INTERNATIONAL STANDARD

ISO 13320-1

First edition
1999-11-01

Particle size analysis — Laser diffraction methods —

Part 1: General principles

Analyse granulométrique — Méthodes par diffraction laser —

Partie 1: Principes généraux

Reference number
ISO 13320-1:1999(E)

Contents

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet iso@iso.ch

Printed in Switzerland

Foreword

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

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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

International Standard ISO 13320-1 was prepared by Technical Committee ISO/TC 24, *Sieves, sieving and other sizing methods*, Subcommittee SC 4, *Sizing by methods other than sieving*.

ISO 13320 consists of the following parts, under the general title *Particle size analysis — Laser diffraction methods*:

— *Part 1: General principles*

— *Part 2: Validation of inversion procedures*

Annexes A to E of this part of ISO 13320 are for information only.

Introduction

Laser diffraction methods are nowadays widely used for particle sizing in many different applications. The success of the technique is based on the fact that it can be applied to various kinds of particulate systems, is fast and can be automated and that a variety of commercial instruments is available. Nevertheless, the proper use of the instrument and the interpretation of the results require the necessary caution.

Therefore, there is a need for establishing an International Standard for particle size analysis by laser diffraction methods. Its purpose is to provide a methodology for adequate quality control in particle size analysis.

Historically, the laser diffraction technique started by taking only scattering at small angles into consideration and, thus, has been known by the following names:

— Fraunhofer diffraction;

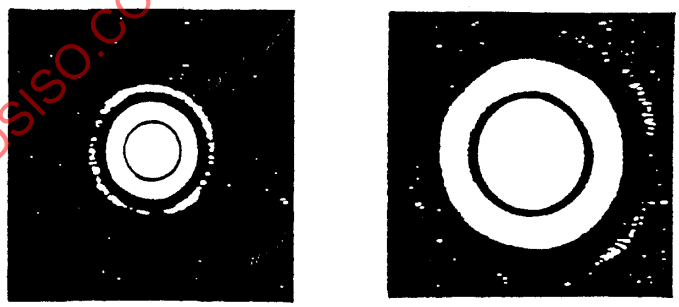
— (near-) forward light scattering;

— low-angle laser light scattering (LALLS).

However, the technique has been broadened to include light scattering in a wider angular range and application of the Mie theory in addition to approximating theories such as Fraunhofer and anomalous diffraction.

The laser diffraction technique is based on the phenomenon that particles scatter light in all directions with an intensity pattern that is dependent on particle size. All present instruments assume a spherical shape for the particles. Figure 1 illustrates the characteristics of single particle scattering patterns: alternation of high and low intensities, with patterns that extend for smaller particles to wider angles than for larger particles [2-7, 10, 15 in the bibliography].

Within certain limits the scattering pattern of an ensemble of particles is identical to the sum of the individual scattering patterns of all particles present. By using an optical model to compute scattering patterns for unit volumes of particles in selected size classes and a mathematical deconvolution procedure, a volumetric particle size distribution is calculated, the scattering pattern of which fits best with the measured pattern (see also annex A).



a) **b)**

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

A typical laser diffraction instrument consists of a light beam (usually a laser), a particulate dispersing device, a detector for measuring the scattering pattern and a computer for both control of the instrument and calculation of the particle size distribution. Note that the laser diffraction technique cannot distinguish between scattering by single particles and scattering by clusters of primary particles forming an agglomerate or an aggregate. Usually, the resulting particle size for agglomerates is related to the cluster size, but sometimes the size of the primary particles is reflected in the particle size distribution as well. As most particulate samples contain agglomerates or aggregates

and one is generally interested in the size distribution of the primary particles, the clusters are usually dispersed into primary particles before measurement.

Historically, instruments only used scattering angles smaller than 14°, which limited the application to a lower size of about 1 μm. The reason for this limitation is that smaller particles show most of their distinctive scattering at larger angles (see also annex A). Many recent instruments allow measurement at larger scattering angles, some up to about 150°, for example through application of a converging beam, more or larger lenses, a second laser beam or more detectors. Thus, smaller particles down to about 0,1 μm can be sized. Some instruments incorporate additional information from scattering intensities and intensity differences at various wavelengths and polarization planes in order to improve the characterization of particle sizes in the submicrometre range.

Particle size analysis — Laser diffraction methods —

Part 1:
General principles

1 Scope

This part of ISO 13320 provides guidance on the measurement of size distributions of particles in any two-phase system, for example powders, sprays, aerosols, suspensions, emulsions and gas bubbles in liquids, through analysis of their angular light scattering patterns. It does not address the specific requirements of particle size measurement of specific products. This part of ISO 13320 is applicable to particle sizes ranging from approximately 0,1 μm to 3 mm.

For non-spherical particles, an equivalent-sphere size distribution is obtained because the technique uses the assumption of spherical particles in its optical model. The resulting particle size distribution may be different from those obtained by methods based on other physical principles (e.g. sedimentation, sieving).

2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this part of ISO 13320. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 13320 are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the lates edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 9276-1:1990, *Representation of results of particle size analysis — Part 1: Graphical representation.*

3 Terms, definitions and symbols

For the purposes of this part of ISO 13320, the following terms, definitions and symbols apply.

3.1 Terms and definitions

3.1.1
absorption
reduction of intensity of a light beam traversing a medium through energy conversion in the medium

3.1.2
coefficient of variation
relative measure (%) for precision: standard deviation divided by mean value of population and multiplied by 100 (for normal distributions of data the median is equal to the mean)

3.1.3
complex refractive index
N_p
refractive index of a particle, consisting of a real and an imaginary (absorption) part

$$N_p = n_p - ik_p$$

3.1.4
relative refractive index
m
complex refractive index of a particle, relative to that of the medium

$$m = N_p/n_m$$

3.1.5
deconvolution
mathematical procedure whereby the size distribution of a particle ensemble is inferred from measurements of their scattering pattern

3.1.6
diffraction
spreading of light around the contour of a particle beyond the limits of its geometrical shadow with a small deviation from rectilinear propagation

3.1.7
extinction
attenuation of a light beam traversing a medium through absorption and scattering

3.1.8
model matrix
matrix containing light scattering vectors for unit volumes of different size classes, scaled to the detector's geometry, as derived from model computation

3.1.9
multiple scattering
subsequent scattering of light at more than one particle, causing a scattering pattern that is no longer the sum of the patterns from all individual particles (in contrast to single scattering)

3.1.10
obscuration
optical concentration
percentage or fraction of incident light that is attenuated due to extinction (scattering and/or absorption) by the particles

3.1.11
optical model
theoretical model used for computing the model matrix for optically homogeneous spheres with, if necessary, a specified complex refractive index, e.g. Fraunhofer diffraction, anomalous diffraction, Mie scattering

3.1.12
reflection
return of radiation by a surface, without change in wavelength

3.1.13
refraction
change of the direction of propagation of light determined by change in the velocity of propagation in passing from one medium to another; in accordance with Snell's law

$$n_m \sin \Theta_m = n_p \sin \Theta_p$$

3.1.14
scattering
general term describing the change in propagation of light at the interface of two media

3.1.15
scattering pattern
angular or spatial pattern of light intensities [$I(\theta)$ and $I(r)$ respectively] originating from scattering, or the related energy values taking into account the sensitivity and the geometry of the detector elements

3.1.16
single scattering
scattering whereby the contribution of a single member of a particle population to the scattering pattern of the entire population is independent of the other members of the population

3.1.17
width of normal size distribution
standard deviation (absolute value) or coefficient of variation (relative percentage) of the size distribution

NOTE For normal distributions about 95 % of the population falls within ± 2 standard deviations from the mean value and about 99,7 % within ± 3 standard deviations from the mean value.

3.2 Symbols

c	volumetric particulate concentration, %
f	focal length of lens, mm
$I(\theta)$	angular intensity distribution of light scattered by particles (scattering pattern)
$I(r)$	spatial intensity distribution of light scattered by particles on the detector elements (measured scattering pattern by detector)
i	indication for imaginary part of refractive index
i_n	photocurrent of detector element n, µA
k	wave number: $2\pi/\lambda$
k_p	imaginary (absorption) part of particle's refractive index
l	illuminated path length containing particles, mm
L	vector of photocurrents (i_1, i_2,..., i_n)
m	relative, complex refractive index of particle to medium
n_m	real part of refractive index of medium
n_p	real part of refractive index of particle
N_p	complex refractive index of a particle
r	radial distance from focal point in focal plane, µm
v	velocity of particles in dry disperser
x	particle diameter, µm
x_{50}	median particle diameter, µm; here used on a volumetric basis, i.e. 50 % by volume of the particles is smaller than this diameter and 50 % is larger
x_{10}	particle diameter corresponding to 10 % of the cumulative undersize distribution (here by volume), µm

x_{90} particle diameter corresponding to 90 % of the cumulative undersize distribution (here by volume), µm

α dimensionless size parameter: $\pi x/\lambda$

θ scattering angle with respect to forward direction

θ_m angle with respect to perpendicular at boundary for a light beam in medium (as used in Snell's law; see refraction)

θ_p angle with respect to perpendicular at boundary for a light beam in particle (as used in Snell's law; see refraction)

