International
Standard

ISO 13317-5

First edition
2025-01

Determination of particle size distribution by gravitational liquid sedimentation methods —

Part 5:
Photosedimentation techniques

Détermination de la distribution granulométrique par les méthodes de sédimentation par gravité dans un liquide —

Partie 5: Techniques de photosédimentation

Reference number
ISO 13317-5:2025(en)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

A list of all parts in the ISO 13317 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The principles of gravitational photosedimentation and its potential use for the granulometric characterization of particle systems have been known for several decades. Recent developments in optoelectronics and data processing have boosted the commercial success and popularity of this measurement technique, which is currently employed in manifold academic and industrial applications.

This document is a part of the ISO 13317 series that provides a general overview on the principles, techniques, methods and underlying physics of particle size analysis by gravitational sedimentation. Photosedimentation employs photometric signals (i.e. transmitted, reflected or scattered light) in order to monitor the changes in the local particle concentration, which arise by the downward or upward particle migration under gravity (called hereafter sedimentation). The temporal or spatial functions of these signals can be directly transformed to distributions of the sedimentation velocity, without referring to model assumptions or being restricted by essential preconditions. Provided the applicability of Stokes' law on particle mobility, one can derive equivalent diameters from the sedimentation velocities (the *Stokes diameter*) and the corresponding particle size distributions. Size fractions are then intrinsically weighted by photometric quantities (e.g. light extinction or scattered light intensity), which is in contrast to the sedimentation techniques described in ISO 13317-2, ISO 13317-3 and ISO 13317-4. However, conversion into volume-weighted distributions is often an integrated part of signal processing, which employs established models for light-particle interactions. A noteworthy feature of gravitational photosedimentation is its ability to finely resolve details in the particle distribution functions. This is related to the physical fractionating of particle systems under gravity and constitutes an advantage compared to spectroscopic ensemble techniques.

Gravitational photosedimentation facilitates the granulometric characterization of dispersed materials of non-zero density contrast to the continuous phase, including solid particles and emulsion droplets. The available measurement range depends on dispersed and continuous phase properties and typically amounts to 200 nm to 100 µm for aqueous samples, whereas the sedimentation velocity can be quantified for the range 0,6 µm/s to 10 mm/s. Also, the working range with regard to particle concentration is strongly affected by material properties and by particle size, yet it is typically well below 1 vol%. The data analysis relies on the assumption that all particles have the same density and comparable shape and do not undergo chemical or physical change in the continuous phase.

In addition, photosedimentation techniques that monitor gravity-induced concentration changes along the complete sample height, e.g. by position-scanning or time-resolved projection, facilitate the characterization of dense dispersion beyond particle size, e.g. with respect to clarification, segregation, agglomeration, consolidation and physico-chemical stability (see ISO/TR 13097). Gravitational photosedimentation is equally applicable in determining particle density (see ISO 18747 series) as well as the formation of sediments and cream layers.

Determination of particle size distribution by gravitational liquid sedimentation methods —

Part 5:
Photosedimentation techniques

1 Scope

This document specifies principles and methods for the use of gravitational photosedimentation techniques for the characterization of dispersed phases of suspensions and emulsions. These techniques monitor the gravity-induced phase separation of particulate materials dispersed in liquids by recording photometric signals (i.e. intensity of transmitted or scattered light) as a function of either vertical position or measurement time, or both.

This document does not cover particle migration by centrifugal, electric or magnetic forces, or sedimentation at high particle concentrations (e.g. zone sedimentation). Moreover, it does not cover the determination of properties other than sedimentation velocity and particle size (i.e. it does not cover particle concentration, particle shape, particle density, zeta-potential or apparent viscosity).

Additionally, this document does not cover alternative techniques for gravitational sedimentation including balance based and X-ray based techniques.

NOTE This document does not purport to address all the safety problems associated with its use.

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*

3 Terms and definitions

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

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

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

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

3.1
sedimentation
directional motion of *particles* (3.7) in a viscous liquid under the action of gravity or centrifugal fields

Note 1 to entry: For a positive *density contrast* (3.17), sedimentation occurs in the direction of gravitational acceleration; it is counter directed to this acceleration for a negative density contrast.

Note 2 to entry: A downward motion under gravity is also called “settling” or “falling”.

Note 3 to entry: An upward motion under gravity is also called “creaming” (e.g. droplets) or more generally, “rising” or “floating”.

[SOURCE: ISO 13317-1:2024, 3.1]

3.2
migration

directional motion of *particles* (3.7) in a viscous liquid under the action of a force field

Note 1 to entry: Migration in gravitational or centrifugal fields is called *sedimentation* (3.1).

[SOURCE: ISO 13317-1:2024, 3.2]

3.3
terminal sedimentation velocity

sedimentation (3.1) velocity in the case that gravity or centrifugal force is completely balanced by buoyancy and drag force

[SOURCE: ISO 13317-1:2024, 3.3]

3.4
Stokes diameter

equivalent diameter of a sphere that has the same *buoyant density* (3.16) and *terminal sedimentation velocity* (3.3) as the real particle in the same liquid under *creeping flow* (3.19) conditions

Note 1 to entry: The general rule that the buoyant density is used for calculating the Stokes diameter applies also to coated particles or multiconstituent particles (such as droplets in multiple emulsions). The buoyant density can be approximated with the *skeleton density* (3.14) for monoconstituent particles.

Note 2 to entry: For porous particles, it is common use to compute particle size based on the *apparent particle density* (3.15). This approach considers the stagnant liquid in the open pores as intrinsic constituent of the dispersed phase. Thus, the obtained size values are hydrodynamic equivalent diameters.

Note 3 to entry: For close-packed *agglomerates* (3.8) or aggregates, the buoyant density can be replaced by the apparent particle density– with particle referring to the agglomerate or aggregate – in order to get the hydrodynamic equivalent diameter.

[SOURCE: ISO 13317-1:2024, 3.4]

3.5
shape correction factor

ratio of the sedimentation velocity of a non-spherical particle to the one of a spherical particle of the same volume and *apparent density* (3.15)

[SOURCE: ISO 13317-1:2024, 3.5]

3.6
hindrance function

ratio of the *terminal sedimentation velocity* (3.3) of a *particle* (3.7) placed in well-mixed dispersion divided by its sedimentation velocity in an infinite vessel for the absence of other particles

[SOURCE: ISO 13317-1:2024, 3.6]

3.7
particle

minute piece of matter with defined physical boundaries

[SOURCE: ISO 26824:2022, 3.1.1, modified — Notes 1, 2 and 3 to entry have been deleted.]

3.8
agglomerate

cluster of *particles* (3.7) held together by weak or medium strong forces with an external surface area, which is similar to the sum of the surface areas of the individual particles

Note 1 to entry: The forces acting between the constituent particles of an agglomerate are relatively weak. They result, for example, from van der Waals attraction or simple physical entanglement.

Note 2 to entry: Agglomerates are also termed secondary particles and the original source particles are termed primary particles.

[SOURCE: ISO 13317-1:2024, 3.8]

3.9
open pore

pore not totally enclosed by its walls and open to the surface either directly or by interconnecting with other pores and therefore accessible to liquid

[SOURCE: ISO 15901-1:2016, 3.11, modified: “fluid” has been replaced with “liquid” in the definition.]

3.10
closed pore

pore totally enclosed by its walls and hence not interconnecting with other pores and not accessible to liquids

[SOURCE: ISO 15901-1:2016, 3.10, modified: “fluids” has been replaced with “liquids” in the definition.]

3.11
dynamic viscosity

measure of flow resistance for Newtonian liquids, calculated as the ratio of the shear stress to the rate of shear for laminar flow exposed to a pre-set shear stress or strain

[SOURCE: ISO 13317-1:2024, 3.11]

3.12
apparent viscosity

measure of flow resistance for non-Newtonian liquids at a defined shear stress or strain, calculated as the ratio of the shear stress to the shear rate

[SOURCE: ISO 13317-1:2024, 3.12]

3.13
true density of the dispersed phase

ratio of mass to volume for a body solely consisting of the dispersed phase without pores, voids, inclusions or surface fissures

[SOURCE: ISO 13317-1:2024, 3.13]

3.14
skeleton density

ratio between sample mass and the volume of the sample including the volume of *closed pores* (3.10) (if present) but excluding the volumes of *open pores* (3.9)

Note 1 to entry: The skeleton density refers to solid *particles* (3.7) and is determined for samples of dry powder.

[SOURCE: ISO 13317-1:2024, 3.14]

3.15
apparent particle density

effective particle density

ratio of mass to volume for a *particle* (3.7) including particulate inclusions, entrapped stagnant liquid and gas in pores, voids and surface fissures as well as surfaces layers and coatings

Note 1 to entry: The apparent particle density is the density of a migrating entity and is calculated as the weighted average of its constituents.

Note 2 to entry: The apparent particle density depends on wettability of *open pores* (3.9) and the kinetics of wetting or replacement of pore liquid. Therefore, it is affected by sample preparation.

Note 3 to entry: The apparent particle density is not identical with the *buoyant density* (3.16). They deviate from each other for porous particles and particle *agglomerates* (3.8) in particular.

[SOURCE: ISO 13317-1:2024, 3.15]

3.16
buoyant density
ratio of mass to volume for a *particle* (3.7) including particulate inclusions, liquid and gas in closed pores and voids as well as surfaces layers and coatings, but excluding the liquid continuous phase that penetrates *open pores* (3.9)

Note 1 to entry: The buoyant density equals the (hypothetical) density of the continuous phase for which the gravitational force acting on the immersed particle is counterbalanced by buoyancy.

Note 2 to entry: The buoyant density of a particle can be experimentally determined (see ISO 18747-1 and ISO 18747-2 for more information)

Note 3 to entry: The buoyant density of monoconstituent particles can be approximated with their *skeleton density* (3.14).

Note 4 to entry: The buoyant density of multiconstituent particles (e.g. coated pigments, droplets of multiple emulsions) can be approximated with the averaged skeleton densities of the single constituents.

Note 5 to entry: The buoyant density is affected by the adsorption of dissolved species at the particle surface and therefore depends on the solvent and its composition.

Note 6 to entry: The buoyant density is not identical with the *apparent particle density* (3.15), particularly for porous particles and particle *agglomerates* (3.8).

[SOURCE: ISO 13317-1:2024, 3.16]

3.17
density contrast
difference between the particle density and the density of the continuous phase

Note 1 to entry: For quantifying the density contrast, the *buoyant* (particle) *density* (3.16) is used, but for porous particles, the *apparent particle density* (3.15) is more appropriate.

[SOURCE: ISO 13317-1:2024, 3.17]

3.18
particle Reynolds number
dimensionless parameter expressing the ratio of inertial to viscous forces within a fluid flowing past a particle

Note 1 to entry: The particle Reynolds number is based on the volume equivalent diameter.

Note 2 to entry: In other contexts, the definition of the particle Reynolds number can refer to different equivalent diameters or to the equivalent radii.

Note 3 to entry: The particle Reynolds number is a characteristic of the flow field and mobility of the particle.

[SOURCE: ISO 13317-1:2024, 3.18]

3.19
creeping flow
type of flow that is solely governed by viscous forces and not affected by inertial effects

Note 1 to entry: For moving *particles* (3.7) or for the flow past a particle, the creeping flow condition applies if the *particle Reynolds number* (3.18) is well below 0,25.

[SOURCE: ISO 13317-1:2024, 3.19]

3.20
Brownian motion
random motion of *particles* (3.7) caused by collisions with the molecules or atoms of the surrounding continuous phase

Note 1 to entry: The trajectory of Brownian motion is not differentiable.

Note 2 to entry: Brownian motion results on a macroscopic level in mass transport of the dispersed phase, e.g. in case of diffusion, thermophoresis or photophoresis.

[SOURCE: ISO 13317-1:2024, 3.20]

3.21

lower size limit

size of the smallest particles that are detectable and with a diffusional particle flux that is negligible compared to the sedimentational particle flux

Note 1 to entry: The ratio of sedimentational flux to diffusional flux (also called Péclet number, Pe) should be > 1.

[SOURCE: ISO 13317-1:2024, 3.21]

3.22

upper size limit

size of the largest particle that satisfies the condition of *creeping flow* (3.19) and of which the *terminal sedimentation velocity* (3.3) is detectable

[SOURCE: ISO 13317-1:2024, 3.22]

3.23

type of quantity

specification of the physical property employed to quantify the individual *particle* (3.7) fractions

Note 1 to entry: The type of quantity is a cumulable property of single particles or disperse systems, such as number, mass, intensity of scattered light (within the single scattering limit), light extinction (within Lambert-Beer-limit), refractive index increment or X-ray attenuation.

Note 2 to entry: The type of quantity is indicated by a numerical or character subscript when symbolising the density and cumulative function of a size distribution. Moreover, the subscript also specifies distribution parameters, such as median, mean and modal values or any quantiles.

Note 3 to entry: The following conventions apply for the subscript of geometric or gravimetric properties:

number: subscript $r = 0$

length: subscript $r = 1$

area: subscript $r = 2$

volume or mass: subscript $r = 3$

Note 4 to entry: The following conventions apply for the subscript of physical properties:

light extinction: subscript toq = “ext”

light intensity: subscript toq = “int”

[SOURCE: ISO 13317-1:2024, 3.23]

3.24

sensitivity

change of instrument response with respect to changes in concentration or absolute quantity of *particles* (3.7) in a specified size class

Note 1 to entry: A concentration or quantity can be given in relative or absolute values in dependence on the detection aim.

Note 2 to entry: Sensitivity depends on the *type of quantity* (3.23).

Note 3 to entry: Sensitivity is a function of size.

[SOURCE: ISO 13317-1:2024, 3.24]

3.25
limit of quantity detection

smallest quantity of specified particle size class for which the instrument response can be distinguished from the background

Note 1 to entry: The limit of quantity detection depends on factors such as size range, precision, noise level, and smoothing algorithms.

Note 2 to entry: The limit of quantity detection affects the *lower size limit* (3.21) and *upper size limit* (3.22).

[SOURCE: ISO 13317-1:2024, 3.25]

3.26
measurement uncertainty

uncertainty of measurement

parameter, associated with the result of a measurement that characterises the dispersion of the values that can reasonably be attributed to the measurand

[SOURCE: ISO Guide 98-3:2008, 2.2.3, modified — Notes 1 to 3 to entry have been deleted and the term "measurement uncertainty" has been added.]

4 Symbols and abbreviated terms

For the purposes of this document, the following symbols apply.

Ar	Archimedes number	dimensionless
b	systematic deviation of measured value from true value	varying
C	transformation coefficient, see Formula (27)	$m^{0,5}\cdot s^{0,5}$
C_{ext}	extinction cross section	
c_M	concentration with respect to extensive property M	varying
D_p	particle diffusion coefficient	$m^2\cdot s^{-1}$
E	extinction	
g	gravitational acceleration	$m\cdot s^{-2}$
h_{sed}	sedimentation distance	m
I	light intensity	
k	coverage factor	dimensionless
K_{ext}	extinction efficiency	
k_B	Boltzmann constant	$J\cdot K^{-1}$
L	optical pathlength	
Lj	Ljaščenko number	dimensionless
M	extensive property indicating the amount of dispersed phase	varying
m	number of bias determinations	dimensionless
N	number of particles	dimensionless

n	number of replicate analyses	dimensionless
Pe	Péclet number	dimensionless
Q_{toq}	cumulative function of distributed quantity, index “toq” indicates the type of quantity, in which the fractions are weighted	dimensionless
q_{toq}	density function of distributed quantity, index “toq” indicates the type of quantity, in which the fractions are weighted	varying
Re_{P}	particle Reynolds number	dimensionless
s	standard deviation	varying
T	absolute temperature	K
t	time	s
t_{observ}	time point of observation	s
t_{sed}	sedimentation time	s
U	expanded uncertainty	varying
u	uncertainty	varying
V_{meas}	measurement volume	
v_{sed}	terminal sedimentation velocity	$\mathrm{m{\cdot}s^{-1}}$
x	particle size (equivalent diameter)	m
x_{Stokes}	Stokes diameter	m
x_V	volume equivalent diameter	m
z	Cartesian coordinate in vertical direction, vertical position	m
$\Delta\rho$	density contrast	$\mathrm{kg{\cdot}m^{-3}}$
δ	thickness	m
η_{c}	viscosity of the continuous phase	Pa·s
ρ_{p}	particle density	$\mathrm{kg{\cdot}m^{-3}}$
ρ_{c}	density of the continuous phase	$\mathrm{kg{\cdot}m^{-3}}$
φ_V	volume fraction	dimensionless

In addition, the following subindices are frequently employed.

app	apparent
c	combined
cr	critical
ext	extinction
int	intensity

lab	laboratory
max	maximum
meas	measurement
psca	partial scattering
ref	reference
rel	relative
rep	repeatability
sca	scattering
Rw	reproducibility
toq	type of quantity

Moreover, this document uses the following abbreviated terms.

