International Standard

ISO 13317-1

Second edition
2024-04

Determination of particle size distribution by gravitational liquid sedimentation methods —

Part 1: General principles, requirements and guidance

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

Partie 1: Principes généraux et orientation

Reference number
ISO 13317-1:2024(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

Page

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*.

This second edition cancels and replaces the first edition (ISO 13317-1:2001), which has been technically revised.

The main changes are as follows:

— core terms and definitions have been revised;

— the explanation of measurement principle and techniques has been revised and expanded;

— sedimentation velocity as measurand has been included;

— a guide for the determination of measurement uncertainty has been included.

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

Gravitational sedimentation has been an established principle of particle size analysis for several decades. It is employed in various academic and industrial fields of application. Numerous national and international standards address gravitational sedimentation techniques and analytical methods.

Although manifold new particle sizing techniques have emerged during the last two decades, sedimentation techniques have been recently rediscovered. This is due to substantial technical advancements and the fact that they are based on a first-principle measurement of the particles' directed motion (migration) under gravity.

The measurands of gravitational sedimentation techniques are the distributions of sedimentation velocity and corresponding particle size. They are derived from observations of phase separation – either by monitoring the deposition of particles or the depletion of dispersion. The physical principles employed to determine the quantity of particles differ widely, whereas sedimentation velocity is in each case computed from the vertically migrated distance and measurement time. This computation does not demand essential preconditions and theoretical assumptions. Yet, the transformation of velocity into particle size relies on the applicability of Stokes' law. As fractionating technique, sedimentation analysis can distinguish between particle fractions of close sedimentation velocity. Accordingly, particle size distributions can be very finely resolved, which is an advantage compared to spectroscopic ensemble techniques.

The ISO 13317 series covers the methods to determine the distributions of sedimentation velocities and particle size of particulate materials by gravitation-induced particle migration in liquids. The direction of this motion depends on the density difference (density contrast) between dispersed and continuous phase. During the measurement, particles should not undergo any physical or chemical change in the continuous phase (liquid).

The primary measurand is the particle velocity distribution, which is converted into size distribution based on established sedimentation theory. The measurement techniques described in the ISO 13317 series are applicable to liquid dispersions, like suspensions and emulsions. The measurable particle size range depends on material properties and typically reaches from 200 nm to 100 µm for aqueous samples, whereas sedimentation velocity can be quantified in the range from 0,6 µm/s to 10 mm/s. Sedimentation analysis is conducted for low particle concentrations. The maximum permissible value depends on the measurement technique and the analysis theory. In general, the volume fraction of particles is well below 1 %.

It is the responsibility of the user of this document to establish appropriate safety and health practices and to determine the applicability of the regulatory limitations prior to its use.

Determination of particle size distribution by gravitational liquid sedimentation methods —

Part 1:
General principles, requirements and guidance

1 Scope

This document specifies the principles of particle size analysis by gravitational sedimentation, the principal types of measurement techniques as well as the general rules for conducting measurements, method validation, determination of the uncertainty budget and representation of results.

This document covers neither particle migration by centrifugal, electric or magnetic forces nor sedimentation at high particle concentrations (e.g. zone sedimentation). Moreover, this document does not deal with the determination of properties other than sedimentation velocity and particle size (i.e. neither particle concentration, particle shape, particle density, zeta-potential nor apparent viscosity).

NOTE This document can involve hazardous materials, operations and equipment. This document does not purport to address all the safety problems associated with its use. Explosion proof analysers are required when examining volatile liquids with a low flash point.

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".

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).

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

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* (3.7) 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* (3.9) 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.

3.5
shape correction factor
ratio of the *sedimentation* (3.1) velocity of a non-spherical *particle* (3.7) to the one of a spherical particle of the same volume and *apparent particle density* (3.15)

3.6
hindrance function
ratio of the *terminal sedimentation velocity* (3.3) of a *particle* (3.7) placed in a well-mixed dispersion divided by its sedimentation velocity in an infinite vessel for the absence of other particles

3.7
particle
minute piece of matter with defined physical boundaries

[SOURCE: ISO 26824:2022, 3.11, 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.