λ wavelength of illuminating light source in medium (i.e. liquid or gas/air), nm

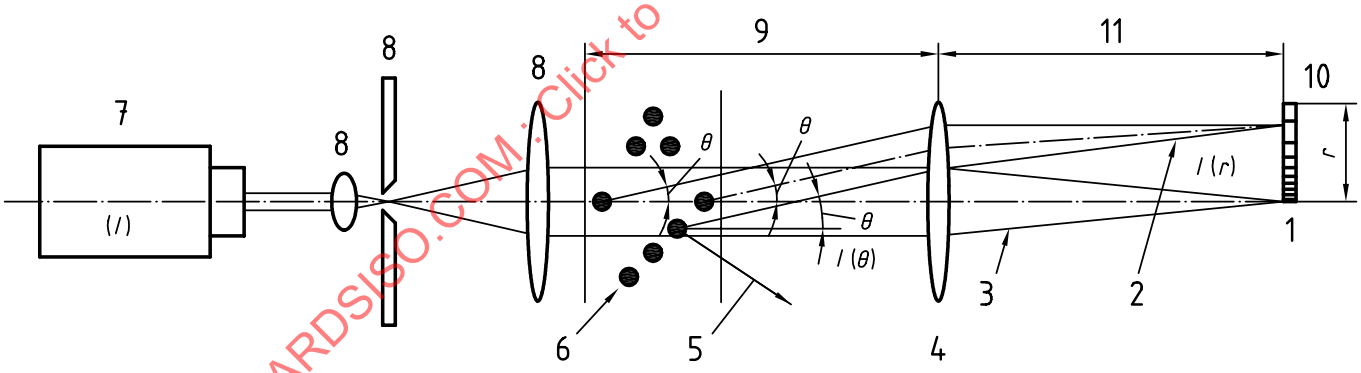
ω rotational velocity of particles in dry disperser

4 Principle

A representative 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 a multi-element detector and numerical values relating to the scattering pattern are then recorded for subsequent analysis. These numerical scattering values are then transformed, using an appropriate optical model and mathematical procedure, to yield the proportion of total volume to a discrete number of size classes forming a volumetric particle size distribution.

5 Laser diffraction instrument

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



Key

1 Obscuration detector
2 Scattered beam
3 Direct beam
4 Fourier lens
5 Scattered light not collected by lens 4
6 Particle ensemble
7 Light source laser
8 Beam processing unit
9 Working distance of lens 4
10 Multi-element detector
11 Focal distance of lens 4

Figure 2 — Example of the set-up of a laser diffraction instrument

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

A representative sample, dispersed at an adequate concentration is passed through the light beam in a measuring zone by a transporting medium (gas or liquid); this measuring zone should be within the working distance of the lens used. Sometimes, the particle stream in a process is illuminated directly by the laser beam for measurement, as in the case of sprays, aerosols and air bubbles in liquids. In other cases (such as emulsions, pastes and powders), representative samples can be dispersed in suitable liquids (see annex C). Often dispersants (wetting agents; stabilizers) and/or mechanical forces (agitation; ultrasonication) are applied for deagglomeration of particles and stabilization of the dispersion. For these liquid dispersions a recirculating system is most commonly used, consisting of an optical measuring cell, a dispersion bath usually equipped with stirrer and ultrasonic elements, a pump and tubing.

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

There are two positions in which the particles can enter the laser beam. In the conventional case the particles enter the parallel beam before and within the working distance of the collecting lens [see Figure 3 a)]. In the so-called reversed Fourier optics case the particles are entered behind the collecting lens and, thus, in a converging beam [see Figure 3 b)].

The advantage of the conventional set-up is that a reasonable path length for the sample is allowed within the working distance of the lens. The second set-up allows only small path lengths but enables measurement of scattered light at larger angles, which is useful when submicrometre particles are present.

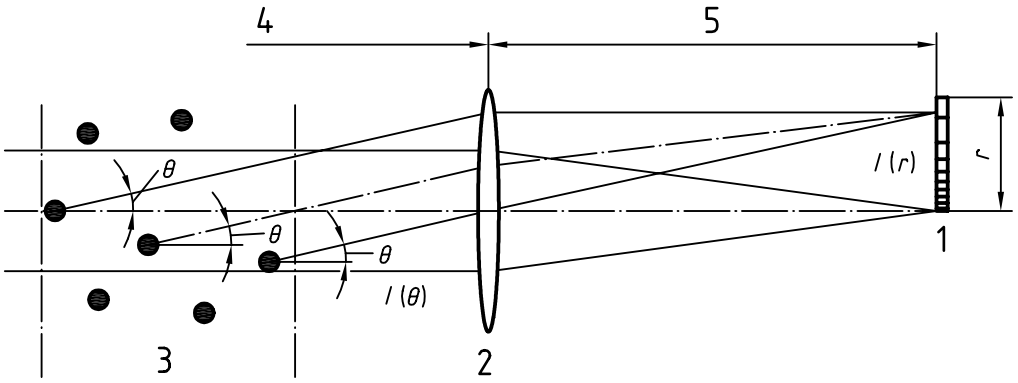
The interaction of the incident light beam and the ensemble of dispersed particles results in a scattering pattern with different light intensities at various angles (see annex A for theoretical background of laser diffraction). The total angular intensity distribution $I(\theta)$, consisting of both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

It is assumed that the recorded scattering pattern of the particle ensemble is identical to the sum of the patterns from all individual single scattering particles presented in random relative positions. Note that only a limited angular range of scattered light is collected by the lens(es) and, thus, by the detector.

The detector generally consists of a number of photodiodes; some instruments apply one photodiode in combination with moving slits. The photodiodes convert the spatial intensity distribution $I(r)$ into a set of photocurrents i_n. Subsequent electronics then convert and digitize the photocurrents into a set of intensity or energy vectors L_n, representing the scattering pattern. A central element measures the intensity of the non-scattered light and, thus, with a calculation, provides a measure of optical concentration or obscuration. Some instruments provide special geometries of the central element in order to automatically re-centre or re-focus the detector by moving the detector or the lens. It is desirable that the detector elements are positioned so as to prevent the light reflected from the surface from re-traversing the optical system.

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

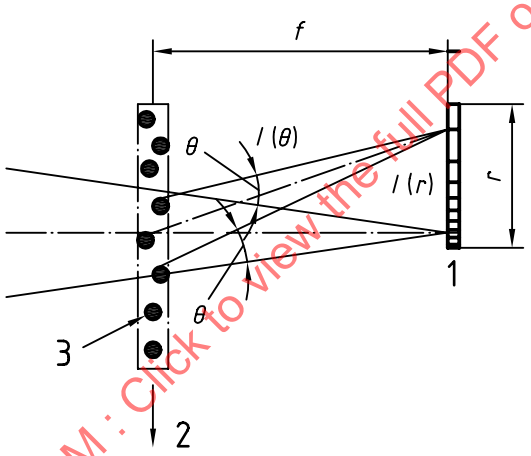
Several significant differences exist, both in hardware and software, not only between instruments from different manufacturers but also between different types from one company. The instrument specifications should give adequate information for proper judgement of these differences. In annex B recommendations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



Key

1 Detector
2 Fourier lens
3 Particle ensemble
4 Working distance
5 Focal distance

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



Key

1 Detector
2 Flow through cuvette
3 Particle

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

Figure 3 — Set-ups of laser diffraction instruments

6 Operational procedures

6.1 Requirements

6.1.1 Instrument location

The instrument should be located in a clean environment that is free from excessive electrical noise, mechanical vibration, and temperature fluctuations and is out of direct sunlight. The operating area should be well ventilated. 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 low power laser can cause permanent eye damage. Never look into the direct path of the laser beam or its reflections. Avoid cutting the laser beam with reflecting surfaces. Observe the local laser radiation safety regulations.

6.1.2 Dispersion liquids

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

If an organic liquid is used for dispersion, observe the local health and safety regulations. Use a cover for the ultrasonic bath when using liquids with a high vapour pressure in order to prevent the formation of hazardous vapour concentrations above the bath and/or the generation of low-temperature zones with fluctuating refractive indices in the fluid by evaporation.

6.1.3 Dispersion gases

For dry dispersion and spray applications a compressed gas is sometimes used. If used, it is essential that it is free from oil, water and particles. To achieve this, a dryer with a filter is required. Any vacuum unit should be located apart from the measurement zone, so that the output of the hot air does not reach the measuring zone. Draught should be avoided in order to avoid unstable particulate streams.

6.2 Sample inspection, preparation, dispersion and concentration

6.2.1 Sample inspection

Inspect the material to be analysed, visually or with the aid of a microscope, firstly to estimate its size range and particle shape and later to check whether the particles have been dispersed adequately.

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

6.2.2 Preparation

For dry powders, prepare a representative sample of suitable volume for the measurement by an adequate sample splitting technique, for instance a rotating riffler. If very small samples are required, or in the case of wet powders, it is also possible to take fractional samples out of a well-mixed sample paste. The consistency of the paste then avoids segregation errors. The pastes are formed by adding dispersant to the sample drop by drop while mixing it with a spatula. As long as the mixture forms lumps, single drops should be added while continuing the mixing after each drop. A good consistency for the paste is one like honey or toothpaste. If the paste becomes too fluid by mistake, it shall not be used, and a new preparation should be initiated.

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

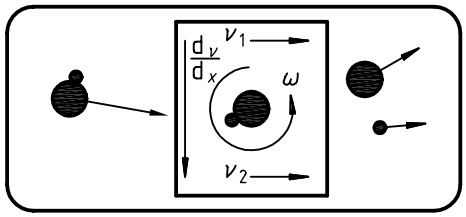
Sprays, aerosols and gas bubbles in liquid should be measured directly, provided that their concentration is at an adequate level (see 6.2.3 and 6.2.4), since sampling or dilution is generally impossible without altering the particle size distribution.