CRM	certified reference material
ILC	interlaboratory comparison
NIR	near infrared radiation
QCM	quality control material
RM	reference material
RTM	representative test material
UVA	ultraviolet A radiation

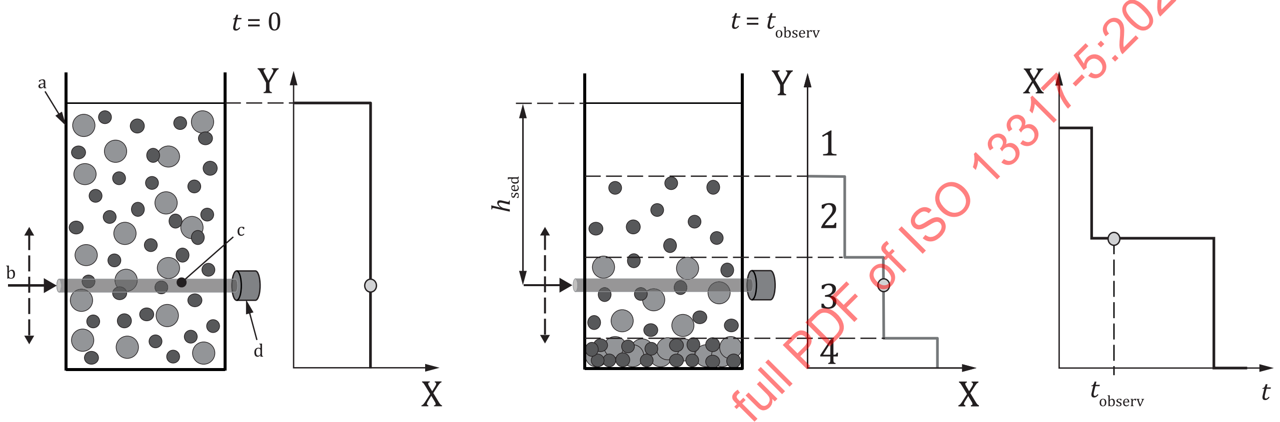
5 Measurement principle and instrumentation

5.1 General measurement principle

Gravitational photosedimentation allows the characterization of liquid disperse systems based on their phase separation under gravity. Unlike other sedimentation techniques, the phase separation is monitored photometrically as the depletion or accumulation of particles at (a) defined vertical position(s) in the initially well-mixed sample.[1] The measurement can be conducted at a fixed position or a continuously varying one (scanning mode) or even at multiple positions for the same measurement time, including the spatially resolved measurement along the vertical axis. The observed quantity is the intensity of light transmitted through, scattered by, or reflected at the sample. These quantities correlate with the local particle concentration at the measurement position(s). Temporal and spatial changes in local particle concentration are entirely attributed to gravitational sedimentation of the particles. The direction of sedimentary motion depends on the density contrast ($\Delta\rho$) between the dispersed and continuous phase (see 3.17); the corresponding particle motion is either called settling and falling ($\Delta\rho > 0$) or creaming, rising and floating ($\Delta\rho < 0$).

NOTE This document refers to photometric measurement techniques that monitor the gradual depletion or accumulation of particles in the continuous phase, but not to techniques that observe the growth of sediment or cream layers by photometric means (see ISO 6344-3 and ISO 8486-2). Moreover, the operational method requires an initially homogeneous dispersion sample [so called homogeneous-start mode (HSM)]; any approach starting with a thin dispersion layer on top or beneath a particle-free liquid (so called line-start mode) is beyond the applicability of this document.

Figure 1 illustrates the measurement principle for the photometric monitoring of transmitted light (for a scattering configuration, see Figure 3) The example assumes a bi-disperse particle system having a positive density contrast. At the beginning of the sedimentation analysis ($t = 0$), the sample is well-mixed, i.e. particles of each size fractions are uniformly distributed along the vertical axis and the local particle concentration is independent from position. However, gravity makes the particle settle downward with a size-dependent velocity. This gives rise to four layers differing in particle concentration. A particle-free liquid layer at the top (zone 1). In zone 2, the coarse particles settled out (segregation) within the time t_{observe} and only the fine particles remain ($c = c_{\mathrm{fine}}$). The particle content in the third layer does not change at all and composition and concentration are not position dependent and remain at its initial value ($c = c_{\mathrm{initial}} = c_{\mathrm{fine}} + c_{\mathrm{coarse}}$). The sediments forms at the bottom (zone 4), where particles have a very high concentration. Composition is not uniform. The sedimentation process is finished when all particles have settled and the formation of the sediment is completed. Nevertheless, the analysis can be stopped when the last of the particles that will migrate due to gravity have passed through the measurement zone [see Figure 1 a)]. In general, measurements can be stopped when photometric signals have reached a stable value, which is associated with the particle-free supernatant.



a) Homogenous mixing state and corresponding concentration profile at $t = 0$

b) Formation of 4 zones and corresponding concentration profile at t_{observ}

c) Evolution of the photometric concentration at the measurement position

Key

X	photometric concentration
Y	position
h_{sed}	sedimentation distance
t	time
t_{observ}	time point of observation
1	zone 1 = particle-free supernatant
2	zone 2 = depleted dispersion phase (due to loss of coarse particles)
3	zone 3 = original dispersion phase
4	zone 4 = sediment
a	Sedimentation cell.
b	Light beam, with fixed or varying position.
c	Measurement zone.
d	Photometric sensor.

The grey area between the light beam and the sensor depicts the measurement zone.

SOURCE: Reproduced with the permission of LUM GmbH©.

Figure 1 — Phase separation due to sedimentation for a bi-disperse sample with positive density contrast and its monitoring via light transmission

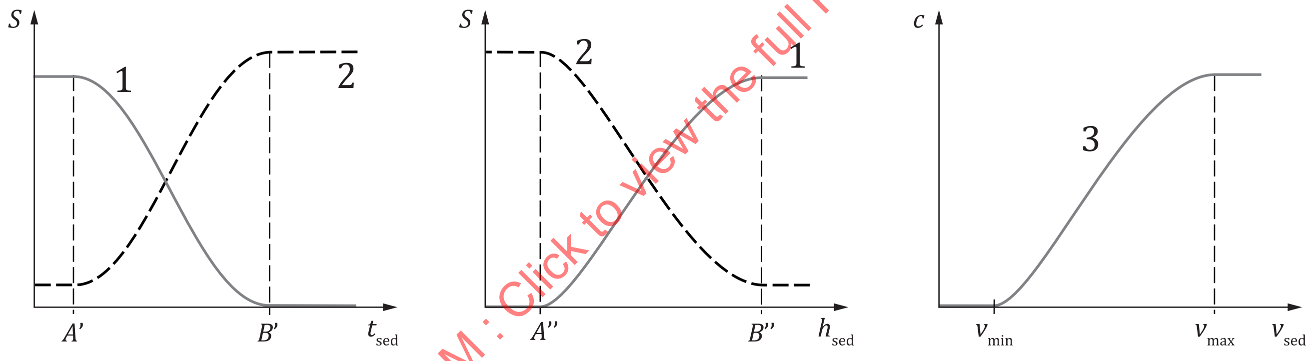
Within the scope of this document, the techniques should only be applied to dilute samples, in which particles settle or rise independently from each other (i.e. no hydrodynamic hindrance, see Reference [2] and ISO 13317-1). This condition offers a chance to quantify individual particle properties, such as size. Yet in principle, photosedimentation techniques also allow the characterization of concentrated samples, e.g. for the purpose of dispersion separation or stability analysis (see Annex E).

5.2 Primary and derived measurement results

The primary measurement data of photosedimentometer are optical signals from the sample contained in a transparent measurement cell (e.g. cuvette). Such signals are either the intensities of transmitted light or scattered light, which are frequently presented as normalized values (e.g. transmittance, relative scattering intensity). In general, they may be registered either as functions of time at a (multiple) vertical cell position(s) or at vertical position(s) at a fixed time(s). Several types of original measurement results are possible:

- time course of the optical signal at a constant vertical position of the sedimentation cell;
- time courses of the optical signal at few vertical positions of the sedimentation cell;
- time courses of the optical signal at different positions obtained by vertical scanning along the sedimentation cell (allows reconstruction of vertical profiles if scanning rate is faster than rate of phase separation);
- time-resolved vertical profiles of the optical signal along the measurement cell (i.e. simultaneous time courses of the optical signals at multiple, finely resolved vertical positions).

Hence, there are two principal types of original measurement results: time courses for a specified position or vertical profiles for a specified time [see Figure 2 a) and b)].



a) Primary measurement: Optical signal vs. sedimentation time

b) Primary measurement: Optical signal along vertical position

c) Derived result: Particle concentration vs. sedimentation velocity

Key

1	scattering signal
2	transmission signal
3	cumulated particle concentration
A'	time, at which the fastest particles have completely passed the vertical measurement position
B'	time, at which the slowest particles have left the zone above ($\Delta\rho > 0$) or below ($\Delta\rho < 0$) the measurement position
A''	distance in the direction of sedimentation, below which the liquid is completely depleted of the fastest particles
B''	distance in the direction of sedimentation, below which the liquid is free of particles
c	particle concentration
h_{sed}	sedimentation distance
S	signal

t_{sed} sedimentation time

v_{sed} sedimentation velocity

The real signal shape of the schematic curves depends on several factors, including particle size distribution, particle shape, wavelength or refractive indices.

Figure 2 — Primary and derived measurement signals of gravitational photosedimentation

The primary optical signals correlate with the particle concentration but are also affected by the optical configuration of the instrument, the optical properties of the measurement cell and the optical properties of the dispersion medium. The quantification of particle fractions, i.e. for photosedimentometer applications within this document, requires a signal transformation to get rid of the signal contributions not caused by particles (see 6.1).

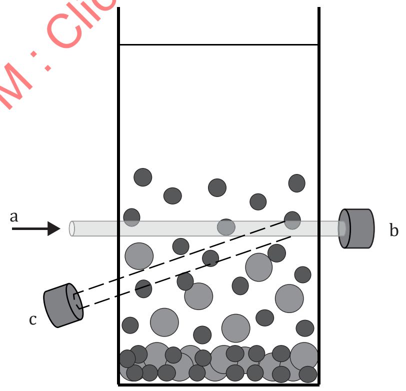
— Transmitted signal intensity is first converted into sample transmission and finally into extinction.

— Scattered intensity is converted into relative excess scattering signals or excess Rayleigh ratio.

The transformed signals are considered to be proportional to the particle concentration, which is prerequisite for the quantification of particle fractions. The evolution of signals with time or vertical position is due to the sedimentational separation and segregation of the dispersed phase as shown in Figure 1. It reflects changes in the composition of the dispersed phase and thus the quantities of particle fractions that have just left the measurement zone. Those fractions migrate with a sedimentation velocity, which is identical to the ratio of sedimentation distance to measurement time and which can be further transformed into an equivalent diameter, the Stokes diameter (see 6.1). Hence, time-curves or profiles of transmitted or scattered signals can be considered as scaled sum functions of the velocity or particle size distribution [see Figure 2 c)].

5.3 Instrumentation

Typical photosedimentometers essentially consist of a vertically aligned measurement cell (or sedimentation column), a unit for adjusting to a constant temperature in the measurement cell (e.g. water bath, contact cooling and heating), an illuminating light source or sources operating at different wavelengths, optical detection system(s) and an electronic signal processing unit.



Key

a Incident beam.

b Transmission detector.

c Scattering detector.

Figure 3 — Transmission and scattering setup

The most important feature for grouping photosedimentometer is whether they employ transmitted light[3],[4] or scattered light[5] for monitoring phase separation. The former has the advantage of a defined measurement volume, which simplifies the “extraction” of particle-induced signal contributions. On the other hand, it principally requires a certain minimum sample opacity and turbidity and allows the quantification of separate particle fractions, i.e. for the determination of velocity distribution or particle size distribution, only if opacity keeps below a critical threshold. Scattered light allows the monitoring of phase separation for fully transparent samples (i.e. low particle concentrations) and, in the case of backscattered (reflected) light, for opaque samples. However, the reliable quantification of separate particle fractions from scattered light requires low optical concentrations.

NOTE 1 Photosedimentometers used for the quantification of separate particle fractions, i.e. for the determination of the velocity distribution or the particle size distribution, are typically operated in transmission mode.

The optical detection system may be comprised of one (or more) detector(s) at fixed vertical position(s) or a movable detector, which scans the sample along the vertical axis. The width of the illuminating light beam(s) can be adjusted to ensure optimum signal-to-noise ratio. An alternative is spatially resolved detectors (e.g. a linear CCD array), which ideally allow the simultaneous observation of concentration changes at each vertical position (STEP Technology[2]). For this purpose, the measurement cell is illuminated with a two-dimensional beam. In practice, each type of detection system can be attributed a certain vertical resolution Δh, which affects the minimum resolution of the distribution functions (see Annex A).

Illumination in photosedimentometers employs radiation from the optical domain including visible light, UVA and NIR:

— at one, fixed wavelength (or a very narrow part of the spectrum);

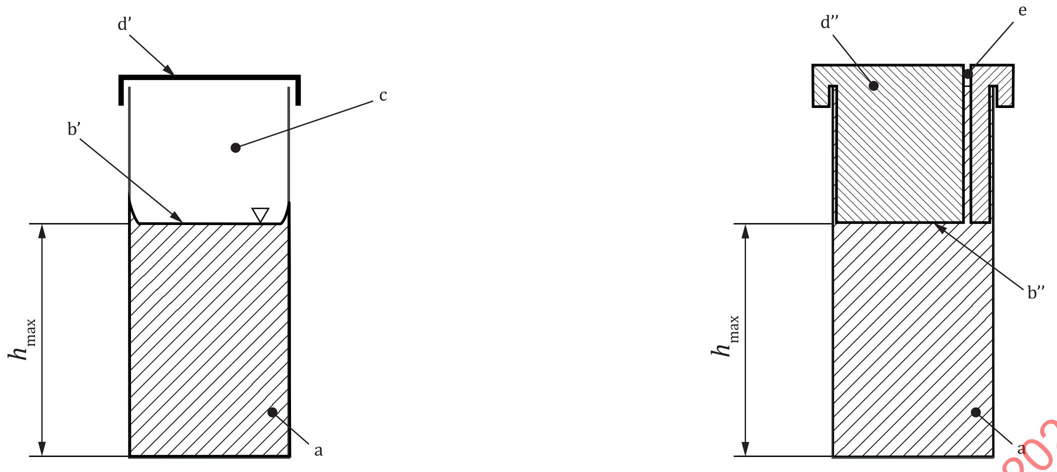
— at multiple, fixed wavelengths;

— with spectral resolution (i.e. for a large number of consecutive wavelengths).

Currently, the first two are the most frequently used.

