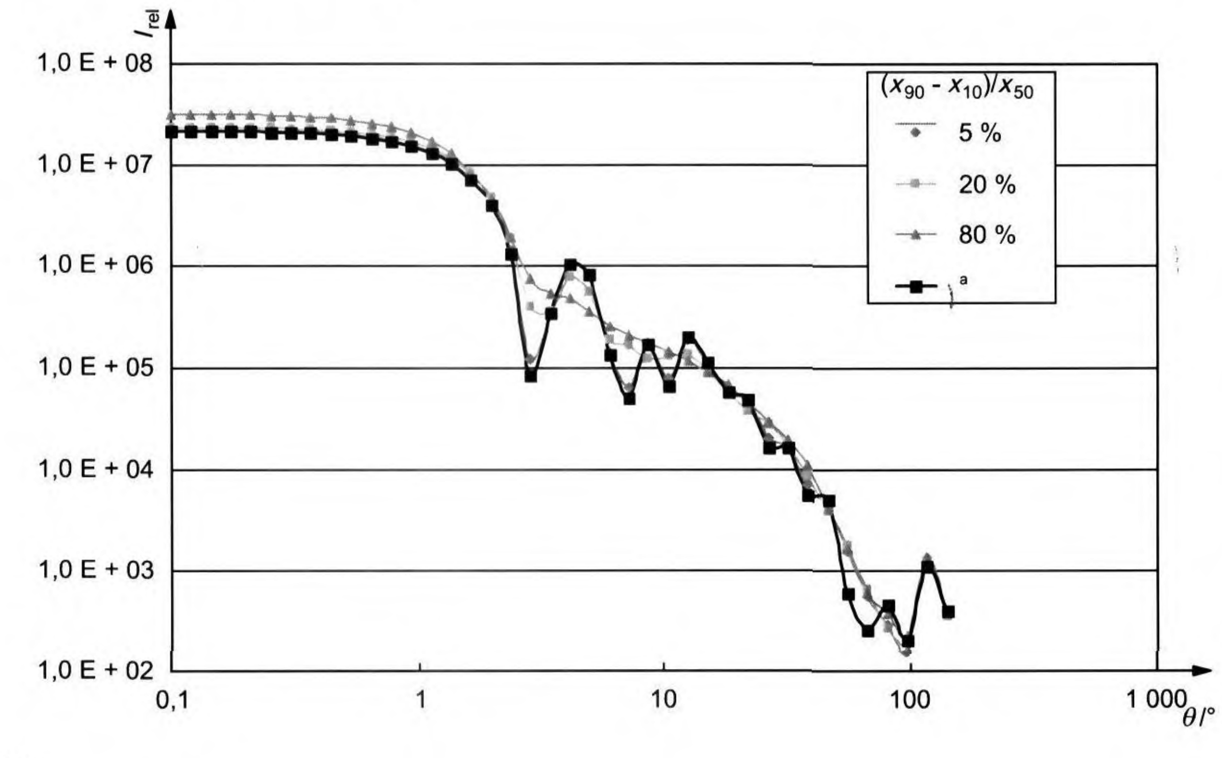
[b] Gray line.

Figure A.9 — Polarization difference plotted against scattering angle and particle size for light of wavelengths 450 nm and 633 nm

A.8 Scattering patterns for PSDs

Figure A.5 illustrates the characteristic features of the scattering signatures of mono-sized particles. The intensity curves show minima and maxima, the angular positions of which are mainly governed by particle size, wavelength and complex refractive index. The scattered light intensity for a unit volume of large particles at small angles is larger than that of the same volume of small particles. This is due to the scattered light energy for large particles being confined to a limited range of angles. Conversely, small particles scatter light to a much wider range of angles. During a measurement, generally only the relative changes of scattering intensities with respect to angle are important, since the absolute intensities are related to particulate concentration. Figures A.3 to A.5 show the general decrease of scattering intensity towards larger angles and the effects of the optical model or refractive index.