6.2.3 Dispersion

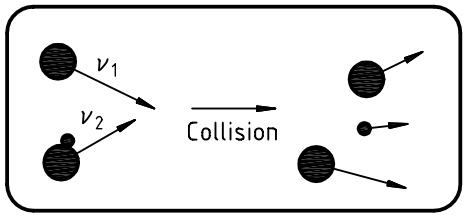
6.2.3.1 Dry powders can be dispersed either in air or in liquid. The dispersion procedure shall be adjusted to the purpose of the measurement, e.g. it has to be decided whether agglomerates should be detected or broken down to the primary particles.

6.2.3.2 An adequate dry disperser should be applied; here, generally compressed air or vacuum is applied for dispersion by shear stress with the assistance of mechanical de-agglomeration by particle-particle or particle-wall collisions (see figure 4). For dry dispersion, the complete fractional sample shall be used for the measurement. Note that the use of large sample quantities can overcome the poor statistical representation of coarse particles in a wide size distribution. It is necessary to check that comminution of the particles does not occur and conversely that a good dispersion has been achieved. This is usually done by direct comparison of dry dispersion with a liquid one: ideally, the results should be the same. Another possibility 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, until a plateau is reached, where the size distribution is nearly constant with increasing energy. At still higher energies the amount of fines may rise again as a result of comminution. On some occasions, agglomeration has

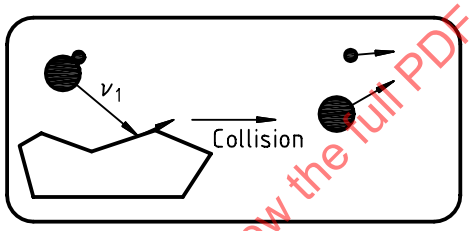
been found at high flow rates through a cascade. The centre of the plateau defines the optimum dispersing energy. Note, however, that a plateau is not always found (for instance for highly aggregated or fragile particles).



a) Velocity gradients caused by shear stress



b) Particle to particle collisions



c) Particle to wall collisions

Figure 4 — Processes involved for dry dispersion of powders

6.2.3.3 For the preparation of liquid dispersions a variety of liquids is available. Annex C presents requirements and some advice. Generally, pasting, stirring and ultrasonication 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 ultrasonication: the measured size distribution should not change significantly if the sample is well dispersed and the particles are neither fragile nor soluble.

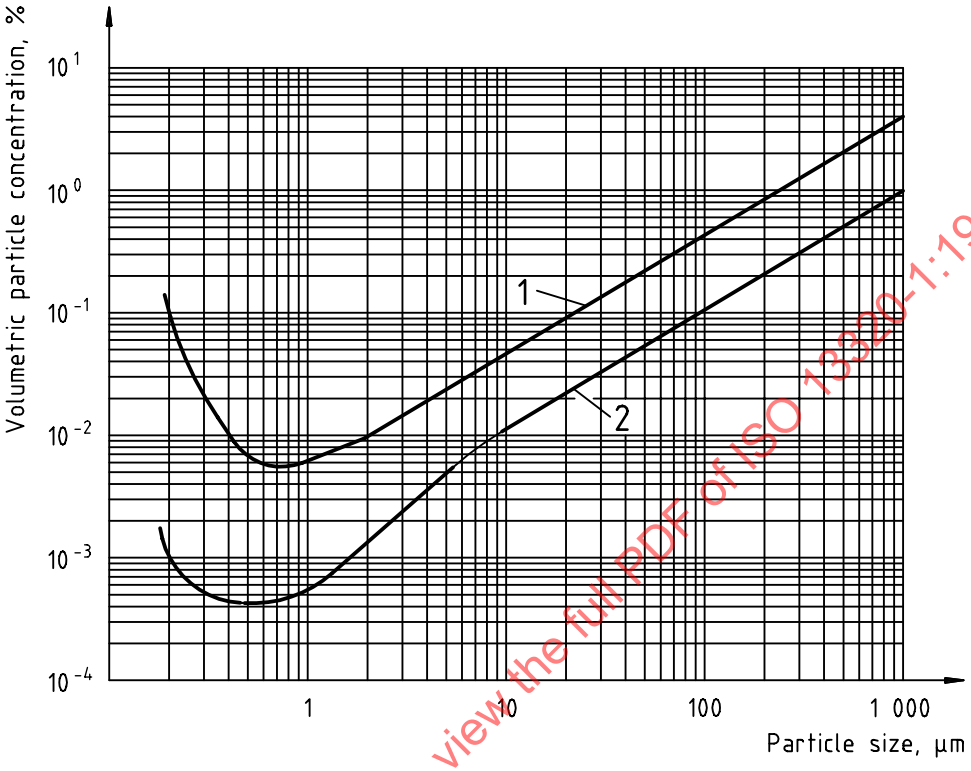
The minimum volume of sample, required for repeatable measurement, increases as the width of the size distribution becomes greater in order to allow a sufficient number of large particles to be present. Accordingly, the volume of the dispersion fluid required to suspend these samples also increases if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

For example, for a sample with particles in the approximate size range of 2 µm to 200 µm, a sample volume of at least 0,3 ml is needed. This will require at least 500 ml of suspension fluid for its dispersion. Also, the measurement time or the number of detector readings within one measurement should be sufficient to reach a reasonable precision. Appropriate measurement conditions should be established experimentally, in relation to the desired precision.

6.2.4 Concentration

The particle concentration in the dispersion should be above a minimum level, which for many instruments will correspond to about 5 % obscuration, in order to produce an acceptable signal-to-noise ratio in the detector. Likewise, it should be below a maximum level, which for many instruments will correspond to about 35 % obscuration for particles larger than about 20 µm, in order to avoid multiple scattering (where light is scattered subsequently at more than one particle).

For particles smaller than about 20 µm, the obscuration value should be kept below about 15 % for the same reason. In general, multiple scattering appears at larger scattering angles. Without multiple scattering correction, the amount of fines calculated will exceed the true value. If work at higher concentrations is required, it should be possible to correct for multiple scattering or systematic errors will arise. A first estimate for the concentration can be observed from figure 5.



Key

1 High limit
2 Low limit

Figure 5 — Typical high and low limits for particle concentration for laser diffraction systems as a function of particle size for narrow size distributions; 2 mm path length (logarithmic abscissa and ordinate)

Figure 5, though only an example, shows that the optimum particulate concentration is nearly proportional to the particle size: smaller particles require lower concentrations. For instance, particles with a diameter of about 1 µm require volumetric concentrations during measurement of about 0,002 %, whereas the concentration for 100 µm particles should be about 0,2 %, in a cell with a 2 mm path length. As a consequence, the width of the particle size distribution influences the optimum sample concentration for measurement. Moreover, the range of concentrations, as shown in figure 5, is influenced by the laser beam width, the path length of the measurement zone, the optical properties of the particles and the sensitivity of the detector elements.

In view of the above, measurements should be performed at different particulate concentrations in order to decide on the optimum concentration range for any typical sample of material.

6.3 Measurement

6.3.1 Procedure

A typical measurement of a particle size distribution by laser diffraction comprises the following steps:

a) Setting up instrument and blank measurement

After selection of the appropriate particle size range and proper alignment of the optical part of the instrument, a blank measurement is performed in which a particle-free dispersion medium is used. Detector data are saved in order to subtract them later from the data obtained with that sample in order to obtain net sample signals.

b) Measurement of the scattering pattern of dispersed sample(s)

Generally, a measuring time allowing for a large number of detector scans or sweeps at short time intervals is used: typically some 2 seconds or 1 000 sweeps. For each detector element an average signal is calculated, sometimes together with its standard deviation. Data are stored in the computer memory. 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 intensity of the central laser beam. The fractional difference between a dispersed sample and a blank experiment is given as an obscuration value, which is indicative of the total amount of scattered light and the particle concentration.

c) Selection of an appropriate optical model

Most often either the Fraunhofer or the Mie theory is used.

Sometimes other approximating theories are applied for calculation of the scattering matrix. When using the Mie theory, the refractive indices of particulate and medium, or their ratio, should be brought into the instrument in order to allow calculation of the model matrix (see annex D for the refractive indexes of liquids and solids). Often, small values of the imaginary part of the refractive index (about 0,01 – 0,1i) are applied to cope with the surface roughness of the particles.

NOTE Small differences in the assumed complex refractive index may cause significant differences in the resulting particle size distributions.

In order to obtain traceable results it is essential that the refractive index values used are reported

d) Conversion of scattering pattern into particle size distribution

This deconvolution step is the inverse of the calculation of a scattering pattern for a given particle size distribution. The fact that short measured data always contain some random and systematic errors, may cause erroneous size distribution results. Several mathematical procedures have been developed for use in the different instruments available [4, 6, 7, 10, 12, 14]. They contain some weighting of deviations between measured and calculated scattering patterns (e.g. least squares), some constraints (e.g. non-negativity for amounts of particles) and/or some smoothing of the size distribution curve. A new procedure [5] uses the observed fluctuations of the detector signals to introduce proper weighting of these data and to calculate confidence intervals for the particle size distribution.

6.3.2 Precautions

Before starting, and during any measurement, the instructions given in the instrument manual should be followed. The following precautions should be taken.