The central part of a photosedimentometer is the measurement cell, in which the liquid dispersion sample is placed for gravitational phase separation. Measurement cells for transmission measurements are typically rectangular in cross-section with the light beam perpendicularly passing two parallel windows, whereas scattering-based photosedimentometry is frequently performed on round cuvettes. The most important characteristics are the height and the optical path (diameter) of the measurement cell. The height limits the sedimentation distance and thus the maximum sedimentation velocity, which can be accessed for a given time resolution. The optical path affects the overall turbidity of the sample and thus restricts the particle concentration, at which the measurements must be run. In some cases, instruments employ different cells (cell heights, path lengths, and material) to increase flexibility regarding measurable samples. In addition, it also sets an upper limit for particle size because the photometric principle of particle quantification relies on a large number of particles in the measurement zone, otherwise signals would reflect stochastic number variations of illuminated particles. On the other hand, to avoid hydrodynamic wall effects, the width should be at least 10 times larger than the coarsest expected particles.[2],[6]

NOTE 2 For the sake of illustration, a transmission configuration can be assumed with a measurement volume of 10 mm path × 2 mm (width of beam) × 1 mm (height of beam) intended to analyse a sample of 10 µm spheres at a volume fraction of 0,1 %. This coincides with approximately 38 200 illuminated particles and, by means of Poisson statistics, the relative standard deviation of this number can be estimated as 0,5 %. For 200 nm and 100 µm nm spheres, the same volume fraction yields an average number of 5×10^9 and 38 illuminated particles, respectively. The corresponding relative standard deviation amounts to 0,01 % and 16 %, respectively.



a) Cap-like lid design, which allows for an air buffer above the liquid sample

b) Stopper-type lid, which completely displaces the air above the liquid sample

Key

$h_{\max}$	maximum sedimentation distance, i.e. height of the liquid column
a	Sample.
b′	Meniscus, i.e. air-sample interface (illustration assumes a lyophilic wall material).
b″	Lid-sample interface.
c	Air.
d′	Cap-like lid.
d″	Stopper-type lid.
e	Degassing channel.

Figure 4 — Different types of lids

Another feature of the measurement cell is whether the lid covers the top of the cell and leaves an air-sample interface or whether the lid touches the sample surface (Figure 4). The latter requires an appropriate lid design, but has the advantage that the top level of the sample (thus the sedimentation distance to the measurement position) remains constant and independent from the operator. The sample volume is rather fixed, as the air must be completely displaced from the zone below the lid (sample volume in the air outflow and the gap between lid and wall is ideally negligible). The second lid-type is simpler in design and allows more flexibility for measurement parameters, yet requires the top level of the sample to be properly identified for each sample (see 6.4).

6 Measurement data and calculation of distribution function

6.1 Primary and derived measurands

The primary measurement results of gravitational photosedimentation are the measured dependencies of photometric signals from the sample on measurement time or vertical position or, more generally, a list of photometric data corresponding to a list of couples specifying time and position.

The photometric signals are the intensities of either transmitted or scattered light (I_{trans} or I_{sca}, respectively). The transmitted signals at a given vertical cell position are normalized with corresponding signals from the pure liquid containing no particles. This is often achieved more practically by using the transmission value of the supernatant of a completely separated sample; with the user being aware of the approximate time necessary for all particles to sediment:

$$E = -\ln\left(T_{\mathrm{sample}}\right) = -\ln\left(\frac{I_{\mathrm{trans,sample}}}{I_{\mathrm{trans,supernatant}}}\right) \tag{1}$$

where

E is the (natural) extinction;

T_{sample} is the sample transmission.

The normalization (background correction) with the signal of the particle free liquid eliminates the influences of the optical setup (e.g. irradiance, photodetector, etc.) and the measurement cell (reflectance at inner and outer walls). Similar reasons require normalization of the scattered signal:

$$I_{\mathrm{sca,rel}} = \frac{I_{\mathrm{sca,sample}} - I_{\mathrm{sca,med}}}{I_{\mathrm{sca,ref}}} \tag{2}$$

where

$I_{\mathrm{sca,med}}$	scattering signal of the dispersion medium/pure liquid;
$I_{\mathrm{sca,ref}}$	scattering signal of a reference liquid/dispersion;
$I_{\mathrm{sca,rel}}$	relative excess scattering intensity;
$I_{\mathrm{sca,sample}}$	scattering signal of sample.

Gravitational photosedimentation starts with a uniform distribution of particles within the sample volume (see 5.1). Accordingly, the initial profiles of photometric signals are also uniform over the entire sample height. Subsequent changes of the photometric signals reflect changes in local particle concentration and are due to phase separation. Within the scope of this document, photosedimentation is applied to measurement conditions, for which phase separation is solely caused by sedimentation of particles, whereas convective flow or Brownian motion may be excluded. In this event, each couple of measurement time and vertical position can be associated with particles that have just passed the measurement zone after having started at the top (settling particles) or bottom (rising particles). These particles migrate with the following sedimentation velocity (see Figure 1):

$$v_{\mathrm{sed}} = \frac{h_{\mathrm{sed}}}{t} \tag{3}$$

NOTE 1 For creaming or rising particles, the relevant travelling distance h_{sed} is defined as vertical distance from the bottom of the vessel. Therefore, a negative sign is assigned to the velocity.

The sedimentation velocity depends on the density contrast between particles and the continuous phase, viscosity of the continuous phase as well as on the particle size. For spherical particles of diameter x, Formula (4) applies, which is named after Stokes based on Reference [7], in the event of creeping flow conditions:

$$v_{\mathrm{sed}} = \frac{g\left(\rho_{\mathrm{p}} - \rho_{\mathrm{c}}\right)}{18\eta_{\mathrm{c}}} x^2 \tag{4}$$

where

g	gravitational acceleration;
η_c	dynamic viscosity of the continuous phase;
ρ_c	density of the continuous phase;
ρ_p	density of the particle.

In the case of non-spherical particles, the sedimentation velocity depends on the particles’ alignment in space. Its orientation-averaged value is smaller than the sedimentation velocity of a volume-equivalent sphere. The ratio between the two velocity values is referred to as the shape correction factor.

In a typical scenario of particle size analysis, particle shape remains an unknown or at least non-quantified factor. Therefore, Formula (4) is used to define the equivalent diameter for particle size analysis with sedimentation techniques, the Stokes diameter:

$$x_\mathrm{Stokes} = \sqrt{\frac{18\eta_\mathrm{c} v_\mathrm{sed}}{g\left(\rho_\mathrm{p} - \rho_\mathrm{c}\right)}} \qquad (5)$$

where the appropriate particle density ρ_p is either the buoyant density for the general case or the apparent particle density for the case of particles having fine, open pores.

NOTE 2 The buoyant density is commonly approximated by the skeleton density, which is frequently reported on data sheets. Such an approximation can be critical in the case of the adsorbed layers of molecules and ions from the continuous phase because relevant data of the layer (e.g. thickness and composition) are typically not known.

The transformation of sedimentation velocity into a spherical equivalent diameter [see Formula (5)] relies on a couple of assumptions, which are discussed in 6.5 (see also ISO 13317-1).

6.2 Intrinsically measured distribution functions

Photosedimentation quantifies the polydispersity of particle systems by means of photometric signals (see Figure 1). Accordingly, the intrinsic types of quantity of photosedimentation measurements are thus (light) extinction [see Formula (1)] or (scattered-light) intensity [see Formula (2)]. Their use as a quantitative description of polydispersity is commonly based on the idea that all particles contribute to light extinction and scattered intensity independently from one another and that their contributions superpose linearly:

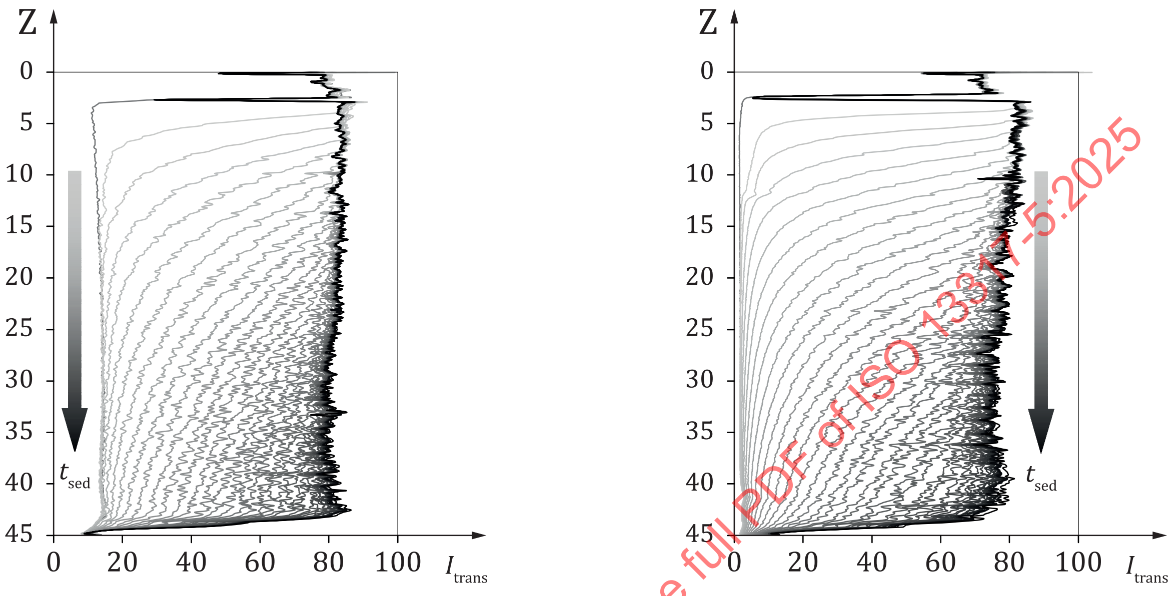
$$E \propto N_\mathrm{part} / A_\mathrm{beam} \propto c_N \cdot L \propto c_V \cdot L \quad \text{(Lambert-Beer law for monodisperse samples)} \qquad (6)$$

$$I_\mathrm{sca,rel} \propto N_\mathrm{part} \propto c_N \cdot V_\mathrm{meas} \propto c_V \cdot V_\mathrm{meas} \quad \text{(single scattering for monodisperse samples)} \qquad (7)$$

where

A_beam	cross-section of the light beam;
c_N	particle number concentration;
c_V	particle volume concentration;
E	(natural) extinction;
$I_\mathrm{sca,rel}$	scattering intensity;
L	length of the optical path;
N_part	number of illuminated particles in the measurement zone;
V_meas	volume of the measurement zone.

This idea only holds true for relatively low sample opacities (corresponding to low particle concentrations). Relatively high sample opacities coincide with nonlinear photometric effects (e.g. multiple scattering or attenuation of scattered light), which leads to underestimating the quantity of coarse particles. Figure 5 illustrates such effects during the sedimentation of glass beads measured in two different cells distinguished by the optical path length. One ensures a sufficiently low obscuration for the homogeneous suspension, so that Lambert-Beer law [see Formula (6)] applies. The other results in an unacceptably high obscuration at the start of the sedimentation process, so that the derived velocity distribution lacks information on the coarsest particles and underestimates the median sedimentation velocity.



a) Acceptable initial transmittance (0,8 wt% in 2 mm cell; apparent median velocity: 40 µm/s)

b) Initial transmittance too low (0,8 wt% in 10 mm cell; apparent median velocity: 36 µm/s)

Key

I_{trans}	transmitted light signal (normalized to clean air), in %
I_{sed}	sedimentation time
Z	vertical coordinate, in mm

NOTE The arrows indicate the evolution of the transmission profiles, which were recorded with an interval of 80 s.

Figure 5 — Profiles of transmitted intensity for sedimentation of glass beads

If Formulae (6) and (7) apply, the time-curves and profiles in Figure 1 a) and Figure 1 b) can be regarded, respectively, as scaled distribution functions. Together with Formula (3), it can be stated:

$$Q_{ext}\left(v_{sed}\right)=\frac{E\left(h_{sed},t\right)}{E_{initial}} \tag{8}$$

$$Q_{int}\left(v_{sed}\right)=\frac{I_{sca,rel}\left(h_{sed},t\right)}{I_{sca,rel}\left(t=0\right)} \tag{9}$$

with $v_{sed}=\frac{h_{sed}}{t}$

The two photometric quantities (extinction and scattering intensity) do not reflect only particle concentration, but also depend on various optical particle properties (e.g. shape and refractive index) and employed instrumentation parameters (e.g. wavelength and aperture angle). This must be considered, when comparing different photosedimentometers or different measurement techniques. For instance, the extinction-weighted distribution of a given sample can significantly change, when the light source is switched from NIR to UVA, in particular if this switch coincides with a qualitative change regarding light absorption.

6.3 Conversion to volume-weighted distribution functions

The intrinsically measured extinction or intensity weighted distribution functions can be converted into volume-weighted functions (for the conversion to number-weighted function, see Annex B), if the relationship between the sedimentation velocity of a particle (or its Stokes diameter) and its photometric response can be quantified by adequate models. The photometric response can be expressed by various quantities.

— Extinction cross-section (C_{ext}): attenuated light flux divided by irradiating light intensity.

— Extinction efficiency (K_{ext}): extinction cross-section divided by the particle's projected area.

— Partial scattering cross-section (C_{psca}): scattered light intensity in a certain direction multiplied with complete solid angle and divided by irradiating light intensity.

— Partial scattering efficiency (K_{psca}): partial scattering cross-section divided by the particle's projected area.

These parameters generally depend on size and shape of the particles, but also on their optical properties, more specifically on their (complex) refractive index. In each case, the computation requires the wavelength of the light source and the refractive index of the liquid (continuous phase) to be known, since the wavelength in the liquid constitutes the length scale for the interaction between light and particles.

The conventional procedure for converting the intrinsically measured distributions functions relies on the assumption of spherical particles and the applicability of Mie's solution for the scattering of electromagnetic waves.[8],[9] The latter includes that the functional relationship between Stokes diameter (x_{Stokes}) and the optical response (i.e. C_{ext} and C_{psca}) remains unaffected by particle shape. This kind of optical computations requires details of the optical setup (e.g. aperture angle or scattering angle) and the knowledge of the refractive indices of particles and continuous phase at the given wavelength.

The starting point of the procedure is the relationship among the contributions of a given size fraction to number or volume and photometric response (i.e. extinction level or scattering intensity):

$$\mathrm{d}Q_{\text{ext}}(x)=\frac{C_{\text{ext}}(x)\,\mathrm{d}Q_0(x)}{\int C_{\text{ext}}(x)\,\mathrm{d}Q_0(x)}=\frac{K_{\text{ext}}(x)/x\,\mathrm{d}Q_3(x)}{\int K_{\text{ext}}(x)/x\,\mathrm{d}Q_3(x)} \qquad (10)$$

where Q_{ext}, C_{ext} and K_{ext} can be replaced by Q_{int}, C_{psca} and K_{psca}, respectively.