In practice, however, fairly wide size distributions are encountered. Figure A.10 shows the influence of size distribution width on scattering pattern for log-normal PSDs. It indicates that only mono-sized and very narrow PSDs show fine structure with maxima and minima in the scattering pattern. For somewhat broader size distributions, this fine structure is lost. Then, smoothing of the maxima and minima occurs, due to the strong dependence of their positions on particle size. This loss of fine structure for broad PSDs causes small errors in the detector signals which may lead to significant differences in such distributions. The effect of such errors is largely dependent on the mathematical procedure, including constraints and smoothing, used in the deconvolution (see also 6.3.1 and 6.7). It also demonstrates the merit of having detectors positioned to *capture the high angles of scattering.*



Key

θ	scattering angle
I_{rel}	relative intensity
$(x_{90} - x_{10})/x_{50}$	width of size distribution

Refractive index of the medium, $n_m = 1,33$; wavelength, $\lambda = 633$ nm.

The particle refractive index, $\underline{n}_p = 1,59 - 0,0$ i.

[a] Mono-size.

Figure A.10 — Influence of size distribution width on scattering pattern (log-normal size distributions around an x_{50} of 10 µm)

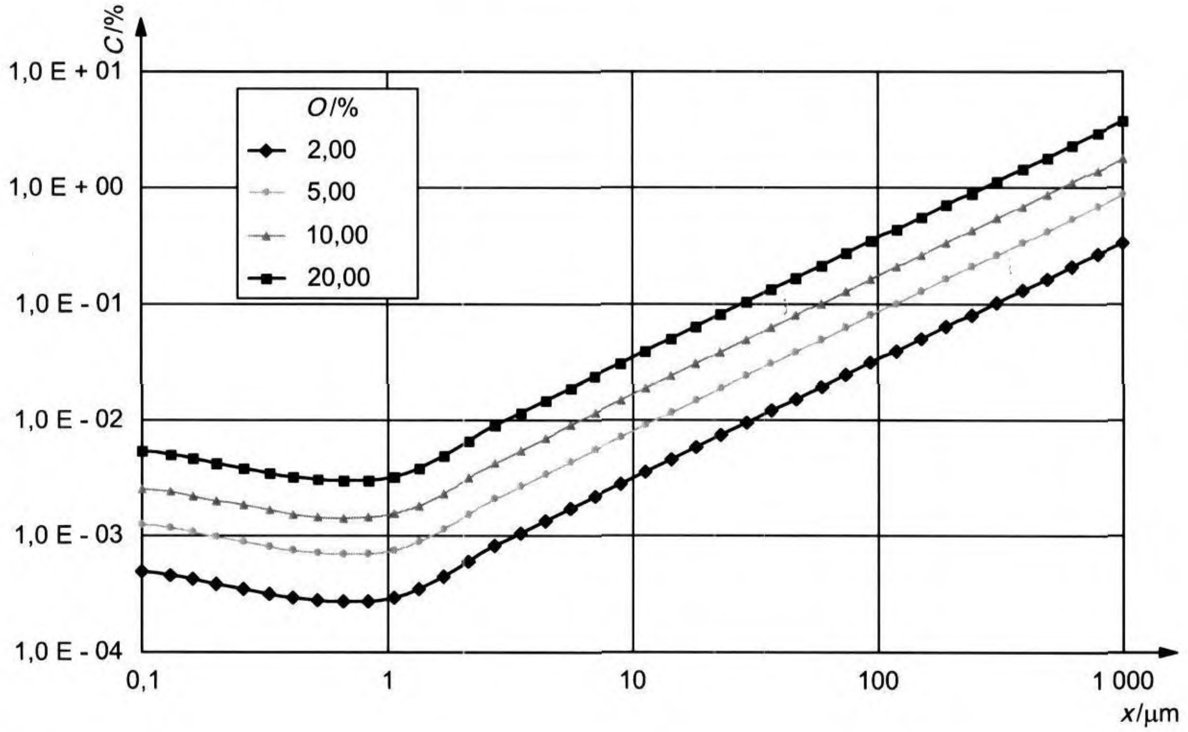
A.9 Concentration

The scattered light intensity from many particles rises in proportion with the number of particles that have that size. In the low concentration region this process is linear. However, at some point the concentration is such that a significant amount of the light scattered by individual particles is further scattered by neighbouring particles. The point at which this multiple scattering changes the size distribution in a significant way marks the maximum allowable particulate concentration for accurate size distribution determination.

In 6.2.4, it was noted that for the same volume of particles, the number of small particles is much larger than that of large particles. Therefore the concentration of the smallest particles in any distribution dominates the point of onset of multiple scattering.

Laser diffraction instruments are often provided with a measure of the attenuation of the incident laser beam due to the presence of particles within the measurement zone. This is referred to as either an obscuration or a transmission detector. Such detectors almost subtend 0° of scattering and, thus, may be regarded as a measured value of extinction.