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

b) After switching the power on, allow sufficient time for the instrument to stabilize. Gas lasers such as the HeNe laser usually have a warm-up time of more than half an hour.

c) Check the instrument status and, if necessary, set up the required measuring range and lens. Ensure, by watching the intensities on the detector, 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) Make sure that the particles are only introduced into the laser beam within the specified working distance of the lens, so that all relevant scattering radiation leaving the particles strikes within the clear aperture of the lens that focusses it on the detector (and thus, vignetting is avoided).

e) Validate the instrument operation with respect to both precision and accuracy at regular time intervals by measuring a control sample of known size distribution (see 6.4 and 6.5.2).

f) In the case of wet dispersion, check that air bubbles are absent in the dispersion liquid. Foaming detergents should be avoided.

g) 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.

h) For aerosols and sprays: make sure that no bright daylight is allowed, either directly or via scattering by particles, into the detector and that the flow of particles/droplets is even.

i) Investigate, if possible, the influence of the optical model (relative refractive index) on the resulting particle size distribution, especially if a significant fraction of the particles is smaller than about 10 µm.

NOTE Occasionally a strong dependency of the results on the refractive index has been found whereby even slightly different values resulted in major systematic errors (see further annexes A and D).

6.4 Repeatability

For samples where the coefficient of variation of the particle size distribution is equal to or less than about 50 % (or ratio of diameter of largest to smallest particle about 10:1) and for measurements performed on at least five different samples from the same batch in the mid-range of any instrument setting, the repeatability of characteristic particle sizes in size distributions should be as follows: for any chosen central value of the distribution, e.g. the median size (x_{50}), the coefficient of variation should be smaller than 3 %. Values at the sides of the distribution, e.g. x_{10} and x_{90}, should have a coefficient of variation not exceeding 5 %. Below 10 µm, these maximum values should be doubled.

6.5 Accuracy

6.5.1 Calibration

Laser diffraction systems are based on first principles, though with idealized properties of the particles (cf. annex A). Thus, calibration in the strict sense is not required. However, it is still necessary and desirable to confirm the correct operation of the instrument by a validation procedure (see 6.5.2).

6.5.2 Validation

6.5.2.1 Primary validation can be made with any certified or standard reference material, acceptable to the practice of the end-users' industries. Here, the total measurement procedure is being examined, including sampling, sample dispersion, sample transport through the measuring zone, measurement and deconvolution procedure [13]. It is essential that the total operational procedure is adequately described in full detail.

Certified or standard reference materials consisting of a known distribution having a range of spherical particles over one decade of size are preferred. They should be certified to mass percentage by an absolute technique, if available, and used in conjunction with an agreed, detailed operation procedure. It is essential that the real and imaginary part of the complex refractive index are precisely specified for the material if the Mie theory is applied in data analysis.

The response of a laser diffraction instrument is considered to meet this standard if the mean value of the x_{50} coming from at least three independent measurements deviates less than 3 % from the certified range of values of the Certified or Standard Reference Material, i.e. the mean value together with its standard deviation; the mean values for the x_{10} and x_{90} should deviate less than 5 % from the certified range of values.

Although use of spherical reference materials is preferable, non-spherical ones may also be used. Preferably, these should have certified or typical values coming from laser diffraction analyses according to an agreed, detailed operational procedure. If the reference values come from other methods than laser diffraction, a significant bias may result. The reason for this bias is that the different principles applied in the various methods may lead to different sensitivity to the properties of the particles and, thus, to different equivalent-sphere diameters for the same non-spherical particle.

In addition to the certified reference materials mentioned above, product samples of typical composition and particle size distribution for a specified class of products can also be applied for validation of instrument behaviour and

operational procedures, provided that their particle size distribution has been proven to be stable over time. Here, the results should comply with previously determined data with the same precision and bias as those for the certified reference materials.

Mixtures in ratios of volume of two or more reference materials having the same properties can be applied to test the accuracy of the reported fractional quantities, the size resolution and the sensitivity to fines or coarse material. Representative sampling from the various materials is here, however, even more important than in the normal case, since the fractional quantities can be very small.

6.5.2.2 For secondary validation of a laser diffraction instrument a suitable reference reticle [1, 8, 9] can be used. Thus, only the quality of instrument optics and software is being examined, leaving out the effects of sample dispersion and handling. For instruments with a focal length above 300 mm, the application of reticles is not reliable due to speckle effects. Of course, the proper use of a reticle includes the requirement that the illuminating beam diameter allows measurement of the full circular area of the dots deposited. Note that some reverse Fourier applications, where the reticle must be placed close to the detector, may fall within this restriction. The response of a laser diffraction instrument is considered to meet the requirements of this part of ISO 13320 if the mean value for the x_{50} coming from at least three measurements deviates less than 2 % from the quoted value and for x_{10} and x_{90} less than 3 %.

6.6 Error sources; diagnosis

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

6.6.2 Errors made in sample preparation are often a main part of the total error. They can be attributed to the following causes:

— improper sampling technique, leading to a non-representative sample in the measurement zone; this type of error is especially significant when using an inadequate sample splitting technique in the case of a large batch of free flowing material having a wide size distribution, but 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;

— incomplete deagglomeration of particles, due to an improper dispersion procedure (liquid; dispersant; ultrasonication);

— comminution of particles by mechanical forces during dispersion (e.g. ultrasonication);

— swelling, re-agglomeration, dissolution or evaporation of particles/droplets before or during measurement;

— inclusion of air bubbles due to foaming dispersants and/or vigorous stirring;

— scattering from differences in refractive index in the dispersing liquid or gas due to temperature fluctuations generated by, for example, evaporation of the dispersing liquid or presence of a flame.

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

— Firstly, most particles in real life do not fulfil the assumption of sphericity. Non-sphericity of particles leads to different cross-sections in different orientations. Since particles are generally measured in all possible orientations, this leads to some broadening of the particle size distribution as compared to the equivalent volume distribution. Moreover, the median and mean diameter may be shifted, often to a larger size.

— Secondly, the particle surface may be rough instead of smooth. This causes diffuse light scattering at the boundary, which often has a similar influence as absorption of light within the particle.

— Thirdly, the particles may be optically heterogeneous, as is the case for porous particles. This may lead to an apparent presence of significant amounts of very small particles, which are non-existent.

— Last but not least, the wrong optical model or parameters may have been chosen. For instance, if the Fraunhofer approximation is applied for samples containing an appreciable amount of small, transparent

particles, a significantly larger amount of small particles may be calculated (see also annex A). Generally, the choice of a wrong model also results in a large difference between particulate concentration as calculated by the instrument and from the mass of sample and the volume of dispersion medium (see also 6.6.6).

6.6.4 Errors in the operational procedure or in the functioning of the instrument can be specified as follows:

— particles with diameters outside the measuring range are present [in this case, adapt the measuring range (change the lens) and/or remove too coarse material, e.g. by presieving];

— the sample is introduced into the laser beam outside the working distance of the lens;

— lens(es) or windows of the measurement cell are dirty and, thus, should be cleaned;

— measurements are conducted with excessive levels of background;

— the optical system has not been aligned properly;

— the particle concentration is too high, causing multiple scattering;

— the mathematical procedure for deconvolution of light intensity values to particle size distribution is inadequate (check with the instrument manufacturer).

6.6.5 The absence of maintaining good control on the above points may also lead to errors of a random nature. Moreover, random errors may result from

— using insufficient measurement time, or readouts of each detector output,

— working at too low a concentration, and

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

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

— Measuring 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.

— Observing the signals from all detector elements during a blank measurement: the background signal should show a smooth behaviour with only small positive or zero values. Negative or overload (100 %) readings 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;

— observing the detector signals from repeated sample measurements, calculating both mean values for each element and their standard deviations and comparing the measured signals for all detector elements with previously measured ones. Thus, an impression is gained of the precision and accuracy of these signals: large systematic differences or zero values for the signals usually 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. Moreover, these data enable, after conversion to light intensity values, comparison of the measured light scattering patterns coming from different instruments, to some extent irrespective of the geometry of the detector elements in these instruments (provided that the geometry is known);

— comparing the actual particulate concentration, as calculated from the sample mass and the volume of the dispersion medium, with a calculated one from the obscuration and particle size distribution, while using the same optical model for calculating the extinction coefficients of the particle size fractions as for the deconvolution; a large difference indicates an inadequate optical model or bad sample handling [11];

— comparing for all detector elements the measured and calculated signals (for the resulting, best-fitting particle size distribution); large systematic differences indicate either a faulty element or an inadequate optical model.

6.7 Resolution; sensitivity

The resolution of the particle size distribution, i.e. the capability to differentiate between different particle sizes, and the sensitivity for small (extra) amounts of particles of certain size are restricted by the following factors:

— number, position and geometry of the detector elements;

— their signal to noise ratio;

— fine structure in the measured scattering pattern;

— difference in scattering pattern between size classes;

— actual size range of the particulate material;

— adequacy of the optical model;

— smoothing applied in the deconvolution procedure.

These factors prevent the laser diffraction technique in its usual design from being a high resolution technique: the minimum width of each size class is usually about 1, 1 to 2 (ratio of upper to lower limit of the size class). Actual values for resolution and/or sensitivity for quality control reasons should be determined by using mixtures of known composition.

7 Reporting of results

Results should be reported in accordance with ISO 9276-1. Moreover, the following information should be reported in order that the measurements can be readily repeated by different operators in different laboratories. Some of the items may be optional for some materials.

a) Sample

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

— sampling procedure, i.e. sampling method and sample splitting procedure;

— sample pretreatment (optional), for instance presieving, type and conditions;

— date of analysis.

b) Dispersion

— dispersion type: dry or wet.

For dry dispersion

— specific details of dispersing device, e.g. injector diameter, primary pressure;

— type of dosing/feeding device;

— feeding rate.