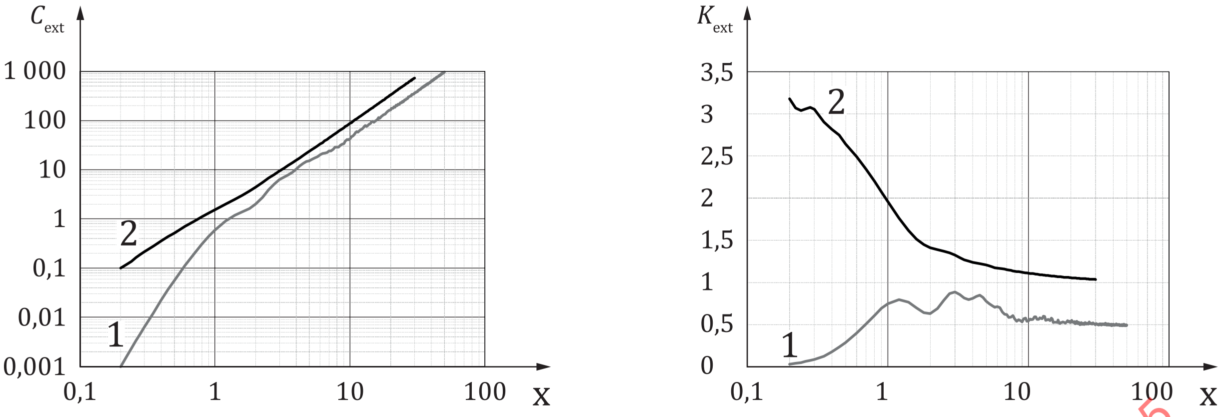
This results in the following expressions for the conversion step:

$$\mathrm{d}Q_3(x)=\frac{x/K_{\text{ext}}(x)\,\mathrm{d}Q_{\text{ext}}(x)}{\int x/K_{\text{ext}}(x)\,\mathrm{d}Q_{\text{ext}}(x)}\ \text{ or }\ \mathrm{d}Q_3(x)=\frac{x/K_{\text{psca}}(x)\,\mathrm{d}Q_{\text{int}}(x)}{\int x/K_{\text{psca}}(x)\,\mathrm{d}Q_{\text{int}}(x)} \qquad (11)$$

In general, all optical cross-sections and efficiencies are non-monotonic functions of particle size with more or less significant oscillations, depending on the material properties and optical configurations. In practice, oscillations are largely dampened by either the aperture of the detection optics or the broadening of the spectral line, or both, but also by the deviation from a spherical shape. For coarse particles > > 1 µm, the following simplification can be employed (see Figure 6):

$$C_{\text{ext}}(x),C_{\text{psca}}(x)\propto x^2\ \text{ or }\ \frac{\mathrm{d}K_{\text{ext}}}{\mathrm{d}x},\frac{\mathrm{d}K_{\text{psca}}}{\mathrm{d}x}=0\ \text{ for x >> 1 µm} \qquad (12)$$

which means that the intrinsically measured distribution functions are essentially area-weighted.



a) Extinction cross-section vs. particle size

b) Extinction efficiency vs. particle size

Key

x	particle size, in µm
C_{ext}	extinction cross-section, in µm^2
K_{ext}	extinction efficiency, dimensionless
1	glass beads
2	iron balls

NOTE The calculation assumes a detector aperture of 14°.

Figure 6 — Mie calculation of size dependency of optical cross-sections and efficiencies for glass beads and iron balls

An alternative to the conventional method based on Formula (11) has been proposed by Weichert[10] for the case of photometric sedimentation monitoring at multiple wavelengths. That procedure does not assume a specific particle shape, nor does it require the optical properties of the particles. However, it relies on the applicability of a dimensionless scaling law, which can limit the spectral range, and a high signal-to-noise ratio in the photometric signals (see Annex C).

Volume-weighted size distribution, in principle, can be further converted into a number-based particle size distribution or the extinction-weighted distribution functions are directly converted to number-weighted ones (Annex B).

6.4 Determination of the start position

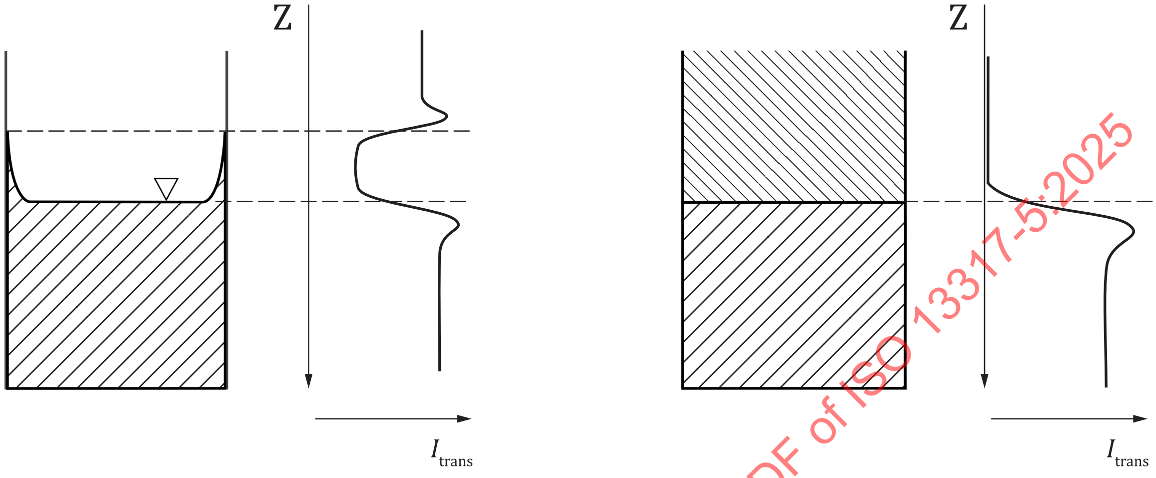
For the calculation of sedimentation velocity [see Formula (3)], the maximum sedimentation distance, which is determined by the detector position and the top level (for settling particles) or cell bottom (for rising particles), must be known. The vertical positions of the measurement zone and the cell bottom depend on the specific instrumentation and are typically well-documented by the manufacturer. In contrast, the position of the top level is an adjustable parameter depending on sample volume, and hence must be determined for each individual sedimentation measurement.

In principle, there are two principal cell configurations that determine the top level (see Figure 4).

— The interface between the liquid dispersion and air (meniscus).

— The liquid dispersion touching the cell lid or upper wall.

The latter can mean that the geometry (including wall positions) is well described, but not necessarily. Inaccuracies can occur if the sample enters into the space between wall and lid. This results in larger sedimentation distances for that particle fraction and, correspondingly, a more tailored size distribution for the fines. On the other hand, free meniscus positions inevitably coincide with variations of the top level. Moreover, menisci are curved surfaces, where the central position commonly lies below the upper line of a thin liquid layer attached to the cell wall by capillary forces [see Figure 7 a)]. This effect hampers the accurate determination of the meniscus position by visual or photometric means. A photometric detection of the top level is generally possible if the sedimentometer provides a spatially resolved photometric signal along the vertical axis. Ideally, menisci would cause a rectangular minimum in the photometric signal, while an interface between the liquid dispersion and an opaque lid would result in a step function. However, diffraction and finite aperture of the optical systems smoothes such profiles and causes some degree of uncertainty on the exact position of the central top level (see Figure 7). This kind of determination of the top level is frequently used and should be guided by the instrument software.



a) Air-liquid interface, i.e. vaulted surface (capillary ascension at the wall causes a signal minimum, which is superposed by diffraction)

b) Lid-liquid interface, i.e. flat interface (the smooth transition in the signal profile is mainly due to diffraction)

Key

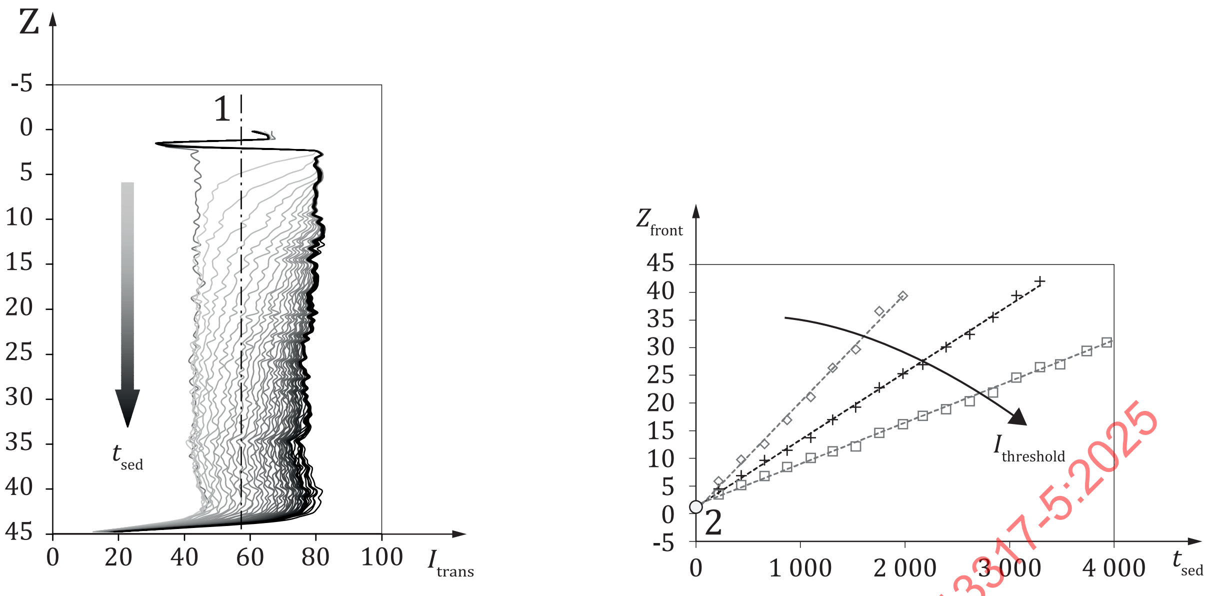
I_{trans}	intensity of the transmitted light signal
Z	vertical coordinate

This figure is not drawn to scale (indicated meniscus curvature applies to lyophilic walls; indicated signal profiles apply to non-opaque liquids).

NOTE The two principal types of start position shown in this figure correspond to those shown in Figure 4.

Figure 7 — Projection of top level in the profiles of the transmitted signals

Apart from using fixed, instrumentation-specific values of the start position or their extraction from photometric signal profiles, a different approach can be used. This relies on the measurement of photometric profiles and employs a simple routine for signal processing called front-tracking. Front-tracking detects the time-dependent location of the sedimentation front (i.e. the interface between supernatant and dispersion phase), which is the vertical position, at which the signal exceeds or falls below a transmission threshold. This position gradually shifts with time; its linear regression intercepts the ordinate at the start position (see Figure 8).



a) Evolution of profiles of the transmitted signals (I_{trans}) with indication of a signal threshold ($I_{threshold}$) used for front tracking

b) Extrapolation of start position (z_{start}) from time curves of the sedimentation front positions (for varying threshold values of the signal intensity)

Key

1	threshold line (at $I_{threshold}$), along which the motion of the sedimentation front is observed
2	starting point with start position z_{start}, used to calculate the sedimentation distance
$I_{threshold}$	threshold value, for which the motion of the sedimentation front is observed
I_{trans}	transmitted light signal (normalized to clean air), in %
t_{sed}	sedimentation time, in s
Z	vertical coordinate, in mm
z_{front}	front position, in mm
z_{start}	start position, in mm

Figure 8 — Derivation of start position from so called front tracking

This alternative procedure has the twofold advantage that the unsharpness of photometric projection can be ignored and that errors in clocking can be largely compensated. “Clocking error” refers to situations in which the phase separation has already started before the measurement time is running or in which the homogenization of particles in the measurement cell is stopped with time delay after triggering the measurement. The former yields a calculated start position beneath the geometric top level, whereas the opposite applies for the latter. Similarly, the procedure can also compensate for lacking temperature adjustment in the initial phase of phase separation. On the other hand, the start position can be determined by the so-called direct boundary method (DBM) approach developed for analytical ultracentrifugation.[11],[12] For details, refer to ISO 13318-1.

6.5 Assumptions behind data analysis in photosedimentation

6.5.1 Assumptions related to Stokes law

Stokes’ formula for the sedimentation velocity of fine particles [see Formula (4)] relies on a couple of assumptions, which relate to the following:

— particle motion:

always in steady-state; balance among gravity, buoyancy and hydrodynamic drag; under *creeping flow* (3.19); no viscous interaction with neighbouring particles and walls;

- particle properties:

  spherical shape; smooth and rigid surface; homogenous density; inert with respect to liquid;

- liquid properties:

  incompressible, Newtonian.

The individual effects are discussed in detail in ISO 13317-1, and References [2] and [6].

Some of the assumptions listed can be addressed by proper sample preparation (see subclauses 7.3 and 7.4). For instance, solvents should show Newtonian behaviour, must not promote dissolution or swelling and may contain dispersing agents that impede particle agglomeration.[6] Other assumptions set limits on the working range (see 6.6) with regard to particle size (e.g. to ensure creeping flow) and concentration (e.g. to avoid either viscous or hydrodynamic particle interactions, or both). Assumptions on the morphological and structural properties of the particles (in particular shape, surface and density) are deliberately considered true when transforming the sedimentation velocity into an equivalent diameter, the Stokes diameter, by Formula (5).

6.5.2 Assumptions related to photometric particle quantification

As explained in 6.2, data analysis in photosedimentation relies on the assumption that all particles contribute independently from each other to light extinction and scattered intensity and that their contributions superpose linearly, which can be briefly expressed by Formulae (6) and (7). Their validity is restricted to a domain in the two-dimensional space spanned by particle size and particle concentration and thus defines the working range of photosedimentation (see 6.6).

The photometric measurement principle is based on the idea that at each instant, a population averaged signal is measured. That means that the measurement zone should contain a sufficiently large number of particles in order to keep the stochastic number variations of illuminated particles very low. This again sets practical limits to the size and concentration of particles that can be analysed with a specific photosedimentometer.

6.6 Working range with respect to particle size and concentration

6.6.1 Limits defined by the applicability of Stokes law

Stokes' Formula (4) applies to the creeping flow definition, which is ensured for fine particles with a particle Reynolds number (Re_p) below 0,25. The corresponding thresholds for Archimedes and Ljaščenko numbers (i.e. dimensionless size and sedimentation velocity, respectively) amount to:

$$Ar_\mathrm{cr}=\frac{g\Delta\rho\rho_\mathrm{c}x_\mathrm{max}^3}{\eta_\mathrm{c}^2}=\frac{g}{v_\mathrm{c}^2}\frac{\Delta\rho}{\rho_\mathrm{c}}\cdot x_\mathrm{max}^3=4{,}68 \text{ and } Lj_\mathrm{cr}=\frac{\rho_\mathrm{c}^2v_\mathrm{max}^3}{g\Delta\rho\eta_\mathrm{c}}=\frac{1}{gv_\mathrm{c}}\frac{\rho_\mathrm{c}}{\Delta\rho}\cdot v_\mathrm{max}^3=0{,}003\,34 \qquad (13)$$

where

Ar_cr	critical Archimedes number, below which creeping flow can be assumed;
g	gravitational acceleration;
Lj_cr	critical Ljaščenko number, below which creeping flow can be assumed;
v_max	sedimentation velocity, below which creeping flow can be assumed;
x_max	particle size, below which creeping flow can be assumed;
η_c	dynamic viscosity of the continuous phase;
v_c	kinematic viscosity of the continuous phase;

ρ_c density of the continuous phase;

ρ_p density of the particle.

Obviously, the corresponding limits to particle size or sedimentation velocity depend on the density contrast and liquid viscosity:

$$x \le \sqrt[3]{\frac{4{,}68 \cdot \nu_c^2}{g(\Delta\rho/\rho_c)}} \text{ and } v_{sed} \le \sqrt[3]{\frac{0{,}00334}{g\nu_c(\Delta\rho/\rho_c)}} \tag{14}$$

In principle, the user should also be aware of a lower size limit, below which particle sedimentation is significantly superposed by Brownian motion. This limit is defined via a critical Péclet number:[13]

$$Pe = \frac{v_{sed} h_{sed}}{D_p} = \frac{\pi g \Delta\rho x^3 h_{sed}}{6 \mathrm{k_B} T} \le 200 \tag{15}$$

$$\text{thus: } x \ge \sqrt[3]{\frac{382 \cdot \mathrm{k_B} T}{g \Delta\rho h_{sed}}} \tag{16}$$

where

Ar_{cr} critical Archimedes number, below which creeping flow can be assumed;

D_p particle diffusion coefficient;

g gravitational acceleration;

h_{sed} sedimentation distance;

$\mathrm{k_B}$ Boltzmann constant;

T temperature;

v_{sed} sedimentation velocity;

x particle size;

$\Delta\rho$ density contrast.

The typical value is in the order of 200 nm (this value applies to $\Delta\rho$ = 2 000 kg/m^3 and h_{sed} = 1 cm at room temperature).

