भारतीय मानक
Indian Standard

IS 101 (Part 10/Sec 1) : 2022
ISO 13320 : 2020

रंग रोगन, वार्निश और संबंधित उत्पादों के लिए नमूने और परीक्षण की पद्धतियाँ

भाग 10 यंत्र विश्लेषण

अनुभाग 1 कण आकार विश्लेषण — लेजर विवर्तन पद्धतियाँ

(पहला पुनरीक्षण)

Methods of Sampling and Test for Paints, Varnishes and Related Products

Part 10 Instrumental Analysis

Section 1 Particle size analysis — Laser diffraction methods

(First Revision)

ICS 19.120

भारतीय मानक ब्यूरो
BUREAU OF INDIAN STANDARDS
मानक भवन, 9 बहादुरशाह ज़फर मार्ग, नई दिल्ली – 110002
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI-110002
www.bis.gov.in www.standardsbis.in

March 2022 **Price Group 15**

Paints, Varnishes and Related Products Sectional Committee, CHD 20

NATIONAL FOREWORD

This Indian Standard (Part 10/Sec 1) (First Revision) which is identical with ISO 13320 : 2020 'Particle size analysis — Laser diffraction methods' issued by the International Organization for Standardization (ISO) was adopted by the Bureau of Indian Standards on recommendation of the Paints, Varnishes and Related Products Sectional Committee and approval of the Chemical Division Council.

While adopting ISO standards on different test methods, it was observed that there was no Indian standard on particle size analysis in the field of surface coatings. Particle size played important role in surface coating and directly concerned with various characteristics and performance of corrosion resistant coating. Considering the importance of laser diffraction analysis, also known as laser diffraction spectroscopy, which is a technology that utilizes diffraction patterns of a laser beam passed through any object ranging from nanometers to millimeters in size to quickly measure geometrical dimensions of a particle, the Committee felt that it would be more convenient to prepare this standard method by adoption of ISO 13320 : 2009 on dual number basis. This process does not depend on volumetric flow rate, the amount of particles that passes through a surface over time.

The already published Indian standards under IS 101 series 'Methods of sampling and test for paints, varnishes and related products' are widely used and known to all concerned. Therefore, to maintain the continuity and also to find the relevant test methods instantly, all test methods are being published under title 'Methods of sampling and test for paints, varnishes and related products'. Since there was no part under IS 101 series for testing by instruments in paints, varnishes and related products, the Committee decided to create new part that is, part 10 for instrumental analysis.

This standard was developed and published in 2018 as (Part 10/Sec 1) of IS 101 series of standards by adopting ISO 13320 : 2009. The other sections of this Indian Standard (Part 10) are:

Sec 2	Electrochemical impedance spectroscopy (EIS) on coated and uncoated metallic specimens — Terms and definitions
Sec 3	Electrochemical impedance spectroscopy (EIS) on coated and uncoated metallic specimens — Collection of data
Sec 4	Electrochemical impedance spectroscopy (EIS) on coated and uncoated metallic specimens — Processing and analysis of data from dummy cells
Sec 5	Electrochemical impedance spectroscopy (EIS) on coated and uncoated metallic specimens — Examples of spectra of polymer — Coated and uncoated specimens

The first revision of this standard has been undertaken to align it with the latest version of ISO 13320 : 2020 version.

The major changes in this revision are as follows:

a) protocols for evaluation of accuracy and qualification of instrument were newly developed;

b) new descriptions for wider applications, such as off-line, online, in-line and at-line have been added;

c) new Annex H (normative) for usage of reference material has been added;

d) some informative parts have been moved to new annexes; and

e) minor revisions and updates have been made throughout the document.

The text of ISO Standard has been approved as suitable for publication as an Indian Standard without deviations. Certain conventions and terminologies are, however, not identical to those used in Indian Standards. Attention is particularly drawn to the following:

a) Wherever the words 'International Standard' appear referring to this standard, they should be read as 'Indian Standard'

b) Comma (,) has been used as a decimal marker, in the International Standard, while in Indian Standards, the current practice is to use a point (.) as the decimal marker.

(*Continued on third cover*)

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 a wide variety of particulate systems. The technique is fast and can be automated, and 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 ISO 13320-1:1999 was first published, 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, it was replaced with the first edition of ISO 13320 in 2009, and since then the method has been developed for a wider application. Additionally, demands raised recently not only on establishment of accuracy of measurements but also on necessity of evaluation of the accuracy and of qualification of instrument by users. Therefore, this document incorporates the most recent advances in understanding.

Indian Standard

METHODS OF SAMPLING AND TEST FOR PAINTS, VARNISHES AND RELATED PRODUCTS

PART 10 INSTRUMENTAL ANALYSIS

Section 1 Particle size analysis — Laser diffraction methods

(First Revision)

1 Scope

This document 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 document 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 spherical and 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. For non-spherical particles 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 documents are referred to in the text in such a way that some or all of their content constitutes requirements 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*

3 Terms, definitions and symbols

3.1 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

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

3.1.2
accuracy
closeness of agreement between a test result or measurement result and the true value

Note 1 to entry: In practice, the accepted reference value is substituted for the true value.

Note 2 to entry: The term “accuracy”, when applied to a set of test or measurement results, involves a combination of random components and a common systematic error or bias component.

Note 3 to entry: Accuracy refers to a combination of trueness and precision.

[SOURCE: ISO 3534-2:2006, 3.3.1]

3.1.3
aspect ratio

ratio of the minimum to the maximum Feret diameter

Note 1 to entry: For not very elongated particles.

[SOURCE: ISO 26824:2013, 4.5]

3.1.4
certified reference material

CRM

reference material (3.1.16) characterised by a metrologically valid procedure for one or more specified properties, accompanied by an RM certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability

Note 1 to entry: The concept of value includes a nominal property or a qualitative attribute such as identity or sequence. Uncertainties for such attributes may be expressed as probabilities or levels of confidence.

Note 2 to entry: Metrologically valid procedures for the production and certification of RMs are given in, among others, ISO 17034 and ISO Guide 35.

Note 3 to entry: ISO Guide 31 gives guidance on the contents of RM certificates.

Note 4 to entry: ISO/IEC Guide 99:2007, 5.14 has an analogous definition.

[SOURCE: ISO Guide 35:2017, 3.2]

3.1.5
complex refractive index

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

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

Note 1 to entry: 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.

Note 2 to entry: In contrast to ISO 80000-7, this document follows the convention of adding a minus sign to the imaginary part of the refractive index.

3.1.6
deconvolution

<laser diffraction> mathematical procedure whereby the size distribution of an ensemble of particles is inferred from measurements of their scattering pattern

3.1.7
diffraction

<particle size analysis> scattering of light around the contour of a particle, observed at a substantial distance (in the ‘far field’)

3.1.8
equivalent spherical diameter
<laser diffraction> particle size reported from a distribution of spherical particles that creates a scattering pattern that matches the light scattering distribution observed from the measurement

Note 1 to entry: The scattering pattern of the spherical particles is calculated according to an optical model.

3.1.9
extinction
<particle size analysis> attenuation of a light beam traversing a medium through absorption and scattering

3.1.10
intermediate precision
<laser diffraction> accuracy and precision under *intermediate precision conditions* (3.1.11)

[SOURCE: ISO 3534-2:2006, 3.3.15, modified — field of application <laser diffraction> has been added.]

3.1.11
intermediate precision conditions
<laser diffraction> conditions where test results or measurement results are obtained on different laser diffraction instruments and with different operators using the same prescribed method

Note 1 to entry: There are four elements to the operating condition: time, calibration, operator and equipment.

3.1.12
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

3.1.13
obscuration
fraction of incident light that is attenuated due to extinction (scattering and/or absorption) by particles

Note 1 to entry: Obscuration can be expressed as a percentage.

Note 2 to entry: When expressed as fractions, obscuration plus *transmission* (3.1.29) equal unity.

[SOURCE: ISO 8130-13:2019, 3.1, modified — words “percentage” and “during a laser diffraction measurement” have been omitted because of context.]

3.1.14
optical model
theoretical model used for computing the model matrix for optically homogeneous and isotropic spheres with, if necessary, a specified complex refractive index

EXAMPLE Fraunhofer diffraction model, Mie scattering model.

3.1.15
precision
closeness of agreement between independent test/measurement results obtained under stipulated conditions

Note 1 to entry: Precision depends only on the distribution of random errors and does not relate to the true value or the specified value.

Note 2 to entry: The measure of precision is usually expressed in terms of imprecision and computed as a standard deviation of the test results or measurement results. Less precision is reflected by a larger standard deviation.

Note 3 to entry: Quantitative measures of precision depend critically on the stipulated conditions. Repeatability conditions and reproducibility conditions are particular sets of extreme stipulated conditions.

[SOURCE: ISO 3534-2:2006, 3.3.4]

3.1.16
reference material
RM

material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process

Note 1 to entry: RM is a generic term.

Note 2 to entry: Properties can be quantitative or qualitative, e.g. identity of substances or species.

Note 3 to entry: Uses may include the calibration of a measurement system, assessment of a measurement procedure, assigning values to other materials, and quality control.

Note 4 to entry: ISO/IEC Guide 99:2007 has an analogous definition but restricts the term “measurement” to apply to quantitative values. However, ISO/IEC Guide 99:2007, 5.13, Note 3 (VIM), specifically includes qualitative properties, called “nominal properties”.

[SOURCE: ISO Guide 35:2017, 3.1]

3.1.17
reflection

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

3.1.18
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

Note 1 to entry: 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.

3.1.19
relative refractive index

m_rel

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

[SOURCE: ISO 24235:2007, 3.3, modified — “absolute refractive index” has been replaced by “complex refractive index” and “the sample” has been replaced by “a particle”.]

Note 1 to entry: In many applications, the medium is transparent and, thus, its refractive index has a negligible imaginary part.

Note 2 to entry: 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.

See *single scattering* (3.1.26).

3.1.20
repeatability

precision under *repeatability conditions* (3.1.21)

Note 1 to entry: Repeatability can be expressed quantitatively in terms of the dispersion characteristics of the results.

[SOURCE: ISO 3534-2:2006, 3.3.5]

3.1.21
repeatability conditions

observation conditions where independent test/measurement results are obtained with the same method on identical test/measurement items in the same test or measuring facility by the same operator using the same equipment within short intervals of time

Note 1 to entry: Repeatability conditions include:

- the same measurement procedure or test procedure;
- the same operator;
- the same measuring or test equipment used under
  - the same conditions;
  - the same location;
- repetition over a short period of time.

[SOURCE: ISO 3534-2:2006, 3.3.6]

3.1.22
method repeatability

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

Note 1 to entry: The variability includes the variabilities of sub sampling technique, of the sampled material together and of the instrument.

3.1.23
scattering

change in propagation of light at the interface of two media having different optical properties

3.1.24
scattering angle

angle between the principal axis of the incident light beam and the scattered light

3.1.25
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

3.1.26
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

3.1.27
single shot

<sample> for an analysis, for which the entire content of a test sample container is used

3.1.28
test sample

sample that is entirely used for a property characterization

[SOURCE: ISO 14488:2007, 3.12]

3.1.29
transmission

<particle size analysis> fraction of incident light that remains un-attenuated by the particles

Note 1 to entry: Transmission can be expressed as a percentage.

Note 2 to entry: When expressed as fractions, *obscuration* (3.1.13) plus transmission equal unity.

3.1.30
true value

quantity or quantitative characteristic supposed to be “true” as the target value of the measurement according to the definition of the measurement

Note 1 to entry: The true value is a theoretical concept and, in general, cannot be known exactly.

Note 2 to entry: For an explanation of the term “quantity”, refer to ISO 3534-2:2006.

3.1.31
trueness

closeness of agreement between the expectation of a test result or a measurement result and a true value

Note 1 to entry: The measure of trueness is usually expressed in terms of bias

Note 2 to entry: Trueness is sometimes referred to as “accuracy of the mean”. This usage is not recommended.

Note 3 to entry: In practice, the accepted reference value is substituted for the true value.

[SOURCE: ISO 3534-2:2006, 3.3.3]

3.2 Symbols

A_i	extinction efficiency of size class *i*
C	particulate concentration, volume fraction
CF	coverage factor
D	particle diameter (*x* may also be used)
$D_{10,3}$	particle diameter corresponding to the 10th percentile of the cumulative undersize distribution (here by volume)
$D_{50,3}$	median particle diameter corresponding to the 50th percentile of the cumulative undersize distribution (here by volume)
$D_{90,3}$	particle diameter corresponding to the 90th percentile of the cumulative undersize distribution (here by volume)
$I(\theta)$	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_1	first order Bessel Function of the first kind
k	wave number in medium: $2\pi n_\mathrm{m}/\lambda$
$\mathrm{i}k_\mathrm{p}$	imaginary (absorption) part of the refractive index of a particle
l_a	distance from scattering object to detector
l_b	illuminated path length 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);
r	radial distance from focal point in focal plane
u_p	standard uncertainty for the parameter and value specified
u_crm	standard uncertainty of the certified value
u_house	standard uncertainty of in-house reference material value
U_crm	expanded uncertainty of the certified value
U_house	expanded uncertainty of in-house reference material value
U_lim	expanded tolerance limit defined by calculation
V_i	volume content of size class i
v	velocity of particles in dry disperser
x	particle diameter (D may also be used)
x_i	geometric mean particle size of size class i
$x_{10,3}$	particle diameter corresponding to 10th percentile of the cumulative undersize distribution (here by volume)
$x_{50,3}$	median particle diameter corresponding to the 50th percentile of the cumulative undersize distribution (here by volume)
$x_{90,3}$	particle diameter corresponding to 90th percentile of the cumulative undersize distribution (here by volume)
$\bar{x}_{1,3}$	volume-weighted mean diameter
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 (see definition 3.1.18)
θ_p	angle with respect to perpendicular at boundary for a light beam in particle (see definition 3.1.18)
λ	wavelength of illuminating light source in vacuum
σ	standard deviation
ω	angular velocity

4 Principle

4.1 General

The laser diffraction or scattering technique[1] for the determination of particle size distributions, PSDs, is based upon the phenomenon that the angular distribution of the intensity of scattered light by a particle (scattering pattern) is dependent on the particle size. When the scattering is from a cloud or ensemble of particles the intensity of scattering for any given size class is related to the number of particles and their optical properties, present in that size class[5][20].

A test 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 an array of photo detectors. The numerical values from each detector are recorded for subsequent analysis. Within certain limits, such as of particle concentration in measuring zone, the scattering pattern of an ensemble of particles is identical to the sum of the individual scattering patterns of all particles. The theoretical scattering patterns of unit volumes of particles in selected size classes are used to build a matrix and together with a mathematical procedure are used to solve the inverse problem, providing a volumetric particle size distribution (PSD), iterated to provide a best fit to the measured scattering pattern[18].