For wet dispersion

— dispersion liquid: identification, volume and, if necessary, temperature;

— dispersant(s): type and quantity;

— sample concentration;

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

— pump speed.

c) Laser diffraction measurement

— instrument type and number;

— software version;

— focal length of lens applied;

— actual size range used for the measurement;

— date of last alignment;

— date of last validation;

— date and time of measurement;

— optical concentration/obscuration;

— trigger thresholds for start/stop conditions (if applied);

— threshold for acquisition of valid data (if applied);

— type of light scattering model applied;

— real and imaginary part of complex refractive index, if the Mie theory is applied;

— (optional) fit parameter resulting from deconvolution (e.g. log difference, chi-squared).

d) Analyst identification

— name and place of laboratory;

— operator's name or initials.

Annex A
(informative)

Theoretical background of laser diffraction

Four types of interaction exist between light and a particle [2-7, 10, 15]:

1) diffraction at the contour of the particle (Fraunhofer diffraction);

2) reflection at the particle's surface, both outside and inside the particle;

3) refraction at the interface coming from medium to particle and vice versa;

4) absorption inside the particle.

These interactions lead to interference phenomena, giving rise to a characteristic scattering pattern, which is dependent on the size, shape and optical properties of the particle. An example is given in figure A.1:

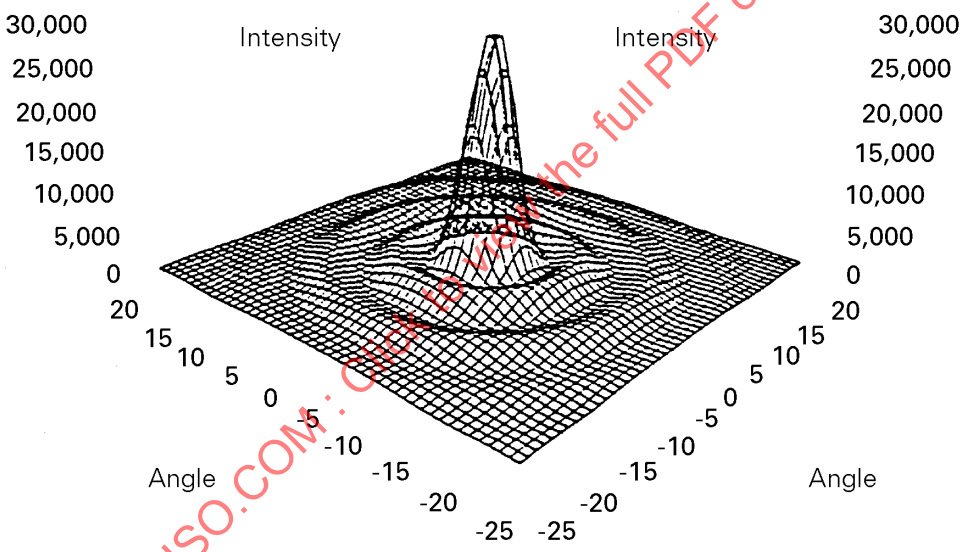


Figure A.1 — Angular intensity spectrum of scattered light for a 3 µm spherical particle [refractive index (RI) 1,60 - 0i; wavelength 633 nm]

It clearly shows the characteristics of the scattering pattern for a single particle.

— The highest intensity is in the 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.

— There is circular symmetry of the scattering pattern of spherical particles. These characteristics form the basis for the application of the laser diffraction technique for the measurement of particle size distributions.

The light scattered by a single spherical particle can be extended to an ensemble of particles provided that

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

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

The interpretation of laser diffraction "spectra" to particle size distributions depends on two major operations. The first requires that mathematical models are created of how homogeneous particles scatter light. The second involves the deconvolution of the angular scattering pattern to a particle size distribution.

The scattering of unpolarized light by a single spherical particle can be written as

$$I(\Theta) = \frac{I_0}{2k^2a^2}\left\{\left[S_1(\Theta)\right]^2 + \left[S_2(\Theta)\right]^2\right\}$$

where

$I(\Theta)$ is the total scattered intensity as a function of angle Θ;

I_0 is the intensity of the incident light;

k is the wavenumber = $2\pi/\lambda$;

λ is the wavelength of I_0 of the illuminating source in air;

a is the distance from scatterer to detector;

$S_1(\Theta)$ and $S_2(\Theta)$ are dimensionless, complex functions defined in general scattering theory, describing the change of amplitude in respectively the perpendicular and the parallel polarized light as a function of angle Θ with respect to the forward direction. Computer algorithms have been developed (see for example [3]) in order to allow computation of these functions and, thus, of $I(\Theta)$.

The intensity of scattered light at a detector element of given geometry by a unit volume of particles in a size class of certain width can now be obtained by integration of $I(\Theta)$ over the number of particles present in that size class and over the geometry of that element. For a series of size classes and detector elements this leads to a model matrix.

NOTE 1 Similar equations can be derived for non-spherical particles having a regular shape. These equations are more complex as the intensities of the scattered light have no circular symmetry, but are dependent also on the azimuthal angle. So far, commercial instruments do not contain models for non-spherical particles; thus, they will not be considered in this part of ISO 13320.

Historically, the **Fraunhofer approximation** was the basis for the first optical model employed for particle size measurement. In this application, besides sphericity of particles, the following restrictive assumptions are made:

a) all particles are much larger than the light wavelength (only scattering at the contour of the particle is considered; this also means that the same scattering pattern is obtained as for thin two-dimensional circular disks);

b) only scattering in the near-forward direction is considered (Θ is small).

For these approximations:

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

and the general formula given above simplifies into the following equation:

$$I(\Theta) = \frac{I_0}{k^2a^2}\alpha^4\left[\frac{J_1(\alpha\sin\Theta)}{\alpha\sin\Theta}\right]^2$$

where

dimensionless size parameter $\alpha = \pi x/\lambda$;

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

NOTE 2 In the expression at the right-hand side often an extra multiplier term $(1 + \cos^2 \Theta)/2$ is added in order to extend it to larger angles.

The advantage of this equation is that it is relatively simple and quick to calculate.

This Fraunhofer approximation does not make use of any knowledge of the optical properties of the material. Therefore, its use is recommended in cases where products are being measured which are mixtures of different materials. In practice, the approximation is valid for large particles (diameter at least about 40 times the wavelength of the light, or $\alpha >> 1$) or somewhat smaller particles that are opaque or have a high refractive index relative to the medium they are suspended in. However, for small particles which have a low relative refractive index, errors occur in the proportion of volume subscribed to a given size. This is caused by the fact that in the Fraunhofer approximation the extinction efficiency relative to the cross-section is assumed to be constant for all particle sizes; in other words, it does not predict that for small particles the intensity of scattering falls more rapidly than the geometric cross-section would predict.

Equations having similar characteristics, but of increasingly more complex form, can be written for both anomalous diffraction and Lorenz-Mie theory.

The **anomalous diffraction approximation** has also found limited application in commercial instruments. Here, it was assumed

a) that all particles are spheres;

b) that all particles are transparent, and

c) that the difference in refractive index between particles and dispersion medium is small [ratio < 1,1 or $(m - 1) << 1$].

This approximation includes an estimate of how the extinction efficiency varies with particle size and, thus, predicts to some degree the variation of scattering efficiency with size. Therefore, its use in circumstances of particles suspended in liquids results in more accurate size distributions in many cases, where the Fraunhofer assumptions are not fulfilled.

The advent of reasonably powerful desk top computers has enabled the rigorous solution from the Mie Theory to the scattering of homogeneous spheres up to a certain size to be coded and calculated in reasonable times. By this means, the assumptions of the previous models have been eliminated (excluding sphericity of particles). However, to exploit this theory to the full, 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 suspending medium. It should be noted that this knowledge is far from always available: especially the imaginary (absorptive) part is often strongly dependent on the wavelength of the light, whereas many crystalline products show differences in refractive index in different crystal orientations. Moreover, the imaginary part of the refractive index is often used in order to account for specific surface structure of the particles, as for example surface roughness. Annex D lists the refractive indices for a large variety of liquids and solids (without the surface structure effects).

Thus, various theories can be used to calculate optical models that predict angular scattering patterns in relation to the sizes of the spherical particles. As different assumptions are made, the various theories differ both in applicable particle size range and in computer time necessary for the calculations. Often, the choice between the theoretical models can be slightly simplified by consideration that particle size, real refractive index, and absorbance (imaginary part of refractive index) are three mutually perpendicular vectors with the following distinctive values:

— particle size: distinctive values between small and medium size 1 µm and between medium and large size 50 µm;

— real part refractive index (particle relative to medium): distinctive value 1,1 (or $m - 1 = 0{,}1$);

— imaginary part refractive index (absorbance) of particle: distinctive value 0,05 i.

If the particle size is larger than about 50 µm, then the Fraunhofer approximation gives good results. The Mie theory can also be used, and, in fact, is preferred for cases where the refractive index of the particles is close to that of the medium. The matrix calculation time for these cases may become extended, as it should be ensured that an adequate number of terms is included in the series expansions and that the scattering of a sufficient range of sizes is integrated to cover each specific size class. For particles smaller than about 50 µm, the Mie theory offers the best

general solution. For medium sized particles (1 µm to 50 µm) with $n_p/n_m > 1,1$ and/or $k_p > 0,05$ the Fraunhofer approximation usually also gives good results. For medium sized particles for which both these values are low, usually the anomalous diffraction approximation gives the same results as the Mie theory. In all cases where the Mie theory is used, good values for the optical properties have to be provided. If it proves impossible to establish a refractive index value for the material in question, then the choice is between the Fraunhofer approximation and a realistic estimate of the complex refractive index for using the Mie theory. The former has the advantage that it is simple and does not need refractive index values, the latter that it usually will provide less biased particle size distributions. In every case, it should be made clear to all parties involved which choices have been made.