Stokes' derivation of particle drag and sedimentation velocity assumes isolated particles. This criterion is approximately met when the volume fraction of the dispersed phase (including immobilised, stagnant fluid in the pores) remains below 0,5 %:

$$\varphi_V \le 0{,}005 \tag{17}$$

6.6.2 Limits defined by the applicability of photometric detection

The photometric quantification of particle fractions requires sufficiently high signals (well above the noise level) and the validity of linear superposition of the individual particles' contributions to scattering and extinction. For extinction-based photosedimentometers, this is usually ensured when the transmitted signal (T_{sample}) for the unseparated sample is lower than 80 % and larger than 10 % of the supernatant's transmittance:

$$0{,}1 \le T_{sample} \le 0{,}8 \tag{18}$$

with $-\ln\left(T_{\text{sample}}\right)=\varphi_V \dfrac{C_{\text{ext}}}{V_{\text{p}}} L=\frac{3}{2}\varphi_V \dfrac{K_{\text{ext}}}{x} L$.

The volume fraction can be then expressed as function of particle size and optical pathlength:

$$\frac{2}{3}\frac{\ln(1{,}25)}{L}\cdot\frac{x}{K_{\text{ext}}(x)} \le \varphi_V \le \frac{2}{3}\frac{\ln(10)}{L}\cdot\frac{x}{K_{\text{ext}}(x)} \text{ or } \frac{0{,}149}{L}\cdot\frac{x}{K_{\text{ext}}(x)} \le \varphi_V \le \frac{1{,}535}{L}\cdot\frac{x}{K_{\text{ext}}(x)} \quad (19)$$

The left hand side of this relation defines minimum particle concentration in the measurement zone and allows an estimation of the limit of quantity detection. In case of a scattering setup, the following are needed:

—a relatively high scattering signal as compared to the signal of the dispersion medium alone;

—a rather high transmittance of light through the cell.

$$I_{\text{sca,sample}} \ge 30 \cdot I_{\text{sca,med}} \text{ and } T_{\text{sample}} > 0{,}8. \quad (20)$$

This allows the formulation of the upper concentration limit:

$$\varphi_V \le \frac{2}{3}\frac{\ln(1{,}25)}{L}\cdot\frac{x}{K_{\text{ext}}(x)} \text{ or } \varphi_V \le \frac{0{,}149}{L}\cdot\frac{x}{K_{\text{ext}}(x)} \quad (21)$$

Setups in perfect reflection mode are not recommended for the quantification of particle fractions.

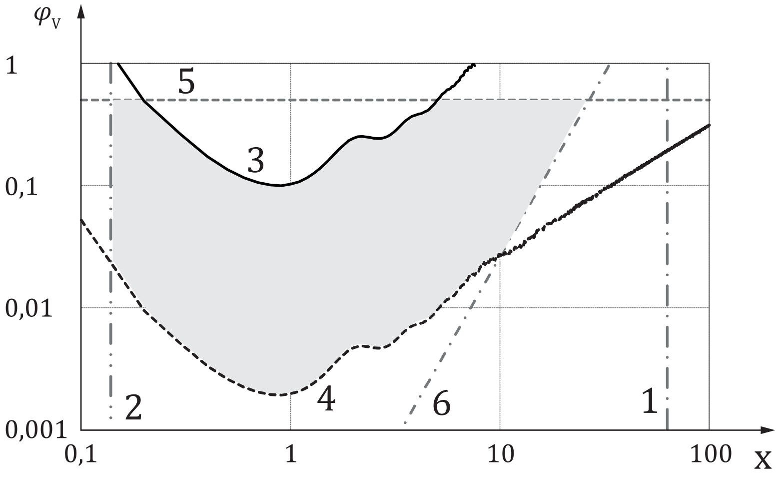
As outlined in 5.3 and 6.5.2, another condition for the operation of photosedimentometer is that the average number of illuminated particles shall be large enough to keep stochastic number fluctuations to a low level. According to Poisson statistics, the relative standard deviation of this number, thus on the extinction level or scattering intensity, can be assessed as the reciprocal square root of the average particle number:

$$s_{N,\text{rel}} = s_{E,\text{rel}} = s_{I_{\text{sca}},\text{rel}} = \frac{1}{\sqrt{N_{\text{part}}}} = \frac{1}{\sqrt{\dfrac{\varphi_V}{V_{\text{p}}}\cdot V_{\text{meas}}}} = \sqrt{\frac{\pi\cdot x^3}{6\cdot\varphi_V\cdot L\cdot A_{\text{meas}}}} \quad (22)$$

Keeping this relative standard deviation below a critical threshold $s_{N,\text{rel,cr}}$ leads to:

$$\varphi_V \ge \frac{\pi\cdot x^3}{6\cdot s_{N,\text{rel}}^2\cdot L\cdot A_{\text{meas}}} \quad (23)$$

Formulae (13) to (23) define the accessible working range for gravitational photosedimentation, which must be determined for each material and optical configuration separately. The working range can be broadened by modifying the wavelength or optical pathlength of the measurement cell. An example of the working range is provided in Figure 9.



Key

x particle size, in µm

φ_V volume fraction in %

1 upper size limit due to creeping-flow condition

2 lower size limit, below which Brownian motion affects particle size analysis

3 upper concentration limit, beyond which Lambert-Beer law (Formula (6)) fails (here: $T_{\text{sample}} < 0{,}1$)

4 lower concentration limit related to signal noise (here: $T_{\text{sample}} > 0{,}8$)

5 upper concentration limit, beyond which particle mutually affect their sedimentation

6 size-concentration limit, beyond which particle number fluctuations adversely affect the signal quality

NOTE Figure 9 shows an example of the working range (filled area) of gravitational photosedimentation for: glass beads dispersed in water; transmission optics with 670 nm wavelength, 14° aperture and beam of 2 mm2; different cells for low and high particle concentration (10 mm and 2 mm, respectively); and for a measurement distance of 4 cm.

Figure 9 — Example of the working range (filled area) of gravitational photosedimentation

7 Performing size analyses

7.1 General

Size analyses with gravitational photosedimentation follow the principles described in more detail in Clause 7 of ISO 13317-1:2024. It starts with a clear specification of the analytical objective(s), including the relevant state of dispersion, the target measurands and their acceptable uncertainty. Pre-consideration regarding sample preparation or material properties employed in data analysis are essentially followed by the different steps of granulometric analysis (see 7.2 to 7.8).

7.2 Sampling

The first step in size analysis consists of taking a representative sample from the powder or liquid dispersion by using adequate sampling techniques and sample splitting (see ISO 14488). Minimum values for sample mass or volume can be derived from the accessible working range of gravitational photosedimentation (see 6.6).

7.3 Dispersion process and primary sample preparation

Sample preparation constitutes a crucial step in granulometric analyses because it adjusts or affects the state of dispersion and thus the measured quantity. Errors and uncertainty in particle size analysis are most commonly caused by improper sample preparation.

The purpose of primary sample preparation consists in producing stock or master suspensions or emulsions, which have experienced a specified dispersion process and are thus defined with respect to their state of dispersion. Hence, primary sample preparation typically modifies the original sample in order to ensure a reproducible granulometric state. Such a master sample can be further divided to conduct multiple measurements with one or different instruments, or comparative analyses with different granulometric techniques.

Powders must first be suspended into an appropriate liquid and then dispersed in it, which includes both distributive and disruptive processes (ISO/TS 22107). The process of suspending can be supported by wetting agents and the liquid may contain dispersing agents, which help to maintain colloidal stability. The liquid should primarily ensure the chemical stability as well as prevent alterations of the physical state (e.g. swelling or shrinkage, dissolution, and agglomeration) of the dispersed phase and its sedimentation (i.e. the density contrast must not vanish). In addition, the liquid should behave indifferent to the measurement cell. Reference [6] lists liquids and dispersing agents, which have proved successful for a couple of solid materials. Finally, the liquid (with or without dispersing agents) in that the particles are dispersed should be sufficiently transparent for the illumination used for the photosedimentation measurement.

If the original material is a liquid dispersion, the original continuous phase (dispersion medium) is usually maintained, although it is possible to replace it with a different solvent. In some situations, it can be helpful or necessary to adjust the density contrast by adding indifferent solutes to the original continuous phase or a mix of different liquids.

Independent from the initial state of the material, the dispersion process constitutes an essential element of sample preparation and can determine the size of the particulate entities that are probed by sedimentation analysis. It is therefore important to describe the dispersion process, i.e. the dispersion technique, the intensity of treatment and the dispersion energy (ISO/TS 22107). These parameters should be selected to best match the state of the particulate material at the relevant process, product application or test scenario.

7.4 Secondary sample preparation (sample conditioning)

The master samples typically require further processing before the measurement can take place. The purpose is to adapt the sample to the measurement conditions without affecting the particle size distribution. Secondary sample preparation can involve, e.g.

- sample splitting and producing aliquots;
- dilution;
- adjustment of viscosity or density of the liquid dispersion medium;
- thermal equilibration of the sample.

It is mainly driven by specific requirements of the instrumentation (e.g. sample volume, working range with respect to particle concentration) and the analytical objectives (e.g. evaluation of the temperature sensitivity).

The most typical task is the adjustment of particle concentration via dilution, notably for performing the analysis in the permissible working range (see 6.6).

7.5 Instrument preparation

Before starting an analysis, the instrument must be readied for operation. Recommendations and instructions of the instrument producer should be followed. They can include a thermal equilibration of the measurement zone for the intended measurement temperature, the specification of measurement parameters in the instrument software (e.g. temperature, wavelength, temporal resolution of signals) and the selection of suitable measurement cells, which can differ with regard to volume, pathlength of measurement zone or solvent resistance. Typically, such procedures are described in detail in the manuals of the specific sedimentometer types. Optimum measurement conditions depend on both the instrumentation and sample, hence their determination can require preliminary experiments.

In a broader sense, instrument preparation also includes regular performance qualification (see 8.3).

7.6 Measurement

As explained in 5.1, gravitational photosedimentation starts with homogeneously mixed samples. Consequently, the measurements conform to the following, general scheme.

a) Thoroughly mix the thermally equilibrated sample in order to ensure a homogenous spatial distribution of the particles.

b) Immediately start the measurement (i.e. with minimal time delay) after homogenization has been completed.

c) Allow the instrument to photometrically monitor the gravity-induced classification of the particle system.

Mechanical vibrations of the measurement cell and temperature gradients in the cell must be prevented during the analysis (e.g. by placing the instrument on a balance table or by proper instrument and cell design). The cell temperature should be kept constant, measured and recorded.

Ensure that the temperature, measurement date and time, as well as baseline values of the sensor system, are recorded and saved together with the measurement data, either by the instrument software or by other means. It is recommended to perform measurements of 6 samples and determine the arithmetic mean and standard deviation. Under routine conditions, measurements of 3 samples are acceptable if the deviation among the individual results is less than 5 %. Such repeated analyses yield statistical measures for the uncertainty due to stochastic variations of the measurement conditions. They cannot replace tests of signal quality and plausibility checks.

Such tests can refer to:

— the position of the liquid surface:
which should not change with time (e.g. due to evaporation) and should correctly detected (if applicable);

— initial and final signals:
usually one can test the plausibility for the start of the measurement (minimum transmittance, maximum scattering signal) and the finished sedimentation process (maximum transmittance, minimum scattering signal); additionally, the requirements expressed by Formulae (18) and (20) must be checked; “final signals” should keep constant over time;

— type of separation:
visual inspection or concentration profiles allow the classification into settling or creaming; for particle size analysis, this should agree with expectation based on material properties:

— shape of time curves or concentration profiles:
time curves of local concentration, of dispersed particles should be monotonic for all types of material; concentration profiles are monotonic for all monoconstituent disperse systems and for multi-constituent samples if the sign of the density contrast agrees for all dispersed constituents; non-monotonic time curves and profiles indicate the presence of at least two dispersed phases with different direction of sedimentational motion; the data analysis of Clause 6 does not apply to such a situation, even though the separate analysis of both sedimentation processes is principally possible.

7.7 Data analysis

Gravitational photosedimentation techniques monitor the sedimentation-induced phase separation in an initially homogeneous liquid dispersion by measuring transmitted or scattered light of the sample. Correspondingly, each data set of the measurement comprises at least 3 parameters: time elapsed after having stopped mixing, position of the measurement zone and the photometric signal. The analysis of these data sets can be considered as a tiered process.

a) Calculation of sedimentation velocities:
From time and position of the data sets based on the physical definition of velocity; it does not require model parameters, yet assumes that the value of the observed quantity is attributed to a time point and space point (i.e. no smearing).

b) Calculation of particle sizes (i.e. Stokes diameters):
From the sedimentation velocity; typically, by assuming spherical particles, a Newtonian liquid, creeping flow condition and an absence of concentration effects; this transformation requires knowledge of the dynamic viscosity (η_c), density contrast ($\Delta\rho$) and gravitational acceleration (see 6.1).

c) Computation of the distribution function with respect to the intrinsic type of quantity (see. 6.2); it does not require model parameters

d) Computation of the distribution function with respect to another type of quantity:
From the distribution function with respect to the intrinsic type of quantity and particle size based on a model that correlates particle size with the observed quantity (see 6.3); this computation frequently requires further model parameters (e.g. the wavelength of radiation and refractive index).

Distributions of sedimentation velocity (weighted by extinction or scattered intensity) can be derived from the measured data without additional model parameters. In contrast, the computation of particle distributions always requires information on the measurement conditions and the material properties, like density contrast, refractive index, etc. Nowadays, users find a large number of the required parameters in databases of the instrument software. In addition, there are several books with tabulated values of material properties (e.g. see References [14] and [15]). Parameters like particle density, liquid density, liquid viscosity or refractive index can be measured by means of established and standardised techniques (e.g. see ISO 18747 series, ISO 15212-1, ISO 2555, ISO 3219 series, and ISO 280).

The data analysis also includes a calculation of the different measures of uncertainty as described in 8.4.

7.8 Reporting

Measurement reports shall:

— allow for a reproduction of the analysis;

— visually emphasize the most important results;

— observe the international conventions in particle characterization as set out in ISO 9276-1.

The test report should refer to ISO/IEC 17025. The test report shall include the following information:

a) a reference to this document, including the date of publication, i.e. ISO 13317-5:2024;

b) file name of the digitally saved measurement data;

c) name and contact information of the customer;

d) name and address of testing laboratory;

e) name of operator;

f) date of testing;

g) file name of report, link to storage of experimental data and unique report identifier (where applicable);

h) sample name (identifier), type of sample (powder, suspension, emulsion) quantity;

i) additional information about sample (e.g. particle shape, agglomeration state, density contrast of particles and liquid, viscosity and type of continuous phase, volume concentration, optical properties if necessary or safety information);

j) ISO standard applied for testing and any other operation not specified in this document which can have influenced the result;

k) instrument type (photosedimentometer based on extinction or scattering) and identifier as well as software version used;

l) sampling place and conditions (if applicable);

m) sample preparation:
   1) either continuous phase (dispersion medium) or dilutant, or both: composition (solvent as well as wetting and dispersing agents) and relevant properties (density, viscosity, refractive index);
   2) either dispersion or homogenization, or both, process and instrumentation, including condition (temperature, energy, time, volume, etc.), if applicable;

n) characteristic parameter for the “average” particle size and its uncertainty, including its unambiguous specification (type of location parameter — e.g. median, mode, arithmetic mean or harmonic mean — and indication of the type of quantity — e.g. weighted by extinction or intensity, volume or particle number) and details of uncertainty evaluation (e.g. number of replicate analyses, standard deviations for in-group-variation and among group variations, intermediate precision);

o) information about polymodality (e.g. bimodal, central size of modes; polydispersity (e.g. index of polydispersity); graphical representation if available;

p) if size quantities depend on particle concentration, size values must be indicated for the lowest concentration or the value extrapolated to infinite dilution;

q) principle of used algorithms (including references, e.g. software module and version) for calculation of the distribution function;

r) conditions of measurement:
   1) particle concentration, if known;
   2) sedimentation time;
   3) temperature of sample during measurement;
   4) measurement cells and sample volume;
   5) wavelength(s) of illuminating light source(s);

s) any deviations from the procedure;

t) any unusual features observed;

u) date of report;

v) name, position of the person releasing the report.