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

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

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

3.14
skeleton density
ratio of the sample mass and the volume of the sample including the volume of closed pores (if present) but excluding the volume 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 12154:2014, 3.3, modified — "as well as that of void spaces between particles within the bulk sample" has been deleted from the definition and Note 1 to entry has been added.]

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 the 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.

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 surface 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 and droplets of multiple emulsions) can be approximated with the averaged 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).

3.17
density contrast
difference between the *particle* (3.7) 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.

3.18
particle Reynolds number
dimensionless parameter expressing the ratio of inertial to viscous forces within a fluid flowing past a *particle* (3.7)

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.

3.19
creeping flow
type of flow 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.

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.

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.

3.22
upper size limit
size of the largest *particle* (3.7) that satisfies the condition of *creeping flow* (3.19) and of which the *terminal sedimentation velocity* (3.3) is detectable

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 the 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”

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 depending 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.

3.25
limit of quantity detection
smallest quantity of specified *particle* (3.7) 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).

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/IEC Guide 98-3:2008, 2.2.3, modified — the term "measurement uncertainty" has been added.]

4 Symbols and abbreviated terms

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

a	edge length	m
Ar	Archimedes number	dimensionless
b	systematic deviation of measured value from true value	varying
C	transformation coefficient, see Formula (34)	$m^{0,5} \cdot s^{0,5}$
C_D	drag coefficient	dimensionless

$c(x)$	concentration density	varying
c_M	concentration with respect to extensive property M	varying
d	diameter	m
D_p	particle diffusion coefficient	$m^2 \cdot s^{-1}$
F_D	drag force (also: hydrodynamic resistance)	N
g	gravitational acceleration	$m \cdot s^{-2}$
h_{sed}	sedimentation distance	m
k	coverage factor	dimensionless
k_B	Boltzmann constant	$J \cdot K^{-1}$
L	length	m
Lj	Ljaščenko number	dimensionless
M	extensive property indicating the amount of dispersed phase	varying
m	number of bias determinations	dimensionless
N	number of replicate analyses	dimensionless
P	resolution ratio	dimensionless
Pe	Péclet number	dimensionless
Q_{toq}	cumulative function of a distributed quantity, for a type of quantity, in which the fractions are weighted	dimensionless
q_{toq}	density function of a distributed quantity, for a type of quantity, in which the fractions are weighted	varying
Re_P	particle Reynolds number	dimensionless
S	saturation of open pores with continuous phase	dimensionless
s	standard deviation	varying
T	absolute temperature	K
t_{sed}	sedimentation time	s
U	expanded uncertainty	varying
u	uncertainty	varying
v_{sed}	terminal sedimentation velocity	$m \cdot s^{-1}$
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	$kg \cdot m^{-3}$
$\dot{\gamma}$	shear rate	s^{-1}
δ_{layer}	layer thickness	m
δ_x	relative error of the calculated particle size	dimensionless
ε	porosity	dimensionless
η_c	viscosity of the continuous phase	$Pa \cdot s$
ρ_p	particle density	$kg \cdot m^{-3}$
ρ_c	density of the continuous phase	$kg \cdot m^{-3}$
ρ_d	true density of the dispersed phase	$kg \cdot m^{-3}$
φ_V	volume fraction	dimensionless

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

aggl	agglomerate, also aggregate
app	apparent
bouy	buoyant
c	combined
incl	inclusion
lab	laboratory
max	maximum
occl	occluded voids
open	open pores
ref	reference
rel	relative
rep	repeatability
Rw	reproducibility
sk	skeleton
sus	suspension
toq	type of quantity
tot	total

For the purposes of this document, the following abbreviated terms apply.