The theoretical predictions of the angular scattering patterns of spherical particles are then used in conjunction with the geometry and the sensitivity of the chosen detector elements to form a matrix which describes how unit volumes of each size class of particles would appear as (energy-)signal at each detector element.

In view of the characteristic features of the scattering patterns, it is advantageous to sample the light intensities over a wide range of angles and, for fairly narrow size distributions, with high resolution with respect to angle. Thus, it seems advantageous to equip instruments with as many detector elements as possible. On the other hand, the signal of each detector element is the product of the intensity of scattered light, the geometric area of the element and its sensitivity. Consequently, any decrease of the geometric area leads to smaller signals and, thus, a lower signal to noise ratio. This is especially important at higher scattering angles, where the intensity of the scattered light is usually very low. Moreover, using more detectors than is required to adequately sample the rate of change of the angular scattering pattern may be counter-productive as more detectors lead to more measurement errors, which will have a detrimental effect on the precision of the calculated size distribution. In practice, this leads to some optimum situation for the number of detector elements, their size and the angular range that they cover. It should be remarked, however, that different designs have been worked out by different instrument manufacturers.

Various scattering diagrams have been calculated in order to illustrate their characteristic features. Figures A.2 and A.3 give three-dimensional angular scattering diagrams, (in which detector output in terms of energy signals for an arbitrary detector geometry, having a strong increase in detector element size with increasing angle, is given) for equal volumes of particles of different sizes. For figure A.2, the Mie theory has been used for the calculation; for figure A.3, the Fraunhofer approximation. Comparison of both figures illustrates the agreement between the two theories for large (latex) particles: above 10 µm to 20 µm the scattering patterns look quite similar, with detector signals shifting towards smaller angles with increasing particle size.

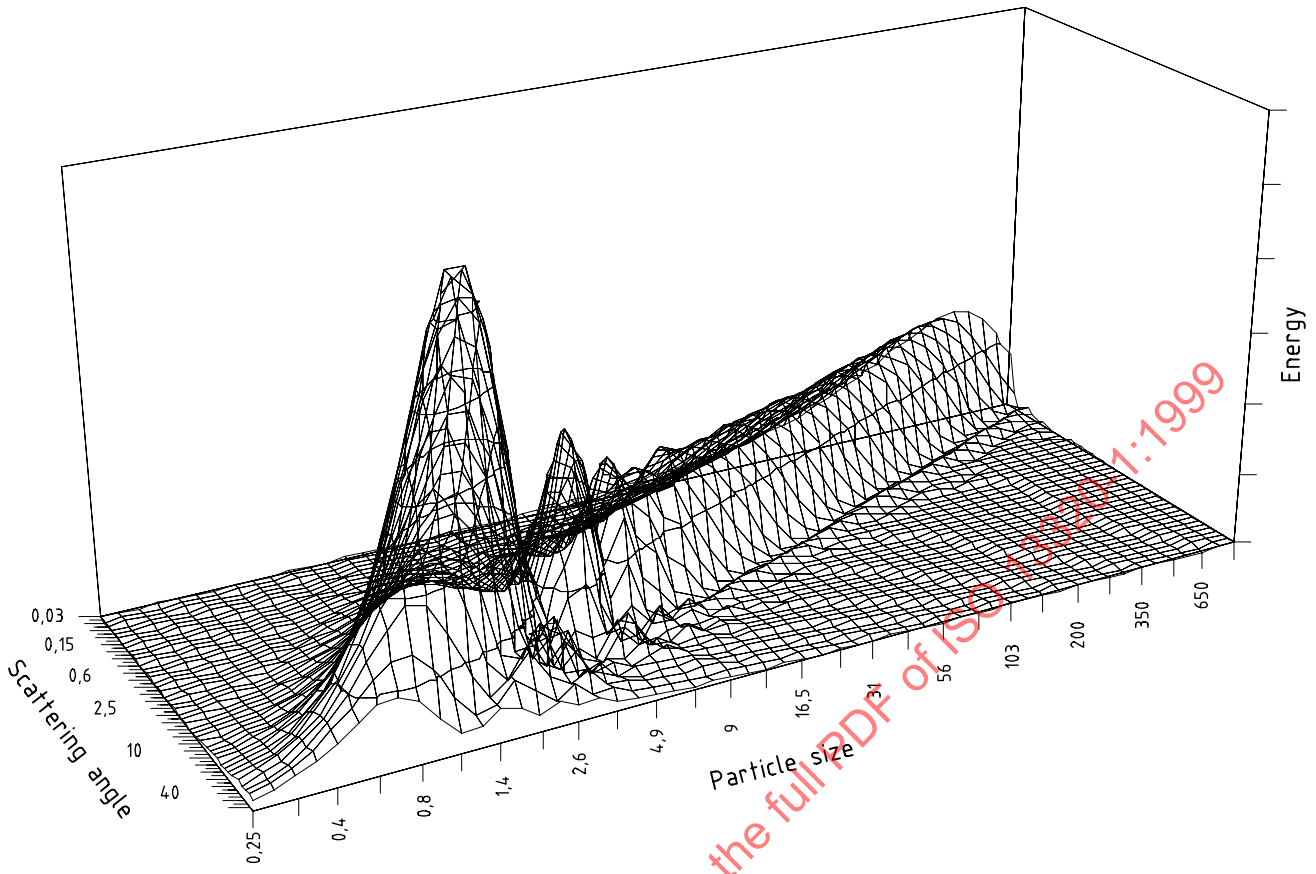


Figure A.2 — Light energy scattering patterns for an arbitrary detector configuration against particle size (µm) and scattering angle (°) for equal volumes of particles (Mie theory, latex particles RI 1,60 - 0,0i, in water RI 1,33)

Also, the differences in detector signals below sizes of about 10 µm for these particles are quite clearly shown: the Fraunhofer theory predicts only small differences at decreasing size, whereas the Mie theory results in strong fluctuations of the maximum intensity in relation to particle size, creating signals that are much higher than the corresponding Fraunhofer ones for some sizes and much lower for others.

Some cross-sections of these types of three-dimensional scattering diagrams are presented in figures A.4 to A.6; note that now the signals are presented in terms of scattered light intensities.

Figure A.4 illustrates clearly some of the characteristic features of the scattering behaviour of almost monodispersed particle size distributions. Firstly, there are the minima and maxima in the intensity curves, the angular positions of which are mainly governed by particle size. For example, the first minimum of 0,5 µm particles lies above 100°, against that for 5 µm particles around 10°. Remember that most early designs of instruments were capable of measuring up to angles of only about 15°. Of course, the presence of this fine structure in the forward direction for larger particles facilitates their discrimination. In contrast, the absence of significant intensity differences in the forward direction for submicrometre particles requires additional information. Therefore, modern instruments, having a measuring range extended to below 1 µm, also collect signals at larger angles than 15°. Note, however, also the secondary influence of the refractive index on the position of minima and maxima.

Secondly, it can be concluded that the scattering intensity for a volume of large particles is larger at small angles, but smaller at large angles than that of the same volume of small particles. Remember, however, that a particle size ratio of 10 leads to a ratio of 1 000 in volume. Also, it should be kept in mind that, during a measurement, generally only the relative changes of scattering intensities with respect to angle are important, since the absolute intensities are also related to particulate concentration.