8 System qualification and quality control

8.1 General remarks

The measurement of the particle velocity by means of photosedimentation is based on first principles and does not require calibration by the user with an RM of a specified velocity or size. Experimentally obtained sedimentation velocity can be transformed into particle size according to Formula (5) by relying on the input quantities gravitational acceleration (g), density contrast ($\Delta\rho$) and liquid viscosity (η_c). As summarized in Figure 10, measured values of particle velocity and its transformation into particle size deviate from the true value due to errors that are related to sample preparation (see subclauses 7.2 to 7.4), instrument design and status quo, measurement procedure, skill of operator and environment conditions. The sources of uncertainty can be of random or systematic nature. Correspondingly, one distinguishes between precision and trueness when assessing the performance of a technical realization of sedimentation analysers. Trueness can be estimated via the systematic deviations of measured size values from the true ones (e.g. known for CRMs). Whereas precision can be quantified from the variation among measurements that are performed for a sufficiently stable QCM and repeated within short time interval. QCMs are RMs of proven homogeneity and stability (including CRMs). Trueness and precision determine the accuracy of the specific sedimentation technique. Quantitative expressions of instrument performance characteristics (performance validation) are the measurement uncertainty estimate based on bias and the standard uncertainty (deviation) according to Reference [16]. It is a quantitative expression of measurement accuracy.

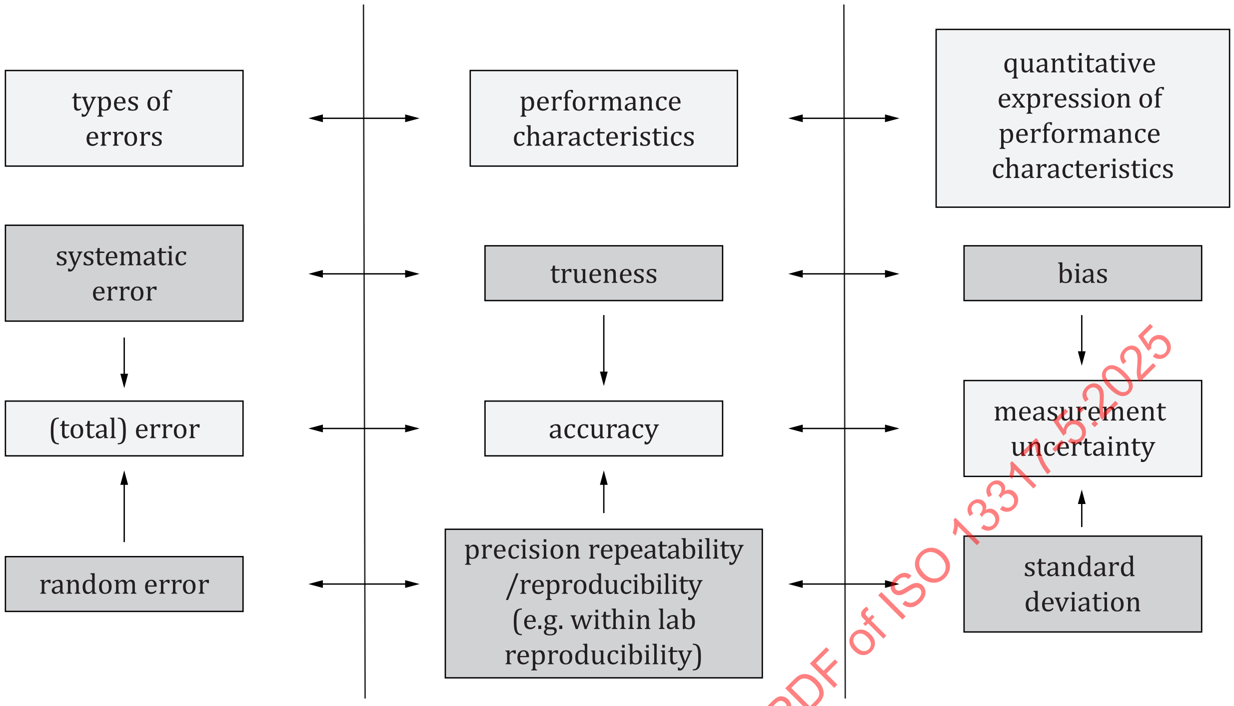


Figure 10 — Interrelations between error types, performance characteristics used to estimate them and expressions of quantitative estimates

Trueness is a necessary qualifying attribute for a sedimentation measuring technique. Yet from a practical viewpoint of the end-user, especially in industry, reproducibility and robustness are more important for industrial applications.

8.2 Reference materials

In general, ISO TS 4807 is intended to support users of reference materials (RMs) for particle size analysis to identify suitable RMs. Specific RMs for sedimentation-based particle sizing shall consist of non-porous particles of homogeneous composition and uniform particle density. Spherical particles and narrow, monomodal size distribution facilitate the comparison among different sedimentation techniques, but are not a prerequisite. Polydisperse RMs are particularly advantageous for the evaluation of sedimentation techniques with regard to the sensitivity for fine and coarse particle detection. According to ISO 13317-1, RMs should meet a few minimum requirements for a given instrumental configuration. These are the negligibility of Brownian motion and hydrodynamic wall effects (see ISO 13317-1) as well as the absence of wall adhesion. In case of CRMs, the certificate should:

a) refer to the distribution of Stokes diameters and clearly indicate this;

b) specify the kind of distribution parameter and the type of quantity (e.g. median of volume-weighted distribution or modal size of extinction-weighted distribution);

c) indicate the material properties used for data analysis (e.g. particle density);

d) reveal the type of sedimentation technique used in the certification process;

e) specify the procedures of sample preparation.

The comparison among different sedimentation techniques and the conversion of a measured distribution function to a different type of quantity can require additional material properties (e.g. the attenuation coefficient or refractive index) and be restricted to spherical particles.

RMs shall be specified regarding useable test liquids and temperature of use. The test liquids (e.g. pure water) should ensure a fast wetting and easy dispersion of the particles (in the case of powder). The test liquids shall preserve the state of dispersion during the time of use, i.e. no swelling, shrinking, dissolution, flocculation or agglomeration (see ISO 14887). Some RM are available as ready-to-use suspensions, which only require a slight re-dispersion of deposited particles before being directly analysed. They avoid, e.g. the risk of destabilization by diluting or segregation due to sampling. If RMs are employed to test the instrument performance for specific materials, they should match the expected size range and resemble the material properties (i.e. particle density and, if relevant, also refractive index).

Qualification tests with CRMs allow for the evaluation of an instrument's bias. The measurement result must not significantly differ from the certified value, taking into consideration both the uncertainty of the certified value of CRM and the measurement uncertainty.[17]

8.3 Performance qualification

Performance qualification of a photosedimentation method shall be implemented on a regular basis and shall be performed in accordance to manufacturer's recommendations. Time intervals should reflect the quality requirements of the organization, where the sedimentation method is employed. National regulations may apply. Beside a general careful visual inspection, performance qualification should cover the full range of equipment capabilities. Additionally, qualification shall be performed after each major change of the instrument (such as repairs, change of location, etc.) or in case of doubt regarding the validity of measurement results. Data of performance measurements accessed periodically are often plotted in time order (see the Shewhart control chart, Figure D.1) to allow for a fast evaluation of instrument qualification and data trends.

8.4 Measurement uncertainty

The true value of the sedimentation velocity for a sample is impossible to know due to deviations in the measurement and preparation method. Achieving accurate sedimentation velocity measurements and the respective calculated particle size distribution requires adherence to "standard theory" (see 6.5) which will minimize introduced errors. Different sources of systematic and random errors in photosedimentation have been identified, which cause a loss of accuracy and thus an increase in the measurement uncertainty. Known sources of error for photosedimentation analysis are:

- technical uncertainties in determining the sedimentation time and sedimentation distance, e.g. determination of meniscus position;
- a non-homogeneous mixing state at the start of sedimentation;
- convective flow due to temperature gradients;
- signal noise;
- adhesion of particles at walls;
- air bubbles at walls, tubing, or adhering to particles.

The most significant contribution to the uncertainty is h_{sed}, due to a lack in an exact spatial and temporal start of the sedimentation experiment. The ideal start position is associated with the instant at which the homogeneous mixing ends and phase separation starts. In practice, a time gap can be encountered between mixing and starting the measurement clock, which means that at the "official" time zero, phase separation has already started, which is equivalent to a shift of the start position. The exact position of air-liquid interfaces (menisci) is difficult to determine due to the curvature of the liquid surface when the cell lid is not in contact with the liquid (see 5.3 and Figure 4). In the case of creaming, a deviation can result, if the cell bottom is not perfectly flat. Uncertainty in the start position has a relatively high impact on the uncertainty of the sedimentation velocity and particle size.

The uncertainty of a measurement indicates the extent sources of error have on the measured value. It quantifies an interval associated with the measured value that characterizes the deviation from the true value and where the true value lies within some degree of probability (see Figure D.2). The basic uncertainty estimation is given in detail in ISO Guide 98-3. Several documents build on ISO Guide 98-3 with the aim to simplify the calculation (see Annex D and ISO 21748). The uncertainty that is related to repeatability can be estimated by repeating the velocity determination n-times ($n \geq 6$) for a given stable sample. Ideally, these measurements take place under the same measurement conditions within a short time interval, typically within a day. The individual results v_j (j = 1...n) yield an arithmetic mean velocity v_{mean} and a standard deviation s_v, under these measurement conditions. The latter constitutes an estimate of the repeatability uncertainty u_{rep}, [see Formula (24)] also called short-term precision (see Annex D).

$$u_{\mathrm{rep}} = s_v = \sqrt{\frac{1}{n-1}\sum_{j=1}^{n}\left(v_j - v_{\mathrm{mean}}\right)^2} \tag{24}$$

Systematic errors within a laboratory method shall be separately estimated as a measure of bias, reflecting the trueness of a device (see Figure 10). The corresponding investigations require a CRM. While repeatability addresses the variation of results for a coherent set of measurements (i.e. identical sample, instrument, skilled operator, measurement procedure) and expresses the corresponding random error under these conditions, reproducibility asks for the measurand obtained under less defined conditions (e.g. different operators, larger time differences between measurements, different batches of chemicals) but the same methodology.

Reproducibility refers to data obtained over the course of different days. Performance qualification, such as control charts and ILC (see Clause D.4), can be used to estimate reproducibility uncertainty u_{Rw} as shown in Formula (25):

$$u_{\mathrm{Rw}} = s_v = \sqrt{\frac{1}{m-1}\sum_{l=1}^{m}\left(v_l - v_{\mathrm{mean}}\right)^2} \tag{25}$$

Reproducibility can be determined over a long period (≥6 months). Reproducibility covers non-intended variation of test conditions, which act as systematic errors for a single set of measurements (i.e. under repeatability conditions). In general, reproducibility refers to the complete analytical method including all steps of sample preparation.

The combined uncertainty, u_{c}, is calculated as the square root of the sum of the squares for each of the sources of uncertainty. The combined uncertainty, u_{c}, spans a range around the arithmetic mean as it is based on the standard deviation and therefore covers only 68,3 % of all measurement results, when normally distributed. To increase that probability, a numerical factor k (coverage factor) is used as a multiplier to u_{c} and estimates the expanded combined uncertainty U_{c} as shown in Formula (26):

$$U_c = k \cdot u_c \, . \tag{26}$$

For the sedimentation velocity, a coverage factor of k = 2 is usually used (which has a probability 95 %, normal distribution) to calculate the expanded uncertainty U_{c}.

The combined sedimentation velocity uncertainty is an expression for the performance characteristic of the photosedimentation method. It is the first step necessary to get the particle size uncertainty. The combined and expanded uncertainty of particle size values can be computed experimentally in a similar fashion to the sedimentation velocity. Alternatively, it is possible to estimate the full combined uncertainty in particle size from the uncertainty of sedimentation velocity and the uncertainty in transforming v_{sed} to x_{Stokes} according to Formula (4). Uncertainty in transforming the measurand can be attributed to the uncertainty of the input quantities, which are the density contrast ($\Delta\rho$), the viscosity of continuous phase (η_c) and the gravitational acceleration (g). Their impact can be consolidated into a transformation factor C as shown in Formula (27):

$$C = \sqrt{\frac{18\eta_c}{g\Delta\rho}} \text{ with } x_{\text{Stokes}} = C \cdot \sqrt{v_{\text{sed}}} \tag{27}$$

The relative uncertainty of the multiplication factor C reads:

$$\frac{u(C)}{C} = \sqrt{\frac{u(\eta_c)^2}{4\eta_c^2} + \frac{u(g)^2}{4g^2} + \frac{u(\Delta\rho)^2}{4\Delta^2\rho}} \tag{28}$$

The combined uncertainty of the size value x_{Stokes} is finally obtained by the standard uncertainties in multiplier C and sedimentation velocity, i.e. $u(C)$ and $u_c(v_{\text{sed}})$. The following expression for the relative combined uncertainty of the Stokes diameter can be derived:

$$\frac{u_c(x_{\text{Stokes}})}{x_{\text{Stokes}}} = \sqrt{\frac{u(C)^2}{C^2} + \frac{u_c(v_{\text{sed}})^2}{4v_{\text{sed}}^2}} \tag{29}$$

Multiplying by the coverage factor k acquires the expanded combined size uncertainty.

Annex A
(informative)

Measurement position

A.1 General considerations on the measurement position

The vertical measurement position is an essential parameter in photosedimentation. Together with the start position, it defines the sedimentation distance h_{sed}, at which the temporal or spatial changes in local particle concentration are monitored. The measurement principle does not specify the sedimentation distance and under ideal conditions, there is no need to do so. Measurement practice, however, has shown that the sedimentation distance should not be either too small or too large. There are a couple of issues that arise, when the sedimentation distance is too small

— Types of error that are related to sample state at the beginning of the measurement (temperature, mixing state, initial convective flow etc.) can become fairly significant (see Clause A.2).

— If the start position needs to be measured (see 6.4), the uncertainty of this measurement contributes to the uncertainty in sedimentation distance, thus to the ones of sedimentation velocity and Stokes diameter (see Clause A.2).

— The smearing effect of Brownian motion is particularly present at low sedimentation distances (see 6.6.1). However, its practical relevance is restricted to particles < < 1 µm.

— Small sedimentation distances reduce the resolution of measured particle size distribution due to the finite width of the measurement zone (see Clause A.3) and imperfect optical projection of the concentration profile (see Clause A.4).

— The maximum sedimentation velocity and the corresponding maximum Stokes diameter that can be reliably quantified can be unacceptably low, i.e. lower than the really existing values of the particle systems.

Moreover, users should also avoid a too large sedimentation distance:

— The measurement time required to reliably detect the finest particles, i.e. the ultimate decline of local particle concentration to zero, can become impractically large.

— A large measurement time, which follows from a large sedimentation distance, can pronounce effects that are related by an improper selection of the liquid dispersion phase (e.g. swelling of particles, liquid evaporation).

The sedimentation distance can be influenced by the start position (e.g. via the filling height) or the measurement position. The latter can be either fixed to a default or an adjustable position, it can systematically change during the measurement (scanning mode) or it can be freely selectable by software or users if the complete concentration profile is recorded in each time step. Hence, the proper selection of the measurement position is a task of manufacturers (either instrument design or device control, or both) and operators.