4.2 Theory

The theoretical scattering pattern of a single spherical homogeneous particle is given by Mie-theory in general[4]. If the particle size is relatively large (in terms of size parameter, $\alpha = \pi \times n_\mathrm{m}/\lambda > 10$) and is opaque, Fraunhofer diffraction theory is available only for small angle forward scattering[4][5]. The Fraunhofer approximation is an analytical method that does not require the optical properties of the material.

Some other theoretical approximations are available for numerical realization of the Mie-theory, and these are called optical models in general. Choosing a relevant optical model for the inverse problem to yield a proper PSD is important.

Laser diffraction records the scattering pattern from the particles presented. This composite pattern is converted to a size distribution of spherical particles that would provide the same composite scattering pattern using an appropriate optical model and data inversion routine. It therefore provides a size distribution of laser diffraction equivalent spheres. If the test sample is not spherical, the same basic procedure is used and the resulting size distribution is formed. Thus, PSD's for non-spherical particles

---

1) Early instruments had very limited computer capacity and were restricted to using a laser with Fraunhofer Diffraction. Often a model form of particle size distribution was iterated to fit the scattering data. The term Laser Diffraction rapidly became the dominant descriptor. This has continued despite the technique having advanced to use different light sources and more sophisticated optical theories and data analysis.

are likely to be different from other particle sizing techniques measuring the same material. The details of the theory are given in Annex A.

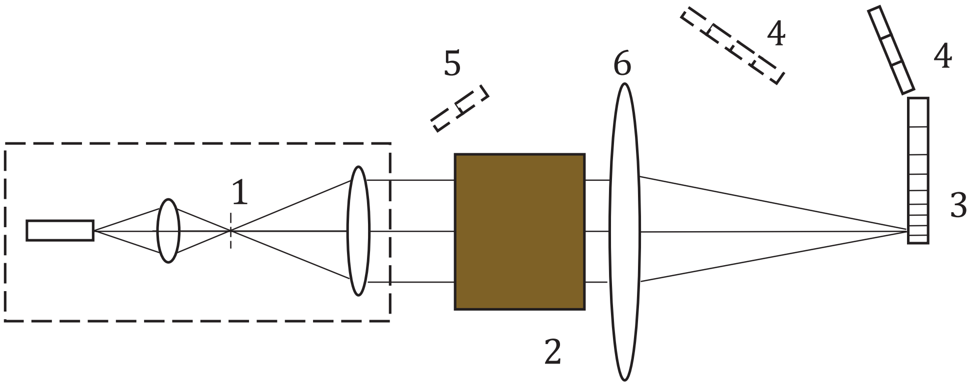
4.3 Typical instrument and optical arrangement

The system consists of a monochromatic light source, sample feeder, optical system, light detectors, and control-calculation device. To extend the applicable range of particle size and its analysis, multiple light sources, additional light detecting systems and related optical systems can be used.

The light source is typically a laser or other narrow-wavelength source to generate a monochromatic beam. This is followed by a beam-processing unit producing an extended and nearly ideal, Gaussian distributed beam to illuminate the dispersed particles. The illuminating light beam passes through the measuring zone of the optical system.

A computer is used to control the measurement, to store and to process the data, and to solve the inversion problem from the data of the detected signals to the particle size distribution. It may provide automated instrument operation.

Typical diagrams of the set-up of laser diffraction/scattering instruments are given in Figures 1 to 4.



Key

1 light source assembly [with one or more light source(s)] including beam expansion and collimation

2 measurement zone (for details, see Figure 2)

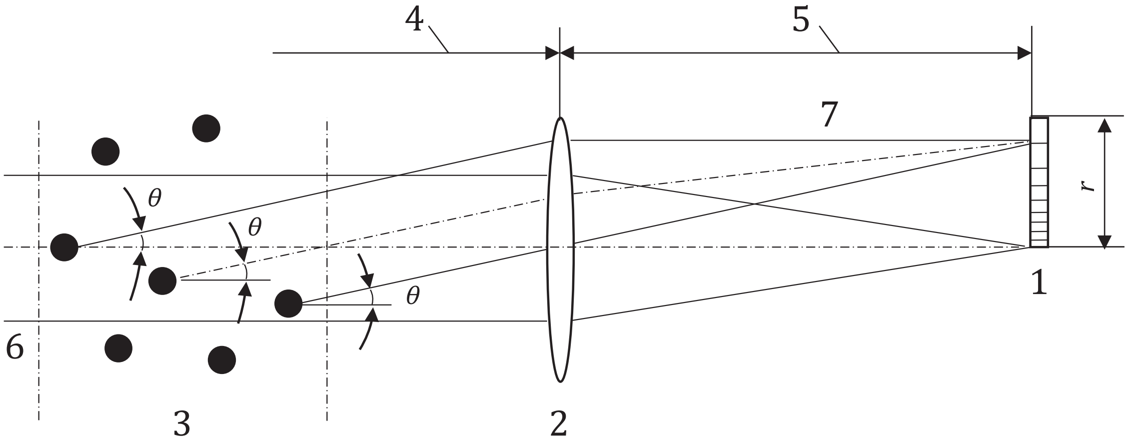
3 forward scattering multi-element detector (with obscuration/transmission detector)

4 wide angle scattering detector(s)

5 back scattering detector

6 Fourier lens

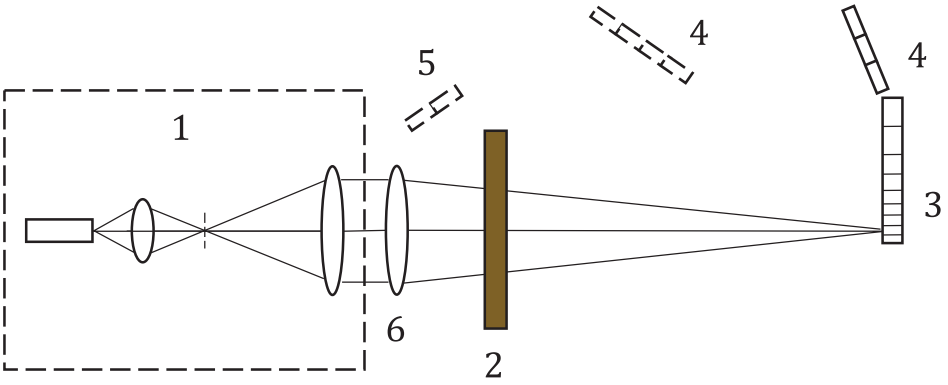
Figure 1 — Fourier optical arrangement



Key

1	forward scattering multi-element detector (including obscuration/transmission detector)	5	focal distance
2	Fourier lens	6	incident light beam
3	ensemble of dispersed particles	7	scattering light
4	working distance within measurement zone	*r*	radius of multi-element detector
		θ	scattering angle

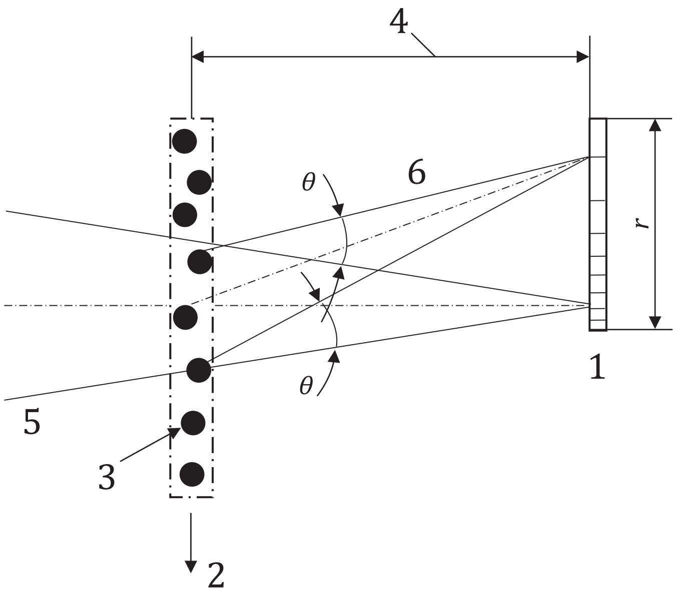
Figure 2 — Fourier optical arrangement — Scattering angle



Key

1	light source assembly [with one or more light source(s)] including beam expansion and collimation	3	forward scattering multi-element detector (with obscuration/transmission detector)
2	measurement zone (for details, see Figure 4)	4	wide angle scattering detector(s)
		5	back scattering detector
		6	reverse Fourier lens

Figure 3 — Reverse Fourier optical arrangement



Key

1	forward scattering multi-element detector (including obscuration/transmission detector)	5	incident light
		6	scattering light
2	flow through cuvette for dispersed particles	*r*	radius of multi-element detector
3	particle(s)	*θ*	scattering angle
4	focal distance		

Figure 4 — Reverse Fourier optical arrangement — Scattering angle

4.4 Measurement zone

The locations of the two possible measurement zones, are illustrated in Figures 2 and 4. The Fourier optical arrangement allows, within certain limits, the particles to traverse the beam in a wide range of positions along the laser axis. By contrast, the presentation of particles within the reverse Fourier optical arrangement shall be confined to a short distance along the laser axis if errors in sizing are to be avoided. The measurement zone shall be located at a defined distance from the low angle detector.

A test sample of particles, dispersed as necessary, is introduced into the measuring zone at an adequate concentration. Scattering theories[20] show that the scattering from each particle can be combined if the concentration is low enough, thus providing single scattering. It also requires that the particles move freely relative to each other. It is also necessary that all particles traverse the laser beam at the same velocity if the effects of velocity bias are to be avoided. Ideally, the selected concentration should remain fairly constant during the measurement.

4.5 Application and sample presentation

The laser diffraction/scattering method is applicable to both wet and dry systems, and also to off-line, online, at-line and in-line measurements. Sprays and gas bubbles in liquid can also be measured directly, provided that their concentration is at an adequate level (see 5.4.4).

a) Off-line; (Laboratory) a sample is removed from the process which may or may not require reducing to a test sample. The test sample is dispersed and manually introduced into the measurement zone, forming a discontinuous measurement sequence whose operational parameters are adapted to the product.

b) At-line; (Laboratory) a test sample is automatically taken, at or close to the process, dispersed and introduced into the measurement zone forming a discontinuous measurement sequence whose operational parameters are most likely dedicated to the product.

c) Online; (Process) a test sample is automatically removed from the process and introduced into the measurement zone. A quasi-continuous real-time measurement, dedicated to close-to-process conditions is made.

d) In-line; (Process) a test sample remains in the process line during the measurement, a quasi-continuous real-time measurement is made under process conditions.

During the introduction of any of the above methods, material inspection and preliminary investigation shall be performed to establish whether appropriate values for sample concentration, dispersion state, resistance to optical fouling and other parameters are being achieved to ensure the desired particle sizing result.

4.6 Off-line measurements

In the case of off-line measurement of wet systems, a test sample is dispersed in an appropriate transparent liquid medium, and transported to an optical (sample) cell, in which the measuring zone is formed. (See Annex B) In off-line measurement, dispersants (wetting agents; stabilizers) and/or mechanical forces (agitation; sonication) are applied for de-agglomeration of the particles and for the stabilization of the dispersion. A recirculation system is often used, consisting of an optical cell, a sample bath (with agitation and/or sonication), a pump and tubing. A small volume cell with limited stirring is also available for particles with very slow sedimentation velocity. Small volume cells should be used with care as the very small test sample volume, required to provide single scattering, may fall below a minimum test sample requirement.

In the case of off-line measurement of dry powder systems, particles are converted into aerosols by a dry powder feeder and a disperser, before being introduced into the measuring zone. The aerosolised particle stream is either blown or sucked through the measurement zone. It is preferred that the concentration of aerosolised powder remains steady during the averaging of the scattered light.

Dispersed dry powders can also be measured online or in-line. Sprays are usually measured in-line. A representative PSD analysis requires that the powder stream is not segregated. Alternatively, the degree of segregation can be measured by analysis of different sections of the powder stream. At all times, the particulate concentration should remain within the concentration limits for single scattering, be fairly stable and all sizes of particles should pass through the measurement zone at the same speed to avoid velocity bias.

4.7 In-line measurements

In the case of in-line measurement, the laser beam illuminates particles in a flowing stream within the process directly. In this case, the measured sample should be representative of the whole stream, the particle concentration should be in an adequate range, and any concentration fluctuation during a single measurement should be within acceptable limits. The particles are presented as produced and may or may not be aggregated. The measuring zone formed by either of the optical arrangements is finite. The influence of potential multiple scattering together with the scattering from particles illuminated by the laser beam but arising from outside of the measurement zone should be evaluated. It is important to remove any influences of outside lighting or laser reflection from the surfaces of optical parts, within the instruments. Such influences may be minimised by subtracting the background measured without particles from the measured scattering pattern when particles are present. In such subtracting procedures, it is always important to confirm the level of signal to noise ratio (S/N). (Routine background subtraction is not always possible in some in-line set ups).

4.8 Online measurements

In the case of online measurement, a test sample is automatically taken from the process. This is often a dedicated arrangement matched to the process. The operational conditions are similar to in-line methods but permit greater control of the measurement environment. Additional methods, to further disperse the particles may be applied. The measurement sequence may be interrupted to permit optical cleaning or other maintenance procedures.

4.9 At-line measurements

In the case of at-line systems the optical measuring system is placed adjacent to a process. This permits the operational arrangements as in the off-line arrangement but carries some risk of contamination from the local environment. Steps should be taken to minimize this with more frequent checks to verify the apparatus remains fit for purpose. (see Annex D).

4.10 Scattering and detectors

The interaction of the incident light beam with the ensemble of dispersed particles results in a scattering pattern with different light intensities scattered at various angles. The detection of the scattered pattern is carried out by a number of photodiodes and/or pixel array detectors. For the range of small angular forward scattering, a multi-element silicon detector is often used. These elements are located concentrically and often having a radius proportional to the distance from the centre. The number of detectors, their locations or optical (detecting) angles, should be set to satisfy the required particle size range and resolution of the measurements. The particles scattering angle is measured with respect to the incident monochromatic beam axis. For particles suspended in a liquid the effect of the measurement cell shall be included into the estimation of scattering angle. The scattering pattern is a continuous function of the light intensity with respect to angle. The intensity falling upon each detector is converted to an energy dependent upon the detector area and its quantum efficiency. The input to subsequent data processing comprises a discrete set of electrical signals whose angular and detection properties are known or have been calibrated[42].