The output of obscuration or transmission can be used to judge the concentration required to avoid significant multiple scattering effects.



Key

C particulate concentration

O obscuration

x particle size

Refractive index of the medium, $n_m = 1,33$; wavelength, $\lambda = 633$ nm; pathlength, $l_b = 2$ mm.

The particle refractive index, $\underline{n}_p = 1,59 - 0,1$ i.

Figure A.11 — Relation of particle size and concentration and its influence on obscuration (Mie calculation of A_i)

The plots shown in Figure A.11 illustrate the relation of particle size and concentration and its influence on obscuration. Its construction is based upon the Lambert-Beer law to give the particulate concentration, C:

$$C = \frac{-2 \ln (1 - O)}{3 l_b \sum_i A_i (\Delta Q_{3,i} / x_i)} \quad \text{(A.3)}$$

where

A_i is the extinction efficiency of class size, i;

l_b is the illuminated pathlength containing particles;

O is the obscuration;

x_i is the geometric mean particle size of class size, i;

$\Delta Q_{3,i}$ is the volume fraction within class size, i.

Any judgement about the concentration to be used to avoid the influence of multiple scattering shall be made with regard to the smallest sizes of particle present in any distribution. Consider also the optical pathlength being filled with particles. Refer to the instrument manual in this regard.

A.10 Data analysis

The prediction of scattering patterns is carried out for unit volume of particles in each size class of given width and for detector elements of given geometry. This is done by integration of $I(\theta)$ over the number of particles present per volume in each size class and over the geometry of each element. For a series of size classes and detector elements, this leads to a model matrix, which is specific for an instrument. It describes how unit volumes of each of n particle size classes would appear as a signal L_j at each of m detector elements:

$$\begin{bmatrix} L_1 \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ L_m \end{bmatrix} = \begin{bmatrix} M_{11} & \cdots & \cdots & M_{1n} \\ \vdots & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ M_{m1} & \cdots & \cdots & M_{mn} \end{bmatrix} * \begin{bmatrix} V_1 \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ V_n \end{bmatrix} \tag{A.4}$$

For example, the first row in the matrix (M_{11} ... M_{1n}) describes the signals for unit volumes of all n size classes on the first detector element, whereas the first column (M_{11} ... M_{m1}) gives the contributions of the first size class on each of the m detector elements. Similar matrices may be constructed for different wavelengths. In matrix notation this can be written as:

$$L = M * V \tag{A.5}$$

In this form, the set of detector signals is seen to be the result of a matrix multiplication of size distribution with the model matrix. In actual measurement practice, however, the inverse of this problem is required. The signals from all detector elements are measured, the computed model matrix is available in the instrument and the PSD is computed by means of a numerical inversion procedure:

$$V = M^{-1} * L \tag{A.6}$$

Equations such as (A.6) are described as ill-posed and ill-conditioned. Even the smallest errors due to measurement make direct inversion without constraint unviable. Therefore, a degree of constraint is necessary which varies from manufacturer to manufacturer dependent upon design and number of detectors, noise levels and experience. Failure to constrain the inversion adequately may lead to solutions of polydisperse distributions showing ripples in the histogram data. Serious lack of constraint can lead to zero or negative values and false modality. On the other hand, over-constraint leads to decreased resolution and widening of the actual PSDs.

A.11 Particle shape

Spherical particles show a scattering pattern with circular symmetry. This relation between particle shape and scattering pattern holds in general: scattering patterns exhibit the same (lack of) symmetry as the particles themselves. Some clear examples are given in Figure A.12, where circular, rectangular and irregular particles and their scattering patterns are shown.