A.2 Initial sample state and uncertainty of start position

The principle of gravitational photosedimentation consists in the photometric monitoring of the local particle concentration over time or along the complete sample height, or both (see 5.1). For the data signal evaluation, it is assumed that particles move only due to gravity, that the velocity of this motion remains constant for the whole measurement and that the process starts with a completely homogeneous mixture [see Figure 1 a)]. In practice, the latter condition can be warranted for dispersed phases of submicrometre particles, for which sedimentation velocities typically amount to (considerably) less than 1 mm per minute, but it can be highly challenging to be fulfilled for particles in the micrometre range.

EXAMPLE Glass beads (lime-soda glass) of 1 µm diameter settle in water (25 °C) with a velocity of 55 µm per minute, whereas 50 µm glass beads settle with 2 mm per second.

Homogeneous mixing is usually achieved by slight agitation up to the moment of starting the measurement, yet the convective flows also need some time (seconds or less) to fade. In conclusion, the real sample state at the beginning of the measurement can significantly deviate from the ideal assumptions; there can already have occurred a segregation of the dispersed phase or the onset of pure sedimentational motion is delayed. This is equivalently to an uncertainty in the start time t_0 of a measurement. A further critical issue in photosedimentation is the determination of the start position – at least for the situation illustrated in Figure 7 a). This leads to an uncertainty in the start position z_0 (see 6.4). Both types of uncertainty are relevant for the sedimentation velocity:

$$v_{\text{sed}} = \frac{h_{\text{sed}}}{\Delta t} = \frac{z - z_0}{t - t_0} \tag{A.1}$$

where

z is the measurement position;

Δt is the measurement time.

The uncertainty in sedimentation velocity is related to the ones of the positions and the measurement time:

$$\delta v_{\text{sed}} = \frac{\delta z}{\Delta t} + \frac{\delta z_0}{\Delta t} + v_{\text{sed}} \cdot \frac{\delta \Delta t}{\Delta t} \tag{A.2}$$

and for the Stokes diameter:

$$\frac{\delta x_{\text{Stokes}}}{x_{\text{Stokes}}} = \frac{1}{2} \cdot \frac{\delta v_{\text{sed}}}{v_{\text{sed}}} \tag{A.3}$$

The uncertainty in measurement position z and clock time t can be neglected:

$$\frac{\delta v_{\text{sed}}}{v_{\text{sed}}} \approx \frac{\delta z_0}{h_{\text{sed}}} + \frac{\delta \Delta t}{\Delta t} = \frac{\delta z_0}{h_{\text{sed}}} + \frac{v_{\text{sed}} \cdot \delta t_0}{h_{\text{sed}}} \tag{A.4}$$

Hence, the relative error in sedimentation velocity decreases with growing sedimentation distance; it rises when the sedimentation velocities increases.

EXAMPLE Assume an uncertainty of 1 s for the start time and 0,1 mm for the start position, which apply to the photosedimentation of glass beads in water. At a sedimentation distance of 3 mm, the relative uncertainty in sedimentation velocity amounts to 3 % and 16 % for 1 µm beads and 20 µm, respectively. For h_{sed} = 10 mm these values are reduced to 1 % and 5 %, respectively.

There can be a further contribution to uncertainty, the source of which is related to the initial phase of sedimentation. That is when the sample temperature, resulting from conditioning (see 7) deviates from the measurement temperature that is controlled by the instrument. In this event, particles settle faster or more slowly in the initial phases of measurement than at later phases, so that the velocity and size of the coarsest particles is either over- or underrated.

A.3 Width of the measurement zone

The measurement volume is located at a certain distance h_{sed} from the start position, but it also has a certain width Δh in vertical direction as to ensure sufficiently high photometric signals. This means that temporal changes in measurement signal at h_{sed} do not only refer to the nominal sedimentation velocity as shown in Formula (A.5):

$$v_{\text{sed}} = \frac{h_{\text{sed}}}{t} \tag{A.5}$$

and its corresponding Stokes diameter as shown in Formula (A.6):

$$x_{\text{Stokes}} = C \cdot \sqrt{v_{\text{sed}}} \tag{A.6}$$

but to narrow fraction of differently sized particles as shown in Formulae (A.7) and (A.8):

$$x_{\text{Stokes}} \cdot \sqrt{1-\tfrac{1}{2}\Delta\eta} \ldots x_{\text{Stokes}} \cdot \sqrt{1+\tfrac{1}{2}\Delta\eta} \tag{A.7}$$

$$\Delta\eta = \frac{\Delta h}{h_{\text{sed}}} \tag{A.8}$$

where $\Delta\eta$ denotes the relative width of the measurement volume.

Hence, the finite width of the measurement zone creates additional polydispersity to the measured size distribution; a monodisperse sample is measured as polydisperse with the full distribution width as indicated by Formula (A.7), which also defines the achievable resolution Δx of the particle size distribution as shown in Formula (A.9):

$$\Delta x / x = \Delta\eta \Big/ \left(\sqrt{1-\tfrac{1}{2}\Delta\eta} + \sqrt{1+\tfrac{1}{2}\Delta\eta} \right) \underset{\Delta\eta<<1}{\approx} \Delta\eta \tag{A.9}$$

In general, the finite width causes measured particle size distributions to appear broader than they are. The apparent distribution function ($Q_{\text{app}}(x)$) is the average over the cumulative distribution function of the nominal Stokes diameters for all sedimentation distances within the width Δh. This yields:

$$Q_{\text{app}}(x) = \frac{2}{\Delta\eta \cdot x^2} \int_{x\sqrt{1-\frac{1}{2}\Delta\eta}}^{x\sqrt{1+\frac{1}{2}\Delta\eta}} \tilde{x} \cdot Q(\tilde{x})\, \mathrm{d}\tilde{x} \tag{A.10}$$

The smearing effect is more pronounced the larger the relative width $\Delta\eta$ and less broad the particle size distribution is. For log-normal distribution, a critical zone width can be estimated above which the logarithmic standard deviation $\sigma_{\ln}$ is increased by more than 25 % as shown in Formula (A.11):

$$\Delta\eta_{\text{cr},25\,\%} \approx \tfrac{1}{2}\sigma_{\ln} \tag{A.11}$$

A.4 Imperfect optical projection

The photometric quantification of local particle concentration assumes that the light signals received at the detector are only originated by particles in the measurement zone (i.e. from the thin vertical slice around the nominal the measurement position). However, small deviation from a parallel light beam, scattered light or light diffraction at a sharp sedimentation front can cause spatial and temporal changes in the photometric signals, which are caused by particles from outside the nominal measurement zone, and they modify the signals originating from particles in the measurement zone. A particular effect is broadening of a sharp sedimentation front (i.e. the transition from particle-free supernatant to the dispersion phase) in the photometric signal by light diffraction. The sharpness of a sedimentation front reflects the degree of polydispersity, but is also affected by the sedimentation distance. Small ones coincide with a relatively narrow transition zone between supernatant and original dispersion phase (zones 1 and 3 of Figure 1, respectively), for which reason the diffraction-related broadening of the PSD is particularly significant and can even exceed the effect of the finite width of the measurement zone.

A.5 Rule of thumb for the measurement position

The most critical situation is a sedimentation distance that is too small. It leads to an overestimation of the distribution width and can sometimes also affect the mean particle size. The artificial broadening reduces the achievable resolution, with respect to details of the PSD, and can be significant for quasi-monodisperse materials or particle systems with multiple narrow size fractions. In order to minimize such effects, it is recommended to work with sedimentation distances above 10 mm.

Annex B
(informative)

Calculation of number-weighted particle size distribution

B.1 Numerical scheme

Starting point of the procedure is the relationship among the contributions of a given size fraction to number, volume and photometric response (i.e. extinction level or scattering intensity) as shown in Formula (B.1):

$$\mathrm{d}Q_{\mathrm{ext}}(x)=\frac{C_{\mathrm{ext}}(x)\mathrm{d}Q_0(x)}{\int C_{\mathrm{ext}}(x)\mathrm{d}Q_0(x)}=\frac{x^2K_{\mathrm{ext}}(x)\mathrm{d}Q_0(x)}{\int x^2K_{\mathrm{ext}}(x)\mathrm{d}Q_0(x)} \tag{B.1}$$

where Q_{ext}, C_{ext} and K_{ext} can be replaced by Q_{int}, C_{psca} and K_{psca}, respectively.

This results in expressions for the conversion step as shown in Formulae (B.2) and (B.3):

$$\mathrm{d}Q_0(x)=\frac{C_{\mathrm{ext}}(x)^{-1}\,\mathrm{d}Q_{\mathrm{ext}}(x)}{\int C_{\mathrm{ext}}(x)^{-1}\,\mathrm{d}Q_{\mathrm{ext}}(x)}\ \text{or}\ \mathrm{d}Q_0(x)=\frac{C_{\mathrm{psca}}(x)^{-1}\,\mathrm{d}Q_{\mathrm{int}}(x)}{\int C_{\mathrm{psca}}(x)^{-1}\,\mathrm{d}Q_{\mathrm{int}}(x)} \tag{B.2}$$

$$\mathrm{d}Q_0(x)=\frac{\left[x^2K_{\mathrm{ext}}(x)\right]^{-1}\mathrm{d}Q_{\mathrm{ext}}(x)}{\int\left[x^2K_{\mathrm{ext}}(x)\right]^{-1}\mathrm{d}Q_{\mathrm{ext}}(x)}\ \text{or}\ \mathrm{d}Q_0(x)=\frac{\mathrm{d}Q_{\mathrm{int}}(x)\Big/\left[x^2K_{\mathrm{psca}}(x)\right]}{\int\mathrm{d}Q_{\mathrm{int}}(x)\Big/\left[x^2K_{\mathrm{psca}}(x)\right]} \tag{B.3}$$

In general, all optical cross-sections and efficiencies are non-monotonic functions of particle size with more or less significant oscillations, depending on material properties and optical configurations. In practice, oscillations are largely damped by either the aperture of the detection optics or the broadening of the spectral line, or both, but also by the deviation of spherical shape. For coarse particles > > 1 µm one can frequently employ the simplification (see Figure 6) shown in Formulae (B.4):

$$C_{\mathrm{ext}}(x),C_{\mathrm{psca}}(x)\propto x^2\ \text{or}\ \frac{\mathrm{d}K_{\mathrm{ext}}}{\mathrm{d}x},\frac{\mathrm{d}K_{\mathrm{psca}}}{\mathrm{d}x}=0\ \text{for x >> 1 µm} \tag{B.4}$$

Hence, Q_{ext} and Q_{int} are area-weighted (surface-weighted) size distributions and can be converted into number-weighted size distributions via:

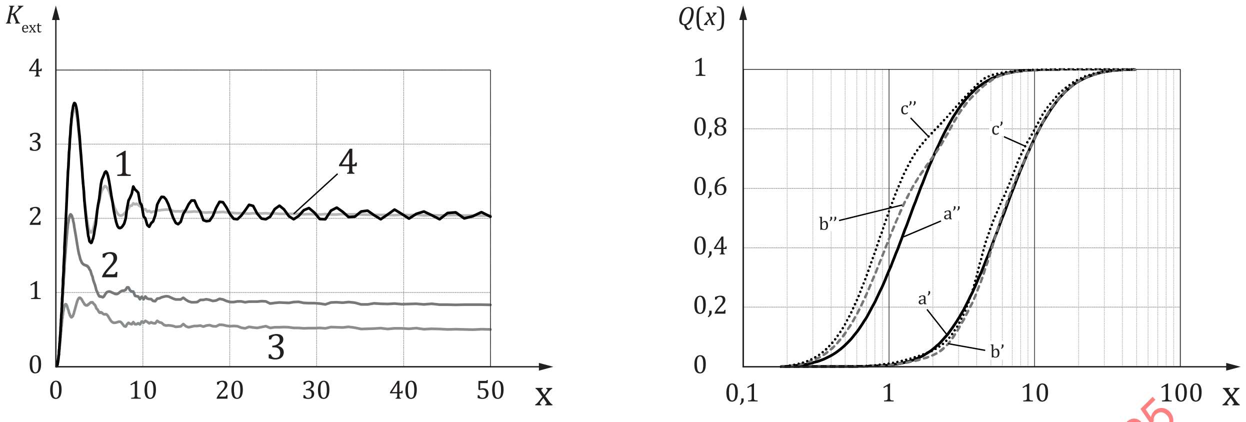
$$\mathrm{d}Q_0(x)=\frac{x^{-2}\mathrm{d}Q_{\mathrm{ext}}(x)}{\int x^{-2}\mathrm{d}Q_{\mathrm{ext}}(x)}\ \text{or}\ \mathrm{d}Q_0(x)=\frac{\mathrm{d}Q_{\mathrm{int}}(x)/x^2}{\int\mathrm{d}Q_{\mathrm{int}}(x)/x^2}\ \text{(for x >> 1 µm)} \tag{B.5}$$

Under the condition shown in Formula (B.4), the velocity-weighted size distributions can also be transformed, regarding the validity of Stokes' Formula (4), as shown in Formula (B.6):

$$\mathrm{d}Q_0(v)=\frac{v^{-1}\mathrm{d}Q_{\mathrm{ext}}(v)}{\int v^{-1}\mathrm{d}Q_{\mathrm{ext}}(v)}\ \text{or}\ \mathrm{d}Q_0(v)=\frac{\mathrm{d}Q_{\mathrm{int}}(v)/v}{\int\mathrm{d}Q_{\mathrm{int}}(v)/v}\ \text{(for x >> 1 µm)} \tag{B.6}$$

B.2 Limits of deriving number-weighted PSDs from gravitational photosedimentation

The determination of number-weighted PSDs by photosedimentation is not just a matter of mathematics as suggested by Formula (B.2). It also requires consideration on the applicability of the underlying model equations and on the error propagation when converting photometric quantities into particle numbers.



a) Extinction efficiency vs. particle size

b) Cumulative distribution function

Key

x	particle size, in µm
K_{ext}	extinction efficiency, dimensionless
$Q(x)$	cumulative distribution function, dimensionless
1	monochromatic illumination (630 nm), zero aperture
2	monochromatic illumination (630 nm), aperture angle = 7°
3	monochromatic illumination (630 nm), aperture angle = 14°
4	polychromatic illumination (median: 630 nm, standard deviation: 66 nm), zero aperture
a'	$Q_3(x)$ for data analysis with correct value of the aperture angle (14°).
b'	$Q_3(x)$ for data analysis with incorrect value of the aperture angle (7°).
c'	$Q_3(x)$ for data analysis with erroneously assuming zero aperture angle.
a''	$Q_0(x)$ for data analysis with correct value of the aperture angle (14°).
b''	$Q_0(x)$ for data analysis with incorrect value of the aperture angle (7°).
c''	$Q_0(x)$ for data analysis with erroneously assuming zero aperture angle.