Often a central detector is set to measure the intensity of the non-extinguished light. This provides a measure of optical concentration or obscuration, after a calculation. Some instruments provide special geometries of the central element in order to automatically re-centre or re-focus the detectors by moving the detectors or lens.

5 Operational requirements and procedures

5.1 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. See IEC 60825-1 regarding laser radiation safety measures.

5.2 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 and has been restored to room temperature. To achieve this, a dryer with a filter and warming system is required. In spray applications, evaporation of the liquid may cause artefacts in the particle size results. Any vacuum unit used to collect the particles should be located well away from the measurement zone, so that the output of the hot air does not disturb the measurement zone. Draughts should be avoided in order to prevent unstable particulate streams or thermal fluctuations within the measurement zone. (See C.1).

5.3 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 B provides information on the dispersion liquids.

Observe health and safety measures 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.

5.4 Sample inspection, preparation, dispersion and concentration

5.4.1 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 or will require further treatment.

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

The inspection of the fully dispersed state of a suspension of particles is difficult to achieve with the naked eye. Any inspection using a microscope should be conducted from a pool of suspension without using a cover slip. Such inspections are very subjective, not definitive but are helpful in many cases.

5.4.2 Preparation

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

Very small test samples can be taken from 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 D.1 to D.7), 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. Rapid 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.

5.4.3 Dispersion

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

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 low 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 reported sizing results.

5.4.4 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. Reference [20] proposes that the onset of multiple scattering commences if particles are regularly separated from their neighbours by 3 times their diameter. As the number of particles increases proportional to D^{-3} for the same volume concentration the smallest particles have the highest number per unit volume. It therefore follows that the smallest sizes in any distribution determine the onset of multiple scattering due to their possible close proximity.

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 path length 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 path length — 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 % (transmission 95 % to 75 %), 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. Annex A (see A.8) provides some information on the relation between particulate concentration, particle size and obscuration.

5.5 Measurement

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

PRECAUTION Before starting and during any measurement, carefully follow the instructions given in the instrument manual. It is also recommended to observe the precautions set out in Annex D.

a) Setting up the instrument, confirming the optical alignment and conducting a blank measurement to establish the background scattering.

b) Determination of the parameters of the sample material to be measured. These include refractive index required for analysis, particle density to facilitate particle transport settings, solubility to help in the choice of liquid dispersant.

c) Sample preparation and introduction into the measurement zone.

d) Data collection to establish the scattering pattern signature.

e) Selection of an appropriate optical model.

f) Conversion of scattering pattern into PSD.

5.5.1 Setting up instrument and blank measurement

After selection of the appropriate particle size range and proper optical alignment, and after allowing a proper warm-up period of the instrument, perform a blank measurement immediately prior to the test sample measurement in which a particle-free dispersion medium is used under the same instrument conditions to be employed for the test sample measurement. These background signals are subtracted later from the detector signals coming from the measurement of the material of interest.

5.5.2 Sample preparation

For wet application, prepare a test sample referring to D.5. 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 de-agglomeration without comminution and to a sufficiently low concentration to ensure single scattering.

5.5.3 Data collection of the scattering pattern

Allow a measuring time for data collection sufficient for statistically adequate representation of the test 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 coordinates (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 this measurement when a dispersed test sample is present and that measured during the blank background experiment is given as a value of obscuration or transmission, which is indicative of the total amount of light scattered or absorbed by the dispersed particles and thus the particle concentration.

5.5.4 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 theory of Mie, the refractive indices of particulate and medium (see Annex F), or their ratio, should be established and entered into the instrument in order to allow calculation of the model matrix[18].

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 transparent particles, where some light is randomly scattered.

A good understanding of the influence of the complex refractive index of the light scattering from particles is strongly advised in order to apply the Mie theory or the Fraunhofer approximation appropriately. 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 is often observed when inappropriate quantities of material are 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.

5.5.5 Conversion of scattering pattern into PSD

This de-convolution step is the inverse of the calculation of a scattering pattern for a given PSD. Several mathematical algorithms have been developed for this purpose (see References [4], [6], [18], [30], [32], [33], [37]). They contain some weighting of deviations between measured and calculated scattering patterns (e.g. least squares) and some constraints on 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 (see 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.

5.5.6 Robustness

It is advised, after a method of measurement has been devised for a specific material, that robustness tests should be performed to avoid the possibility of choosing a set of parameters which leaves the measurement vulnerable to minor errors or changes producing significant and unexpected changes on the final result. (See Annex G)[1].

5.6 Resolution and sensitivity

5.6.1 General

The resolution of the PSD describes the ability of a measuring device to distinguish meaningfully between closely adjacent particle sizes.

Therefore, higher resolution allows an easier discrimination between particles of different size and it allows an unbiased determination of the width of the PSD.

The sensitivity of the PSD describes the ability of a measuring device to distinguish meaningfully between small changes in the amounts of particles in a given size class.

Therefore, higher sensitivity allows a better comparability of mixing ratios and the discrimination of small amounts of large particles at the upper end and small particles at the lower end of the particle size distribution.

However, both resolution and sensitivity, respectively, are strongly dependent on the following items:

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

b) number, width and way of generation of size classes of the PSD;

c) application of the appropriate optical model;

d) fine structure in the measured scattering pattern, especially of narrow-sized PSDs;

e) actual size range and distribution width of the particulate material;

f) possible smoothing and regularisation effects applied to intensity signals and/or to the deconvolution procedure in the evaluation;

g) signal-to-noise ratio, etc.

All these factors have significant influence on resolution and sensitivity. Therefore, there is no simple way to describe procedures and measures needed for resolution and sensitivity. If instruments are comparable in the sense of the items listed above, actual values for resolution and sensitivity may be determined by using mixtures of known composition, e.g. for quality control reasons.

5.6.2 Resolution

Due to the light scattering signature arising from an ensemble of particle sizes and the need to carry out a matrix inversion, constrained to zero or positive values, the resolution of the technique is limited. The resolution achievable is also influenced by the particle size range and the optical properties of the material being measured. Under cooperative circumstances mono-sized particles separated in size by a factor of 2, can be partially separated over the mid-range of sizes. The resolution at the very highest size is limited by the solid angle of scattering due to the finitely small optical detectors. The resolution of the very smallest size is limited by the very weak scattering properties of particles having those sizes.

5.6.3 Sensitivity and result variability

Sensitivity in this context refers to the ability of the laser diffraction measurement instrument to discriminate or detect small changes in both size and quantity. As a result of the scattering characteristics of various sizes of particles coupled with limitations in both the number and angular extent of some detectors together with the limitations of the data inversion stage, the sensitivity is far from uniform over the range of particle sizes covered.

The largest particles in any distribution will only be present in small numbers. To avoid uncertainty in the higher percentiles of the distribution the minimum mass of test sample should be considered[29][40].

The measurement of a fine particle distribution can be compromised by the odd large bubble or large particle contaminant. This might be regarded as an unfortunate sensitivity to the strong scattering properties of large particles. Equally because very small particles scatter weakly the sensitivity to their presence can be significantly reduced when poly-disperse particle size distributions containing larger particles are present. It is not realistic to be very specific about these effects as they vary dependent upon size range, optical properties, the degree of poly-dispersity, particle shape and particle concentration.

6 Accuracy repeatability and instrument qualification

6.1 General

Before commencing any of the tests specified in this subclause, the operator should have considered the protocol of measurement and the recommendations of Clause 5 and Annexes D and H. In general, the tests may be applied to both liquid and dry dispersions. A test of instrument repeatability does not generally apply to dry dispersion as the particles are not re-circulated and different aliquots of single shot samples can be used.

However, repeated dry measurements, of the same sample, employing a gravity dispersion accessory fitted with a total sample capture provision and used together with fully free flowing, and non-cohesive reference materials, may be employed in 6.3. The same gravity method may be used to meet the accuracy test set out in 6.2 using a certified reference material.

The verification of laser diffraction units designed for spray measurements require a different protocol as no reference spray is available. If a flow cell or a dry dispersion system can be added, then a test for accuracy as described in 6.2 may be applied. Alternatively, a reference reticule[19] that has been fully characterized using a laser diffraction unit that has met the accuracy test in 6.2, may be employed to determine the intermediate precision.

For the purposes of this document both terminologies “method of moments” and “moment-ratio” which are commonly used, are used for each parameter described.

The total value of the uncertainty associated with each parameter which are used as the final acceptance/rejection limits shall be calculated using Formula (1) (see H.1 to H.3):

$$U_{\mathrm{lim}} = \pm CF \cdot \sqrt{u_{\mathrm{crm}}^2 + u_{\mathrm{p}}^2} \qquad (1)$$

where U_{lim} is the acceptance limits for test 6.2 and 6.5.

The requirements for acceptable instrument uncertainty values, u_{p}, for a laser diffraction system and the value for the coverage factor *CF* are given in Table 1. The term u_{crm} is given in the certified reference material documentation. The value of the coverage factor *CF* is usually a number between 2 and 3 and shall be chosen by users on the basis of the desired level of confidence, and which shall be documented.

Table 1 — Parameters for the calculation of the tolerance limits

Parameters required	Nomenclature	Maximum acceptable instrument uncertainty, u_{p}	Coverage factor, *CF*
10th percentile	$D_{10,3}$ or $x_{10,3}$	2 %	2–3
50th percentile	$D_{50,3}$ or $x_{50,3}$	1,5 %	2–3
90th percentile	$D_{90,3}$ or $x_{90,3}$	2,5 %	2–3

6.2 Accuracy

6.2.1 Introduction

Certified reference materials with assigned values by laser diffraction as defined in H.1 to H.3 and applying to the laser diffraction method shall be used for the system qualification (OQ: operation qualification, PQ: performance qualification)[41][42] and for the test of accuracy using the wet or dry dispersion method.

The dry dispersion method uses a large quantity of sample per test. In order to mitigate against the cost of the increased reference material consumption, in-house reference material, certified in accordance with the method set out in H.1 to H.3 inclusive may be used for the test of accuracy of the dry dispersion method.

The tolerance limits shall be calculated for the parameters $D_{10,3}$ or $x_{10,3}$; $D_{50,3}$ or $x_{50,3}$; $D_{90,3}$ or $x_{90,3}$ using the formula; $U_{\mathrm{lim}} = \pm CF \cdot \sqrt{u_{\mathrm{crm}}^2 + u_{\mathrm{p}}^2}$, where the values of u_{crm} are taken from the certified reference material documentation and the values of CF and u_{p} are obtained from Table 1.

6.2.2 Accuracy test

At least 3 separate test samples shall be measured, 5 separate test samples are preferred. Each test shall be conducted at an adequate sample concentration and signal integration period to allow a sufficient number of particles to be analysed (see ISO 14488).

The average cumulative volume distribution value from the 3 or 5 tests, at the required percentile shall not exceed the pre-calculated tolerance limits U_{lim} for each of the parameters $D_{10,3}$ or $x_{10,3}$; $D_{50,3}$ or $x_{50,3}$; $D_{90,3}$ or $x_{90,3}$.

In the event of a failure of this test, then all aspects of the measurement method adopted by the operator and of that of the instrument should be examined extensively.

6.3 Instrument repeatability

6.3.1 Introduction

For the wet dispersion method, this test is carried out using one instrument, a single operator and the same dispersed sample. For the dry dispersion method only, the method repeatability described in 6.4 can be used for this test. Well behaved dry samples which have been correctly split into subsamples with a very low sample to sample variability should also be able to fulfil the tolerances in this section.

Any material being either spherical or of “limited shape”, but in accordance with the requirements of Annex H may be employed for this test.

6.3.2 Repeatability test

Perform at least 6 consecutive measurements, in a short time period, with the same dispersed test sample at an adequate sample concentration and signal integration period to allow a sufficient number of particles to be analysed (see ISO 14488)[8].

The average values of $D_{10,3}$ or $x_{10,3}$; $D_{50,3}$ or $x_{50,3}$ and $D_{90,3}$ or $x_{90,3}$ from the 6 measurements shall be calculated.

a) The reported cumulative volume distribution value from each test at the 10th percentile $D_{10,3}$ or $x_{10,3}$ shall not deviate from the average value of the 6 measured results values by more than ± 2 %.

b) The reported cumulative volume distribution value from each test at the 50th percentile $D_{50,3}$ or $x_{50,3}$ shall not deviate from the average value of the 6 measured results values by more than ± 1,5 %.

c) The reported cumulative volume distribution value from each test at the 90th percentile $D_{90,3}$ or $x_{90,3}$ shall not deviate from the average value of the 6 measured results values by more than ± 3 %.

In the event of a failure of this test, then all aspects of the measurement method adopted by the operator and of that of the instrument should be examined extensively.

6.4 Method repeatability

6.4.1 Introduction

This test is carried out using one instrument and a single operator, using different aliquots of the same sample. It is applicable to both the wet and dry dispersion methods. This type of repeatability includes variability due to sampling and dispersion. However, in all cases the written measurement protocol should be followed which has been prepared incorporating the recommendations of Clause 5.

Any material being either spherical or of "limited shape", but in accordance with the requirements of H.2 may be employed for this test.

6.4.2 Method repeatability test

Perform at least six consecutive measurements with the dispersed single shot test samples. Each test shall be conducted at an adequate sample concentration and signal integration period to allow a sufficient number of particles to be analysed (see ISO 14488).

The average values of $D_{10,3}$ or $x_{10,3}$; $D_{50,3}$ or $x_{50,3}$ and $D_{90,3}$ or $x_{90,3}$ from the 6 measurements shall be calculated.

a) The reported cumulative volume distribution value from each test at the 10th percentile $D_{10,3}$ or $x_{10,3}$ shall not deviate from the average value of the 6 measured results values by more than ± 3 %.

b) The reported cumulative volume distribution value from each test at the 50th percentile $D_{50,3}$ or $x_{50,3}$ shall not deviate from the average value of the 6 measured results values by more than ± 2,5 %.

c) The reported cumulative volume distribution value from each test at the 90th percentile $D_{90,3}$ or $x_{90,3}$ shall not deviate from the average value of the 6 measured results values by more than ± 4 %.

In the event of a failure of this test then, all aspects of the measurement method adopted by the operator and of that of the instrument should be examined extensively.

6.5 Accuracy under intermediate precision conditions

6.5.1 General

The tests described below permit comparison of a wide range of instruments having similar properties as well as operators having variable levels of training with an in-house reference material, preferably that meets the requirements set out in H.2 and characterized in accordance with the protocol set out in H.3. However, in all cases the written measurement protocol should be followed which should be drafted in conjunction with the recommendations of Clause 5. This protocol should describe an adequate sample concentration and signal integration period to allow a sufficient number of particles to be analysed (see ISO 14488).