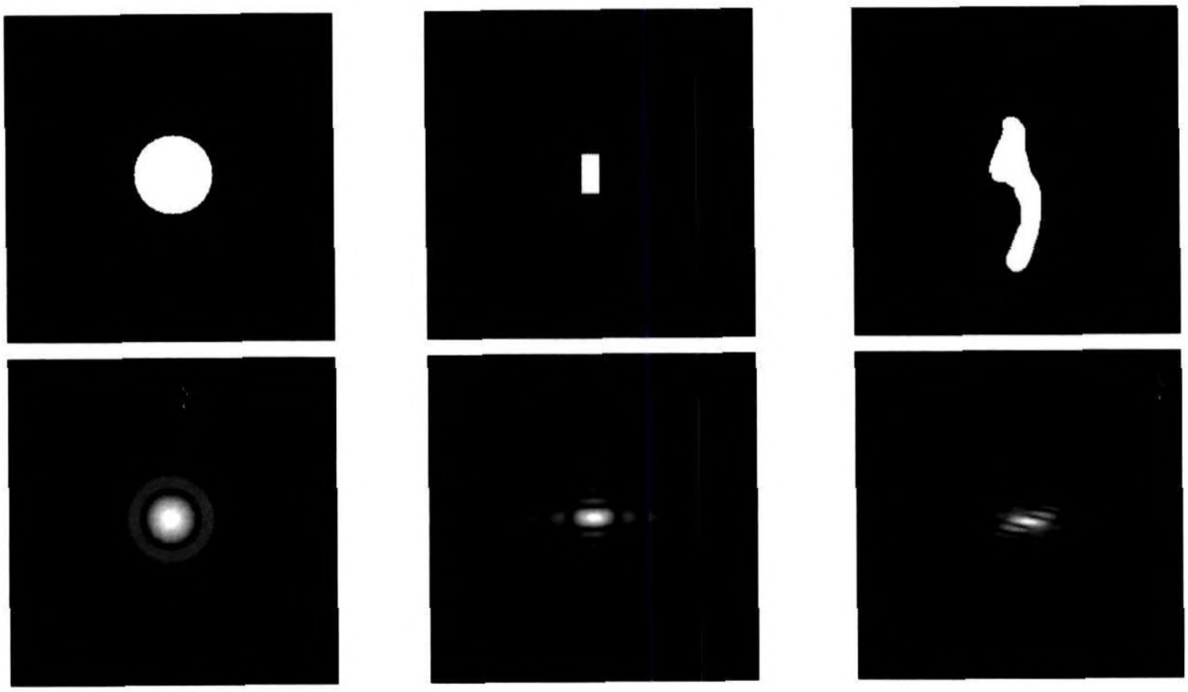


Figure A.12 — Circular, rectangular and irregular particles and their scattering patterns (simulated images)

Collectives of non-spherical particles are represented by mixtures of spheres that produce a similar scattering pattern. Their sizing result depends on:

a) aspect ratio of the particles;

b) flow conditions in the measurement zone;

c) orientation and geometry of the detector elements.

Particles having an aspect ratio of about 1 can be assumed to take random positions during measurement. For particles with an aspect ratio larger than about 5, the flow conditions in the measurement zone determine the possibilities to take all possible cross-sections. It has been shown that such particles in liquid dispersions usually have a preferred orientation in the measurement zone of laser diffraction instruments (Reference [3]). This holds especially for fibres and flakes. It results in a limited set of preferred cross-sections seen by the laser beam. Moreover, the corresponding scattering patterns do not have circular symmetry, as shown in Figure A.12. Thus, the geometry and orientation of the detector determine which part of these scattering patterns is measured and interpreted in terms of a PSD. Therefore, the sizing result for particles having large aspect ratios depends on the actual flow conditions in the measurement zone as well as on the type of detector (instrument) used.

This demonstrates the vital necessity of having a good quality microscope available in each facility engaged in particle sizing to facilitate the understanding and the interpretation of the PSD obtained.

Annex B
(informative)

Recommendations for instrument specifications

It is recommended that manufacturers of instruments provide specifications for laser diffraction instruments concerning the items listed in Clauses B.1 to B.10.

B.1 General

Power requirements

Mass

Dimensions

Specific requirements, e.g. temperature, humidity, vibration, safety, etc.

B.2 Light source(s)

Type; wavelength

Power output

Intensity stability (accepted level of fluctuation)

Parallel and/or convergent beam

Beam width/dimension(s) in sample

Polarization

Typical lifetime

B.3 Sample module

Sample pathlength in laser beam

Liquid pump rate, or particulate and air rate for dry dispersers

Sonication power/frequency

Volume of recirculation system and cell

Materials of system in contact with particles and dispersion liquids

Maximum particle size/density which can be dispersed/handled

B.4 Lens

Focal length(s)

Working distance

Whether fixed, or require changing

B.5 Detector

Number of elements

Indication of detector geometry and orientation (e.g. half or quarter rings, segments, etc.)