ALS	angular light scattering
DLS	dynamic light scattering
CRM	certified reference material
FBRM	focussed beam reflectance method
HSM	homogeneous-start method
LSM	line-start method
OV	occluded void
PTA	particle tracking analysis
QCM	quality control material
RM	reference material
SOP	standard operating procedure

5 Measurement principle and technical realisations

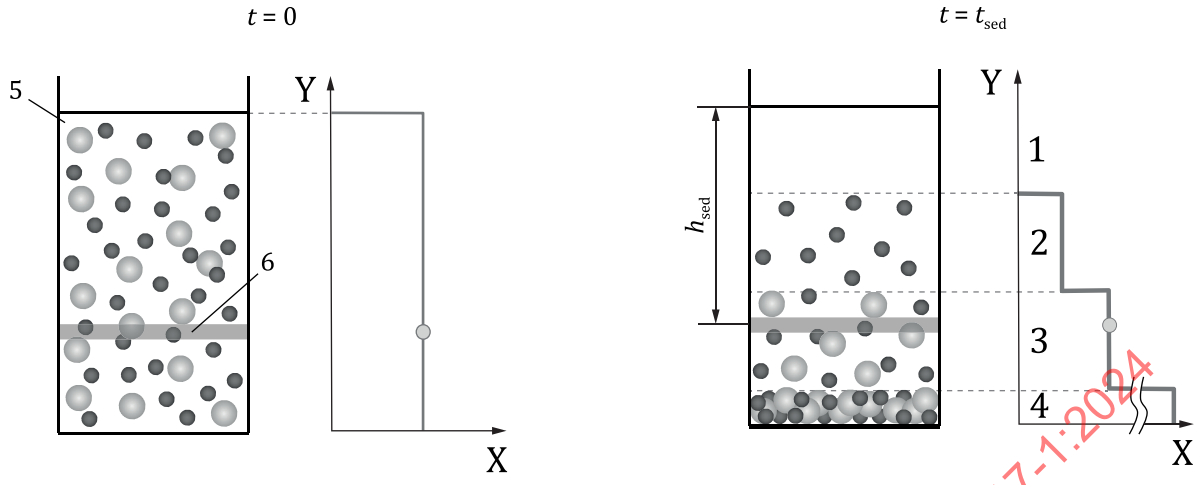
5.1 General measurement principle

Gravitational liquid sedimentation techniques are established tools for the characterisation of suspensions and emulsions. They quantify the separation of particles (the dispersed phase) from the continuous phase (also called: dispersion medium or dispersion liquid) under the presence of gravity. This phase separation relies on the directional, migratory motion of each particle, called sedimentation. Its rate, the sedimentation velocity, depends on the particle size and thus offers a chance for the granulometric characterisation of particle systems.

NOTE 1 Gravitational liquid sedimentation techniques are generally called “sedimentation techniques” in this document.

Sedimentation occurs for any particle dispersed in a quiescent viscous liquid, as long as a density contrast exists. It is driven by gravity, which acts on the particle (weight) and the displaced liquid (buoyancy). The resulting net force (excess force) causes a migratory particle motion, which is retarded by a frictional force (also called the drag force), which increases linearly with the sedimentation velocity and eventually leads to a steady-state of zero net force, at which particles move with a terminal sedimentation velocity (see Reference [43], chapter 6.4). Theoretically, terminal velocity is never reached. Sedimentation time to reach 99 % of the terminal velocity is generally very fast and depends on the ratio of particle density and liquid viscosity and the particle size squared for particle systems and operational conditions considered within this document (i.e. for creeping flow). It amounts to 0,2 µs and 49 ms for spherical gold particles (r_p = 19 300 kg/m^3) of 0,3 µm and 100 µm, respectively, settling in water. If the excess force is positive (i.e. weight is greater than buoyancy), the particle motion is called falling or settling. In the opposite case, it is called rising, creaming or floating.

Sedimentation results in a depletion of the dispersed phase and the formation of a (fixed) layer of separated particles – either at the bottom (sediment) or at the air-liquid interface (cream, foam).



a) Homogeneous dispersion and corresponding concentration profile at $t = 0$

b) Formation of four zones and corresponding concentration profile at t_{sed}

Key

X concentration
Y position
1 zone 1 = particle-free supernatant
2 zone 2 = depleted dispersion (due to loss of coarse particles)
3 zone 3 = original dispersion
4 zone 4 = sediment
5 sedimentation cell
6 measurement zone
h_{sed} sedimentation distance
t_{sed} sedimentation time

Figure 1 — Schematic illustration of phase separation due to sedimentation for a bidisperse sample with positive density contrast and its monitoring by an incremental sensing technique