The in-house characterized material shall be accompanied by the values of the specified property and the associated standard uncertainties, u_{house}, required for the acceptance test in this section as well as by a measurement method describing all experimental details for its application in laser diffraction measurement.

6.5.2 Intermediate precision conditions (general test)

For this test, an ‘in-house’ reference material which has been characterized on several similar laser diffraction instruments (‘different laboratories’) with different operators using the same prescribed method is used. This in-house material may then be used to qualify the performance of laser diffraction units of the same kind following the procedure described below. As the same kind of instruments are involved in the characterization of the in-house material, differences in instruments and methods are already included in the associated uncertainties of the characterized material. Therefore, u_p is not required as in 6.2 for the calculation of U_{lim}. The tolerance limits are given by the expanded uncertainty U_{house} of u_{house}

$$U_{\text{lim}} = \pm U_{\text{house}} = \pm CF \cdot u_{\text{house}} \tag{2}$$

where a coverage factor of $CF = 3$ should be chosen in order not to exclude 5 % of the instruments involved.

At least 3 separate test samples shall be measured, 5 separate test samples are preferred.

Each test shall be conducted at an adequate sample concentration and signal integration period to allow a sufficient number of particles to be analysed (see ISO 14488).

The average cumulative volume distribution value from the 3 or 5 tests, at the required percentile shall not exceed the pre-calculated tolerance limits U_{lim} for each of the parameters $D_{10,3}$ or $x_{10,3}$, $D_{50,3}$ or $x_{50,3}$ and $D_{90,3}$ or $x_{90,3}$.

In the event of a failure of this test then, all aspects of the measurement method adopted by the operator and of that of the instrument should be examined extensively.

7 Reporting of results

7.1 General

Report results in accordance with ISO 9276-1 and ISO 9276-2. 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 $D_{5,3}$ or $x_{5,3}$ and above $D_{95,3}$ or $x_{95,3}$ 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 a $D_{100,3}$ or $x_{100,3}$ value or a number distribution by laser diffraction shall not be permitted.

The report of results should contain some or all the following information: Items marked * are mandatory.

7.2 Sample

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

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

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

d) amount of sample,

e) date of analysis. *

7.3 Dispersion

for dry dispersion:

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

b) type of dosing/feeding device, *

c) dosing rate,

d) dispersion pressure; *

for wet dispersion:

e) dispersion liquid: identification, volume and, if necessary, temperature, *

f) dispersant(s): type and concentration,

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

h) pump and stirring speed, *

i) optical path length.

7.4 Laser diffraction measurement

a) instrument type and number, *

b) software version,

c) volume of dispersion unit,

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

e) date and time of last alignment,

f) date of last qualification test, *

g) date and time of measurement,

h) optical concentration/obscuration, *

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

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

k) type of light-scattering model applied, *

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

m) real part of the refractive index of the fluid employed, if the Mie theory is applied, *

n) (optional) fit parameter resulting from de-convolution (e.g. log difference, chi-squared, percent residual);

o) sonication settings and duration, *

p) pump and stirring settings, *

q) obscuration/transmission levels employed. *

7.5 Analyst identification:

a) name and address of laboratory,

b) operator's name or initials. *

Annex A
(informative)

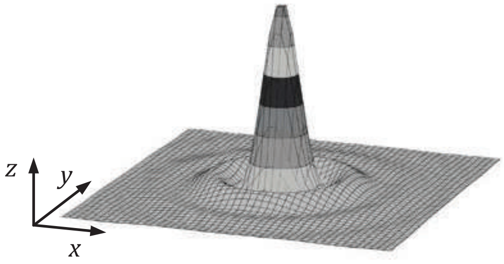
Theoretical background of laser diffraction

A.1 Introduction

Four types of interaction between the incident light and the particle influence laser diffraction measurements[5];

- diffraction at the contour of the particle;
- 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 within the particle.

These interactions lead to interference phenomena, which cause a characteristic pattern of scattered light. 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 – 0,0i.

NOTE The centre of the detector area corresponds to zero degrees. The detector elements correlate with angle.

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

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

- the highest intensity is at zero angle (forward direction) and the intensity gradually decreases towards larger scattering angles;

- — there are large differences in light intensities, with characteristic maxima and minima at different angles in relation to particle size;
- — 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;
- — 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 shall be extended to an ensemble of particles. This is possible provided that:
  - a) each particle scatters as an independent entity, i.e. there is no significant multiple scattering, which means that particle concentration should be low, and
  - b) there is no optical interference between the scattered radiations 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 [20] gives an explanation for the apparent paradox of the factor two. Reference [20] 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 extinction efficiency, expressed as the ratio of extinction 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 and shape (scattering cross-section);

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

c) wavelength of the illuminating source;

The refractive index value of particles ($\underline{n}_\mathrm{p} = n_\mathrm{p} - \mathrm{i}k_\mathrm{p}$) is a complex number with a real term, n_p, and an imaginary term, $\mathrm{i}k_\mathrm{p}$.

EXAMPLE Polystyrene ‘latex’ particles have $\underline{n}_\mathrm{p}$ = 1,59 – 0,0i, λ = 633 nm. 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 $\underline{n}_\mathrm{p}$. The refractive index of non-absorbing dispersion media contains only a real part.

Some information on refractive index values is given in Annex F. The real part can be established by direct measurement using one of several techniques. The determination of the imaginary part is more often empirically arrived at.

The imaginary part might be considered as apparent absorption where light energy is dissipated as heat. In addition, at irregular internal 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 shall 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 together with the influence the 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 irregularly shaped particles has yet to be fully implemented and thus 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 laser diffraction 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 “irregularly shaped objects”.

NOTE ISO 9276-2 adopts the convention that the diameter of the equivalent sphere is described as x or D.

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

See References [4], [5], [18], [20], [30], [42].

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 de-convolution of the measured scattering pattern into a PSD.

Light is an electromagnetic wave with the electric and magnetic vectors at 90 degrees to each other. The influence of these two vectors are expressed in the terms $S_1(\theta)$ and $S_2(\theta)$.

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

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

where

k is the wave number in the medium;

l_a is the distance from scattering object to detector;

I_0 is the intensity of the incident polarized 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 to the scattering plane respectively, as a function of angle θ with respect to the forward direction.

The Fraunhofer approximation was the first optical model employed for particle size measurements. 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[20], 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:

The advantage of the Fraunhofer approximation 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 $\alpha >> 1$). 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. By assuming diffraction is the only scattering component then $S_1(\theta)$, $S_2(\theta)$ are assumed to be equal and Formula (A.2) can be formulated.

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

where

α is a dimensionless size parameter, $\alpha = \pi x n_\mathrm{m}/\lambda$;

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 Formula (A.2) in order to extend it to larger angles.

When a plane wave interacts with a spherical particle, some of the wave may pass through the particle, which having a different refractive index to the surrounding media, introduces refraction. Under these conditions the dimensionless, complex functions as set out by Mie theory and for the far field, are as follows;

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 $S_2(\theta)$. Mie theory provides a rigorous solution that is valid for all sizes of spheres (References [4], [5], [18], [20]). 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 shall 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. (see Annex G).

$S_1(\theta)$and $S_2(\theta)$ are given as,

$$S_1(\theta)=\sum_{n=1}^{\infty}\frac{2n+1}{n(n+1)}\left[a_n\pi_n(\cos\theta)+b_n\tau_n(\cos\theta)\right] \tag{A.3}$$

$$S_2(\theta)=\sum_{n=1}^{\infty}\frac{2n+1}{n(n+1)}\left[a_n\tau_n(\cos\theta)+b_n\pi_n(\cos\theta)\right] \tag{A.4}$$

Fortunately, the complex Formulae (A.3) and (A.4) have been encoded into open source software available by a search of the 'World Wide Web' and yields Mie calculation facilities.

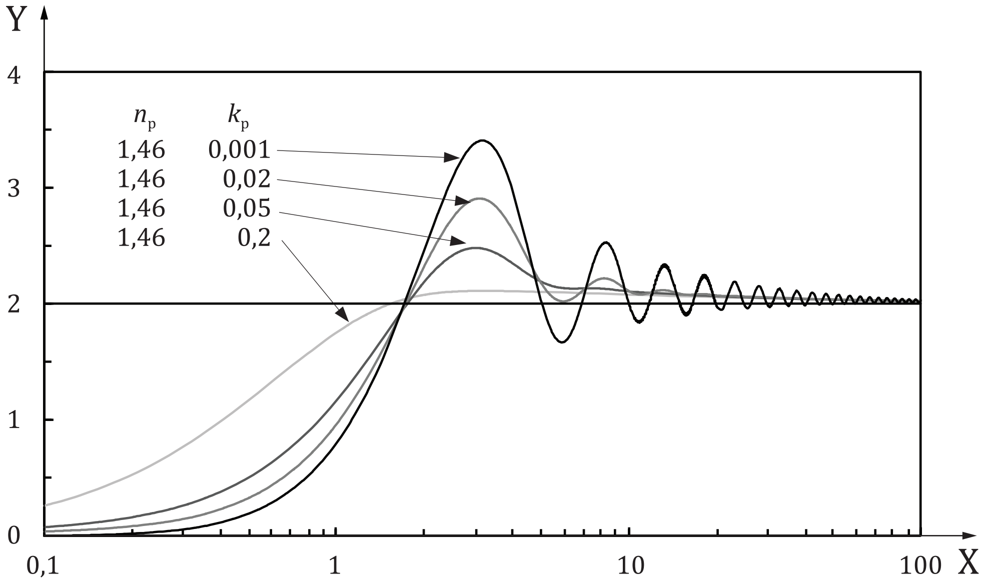
A.5 Model selection

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.

Figures A.2 and A.3 compare the extinction efficiencies according to Mie and Fraunhofer models for both transparent and absorbing particles.



Key

X particle size (µm)

Y extinction efficiency (–)

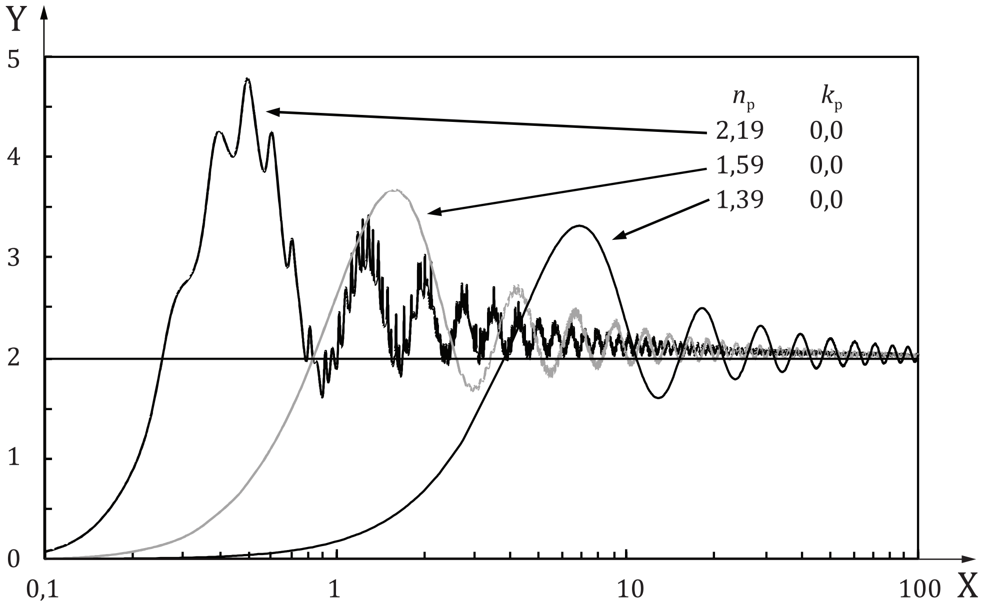
n_p real part of the refractive index

k_p coefficient of the imaginary part of the refractive index

Refractive index of the medium, n_{H_2O} = 1,33; wavelength, λ = 633 nm. The complex refractive index is given by $\underline{n}_p = n_p - ik_p$.

NOTE Fraunhofer assumes an extinction efficiency of 2 for all particle sizes.

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



Key

X	particle size (µm)
Y	extinction efficiency (–)
n_p	real part of the refractive index
k_p	coefficient of the imaginary part of the refractive index

Refractive index of the medium, n_{H_2O} = 1,33; wavelength, λ = 633 nm. The complex refractive index is given by $\underline{n}_p = n_p - ik_p$.

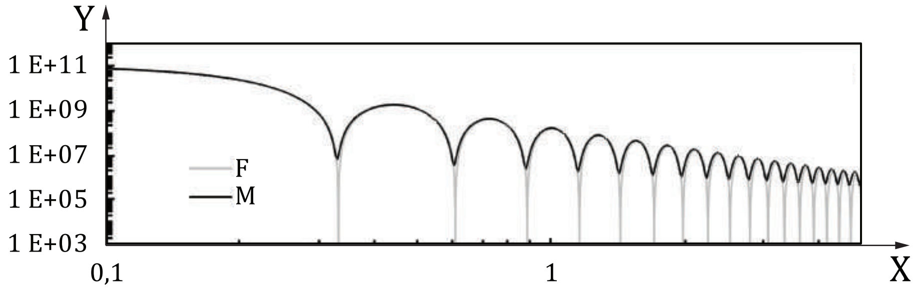
NOTE Fraunhofer assumes an extinction efficiency of 2 for all particle sizes.

Figure A.3 — Extinction efficiencies in relation to particle size and refractive index (Mie model, transparent)

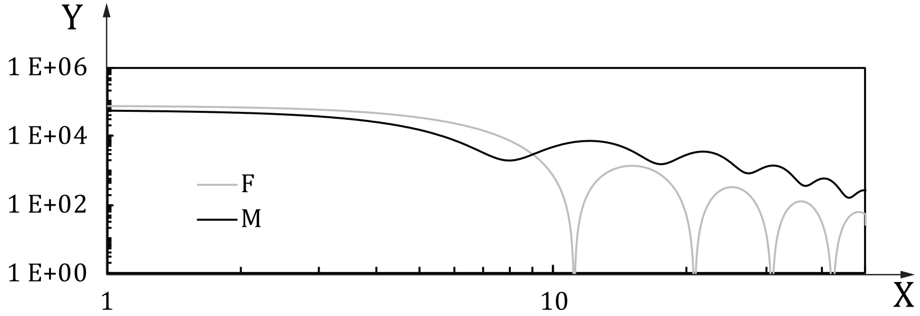
Figures A.2 and A.3 show good agreement between the Mie and Fraunhofer theories for transparent particles larger than about 50 µm and for opaque particles (k_p > 0,2) larger than about 2 µm. Note that Fraunhofer assumes an extinction efficiency of 2 for all particle sizes. In the range 2 µm to 50 µm, 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.