Alignment, automatic or manual

Information on calibration of detector elements

Indication for normal detector signals for blank experiments and their maximum allowable limits

Detector saturation indicators

B.6 Measurement

Typical measurement time

Minimum time between successive measurements

Typical particulate concentration range during measurement

B.7 Computer

Processor type; memory size

Speed; operating system

Presence of facility for calculation of model matrix

Presence of facility for multiple scattering correction

B.8 Deconvolution

Type of optical model(s) that can be applied

Indicative description of mathematical procedure, for example weighting, constraints and smoothing

B.9 Output

Measurement range(s), overall and during each analysis

Size class ranges; also whether fixed or adjustable

Types of output, e.g. differential and cumulative distributions; values for sizes at given percentages and/or vice versa; moments; fits to distribution models

Data storage; availability of background and sample light-scattering fluxes

B.10 Performance

Repeatability, within instrument

Resolution and number of size classes

Lower detection limit for small proportions of small and large particles in size distributions (within measuring range)

Indication for the presence of particles with diameters outside measuring range

Annex C
(informative)

Dispersion liquids for the laser diffraction method

The liquid chosen for the dispersion of powders should:

a) be transparent at the wavelength of the light source(s) employed (e.g. for He:Ne laser, 633 nm);

b) be compatible with the materials used in the instrument (O-rings, tubing, etc.);

c) not dissolve or alter the size of the particulate material;

d) be essentially free from air bubbles or other particles;

e) favour easy and stable dispersion of the particulate material;

f) have a refractive index which differs significantly from that of the particulate material;

g) have suitable viscosity in order to enable recirculation;

h) not be hazardous to health and meet safety requirements.

Water is often used. A low-foaming surfactant may be added to lower the surface tension of water (and, thus, facilitate wetting of the particles), whereas a dispersant (often a polyelectrolyte) may be used to stabilize the dispersion. Organic liquids can be chosen, such as ethanol, 2-propanol (isopropyl alcohol), *n*-hexane or isooctane. Guidance on dispersion is given in ISO 14887 and in References [22] and [23]. Annex D lists refractive indices for a variety of liquids.

Annex D
(informative)

Refractive index, n_m, for various liquids and solids

The values are quoted relative to air = 1, at temperatures of 20 °C to 25 °C (see References [10], [17], [18], [19], [20]).

The refractive indices of solids are very sensitive to impurities. The values listed are recommended for pure materials so as to allow consistent reporting between laboratories. Other reference works may document different values. All refractive index values used should be reported.

Refractive indices are usually dependent on the wavelength of the light. Thus, when a light source of another wavelength is used, consult the literature to find out whether data are available.

D.1 Liquids

Table D.1 — Refractive index for liquids

Designation	Refractive index n_m	Wavelength in air nm
Acetone	1,359	589
Carbontetrachloride/tetrachloromethane	1,460	589
Castor oil	1,477	589
Chloroform/trichloromethane	1,446	589
Cyclohexane	1,424	589
Decaline/decahydronaphthalene *(trans/cis)*	1,47 to 1,48	589
n-Decane	1,409	589
Diethylene glycol	1,447	589
Diethylether/ethoxyethane	1,353	589
Ethanol (check refractive index w.r.t. wavelength)	1,361	589/687
Ethylbenzene	1,496	589
Ethylene glycol/1,2-ethanediol	1,432	589
Fluorocarbon 112	1,413	589
Glycerol/1,2,3-propanetriol	1,475	589
n-Heptane	1,386	589
n-Hexane	1,373	589
iso-Propyl alcohol/2-propanol	1,378	589
Linseed oil	1,478	589
Methanol	1,329	589
Methyl(ethyl)ketone (MEK)/2-butanone	1,379	589
Olive oil	1,468	589
Polyethylene glycol 300	1,47	
Silicone oil (dimethyl)	~ 1,40	589
Silicone oil (methyl-phenyl)	1,42 to 1,53	589
Toluene	1,497	589
Trichloroethylene/trichloroethene	1,477	589
2,2,4-Trimethylpentane	1,391	589
Water	1,333	589

D.2 Solids

Most of the (mineral) components indicated in Table D.2 come from natural sources. Consequently, their chemical composition may show deviations. Moreover, most of these materials are anisotropic. Either or both effects lead to the range of refractive indices indicated.

Surface roughness of transparent particles is often accounted for by assuming an imaginary part of the refractive index to be in the range 0,01 i to 0,03 i. Therefore, in Table D.2, an asterisk (*) is used for those materials for which the literature does not provide a value.