Figure B.1 — Impact of optical settings on the extinction efficiency of glass beads dispersed in water and the consequences for analysing photosedimentation data

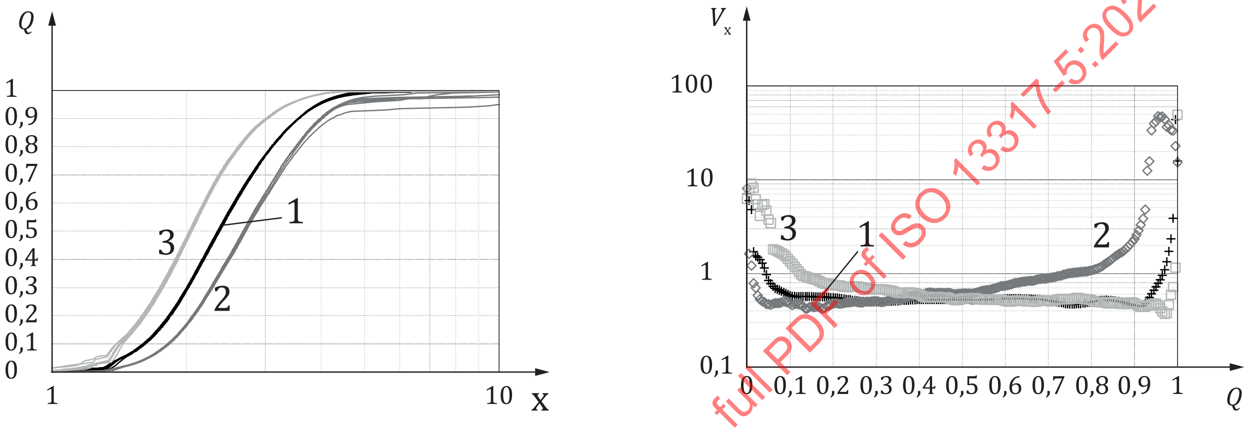
The computation of volume-weighted PSDs (see 6.3) or number-weighted ones relies on an appropriate model that relates particle size (more specifically the Stokes diameter) with the extinction or scattering properties of single particles (e.g. the extinction cross-section C_{ext}). Most frequently, these models are based on the Mie solution of light scattering on spheres or on the approximation in Formula (B.4). The latter works fine in the size range > 5 µm for a lot of materials, especially when being opaque at the relevant wavelength (e.g. metals, natural minerals, etc.) and can be even used for non-spherical particles. This holds true independent from instrumental parameters such as light wavelength and optical aperture. However, the approximation in Formula (B.4) fails for fine particles considerably below 10 µm, where the extinction efficiency is a nonlinear function of particle size and significantly affected by source of illumination (i.e. wavelength distribution) and optical aperture [see Figure B.1 a)] as well as by the shape and refractive index of particles. Although most particle systems consist of non-spherical particles, the data processing employs the Mie solution, for which reason the shape of the derived number-weighted size distributions is typically biased. Moreover, incorrect values of the model parameters constitute another source of such kind of bias. This is illustrated in Figure B.1 b).

Beside inadequate model equations or incorrect values of model parameters, another practical issue can be encountered when computing number-weighted PSDs from photosedimentation: the error propagation with regard to the uncertainty in particle quantities. Uncertainties in the extinction weights ($\delta(\Delta Q_{ext})$ or δq_{ext}) of a given size fraction lead to uncertainties in their volume weights (δq_3) and number frequencies (δq_0)[18] as shown in Formula (B.7) and (B.8):

$$\delta q_3 = \frac{x^3 / C_{\text{ext}}(x)}{\int x^3 / C_{\text{ext}}(x) \mathrm{d}Q_{\text{ext}}} \cdot \delta q_{\text{ext}} \tag{B.7}$$

$$\delta q_0 = \frac{C_{\text{ext}}(x)^{-1}}{\int C_{\text{ext}}(x)^{-1} \mathrm{d}Q_{\text{ext}}} \cdot \delta q_{\text{ext}} \tag{B.8}$$

Since $C_{\text{ext}}(x)$ is a rising function [e.g. Figure 6 a)], uncertainties at the fine edge of a measured extinction-weighted PSD should be expected to be magnified at conversion, whereas uncertainties at the coarse edge are diminished (see Figure B.2).



a) Extinction efficiency vs. particle size **b) Cumulative distribution function**

Key

x particle size, in µm
Q cumulative weights, dimensionless
V_x relative standard deviation of the quantiles from replicate analyses, dimensionless
1 extinction-weighted particle size distribution
2 volume-weighted particle size distribution
3 number-weighted particle size distribution

Figure B.2 — Impact of conversion on the repeatability of quantiles; for photosedimentation data of SiC particles in water

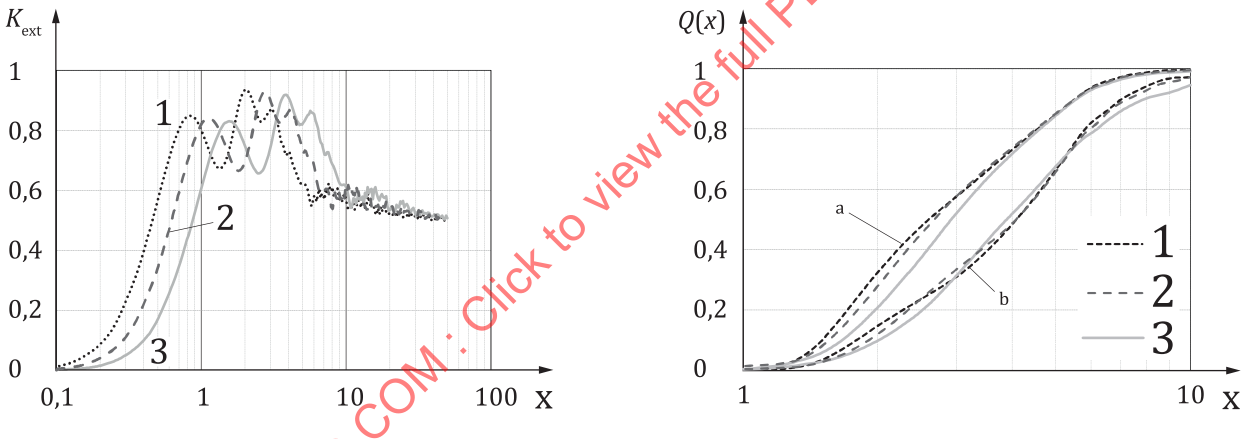
Annex C
(informative)

Detailed multi-wavelength approach

Some photosedimentometers allow to monitor the changes in local particle concentration via an optical setup employing multiple wavelengths. That means that the particle system can be described by a set of extinction-weighted PSDs, each of them corresponding to one of wavelengths employed (see 6.2). In general, these distributions differ slightly because the relationship between a particle's impact on light propagation (e.g. its extinction cross-section) and its size (i.e. Stokes diameter) is affected by wavelength [see Figure C.1 a)]. When converting to volume-weighted PSDs, one can expect that all distribution functions perfectly match as they reflect the same sedimentation process.

NOTE Formula (18) (see 6.6.2) must be fulfilled for all wavelength.

Prerequisite for the conversion is the availability of adequate optical models and the accurate knowledge of the materials' optical properties, i.e. the (complex) refractive indices of particles and liquid dispersion medium, which are functions of wavelength. In practice, both requirements are rarely fulfilled, for which reason the application of a multiple wavelength setup results in (slightly) different solutions for the volume-weighted PSDs [see Figure C.1 b)].



a) Extinction efficiency vs. particle size

b) Exemplary result of multi-wavelength photo-sedimentation, conventional approach

Key

x	particle size, in µm
K_{ext}	extinction efficiency, dimensionless
$Q(x)$	cumulative distribution function, dimensionless
1	monochromatic illumination (470 nm), aperture angle = 14°
2	monochromatic illumination (630 nm), aperture angle = 14°
3	monochromatic illumination (870 nm), aperture angle = 14°
a	Extinction-weighted PSD.
b	Volume-weighted PSD.

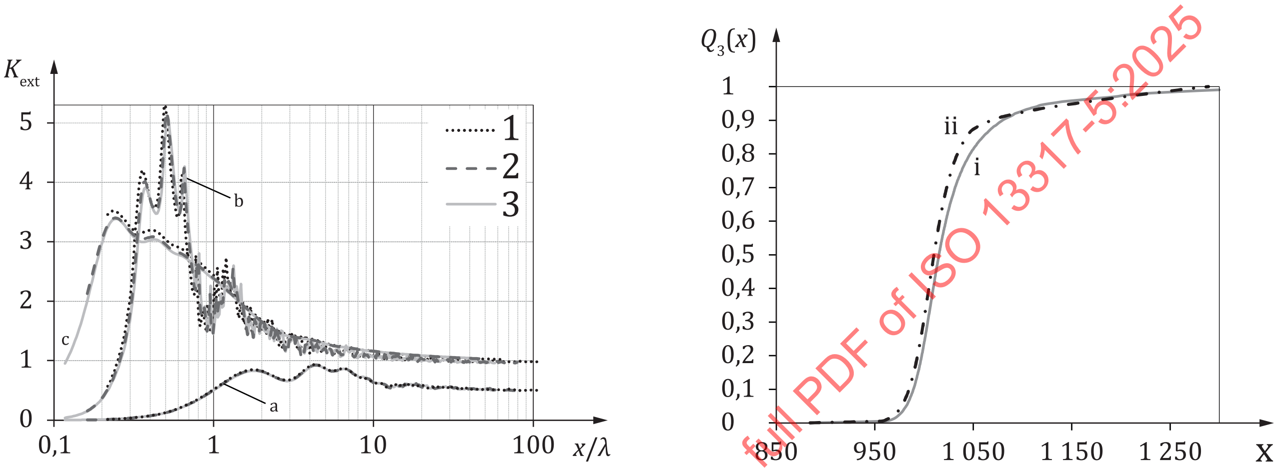
Figure C.1 — Wavelength dependency of extinction efficiency and volume-weighted PSDs from photosedimentation; for glass beads in water

However, multi-wavelength measurements allow to replace the conventional route of data analysis as described in subclauses 6.2 and 6.3 by an alternative method, which simultaneously processes the primary measurement signals or the extinction-weighted PSDs of all wavelengths. This way of data processing does not need a specific optical model, nor does it require values for the optical properties. It only assumes the following relationship for the optical efficiency functions [see Figure C.2 a)]:

$$K_{\text{ext/sca}}(x,\lambda)=\text{funct.}(x/\lambda) \tag{C.1}$$

and that spectral functions of the refractive indices are similarly shaped for particles and liquid dispersion medium. This approach has been proposed by Weichert al.[10],[19] for the case of photometric centrifugal sedimentation (see ISO 13318-2) and can be easily transferred gravitational photosedimentation.[20]

Figure C.2 b) shows results from multi-wavelength measurements. They prove good conformity between the conventional approach of employing optical models and the Weichert algorithm.



a) Extinction efficiency vs. dimensionless particle size, various materials

b) Measurement results for multi-wavelength approach and classical analysis based on Mie theory and material properties

Key

x	particle size, in µm
K_{ext}	extinction efficiency, dimensionless
$Q_3(x)$	cumulative distribution function, dimensionless
λ	wavelength, in µm
1	monochromatic illumination (470 nm), aperture angle = 14°
2	monochromatic illumination (630 nm), aperture angle = 14°
3	monochromatic illumination (870 nm), aperture angle = 14°
i	derived from photosedimentation by employing a model for particle extinction and providing the refractive indices of dispersed and continuous phase (for 870 nm data)
ii	derived from a multi-wavelength measurement without referring to an optical model and material properties
a	Glass bead in water.
b	SiC particles in water.
c	Steel balls in water.

NOTE Measurement data were obtained for a silica sample with LUMiReader operating at 870 nm, 630 nm and 470 nm.

SOURCE: Reproduced with the permission of Dr. Lerche KG©.

Figure C.2 — Background and performance of the multi-wavelength particle size analysis (which does not refer to an optical model)

Annex D
(informative)

Guide to uncertainty determination

D.1 General

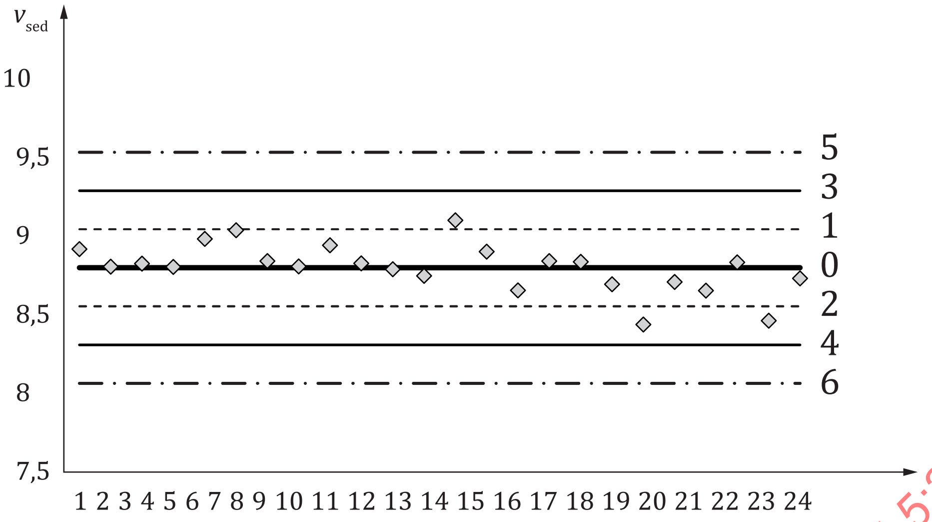
Estimation of measurement uncertainty can be achieved through various approaches. The fundamental uncertainty estimation is detailed in ISO Guide 98-3 covering a bottom-up approach that necessitates estimating the uncertainty for each source of error, component by component. This process can be time-consuming and challenging in determining all of the sources of error.

To simplify this approach several documents have expanded upon the principles of ISO Guide 98-3. Instead of quantifying all uncertainty components individually, these methods involve measuring samples in a way that combines all uncertainties. One such approach is outlined in the NordTest Guide NT TR 537, which employs long-term reproducibility measurements and reproducibility bias measurements to estimate combined uncertainties. Unlike the GUM method, if errors are discovered, it is difficult to unbundle the source of the error from the results. Although this method offers convenience and can be performed by a single laboratory, it requires the use of CRM samples to accurately determine the bias. In cases where a CRM is unavailable for the specific measurand, an alternative option is an ILC. In an ILC, different laboratories use the same method to measure the sample of interest, and the estimate of uncertainty is then calculated as the mean standard deviation of all participants in the interlaboratory test. However, organizing an ILC can be challenging, and can result in an overestimate of bias uncertainty. Despite these potential challenges, using appropriate methods for uncertainty estimation is crucial to ensure accurate and reliable results in scientific measurements.

D.2 Available methods for uncertainty estimation in sedimentation experiments

An exemplary procedure for computing the full combined uncertainty experimentally from gravitational photosedimentation experiments using the NT method and 1 000 nm silica nanoparticles can be found in Annex D of ISO 13317-1:2024 and, more completely, in Reference [21]. These examples indicate how a lab can estimate a value of uncertainty for both the sedimentation velocity and the Stokes diameter of the particles based on the gravitational photosedimentation method. A brief summary of the factors necessary for determining the combined uncertainty by the NT method will be described in this annex.

Another useful estimation of the uncertainty of a sample based on long-term measurements can be calculated by regularly taking measurements of a sample over a long time frame as a proficiency qualification. This particular method is often used for continuous production of samples in batches. Plotting the measurand values against their run date and evaluating the mean value, the standard deviation, twofold and threefold the standard deviations allow for the creation of a control chart in which trends can be observed in the measurement, see 8.3. The value of twice the standard deviation is a good estimate of the expanded uncertainty when the time frame of the measurements has exceeded 6 months. One commonly used control chart is the Shewhart control chart as shown in Figure D.1.



Key

v_{sed}	sedimentation velocity in µm/min
0	arithmetic mean value
1	mean value + standard deviation
2	mean value - standard deviation
3	upper warning
4	lower warning
5	upper control limit
6	lower control limit

NOTE Figure D.1 shows a Shewhart control chart, wherein the performance velocity data (in µm/min) are accessed periodically (abscissa: time-wise sequence number of the performance qualification) for a quality control material (nominal velocity 8,84 µm/min).

SOURCE: ISO 13317-1:2024, Figure 7.

Figure D.1 — Shewhart control chart

D.3 Experiments for deriving precision, trueness and reproducibility based on a bottom-up method

An overview of the terms used in describing the relationship between the true value of a sample, the measured value, measurement error and uncertainty range are described in Figure D.2.[22] A full explanation of the terms and their use in measurement uncertainty can be found in.[21]

Precision according to Figure 10 is a measure of random errors and represented by the standard deviation, i.e. the breadth of the results normally distributed around the mean value. Precision under repeatability conditions is the so-called short-term precision and refers to the closeness of results from replicate measurements, i.e. the same operator, determined within consecutive measurements (i.e. measurements without significant time delays between measurements), and with the same photosedimentation device. Repeatability tests can be checked to determine the significance of any systematic errors through evaluating the trueness of a method by determining the bias, the mean measured values of the CRM compared with the certified value of the CRM.