Figures A.2 and A.3 illustrate 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.4 compares the Mie and Fraunhofer predictions for the scattering patterns for 100 µm (opaque) and 3 µm (transparent) particles.



a) $x = 100\ \mu\mathrm{m}$, $\underline{n}_{\mathrm{p}} = 1{,}59 - 2{,}0\mathrm{i}$



b) $x = 3{,}0\ \mu\mathrm{m}$, $\underline{n}_{\mathrm{p}} = 1{,}59 - 0{,}0\mathrm{i}$

Key

X	angle (degree)
Y	relative intensity (–)
F	Fraunhofer model
M	Mie model

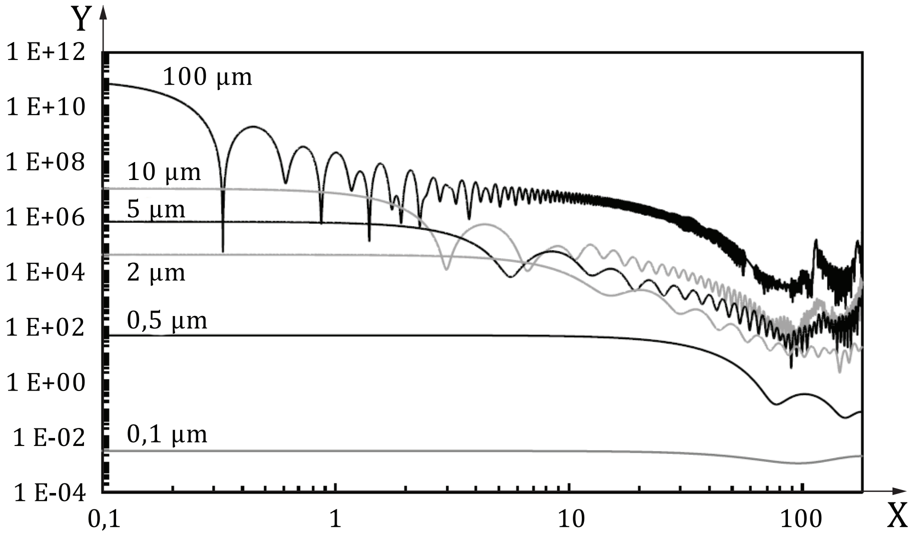
Refractive index of the medium, $n_{\mathrm{H_2O}} = 1{,}33$; wavelength, $\lambda = 633$ nm.

Figure A.4 — Comparison of scattering patterns of absorbing and 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.

The intensity of scattered light with respect to the angle of observation for various single particle sizes is shown in Figure A.5.



Key

X angle (degree)

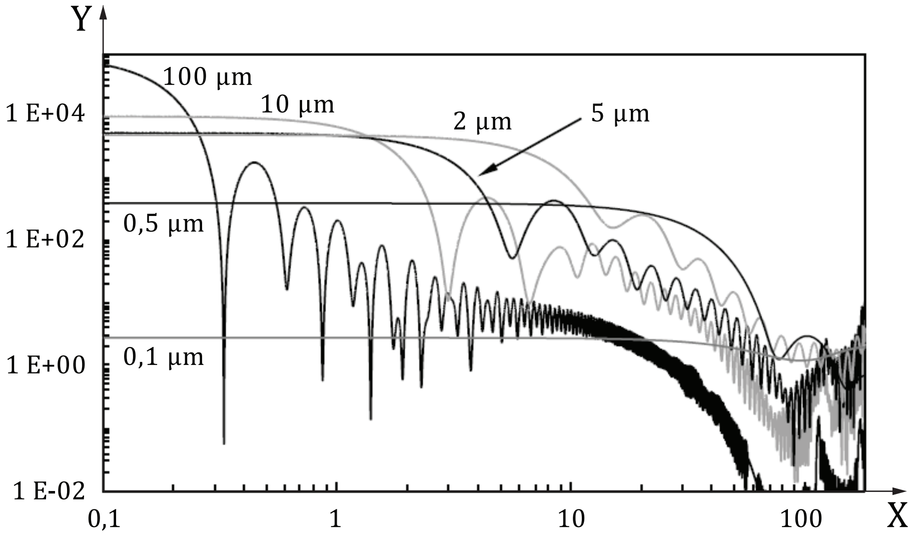
Y relative intensity (–)

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

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

Figure A.5 — 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.6.



Key

X angle (degree)

Y relative intensity (–)

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

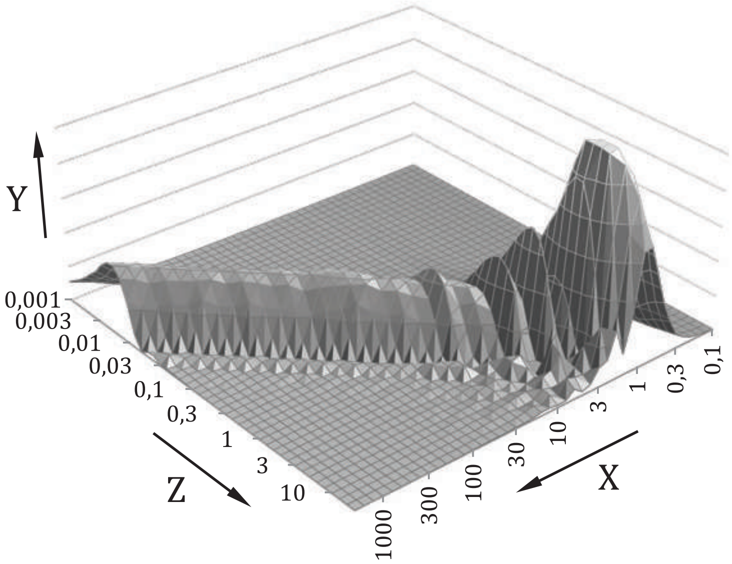
The particle refractive index, $\underline{n}_p$ = 1,59 – 0,0i.

Figure A.6 — 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. It should be understood that current laser diffraction designs use a limited number of detectors, typically less than 100. The limited detector number results in the fine detail shown in the scattering graph being lost due to spatial averaging. 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 integrated over 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.7. A matrix of relative energy data that has the property of diagonal symmetry and a uniform relationship between particle size and angle of observation has significant advantage during the numerical inversion process.



Key

X particle size (µm)

Z angle (degree)

Y relative energy (arb.)

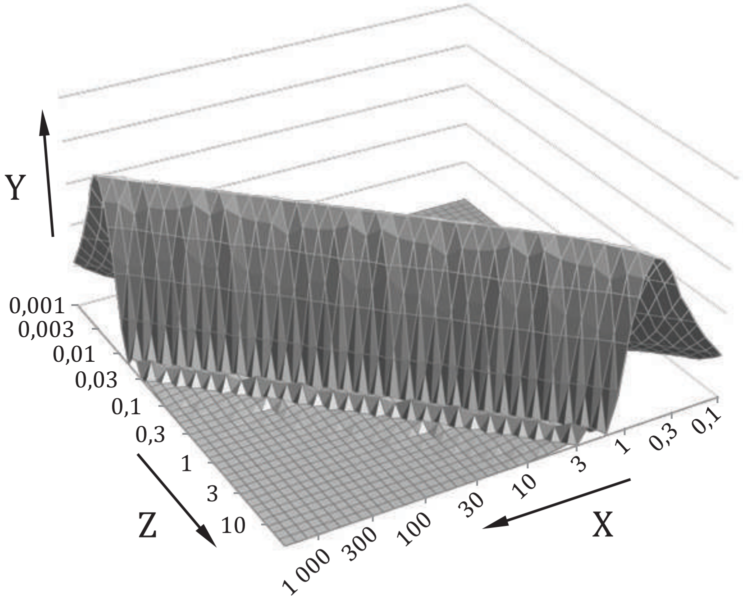
Refractive index of the medium, n_m = 1,33; wavelength, λ = 633 nm.

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

Figure A.7 — 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.8.



Key

X	particle size (µm)
Z	angle (degree)
Y	relative energy (arb.)

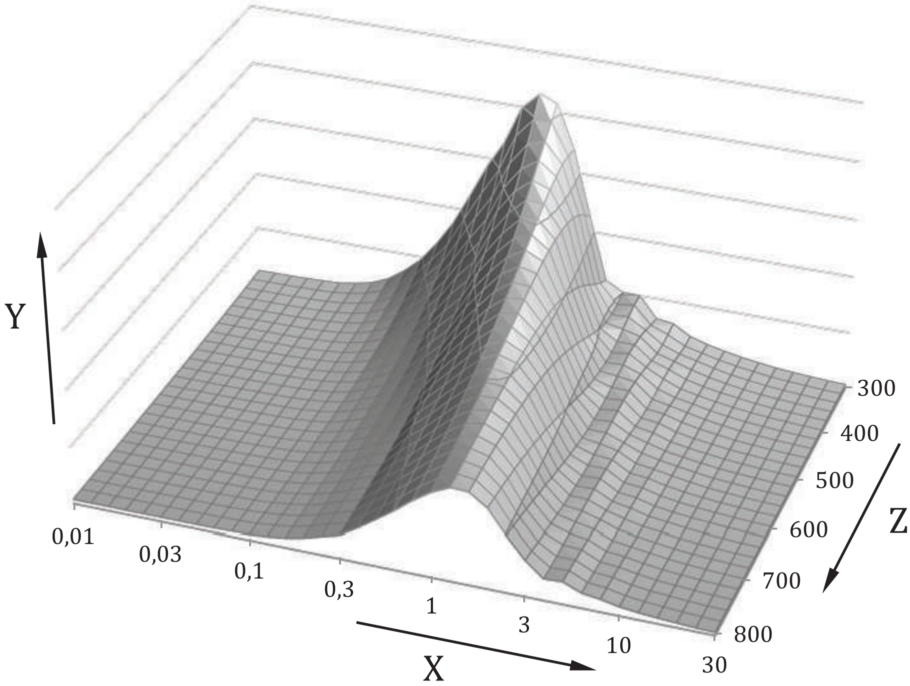
Figure A.8 — Scattering patterns for an optimum detector configuration against particle size for equal volumes of particles (Fraunhofer model)

Figures A.7 and A.8 illustrate regions of agreement and differences between Mie and Fraunhofer theory for large and small particles, respectively.

A.6 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.9.



Key

X particle size (µm)

Z wavelength (nm)

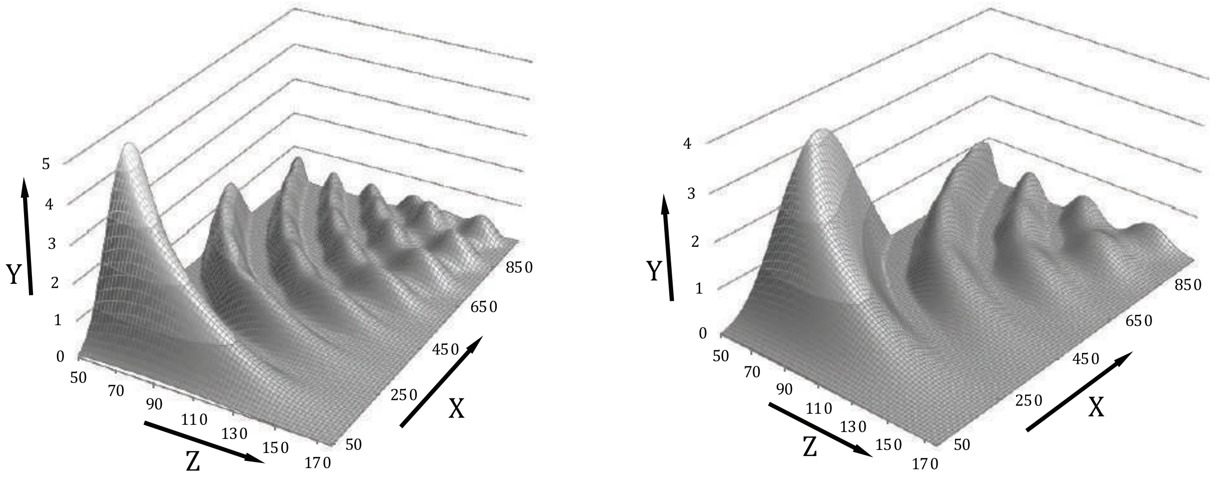
Y relative extinction (arb.)

Refractive index of the medium, n_m = 1,33; the particle refractive index, $\underline{n}_p$ = 1,59 – 0,01i.

Figure A.9 — 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 also varies strongly with size. The combined influence of polarization difference and wavelength is illustrated in Figure A.10 a) and b)[42].

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.



a) b)

Key

X particle size (nm)

Z angle (degree)

Y relative polarization energy difference per unit volume, $(I_v^2 - I_h^2)/x^3$, (arb.)

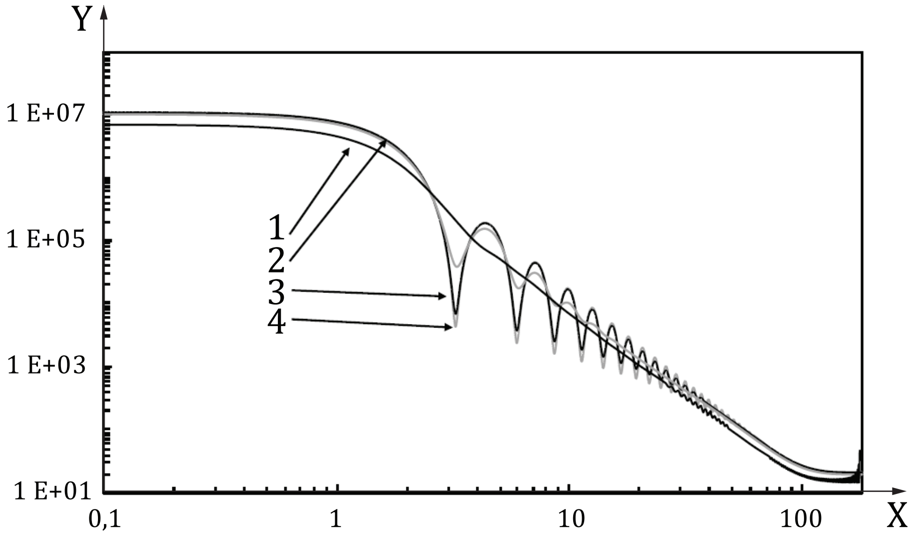
Refractive index of the medium, n_m = 1,33; the particle refractive index, $\underline{n}_\mathrm{p}$ = 1,59 – 0,01i

Figure A.10 — Polarization difference plotted against scattering angle. Particle size of equal volume, for light of wavelengths a) 450 nm and b) 633 nm

A.7 Scattering patterns for PSDs

Figure A.6 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.4 to A.6 show the general decrease of scattering intensity towards larger angles and the effects of the optical model or refractive index.