Table D.2 — Refractive index for solids

Name	Description	Refractive index		Wavelength in air
		Real n_p	**Imaginary** k_p	nm
Acetylene soot	—	1,56 to 1,99	0,3 to 0,5	633
Agate	Quartz (impure)	ca. 1,54	*	589
Aluminite	$Al_2(SO_4)(OH)_4 \cdot 7H_2O$	1,46 to 1,47	*	589
Aluminium	Al	1,48	3,9	657
Aluminium (hydr)oxides	Bauxite	1,56 to 1,75	*	589
	Boehmite	1,64 to 1,67	*	589
	Corundum	1,76 to 1,77	*	589/668
	Diaspore	1,68 to 1,75	*	589
	Gibbsite	1,56 to 1,60	*	589
	Ruby	1,76 to 1,77	*	589/668
	Sapphire	1,76 to 1,77	*	589/668
Alunite	$(K,Na)Al_3(SO_4)_2(OH)_6$	1,57 to 1,59	*	589
Analcite	$NaAlSi_2O_6\ H_2O$	1,48 to 1,49	*	589
Anatase	TiO_2	2,49 to 2,56	*	589
Andalusite	Al_2OSiO_4	1,63 to 1,65	*	589
Anhydrite	$CaSO_4$	1,57 to 1,61	*	589
Anorthoclase	$(Na,K)AlSi_3O_8$	1,52 to 1,53	*	589
Apatite	$Ca_5(PO_4)_3(OH,F,Cl)$	1,63 to 1,67	*	589
Aragonite	$CaCO_3$	1,53 to 1,69	*	589
Barite	$BaSO_4$	1,64 to 1,65	*	589
Barium compounds	Barite	1,64 to 1,65	*	589
	Barium yellow	1,94 to 1,98	*	589
	Witherite	1,53 to 1,68	*	589
Barium yellow	$BaCrO_4$	1,94 to 1,98	*	589
Bauxite	$AlO(OH)$	1,56 to 1,75	*	589
Beeswax (white)		1,45 to 1,47	*	589
Beryl	Emerald	1,56 to 1,60	*	589

Table D.2 *(continued)*

Name	Description	Refractive index		Wavelength in air
		Real n_p	Imaginary k_p	nm
Boehmite	$AlO(OH)$	1,64 to 1,67	*	589
Borax	$Na_2B_4O_7 \cdot 10H_2O$	1,45 to 1,47	*	589
Brookite	TiO_2	2,58 to 2,70	*	589
Brucite	$Mg(OH)_2$	1,56 to 1,60	*	589
Calcite	$CaCO_3$	1,49 to 1,74	*	589/643
Calcium compounds	Anhydrite	1,57 to 1,61	*	589
	Apatite	1,63 to 1,67	*	589
	Aragonite	1,53 to 1,69	*	589
	Calcite	1,49 to 1,74	*	589/643
	Chalk	1,51 to 1,65	*	589
	Dolomite	1,50 to 1,68	*	589
	Fluorite	1,43 to 1,44	*	589
	Gypsum	1,52 to 1,53	*	589
	Vaterite	1,55 to 1,65	*	589
	Wollastonite	1,62 to 1,65	*	589
Cadmium yellow	CdS	2,35 to 2,53	*	589/625
Carbon	C	2,0	1,0	633
Carbon black		1,6 to 2,0	0,3 to 0,8	633
Carnauba wax		1,47	*	589
Chalk	$CaCO_3$	1,51 to 1,65	*	589
Chalcedony	Quartz (impure, fibrous)	1,54	*	589
China clay	Kaolinite	1,56	*	589
Corundum	Al_2O_3	1,76 to 1,77	*	589/668
Diamond	C	2,41 to 2,42	*	589/644
Diaspore	$AlO(OH)$	1,68 to 1,75	*	589
Dolomite	$CaMg(CO_3)_2$	1,50 to 1,68	*	589
Emerald	$Be_3Al_2Si_6O_{18}$	1,56 to 1,60	*	589
Fluorite	CaF_2	1,43 to 1,44	*	589/644
Garnet	Mixed aluminium silicate	1,71 to 1,89	*	589
Gibbsite	$Al(OH)_3$	1,56 to 1,60	*	589
Glass, borosilicate	NIST -SRM 1820	1,487	*	436
Glass, soda lime	NIST -SRM 1822	1,529	*	436
Glass, heavy silicate flint		1,65	*	589/656
Glass, very heavy silicate flint		1,89	*	589/656
Goethite	$FeO(OH)$	2,26 to 2,52	*	589