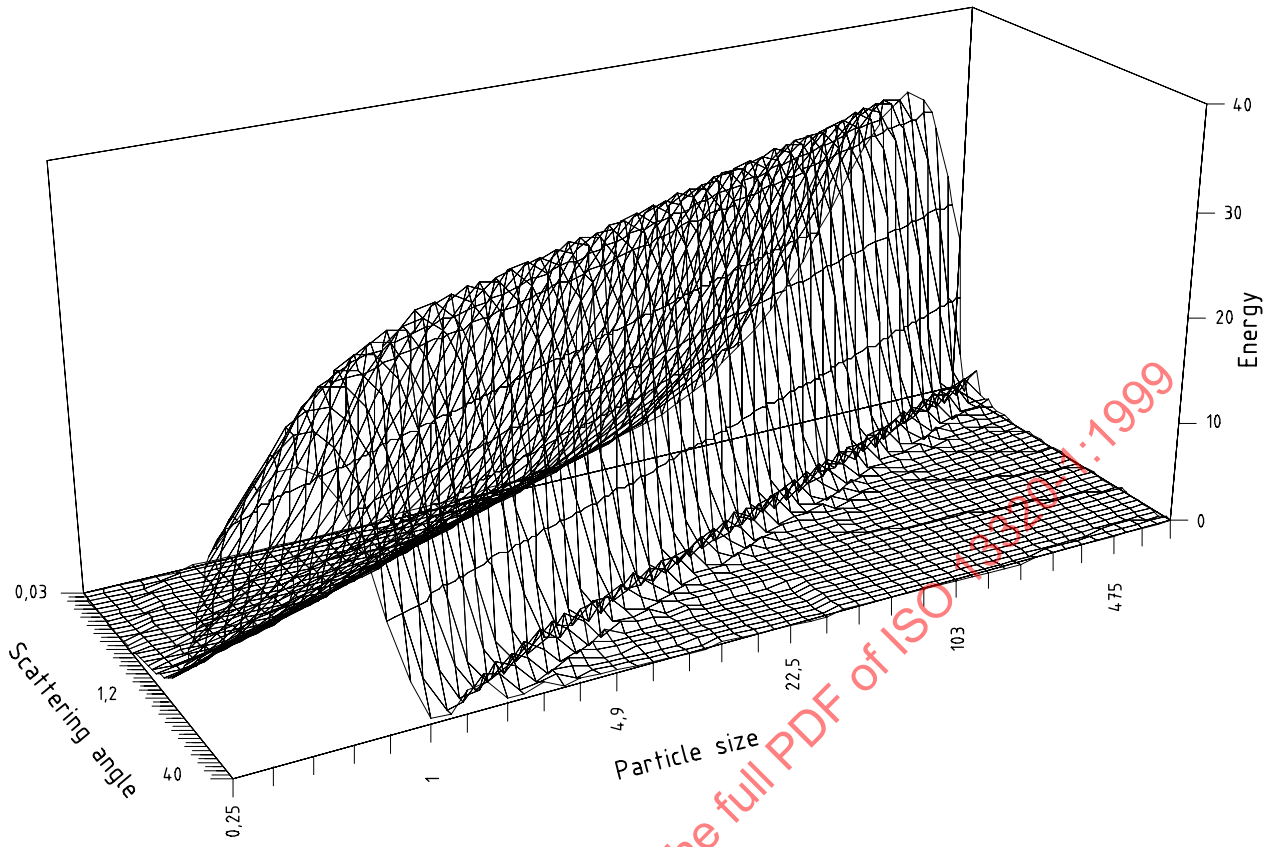


Figure A.3 — Light energy scattering patterns for an arbitrary detector configuration against particle size (µm) and scattering angle (°) for equal volumes of particles (Fraunhofer theory)

Thirdly, figures A.4 and A.5 show the general decrease of scattering intensity towards larger angles and the effects of the optical model or refractive index. For example, it is indicated that the presence of a small amount of absorption of light by the particles (imaginary part of refractive index) leads to both lower intensities and more fine structure as compared to transparent particles.

This effect is usually even stronger for the Fraunhofer approximation. Also, the conclusion can be drawn from figures A.4 and A.5 that application of the wrong optical model, for example the Fraunhofer approximation or some absorbance to transparent particles, leads to necessity for compensation of too small amounts of light scattered at large angles through "apparent" addition of fines. Finally, figure A.6 indicates that only monosized and narrow size distributions of particles show fine-structure in the angular scattering pattern. For somewhat broader size distributions, this fine structure is lost. This can be explained from the strong influence of particle size on the position of minima and maxima. As a result, the minima and maxima for different sizes will compensate, which leads to smoothing of the angular scattering pattern for broader particle size distributions. For example, for size distributions around 10 µm having a width of 30 % (expressed as a coefficient of variation), the decrease of intensity with angle up till about 90° proceeds smoothly and without maxima and minima. Altogether, these figures indicate that high resolution with respect to size is not to be expected for broad size distributions from the laser diffraction technique. Furthermore, it can be concluded that small errors in the detector signals may lead to significant differences in the resulting particle size distribution when dealing with the normal case of broad size distributions. The effect of such errors, of course, is largely dependent on the mathematical procedure, including constraints and smoothing, used in the deconvolution (see also 6.3.1 and 6.7).

So far, the prediction of scattering patterns for various particle sizes has been discussed. These are usually implemented in instruments in conjunction with the geometry of the chosen detector elements in the form of a matrix, which describes how unit volumes of each of m particle size classes would appear as a signal at each of n detector elements:

$$\begin{bmatrix} L_1 \\ : \\ : \\ : \\ : \\ : \\ L_n \end{bmatrix} = \begin{bmatrix} M_{1,1} & .. & .. & .. & .. & .. & M_{1,m} \\ : & \backslash & & & & & : \\ : & & \backslash & & & & : \\ : & & & \backslash & & & : \\ : & & & & \backslash & & : \\ : & & & & & \backslash & : \\ M_{n,1} & .. & .. & .. & .. & .. & M_{n,m} \end{bmatrix} x \begin{bmatrix} S_1 \\ : \\ : \\ : \\ : \\ : \\ S_m \end{bmatrix}$$

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

$$L = M \times S$$

In this form, the set of detector signals is seen to be the result of a matrix multiplication of size distribution with the scattering matrix. In the actual measurement practice, however, the inverse of this problem is required. The signals from all detector elements are measured, the computed matrix is available in the instrument and the particle size distribution is expected from the calculation:

$$S = \mathrm{M}^{-1} \times L$$

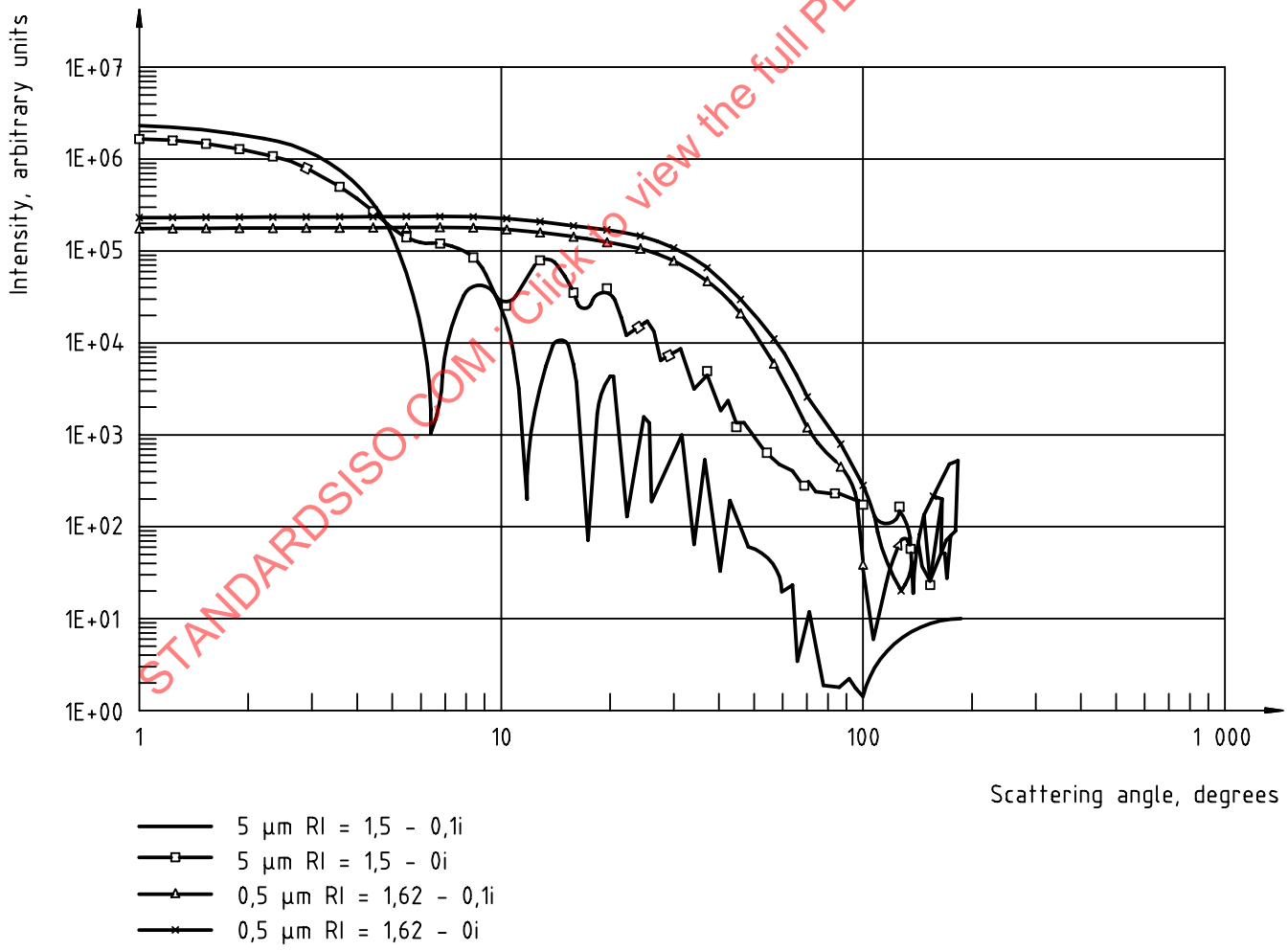


Figure A.4 — Influence of particle size on angular light intensity scattering patterns for equal volumes of particles (medium water, RI 1,33) — Normal size distributions by volume; width 1 % (coefficient of variation)

Such equations are described as badly posed and badly conditioned due to measurement errors making 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 leads to solutions of polydisperse distributions showing ripples in the histogram data. Serious lack of constraint can lead to zero or negative values and false modality. On the other hand, overconstraint will lead to decreased resolution and widening of the actual particle size distributions.