In practice, however, wide size distributions are encountered. Figure A.11 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 results in even small errors in the detector signals leading 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 de-convolution (see 5.5.5). It also demonstrates the merit of having detectors positioned to capture the high angles of scattering.



Key

X	angle (degree)	1	80 %
Y	relative intensity (–)	2	20 %
		3	5 %
		4	mono-size

Percentage width of size distribution = (100 %) × ($x_{90,3}$ - $x_{10,3}$)/$x_{50,3}$.

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

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

Figure A.11 — Influence of size distribution width on scattering pattern (log-normal size distributions around an x_{50} of 10 µm)

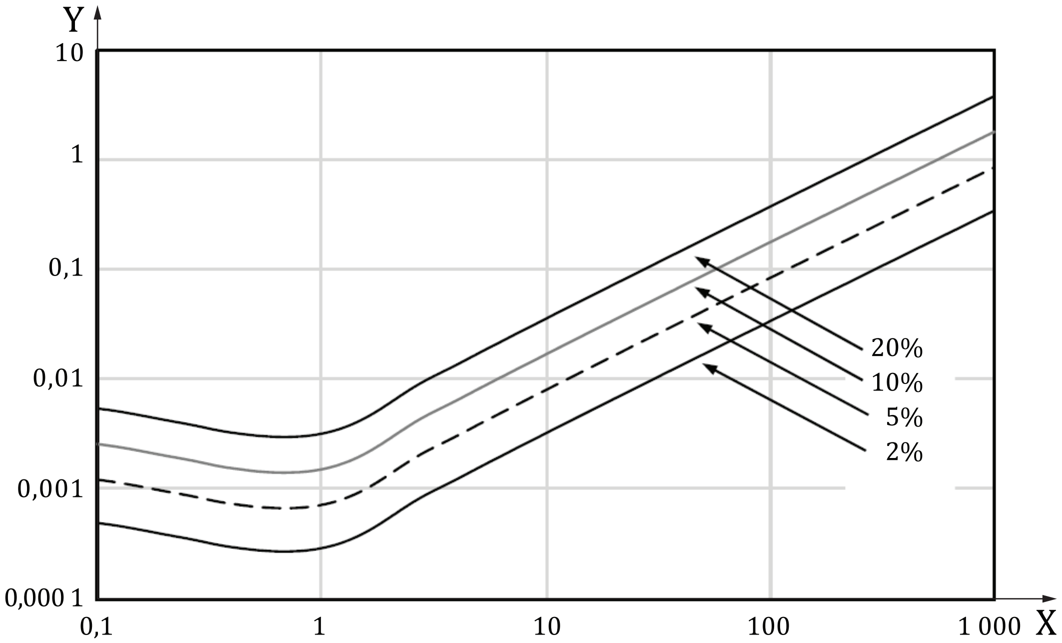
A.8 Concentration

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[20].

In 5.4.4, 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

X particle size (μm)

Y volume concentration (%)

Lines are for each obscuration (%)

Refractive index of the medium, n_m = 1,33; wavelength, λ = 633 nm; path length, l_b = 2 mm.

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

Figure A.12 — Relation of particle size and concentration and its influence on obscuration (Mie calculation)

The plots shown in Figure A.12 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:

$$C = \frac{-2\ln(1-O)}{3l_\mathrm{b}\sum_i A_i\left(\Delta Q_{3,i}/x_i\right)} \qquad \text{(A.5)}$$

where

A_i is the extinction efficiency of size class, i;

l_b is the illuminated path length containing particles;

O is the obscuration;

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

$\Delta Q_{3,i}$ is the volume fraction within size class, 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 path length being filled with particles. Refer to the instrument manual in this regard[28].

A.9 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 conducted by integration of $I(\theta)$ over the number of particles present per volume in each size class and over the geometry of each element. This process is carried out for each series of size classes and detector elements, this leads to a model matrix, which is specific for each instrument. It describes how unit volumes of each of n particle size classes would appear as a signal $\boldsymbol{L}_j$ at each of m detector elements:

$$\begin{bmatrix} \boldsymbol{L}_1 \\ : \\ : \\ : \\ : \\ : \\ : \\ \boldsymbol{L}_m \end{bmatrix} = \begin{bmatrix} \boldsymbol{M}_{11} & : & : & : & : & : & : & \boldsymbol{M}_{1n} \\ : & : & & & & & & : \\ : & & : & & & & & : \\ : & & & : & & & & : \\ : & & & & : & & & : \\ : & & & & & : & & : \\ : & & & & & & : & : \\ \boldsymbol{M}_{m1} & : & : & : & : & : & : & \boldsymbol{M}_{mn} \end{bmatrix} * \begin{bmatrix} \boldsymbol{V}_1 \\ : \\ : \\ : \\ : \\ : \\ : \\ \boldsymbol{V}_n \end{bmatrix} \tag{A.6}$$

For example, the first row in the matrix ($\boldsymbol{M}_{11}$ ... $\boldsymbol{M}_{1n}$) describes the signals for unit volumes of all n size classes on the first detector element, whereas the first column ($\boldsymbol{M}_{11}$ ... $\boldsymbol{M}_{m1}$) 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:

$$\boldsymbol{L} = \boldsymbol{M}\,\underline{\boldsymbol{V}} \tag{A.7}$$

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[18][32][33][37][42]:

$$\underline{\boldsymbol{V}} = \boldsymbol{M}^{-1}\,\boldsymbol{L} \tag{A.8}$$

Formulae such as Formula (A.8) 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 poly-disperse 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.10 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.13, where circular, rectangular and irregular particles and their scattering patterns are shown.

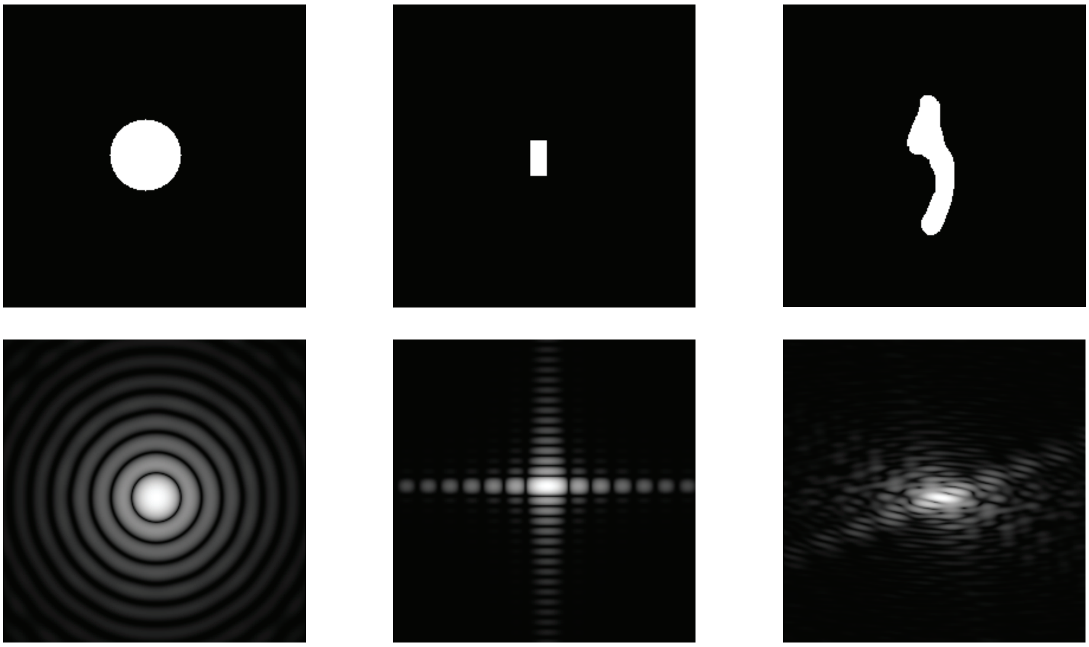


Figure A.13 — Circular, rectangular and irregular particles and their scattering patterns (simulated images)

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 smaller than about 0,2, 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.13. 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)

Advice on dispersion liquids

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 dispersion and 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 References [27] and [42], list refractive indices for a variety of liquids.

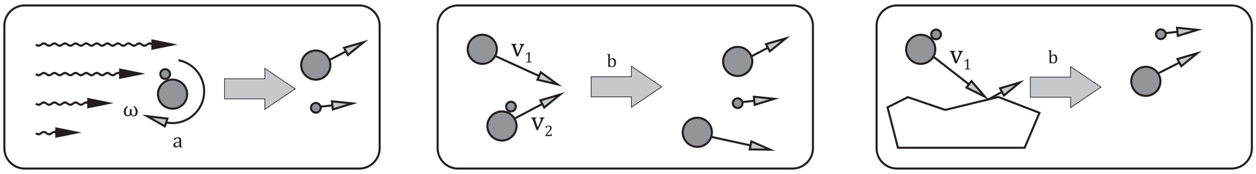
Annex C
(informative)

Dispersion methods — Recommendations

C.1 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 de-agglomeration by particle-particle or particle-wall collisions (see Figure C.1). The complete test 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 combination 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 attrition. If such a plateau is reached, its centre defines the optimum dispersing energy.

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



a) Velocity gradients caused by shear stress

b) Particle-to-particle collisions

c) Surface impacts

Key

V_1, V_2	velocity
ω	angular rotation
[a]	Flow gradient.
[b]	Collision.

Figure C.1 — Processes involved in dry dispersion of powders

C.2 Dispersion in liquid media

For the preparation of liquid dispersions, refer to ISO 14887. A variety of liquids is available. Annex B contains guidelines on the selection of an appropriate liquid for wet dispersion. Generally, pasting, stirring and sonification 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 sonification: 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 measurements 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)[29][40]. 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.

Annex D
(informative)

Instrument preparation — Recommendations

WARNING — 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.

D.1 Warm up

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).

D.2 Status check

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.

D.3 Working zone

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 is captured within the clear aperture of the lens that focuses it on the detector.

D.4 Qualify

Qualify the instrument performance with respect to both precision and accuracy at regular time intervals by measuring a reference material of known size distribution and record the date and results. (see Clauses 5 and 6).

D.5 Wet dispersion

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).

D.6 Dry dispersion

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.

D.7 Sprays

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.

D.8 Optical model

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

Annex E
(informative)

Error sources and diagnosis

E.1 Sampling and sample preparation

a) 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. See ISO 14487.

b) Incomplete de-agglomeration of particles, due to an improper dispersion procedure (liquid, dispersant, sonication).

c) Clustering 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.

d) Swelling, re-agglomeration, dissolution or evaporation of particles/droplets before or during measurement.

e) Inclusion of air bubbles due to foaming dispersants and/or vigorous stirring.

f) 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.

E.2 Errors and bias from sources related to particle properties

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

a) 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 small aspect ratio. Often, such particles have a preferred orientation.

b) 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.

c) Optical heterogeneity: The particles may be optically heterogeneous, as is the case for aggregated 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.

d) 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.

e) Inappropriate optical model or parameters: 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 5.5.4).

E.3 Errors from procedure

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 de-convolution of light intensity values to PSD for the elected measurement (check with the instrument manufacturer);

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

j) working at significantly different obscuration;

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

E.4 Error diagnosis

Errors in specific parts of the procedure may be diagnosed by the following operations:

a) 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.

b) 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.

c) 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 shall elapse to allow the fluctuations to die down.

d) 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.

e) Comparison of known particulate concentration with the theoretical value. For particle systems where all the particles have an aspect ratio of greater than about 0,25 (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 formula shown in A.9 may provide guidance as to the appropriate choice of optical model and refractive index values. For particle systems having aspect ratios close to 1, 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.

f) 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.

Annex F
(informative)

Refractive index — Recommendations

F.1 General

Laser Diffraction/Scattering is essentially an optical method where both the size and the quantity of the particles in the distribution, described by this method, depend upon the optical characteristics of both the particles and the suspending medium. The scattering intensity from a particle depends upon its size, relative refractive index with respect to the suspending fluid and the wavelength of illuminating source.

The refractive index of a material is wavelength and to a degree, temperature dependent. The rate of change of both the refractive index value with respect to wavelength and temperature is also material dependent.

When $\left|Re\left(m_{\text{rel}}-1\right)\right|>0{,}05$, then the real part of the refractive index is usually only required to 2 decimal places.

The positive imaginary (absorption) part of the refractive index of a particle k_{p} has typical values between 0,001, to 0,1.

Where a rough particle surface is expected, as in crushed fully transparent glass, a value of k_{p} of 0,01 to 0,03 may be applied.

A k_{p} of zero is applied for measurements of reference latex beads.

Refer to Annex G, Robustness, of the final value of refractive index selected. Specify the required maximum standard error in the calculated result.

The wavelength used to determine the value of refractive index may not be the same as the light source wavelength used within the laser diffraction apparatus being employed.

F.2 Sources of reference for n_{p} real part of refractive index

a) General literature sources of reference for organic and inorganic materials are as follows: References [10], [12], [13], [14], [23], [27].

b) References for glass and other optical materials can be found in References [12], [13] and [27].

c) Geological and other minerals: References [3], [10], [11], [15], [17], [23], [43].

d) Polymers and pigments: References [7], [26], [36].

e) Refractive index values by microscopic determination: References [2], [9], [16], [24], [30], [31], [34], [35], [38].

f) The microscopic method is assisted with a range of index matching fluids: References [22], [43].

g) Refractive index matching may also be achieved by using binary mixtures e.g. propan-2-ol and 2-methylnapthalene. This method requires that the particles are not resoluble in either liquid. Other binary mixtures have also been used.

h) Refractive index determination by extrapolation of solutions to 100 % solids: Reference [9].

i) Refractive index determination using a refractometer: Reference [17].

j) Molecular refractivity is provided by References [25], [39]. Molar refractivity software is available.

k) Refractive index estimations are provided for pharmaceutical products: Reference [9].

F.3 Imaginary part of the refractive index

In general, the imaginary part is often established empirically or by experience.

There are a limited number of methods to establish the imaginary part of the refractive index. Such methods are based upon ellipsometry of thin films. Values established for thin films can only be an initial guess as they may not be suitable at particle dimensions.