Table D.2 (*continued*)

Name	Description	Refractive index		Wavelength in air
		Real n_p	Imaginary k_p	nm
Gold	Au	0,28	2,2	600
Gold	Au	0,31	2,7	650
Graphite	C	1,8	0,6 to 0,8	633
Greenockite	CdS	2,51 to 2,53	*	589
Gypsum	$CaSO_4{\cdot}2H_2O$	1,52 to 1,53	*	589
Halite	NaCl	1,544	*	589
Hausmannite	Mn_3O_4	2,1 to 2,5	*	671
Hematite	Fe_2O_3	2,9 to 3,2	0,01	589
Illite (clay)	KAl silicate	1,54 to 1,61	*	589
Iron	Fe	1,51	1,6	589
Iron	Fe	1,70	1,8	668
Jarosite	$KFe_3(SO_4)_2(OH)_6$	1,72 to 1,82	*	589
Kaolinite	$Al_4Si_4O_{10}(OH)_8$	1,53 to 1,57	*	589
Kieserite	$MgSO_4{\cdot}H_2O$	1,52 to 1,58	*	589
Leucite	$KAlSi_2O_6$	1,51	*	589
Magnesite	$MgCO_3$	1,51 to 1,78	*	589
Magnesium compounds	Brucite	1,56 to 1,60	*	589
	Dolomite	1,50 to 1,68	*	589
	Kieserite	1,52 to 1,58	*	589
	Magnesite	1,51 to 1,78	*	589
	Periclase	1,735	*	589
	Serpentine	1,53 to 1,57	*	589
	Spinel	1,71 to 1,72	*	589/656
	Talc	1,54 to 1,60	*	589
Magnetite	Fe_3O_4	2,42	*	589
Malachite	$Cu_2(OH)_2(CO_3)$	1,65 to 1,91	*	589
Mascagnite	$(NH_4)_2SO_4$	1,52 to 1,53	*	589
Mica	Mixed aluminium silicate	1,53 to 1,70	*	589
Moissanite	SiC	2,65 to 2,69	*	589
Opal	$SiO_2{\cdot}nH_2O$	1,41 to 1,46	*	589
Orthoclase	$KAlSi_3O_8$	1,52 to 1,54	*	589
Periclase	MgO	1,735	*	589
Platinum	Pt	2,2	2,1	633
Polycarbonate		1,59	*	687
Polymethylmethacrylate		1,49	*	589

Table D.2 (*continued*)

Name	Description	Refractive index Real n_p	 Imaginary k_p	Wavelength in air nm
Polystyrene		1,59 to 1,60	*	589
Polystyrene-butadiene		1,52 to 1,59	*	540/589
Polyvinylchloride (PVC)		1,52 to 1,55	*	589
Quartz	SiO_2	1,54 to 1,55	*	589/768
Rock salt	NaCl	1,544/1,541	*	589/640
Ruby	Corundum	1,76 to 1,77	*	589/668
Rutile	TiO_2	2,56 to 2,90	*	589/691
Sapphire	Corundum	1,76 to 1,77	*	589/668
Serpentine	$Mg_3Si_2O_5(OH)_4$	1,53 to 1,57	*	589
Silica (fused)	SiO_2	1,46	*	589/644
Silicon	Si	4,2	0,1	589
Silicon carbide	SiC	2,64 to 2,65	*	589/616
Silicon oxides	Agate	ca. 1,54	*	589
	Chalcedony	1,54	*	589
	Various glasses	1,49 to 1,89	*	436 to 656
	Opal	1,41 to 1,46	*	589
	Quartz	1,54 to 1,55	*	589/768
	Silica (fused)	1,46	*	589/644
	Tridymite	1,47 to 1,48	*	589
Silver	Ag	0,13	3,99	633
Spinel	$MgAl_2O_4$	1,71 to 1,72	*	589/656
Sulfur	S	1,96 to 2,25	*	589
Sylvite	KCl	1,49	*	589
Talc	$Mg_3Si_4O_{10}(OH)_2$	1,54 to 1,60	*	589
Tenorite	CuO	2,63	*	589
Titanium dioxide	Anatase	2,49 to 2,56	*	589
	Brookite	2,58 to 2,70	*	589
	Rutile	2,56 to 2,90	*	589/691
Topaz	$Al_2SiO_3(OH,F)_2$	1,61 to 1,64	*	589
Tridymite	SiO_2	1,47 to 1,48	*	589
Tungsten	W	2,76	1,0	578
Vaterite	$CaCO_3$	1,55 to 1,65	*	589
Witherite	$BaCO_3$	1,53 to 1,68	*	589
Wollastonite	$CaSiO_3$	1,62 to 1,65	*	589
Zircon	$ZrSiO_4$	1,92 to 2,02	*	589