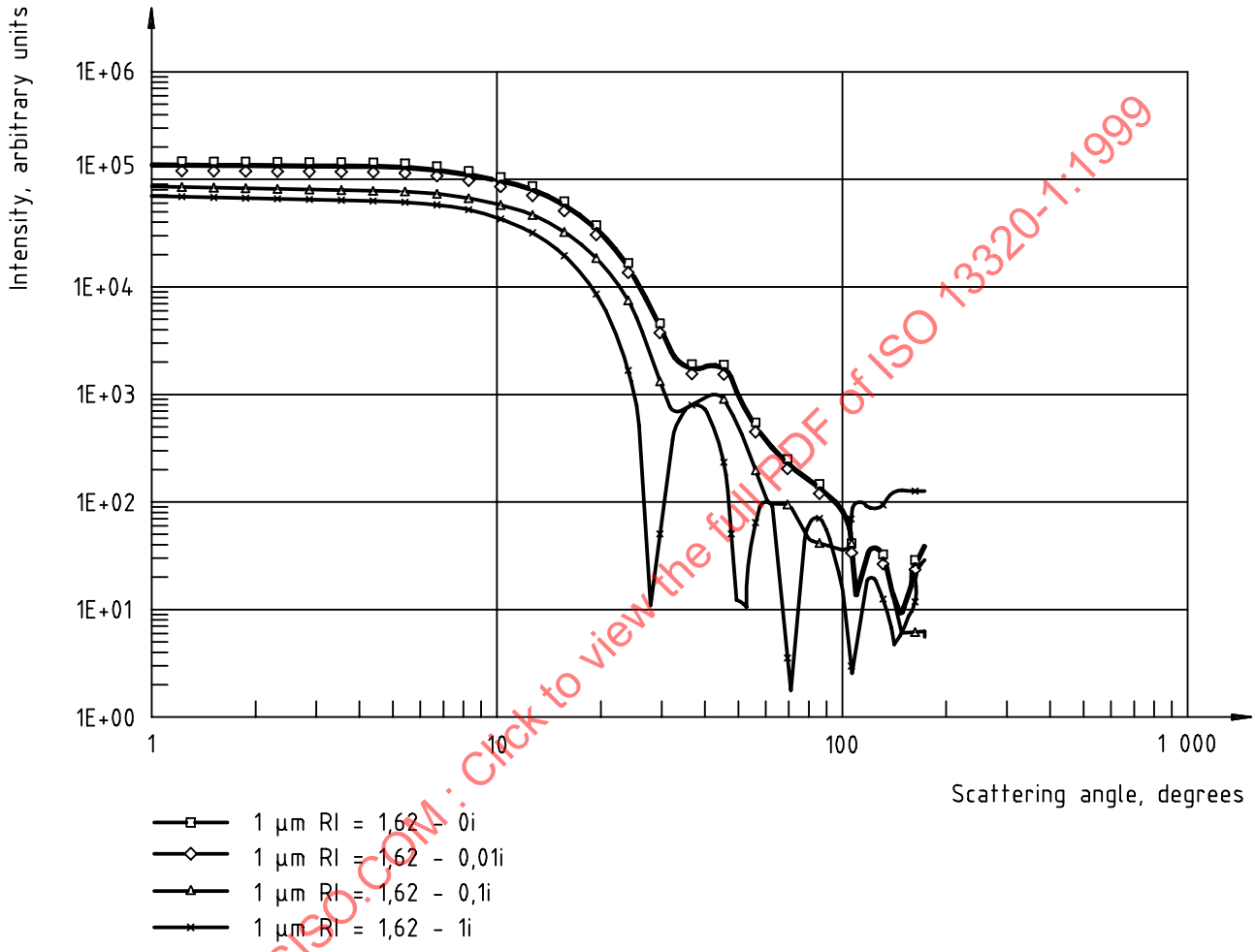


Figure A.5 — Influence of imaginary parts of RI (absorbancies) on angular light intensity scattering patterns for about 1 µm particles (medium: water, RI 1,33) — Normal size distributions by volume; width 1 % (coefficient of variation)

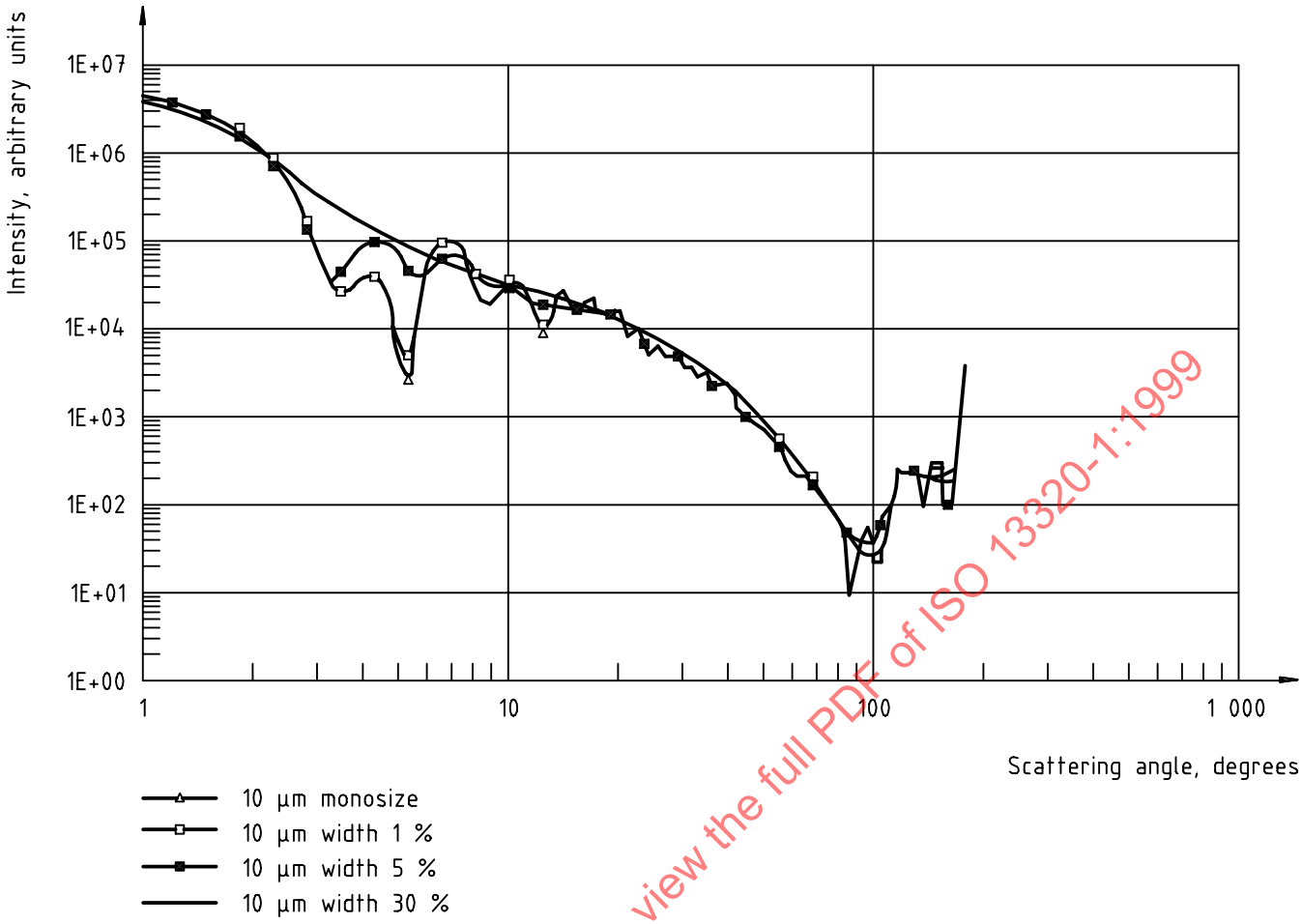


Figure A.6 — Influence of distribution width on angular light intensity scattering patterns of normal size distributions around 10 µm (particle RI = 1,62; medium water RI = 1,33)

Annex B
(informative)

Recommendations for instrument specifications

It is recommended that manufacturers of instruments provide specifications for laser diffraction instruments concerning the following items.

B.1 General

— power requirements;

— weight;

— dimensions;

— specific requirements, e.g. temperature, humidity, vibration, safety, etc.

B.2 Light source/laser

— type;

— wavelength;

— power output;

— intensity stability (accepted level of fluctuation);

— parallel and/or convergent beam;

— beam width/dimension(s) in sample;

— polarization;

— typical lifetime.

B.3 Sample circuit

— sample path length in laser beam;

— liquid pump rate, or particulate and air rate for dry dispersers;

— sonication power/frequency;

— volume of recirculation system and cell;

— materials of system in contact with particles and dispersion liquids;

— maximum particle size/density which can be dispersed/handled.

B.4 Lens

— focal length(s);

— working distance;

— whether fixed, or require changing.

B.5 Detector

— number of elements;

— detector geometry indication (e.g. half or quarter rings, segments, etc.);

— alignment, automatic or manual;

— whether or not detector elements have been calibrated;

— indication for normal detector signals for blank experiments and their maximum allowable limits;

— overload level for detector elements.

B.6 Measurement

— typical measurement time;

— minimum time between successive measurements.

B.7 Computer

— processor type;

— memory size;

— speed;

— operating system;

— disc type and size;

— monitor type;

— keyboard type;

— real time interfaces printer type/protocol;

— network functions/protocol;

— presence of facility for calculation of model matrix;

— presence of facility for multiple scattering correction.

B.8 Deconvolution

— type of optical model(s) that can be applied;

— indicative description of mathematical procedure, for example weighting, constraints and smoothing.

B.9 Output

— measurement range(s), overall and during each analysis;

— size class ranges; also whether fixed or adjustable;

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

— data storage; availability of background and sample light scattering fluxes.

B.10 Performance

— repeatability, within instrument;

— reproducibility, instrument to instrument;

— resolution and number of size classes;

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

— how presence of particles with diameters outside measuring range is indicated.