F.4 Methods of estimating refractive index for material mixtures

a) A composite value for the real part of the refractive index may be estimated by adding the individual refractive index values for each component multiplied by the volume fraction of each material component in the sample (a knowledge of each components density is required to relate weight to volume) i.e.

$$\text{Composite } RI = n_{\mathrm{p}1} VF_1 + n_{\mathrm{p}2} VF_2 + \cdots$$

where

$n_{\mathrm{p}1}$ refractive index of sample material component 1;

$n_{\mathrm{p}2}$ refractive index of sample material component 2;

VF_1 volume fraction of sample material having refractive index $n_{\mathrm{p}1}$;

VF_2 volume fraction of sample material having refractive index $n_{\mathrm{p}2}$.

b) The Gladstone-Dale approximation (best for minerals and mixtures only)[3], may also be used. Such a composite value should be tested to ensure it also corresponds to the lowest residual between the measured and calculated light energy fit.

Annex G
(informative)

Laser diffraction robustness and ruggedness

G.1 Robustness

A robust analytical method is one which exhibits insensitivity to changes of the operational parameters. This should be ascertained during the method development and determines the allowable (acceptable) limits for all critical parameters that affect the final result[1].

G.2 Ruggedness

A rugged analytical method is one which exhibits insensitivity against inadvertent changes of known operational variables. These variables often make themselves known when transferring methods between sites, even if results on a single site were acceptable. Experiments are normally conducted, using well defined procedures following robustness testing and provides information on a procedure's inter-laboratory transferability.

G.3 Investigation of parameters

From a fundamental measurement perspective, laser diffraction is a robust technique. If the same scattering pattern is measured, the same result will always be obtained using the same optical model. However, if there is variation in the measured scattered light, there will be variation in the results. Many of sources of variation/poor robustness are related to the sample preparation/sampling of the material.

An ideal time to study the robustness of a method is during its development, but sometimes investigations may occur as part of a troubleshooting exercise.

When considering the parameters that should be examined in order to make a robust laser diffraction procedure, it is recommended that a quality by design (QbD) approach as pioneered by Juran[21] is adopted. A case study in the development of QbD to laser diffraction method development was outlined by Adamson[1].

When embarking upon method development, the first step is to determine the end goals. If the aggregated or agglomerated state is of interest, then care should be taken not to disperse the clusters. Conversely if the dispersed state is of interest, then the agglomerates should be fully dispersed. By following the guidelines presented elsewhere in this document and in the operating manuals/literature of the manufacturer in question a rough method can be defined. To improve the robustness of a method, a fuller understanding of the parameters that can influence the final result is needed. A decision can then be made as to which ones are key for the product in question. This is essentially a risk assessment.

Each parameter can be classified into defined types. Each of these parameters can also be classed as being either;

a) Noise factors: unintentional variations which if identified as potentially critical may require ruggedness testing to assess their impact. These may be able to be controlled in a broad sense. Small variation may show up as small unavoidable differences in results.

b) Control factors; these are factors which form a crucial part of the method (such as the sample preparation procedure). They should be well defined (by describing them in detail) by a method.

c) Experimental factors; are those that should be varied as part of method development to find the most appropriate ones for the procedure in question.

These factors can be illustrated by using what is called an Ishikawa or fishbone diagram. Below we will see separate diagrams for wet, dry and spray methods (see Figure G.1).

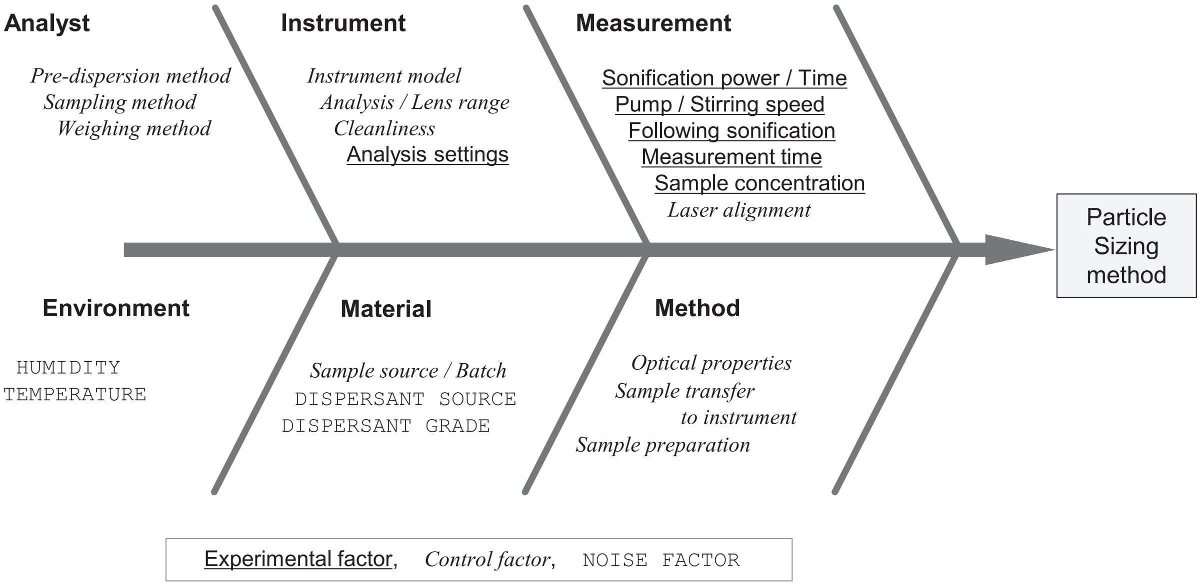


Figure G.1 — Risk factor for wet dispersion method

Analyst variables; describe how a sample is obtained and pre-dispersed.

Environmental variables; describe the conditions in the laboratory where the measurement will be made. Is the temperature constant? Is the temperature or humidity similar to other laboratories measuring this compound if doing a method transfer/comparison? Is the laboratory humidity different to previous occasions where measurements were performed?

Material variables; describe the source of sample, dispersant and any reference materials used for the measurement. Are the dispersants used of an appropriate grade and free of contamination? Is the material being measured produced so its surface chemistry is consistent? Do its surface properties vary? Has it been washed differently? Is it drier or wetter than usual?

Instrument variables; describe the set up of the instrument and its basic function. Is the instrument model the same? Have the appropriate analyses and size ranges or lens been selected? Is the system in a state appropriate for measurement?

Method variables; describe parameters associated with the method set up and selection process. Is the method which defines how to prepare the sample and add to the dispersion unit appropriate? Is the selection of the optical model appropriate? Is the amount of sample added sufficient to get good signal to noise, but not enough to get sufficient multiple scattering.

The user should be able to determine which are the critical factors and come up with a series of experiments to determine the most appropriate settings (stir speed titration, examination of repeatability as a function of measurement time, ultrasound power and duration, etc).

For dry measurements (Figure G.2), the same guidance as for the wet measurement applies, but the key measurement parameters will be feed rate, dispersion pressure, moisture content, amount of sample, with minimal temperature fluctuations of propelling gas. Guidance on setting these can be found in Annex C.

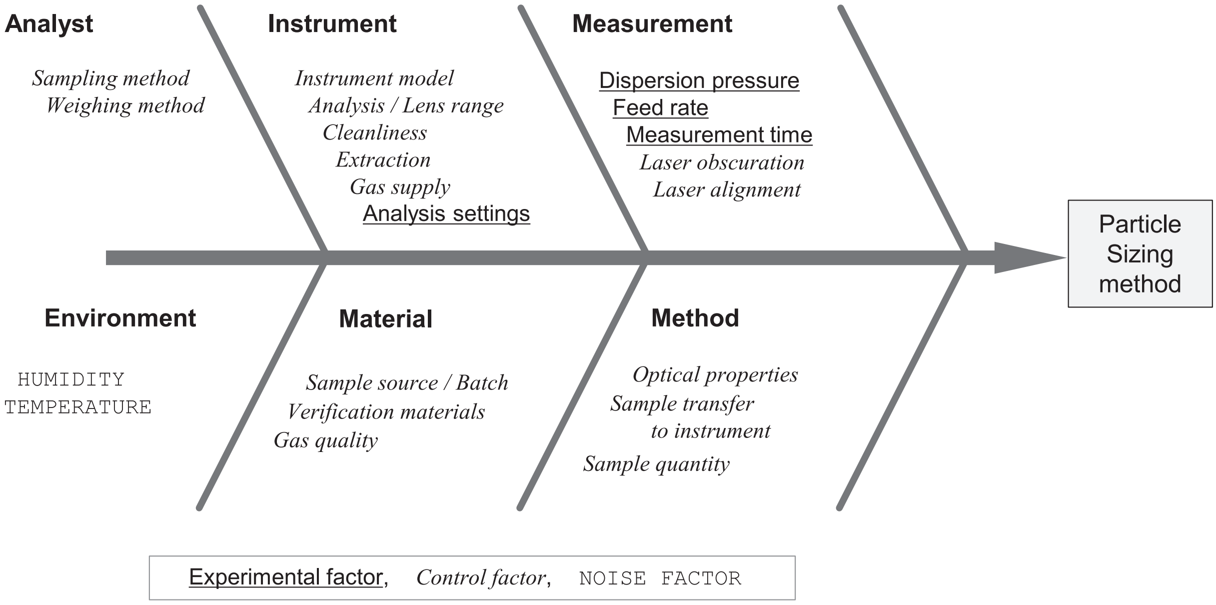


Figure G.2 — Risk assessment for dry dispersion methods

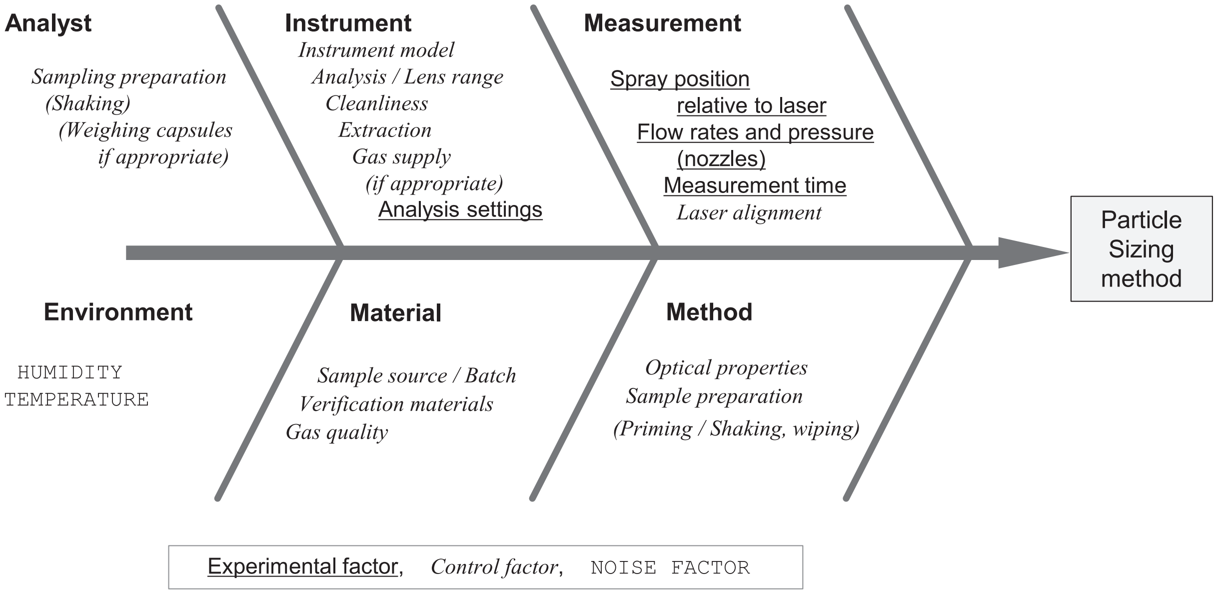


Figure G.3 — Risk assessment for spray methods

For sprays (see Figure G3), the type of spray will determine the critical parameters. For nozzle characterization, flow rate and pressure are critical, for nasal sprays device priming and shaking are important. For any spray measurement the most important parameter is the position of the spray relative to the laser. (This affects many parameters, sampling in the plume, potential loss of light and the chance to coat the measurement optics in the device with spray). Additionally, the spray should emit into a moving airstream to minimize velocity bias.

The analysis conditions can determine the range of detectors used, as beam steering due to evaporating propellant or drops needs to be removed from the analysis to reveal the scattering exclusively due to the droplet size distribution.

Annex H
(normative)

Certified reference materials, reference materials and comparison parameters

H.1 General

Particle size determination by laser diffraction, describes the size of three-dimensional objects with a single value of length, the 'equivalent spherical diameter (laser diffraction)'. For this reason, the equivalent spherical diameters reported for non-spherical particles depend upon the technique employed. The sphere is the only shape whose properties can be fully defined by a single dimension of length and volume, without ambiguity.

This document requires that a certified reference material whether spherical or non-spherical be employed for the determination of accuracy in 6.2 and 6.5. While ISO 17034 recognizes the possibility to assign method defined certified values, they do not provide specific detail on how this can be achieved for laser diffraction analysis.

This annex explains the differences between different kinds of reference materials as well as set out both the material requirements together with the route to providing a metrologically valid traceable procedure for the creation of the assigned values complete with the standard and extended uncertainties for laser diffraction.

Three types of reference materials can be discriminated for application to laser diffraction instruments:

a) Certified Reference Materials composed of spherical particles: Due to the sphericity of the particles, the PSD properties of the material are independent of the method and have been obtained by methods that deliver results directly traceable to the International System of Units (SI), typically imaging methods. The certified values have assigned uncertainties derived from the summation of all input factors of the measurement model.

b) Certified Reference Materials that may consist of spherical or non-spherical particles and have certified values for the equivalent spherical diameter as obtained by this document: The PSD properties have been established by a network of competent laboratories, i.e. by well-trained analysts using laser diffraction instruments, the proper functioning of which has been demonstrated by e.g. the use of CRMs described in (a). Due to the demonstration of the proper functioning of the instrument and adherence to this standard, the certified values are traceable to the International System of Units (SI) and the uncertainties comprise all influence factors expected for laser diffraction. The procedure to derive the certified values and their uncertainties shall be described in full detail.

c) In-house Reference Materials: These materials may consist of spherical or non-spherical particles; typically, their composition is close to one of the company's products. PSD properties for laser diffraction application have been established by a well-trained analyst on a laser diffraction instrument, the quality of which has been demonstrated, e.g. by using a CRM of type (a) or (b) above. The assigned values are valid for the instrument model used for value assignment only and the uncertainty comprises all influence factors for the instrument model in question. The measurement procedure shall be described as required by this document and by ISO/IEC 17025.

NOTE Irregular particles are prone to flow orientation and the conversion of the scattering pattern to a size or to a size distribution is more dependent on the method employed when compared with spherical particles. This is reflected either in an increased uncertainty of the assigned values of the certified material or in an increased systematic deviation of the test result, which may not be covered by u_p as provided in Table 1.