Annex E
(informative)

Recommendations to reach optimum precision in test methods

E.1 A robust test method for laser diffraction analysis of PSDs should fulfil the requirements listed in E.1.1 to E.1.10:

E.1.1 Test products should have adequate quality: little or no segregation, adequate dispersability, non-fragile, no extreme aspect ratios (such as fibres or thin plates), homogeneous, known optical properties and an x_{90}/x_{10} ratio of 1,5 to 4.

E.1.2 Characteristic PSD parameters should be chosen to lie in between 5 % and 95 % of the volume-based PSD. Outside this range, decreased precision is expected. Claims about an x_{100} are deprecated by this International Standard.

E.1.3 The sample ultimately measured in the instrument should be representative of the product within given limits. Sample splitting by the use of a riffle splitter is the preferred method of creating a test portion from a laboratory sample. A sufficient test portion mass should allow for the required precision of the PSD parameter of interest (cf. ISO 14488).

E.1.4 The dispersion method should fully disperse the particulate product into a stable dispersion of primary particles, in which no agglomerates remain or reform and neither dissolution nor breakage occurs (cf. ISO 14887). No air bubbles should be present.

E.1.5 The dispersion method should be insensitive to small variations of the dispersion conditions.

E.1.6 The instrument should be located on a stable, rigid bench, out of direct sunlight, and in an area where the temperature fluctuations are smaller than ± 1 °C.

E.1.7 The test method should include adequate attention to the instrument requirements: sufficient warm-up time, clean windows and optical components, proper alignment of the optics, and proper settings of the mechanical system for dispersed material transport to prevent particle segregation.

E.1.8 The test method should take differences between instrument brands or models into consideration, if it is meant for analysis at different locations.

E.1.9 A proper optical model should be selected for the product in view of particle size and complex refractive index.

E.1.10 The operator should have received adequate training to perform the PSD analysis. This competence can be demonstrated in a detailed report. This report should contain all relevant product properties, procedures and instrument settings, the repeatability at the chosen optimum conditions, the critical aspects in the procedure and the effects of all variables tested.

E.2 Several stages are involved in method development. See E.2.1 to E.2.7.

E.2.1 A preliminary judgement is made on whether a relevant PSD for the product can be measured by laser diffraction. This includes whether measurement in dry state or liquid dispersion is preferred and which PSD parameter(s) represent(s) product performance. A microscopic inspection of the product is helpful to obtain information on particle size and shape.

E.2.2 A laboratory sample is collected that is sufficiently large for all method development activities and future testing. A technique for laboratory sub-sampling is selected to obtain representative test portions. Segregation according to size is to be expected if most particles are larger than about 50 µm.

E.2.3 Preliminary tests on instrument behaviour and settings are performed and optimum settings selected.

E.2.4 Optimum conditions for dry dispersion (device, pressure, sample amount, feeding rate) or wet dispersion (sample amount, dispersion liquid, surfactant, sonication time and power, pumping speed) are selected by performing analyses at varying conditions. These investigations should include tests of the degree of solubility of the product in the liquid. Completeness of liquid dispersion and particle fragility can be checked both under a microscope and by performing analyses at different times and conditions in the instrument. Adequate dispersion of dry powders in both air and liquid is increasingly difficult if the particle size becomes much smaller than 10 µm.

E.2.5 At least five independent test samples of sufficient sample size should be analysed to calculate the PSD parameters, standard deviation, and CV. If necessary, different instruments are to be involved in the tests.

E.2.6 The precision of the results is compared with the requirements in view of product performance. If necessary, critical aspects of the method are reconsidered and improved.

E.2.7 All details of procedures, instrument settings and results are written down in a report (protocol).

E.3 Once a successful method for a given product has been developed, the same product can be used for training of operators or for future instrument testing (for repeatability, reproducibility and/or accuracy). In the case of instrument testing, all results should be properly stored to act as historical proof of its good quality.

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