H.2 General requirements for reference materials suitable for laser diffraction

H.2.1 General

Reference material particles for use in particle size measurements by laser diffraction may be spherical or non-spherical, certified in relation to the specific goal of their application. In addition to being produced in compliance with the general requirements for reference materials (see ISO Guide 35) they shall comply with the following properties.

H.2.2 Size distribution width

The width of the PSD ($x_{90,3}/x_{10,3}$ ratio) shall be in the range of 1,5 to 10.

H.2.3 Aspect ratio, shape

The aspect ratio of the particles shall be greater than 0,5 in the X, Y and Z plane.

H.2.4 Optical properties, refractive index

The optical homogeneity of the material shall be as uniform as possible. The complex refractive index of the particles shall be provided for the wavelength used.

H.2.5 Apparent density (wet application)

The apparent density of the material shall exceed the density of the dispersing liquid for the particles not to float in wet applications. Furthermore, the apparent density should not be too high for avoiding sedimentation effects. Therefore, a value within the range 1 100 – 2 500 kg/m^3 seems to be optimal for aqueous applications. Particles of higher densities can be used if a liquid with higher density or viscosity is applied.

H.2.6 Stability (chemical/mechanical/long term)

For wet application the particles shall have a high chemical stability and be non-soluble and non-swelling in dispersant media. The particles should not be disrupted by ultrasound pressure in dispersant media. For dry application the mechanical strength shall be as high as possible since the material should be able to withstand a typical dry dispersion procedure without breakage. The material should provide a shelf life of at least 2 years after production without measurably changing its physical properties.

H.2.7 Dispersibility (wet application)

The material shall be easily dispersible in the chosen liquid. No particle agglomerates or flocculation should be detectable after dispersion. It is allowed to support the particle dispersion using dispersing agents or ultrasound.

H.2.8 Dispersibility (dry application)

The particles should not agglomerate under normal environmental conditions. Their electrostatic behaviour should not cause any significant deposition on a feeding mechanism.

H.2.9 Quantity, sampling, sub sampling

A significant quantity of material should be stocked to guarantee a prolonged period of application. Collecting test samples from the reference material stock shall be carried out by use of a suitable splitting method (see ISO 14488).

H.2.10 Documentation, protocol

The chosen reference material shall possess sufficient and robust, written sampling/dispersion/measurement protocols, suitable for laser diffraction analysis.

H.2.11 Required property values

For system qualification on accuracy (OQ) (6.2) and on accuracy under intermediate precision conditions (PQ) (6.5) the following assigned particle size parameters are required: $D_{10,3}$ or $x_{10,3}$, $D_{50,3}$ or $x_{50,3}$ and $D_{90,3}$ or $x_{90,3}$. The standard uncertainty, u_{crm}, or the expanded uncertainty, U_{crm}, of each particle size parameter should be quoted. Additional property values may be added for better relation to product properties.

H.3 Procedure to create other traceable reference properties for spherical and non-spherical reference materials using laser diffraction instrument

The laser diffraction apparatus selected as well as the measurement procedure to provide the assigned values of the in-house reference material shall demonstrate their fitness for purpose by completing and fully documenting the procedure followed. Subsequently, the value applicable for the specific instrument model and set-up is determined. The approach is basically the set-up of a Shewhart control chart, with the assigned value being the average of the results and the assigned standard uncertainty being the standard deviation of the results obtained. The values obtained following this approach are valid for one specific instrument model and for specific instrument settings.

- The proper operation of the laser diffraction instrument shall be established with a spherical certified reference material (3 to 5 measurements). The measured data shall fully agree with the certified results within the expanded uncertainty values provided by the certificate.
- Variables related to particle transport mechanisms, such as pumping and stirring speeds for liquid dispersions and pressure and output nozzle choice in dry powder systems, shall be optimized to minimize the effects of e.g. particle alignment and velocity bias (all particles should take random orientation and traverse the measurement zone at the same speed).
- Test samples of a new reference material shall be used in a sufficient quantity in order to guarantee that they are representative for the stock of material within a stated confidence interval (see ISO 14488). At least 10 test samples of the new material shall be measured to yield average values for the size parameters $D_{10,3}$ or $x_{10,3}$, $D_{50,3}$ or $x_{50,3}$ and $D_{90,3}$ or $x_{90,3}$, as well as their uncertainty (the standard deviation of the results). During these measurements, as many factors as possible that might have an influence on the result should be varied. This means measurements should be performed on different days, by different operators (if available), on different instruments of the same model (if available), etc.

The whole procedure and all values obtained shall be fully documented.

Bibliography

[1] Adamson J.T., A Quality By Design Approach for Particle Size Analysis of an Active Pharmaceutical Ingredient. s.l.: *American Pharmaceutical review*, July 2013

[2] Allaby A., Allaby M., *"Becke line test": A Dictionary of Earth Sciences*, Oxford University Press, 1999

[3] Battey M.H. *Minerology for Students.*: Longman, 1981

[4] Bohren C.F., Hufman D.R. *Absorption and scattering of light by small particles.*: Wiley, 1983. p. 530

[5] Born M., Wolf E. *Principals of Optics: Electromagnetic theory of propagation, Interference and diffraction of light*, 7th Edition. Cambridge UK: Cambridge University Press, 1999

[6] Boxman A., Merkus H.G., Verheijen P.J.T., Scarlett B. *Deconvolution of light-scattering patterns by observing intensity fluctuations.: Appl. Opt. 30*, 1991. pp. pp. 4818–4823

[7] Branrup J., Immergut E.H., Gruike E.A. *Polymer Handbook.*: Wiley Interscience, 1999

[8] Burgess C. Pharmaceutical Technology: *Pharmaceutical Technology*, June 2014. Vols. Volume 38, Issue 6

[9] Cao X., Hancock B.C., Leyva N., Becker J., Yu W., Masterson V.M., Estimating the refractive index of pharmaceutical solids using predictive methods.: *International Journal of Pharmaceutics*, **368**, 2009. pp. 16–23

[10] Dana J.D., Dana E.D. *The System of Minerology*, Longman, 1981. Vols. Vol. 1: Elements, Sulfides, Sulfosalts, Oxides; Vol. 2: Halides, Nitrates, Borates, Carbonates, Sulfates, Phosphates, Arsenates, Tungstates, Molydbates, etc.

[11] Deer W.A., Howie R.A., Zussman J., An Introduction to the Rock Forming Minerals.: Longman, 14th Impression, 1983

[12] Driscoll W.G., Vaughan W. *Handbook of Optics.* New York: McGraw-Hill, 1978

[13] Fanderlick I. *Optical Properties of Glass.* New York: Elsevier, 1983

[14] Gibb T.R.P.Jr, Optical Methods of Chemical Analysis.: McGraw Hill, First Edition 1942

[15] Gladstone J.H., Dale T.P., Researches on the refraction, dispersion and sensitiveness of liquids.: *Philosophical Transactions of the Royal Society* **153**, 1863, pp. 317–343

[16] Hartshorne N.H. C*rystals and the Polarising Microscope — A Handbook for Chemists and Others*. London: Edward Arnold, 2nd Edition, Stuart A., 1950

[17] Herbert-Smith G.F. *Gem-Stones and their distinctive characters.* London: Methuen & Co, 2nd Edition 1913

[18] Heuer M., Leschonski K. *Results obtained with a new instrument for the measurement of particle size distributions from diffraction patterns: Part. Charact. 2*, 1985. pp. pp. 7–13

[19] Hirleman E.D., On-line calibration technique for laser diffraction droplet sizing instruments. New York, NY: Am. Soc. Mech. Eng, 1983. pp. Paper 83-GT 232. Vol. 28th Int. Gas Turbine Conference

[20] Van de Hulst H. C. *Light scattering by small particles.* New York: Dover, 1981. p. 470

[21] Juran J.R. *Quality by Design: The New Steps for Planning Quality into Goods and Services.* New York: Free Press, 1992

[22] KATRITZKY A.R., SILD S., KARELSON M., pp. General Quantitative Structure-Property Relationship Treatment of the Refractive Index of Organic Compounds. pp. 840–848

[23] KERR P. F. *Optical Minerology.* New York: McGraw-Hill, 1977

[24] LARSEN E.S., BERMANN H., The Microscopic Determination of the non-opaque Minerals United States Second Edition Department of the Interior Geological Survey Bulletin 848.: United States Government Printing Office, 1934 (First edition dates from 1921)

[25] LE FÈVRE R.J.W., Molar refractivity and polarizability. [ed.] V Gold.: Academic Press, 1965. Vols. Volume 3

[26] LEWIS P.A. *Pigment Handbook.* New York: John Wiley, 1988

[27] LIDE D.R., CRC Handbook of Chemistry and Physics. Boca Raton: CRC Press, 2004–2005

[28] LIPS A., HART P.M., EVANS I.D., On the characterization of food emulsions and dispersed hydrocolloid particles by optical methods. [ed.] K Leschonski: Proceedings of the 5th European Symposium on Particle Characterization (PARTEC). pp. 443–451. Nürnberg Messe, Nürnberg, 1992

[29] MASUDA H., GOTOH K., Study on the sample size required for the estimation of mean particle diameter. *Advanced Powder Technol.* **10** (1999) 159–173

[30] MERKUS H.G. *Particle Size Measurements*: Springer, 2009

[31] MERMUYS HD., THAS O., VAN DER MEEREN P., Determination of the Refractive Index of Water-dispersible Granules for Use in Laser Diffraction Experiments.: Part, Part Charac, 19(6), 2002. pp. 426–432

[32] PHILLIPS D.L., A technique for the numerical solution of certain integral equations of the first kind.: J. Assoc. Comput. Mach, 1962. pp. 9, pp. 84–97

[33] PIKE E.R., MCWHIRTER J.G., BERTERO M., DE MOL C., Generalised information theory for inverse problems in signal processing.: IEE Proc. F: Commun. Radar Signal Proc, 1984. pp. 131, pp. 660–667

[34] ROTH W.A., EISENLOHR F., LÖWE F. *Refraktometrisches Hilfsbuch.* Berlin: Walter de Gruyter & Co, 1952

[35] SCHROEDER VAN DER KOLK J.L.C. *Tabellen zur mikroskopischen Bestimmung der Mineralien nach ihrem Brechungsindex*. Wiesbaden: Kreidel's Verlag, 1906. Vols. 2nd Edition Beekman, E.H.M

[36] TILLEY R. *Colour and the Properties of Materials.* New York: John Wiley, 2000

[37] TWOMEY S., On the numerical solution of Fredholm integral equations of the first kind by the inversion of the linear system produced by quadrature.: J. Assoc. Comput. Mach., 1963. pp. 10, pp. 97–101

[38] VAN HILTEN D., Refractive indices of minerals through the microscope: a simpler method by oblique observation.: *American Mineralogist*, **66**, 1981. pp. 1069–1091

[39] VOGEL A. *Physical Properties and Chemical Constitution. Part XXIII Miscellaneous Compounds Investigation of So-Called Coordinate or Dative Link in Esters of Oxy-Acids and in Nitro-Paraffins by Molecular Refractivity Determinations Atomic, Structural, and Group Para.: j.* Chem Soc, 1948. pp. 1833–1855

[40] WEDD M., Procedure for Predicting a Minimum Volume or Mass of Sample to Provide a Given Size Parameter Precision.: *Part. Part. Syst. Charact.*, **18** (2001) 109–113

[41] WINCHELL A.N., WINCHELL H. *Elements of Optical Minerology*. New York: John Wiley, 1929. Vol. Second Edition Part 111

[42] Xu R. *Particle characterization: Light scattering methods*. Dordrecht: Kluwer, 2000. p. 397 p. . Vols. Powder Technology Series, Vol. 13

[43] The *United States Pharmacopeia,* Thirty-Seventh Revision, and the *National Formulary*, Thirty-Second Edition, *USP 37–NF 32*. Section 1058

[44] ISO 3534-2, *Statistics — Vocabulary and symbols — Part 2: Applied statistics*

[45] ISO 8130-13, *Coating powders — Part 13: Particle size analysis by laser diffraction*

[46] IEC 60825-1, *Safety of laser products — Part 1: Equipment classification and requirements*

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

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

[49] ISO 17034, *General requirements for the competence of reference material producers*

[50] ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

[51] ISO 24235, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of particle size distribution of ceramic powders by laser diffraction method*

[52] ISO 26824, *Particle characterization of particulate systems — Vocabulary*

[53] ISO 80000-7, *Quantities and units — Part 7: Light and radiation*

[54] ISO Guide 31, *Reference materials — Contents of certificates, labels and accompanying documentation*

[55] ISO Guide 35, *Reference materials — Guidance for characterization and assessment of homogeneity and stability*

[56] ISO/IEC Guide 99, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

This page has been intentionally left blank

(*Continued from second cover*)

The technical committee has reviewed the provisions of the following International Standards referred in this adopted standard and has decided that they are acceptable for use in conjunction with this standard:

International Standard	*Title*
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

In reporting the result of a test or analysis made in accordance with this standard, if the final value observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

This Indian Standard has been developed from Doc No.: CHD 20 (17807).

Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected

BUREAU OF INDIAN STANDARDS

Headquarters:

Manak Bhavan, 9 Bahadur Shah Zafar Marg, New Delhi 110002
Telephones: 2323 0131, 2323 3375, 2323 9402 *Website*: www.bis.gov.in

Regional Offices: *Telephones*

Central : 601/A, Konnectus Tower -1, 6th Floor, DMRC Building, Bhavbhuti Marg, New Delhi 110002 — 2323 7617

Eastern : 8th Floor, Plot No 7/7 & 7/8, CP Block, Sector V, Salt Lake, Kolkata, West Bengal 700091 — 2367 0012, 2320 9474

Northern : Plot No. 4-A, Sector 27-B, Madhya Marg, Chandigarh 160019 — 265 9930

Southern : C.I.T. Campus, IV Cross Road, Taramani, Chennai 600113 — 2254 1442, 2254 1216

Western : Plot No. E-9, Road No.-8, MIDC, Andheri (East), Mumbai 400093 — 2821 8093

Branches : AHMEDABAD. BENGALURU. BHOPAL. BHUBANESHWAR. CHANDIGARH. CHENNAI. COIMBATORE. DEHRADUN. DELHI. FARIDABAD. GHAZIABAD. GUWAHATI. HIMACHAL PRADESH. HUBLI. HYDERABAD. JAIPUR. JAMMU & KASHMIR. JAMSHEDPUR. KOCHI. KOLKATA. LUCKNOW. MADURAI. MUMBAI. NAGPUR. NOIDA. PANIPAT. PATNA. PUNE. RAIPUR. RAJKOT. SURAT. VISAKHAPATNAM.

Published by BIS, New Delhi