Particles settle at different velocities in the dilute regime based on their difference in size. As a result, four particle concentration zones are progressing (see Figure 1). The top layer, the supernatant (zone 1), has already become free of particles ($c = 0$). The next layer (zone 2) is depleted of the large particles and the dispersed phase consists only of the fine particle fraction ($c = c_{fine}$). Simultaneously, a sediment (zone 4) develops at the bottom. In the early stages of phase separation, it is predominantly built up by fast settling, coarse particles. In the layer just above the sediment (zone 3), the concentration does not change at all with time ($c = c_{initial} = c_{fine} + c_{coarse}$) in the case of gravity sedimentation until the coarse fraction has completely entered the sediment (zone 4). The sedimentation process is finished when all particles have settled down and the formation of the sediment is completed. In the case of a negative excess force, the opposite picture is observed, i.e. particle concentration decreases at the bottom and increases at the top.

In general, sedimentation techniques quantify either the changes of local particle concentration in the measurement zone (detection level) or the growth of the layer of separated particles (e.g. at the bottom of a detection tray for the balance method, see ISO 13317-4). The vertical position of measurement zone (see Figure 1) and the time elapsed since starting the separation define the sedimentation velocity (first measurement principle). Further preconditions or assumptions are not needed for attributing the sedimentation velocity to a point of the measurement data (e.g. be it the temporal evolution of local particle concentration, the local variation of particle concentration at a given time, the time function of sediment weight). The sedimentation velocity itself constitutes an essential characteristic for several applications,

which goes far beyond a granulometric characterisation (e.g. analysis of suspension stability, segregation phenomena, flocculation processes and phase separation of highly concentrated slurries).

The sedimentation velocity depends on the properties of the continuous phase (density, rheological behaviour) and on characteristics of the particles (i.e. size, density and shape). This allows its conversion into particle size based on the Stokes' law and corresponding presumptions (see 6.2.1). This (indirect) quantification yields an equivalent diameter with respect to sedimentation velocity, called Stokes diameter, x_{Stokes}. It reflects the weight or volume of the particles as well as their mobility or drag coefficient. It is typically one of the smallest equivalent diameters of a given particle. According to Leschonski[44], Formula (1) applies:

$$x_{\mathrm{Stokes}} < x_V < x_S = x_{\mathrm{proj,m}} < x_{\mathrm{proj,st}} \tag{1}$$

where

$x_{\mathrm{proj,m}}$ is the projected area equivalent diameter for mean orientation;

$x_{\mathrm{proj,st}}$ is the projected area equivalent diameter for stable orientation;

x_S is the surface equivalent diameter;

x_V is the volume equivalent diameter.

The difference between these equivalent diameters is particularly pronounced for particle aggregates and agglomerates, where Formula (2) applies[45]:

$$x_{\mathrm{Stokes}} << x_{\mathrm{hd}} < x_{\mathrm{gyr}} < x_{\mathrm{Feret,max}} \tag{2}$$

where

$x_{\mathrm{Feret,max}}$ is the maximum Feret diameter;

x_{gyr} is the diameter of gyration;

x_{hd} is the hydrodynamic equivalent diameter.

NOTE 2 The Stokes diameter is not identical to the hydrodynamic or mobility equivalent diameter, which solely refers to the particles drag coefficient. Colloid scientists often use the radius of gyration (i.e. $0{,}5 \cdot x_{\mathrm{gyr}}$).

An essential feature of each sedimentation technique is the way of quantifying the particles and thus particle size fractions. It occurs separately from the physical process of particle classification via sedimentation and can employ very different measurands (e.g. local mass concentration, local X-ray attenuation or light obscuration, sediment weight, sediment height). The primary measurement results of sedimentation techniques are typically time-curves of these measurands and sometimes they can also be the distribution of these measurands along the vertical coordinate (i.e. profiles). The positions at which time-curves are measured or the instants at which a profile is acquired can be adjusted by operators or are fixed by instrumentation. The time axis or the vertical measurement positions can be easily transformed into an axis of sedimentation velocity on which the measured quantity is projected. Hence, the above-mentioned measurands define the intrinsic type of quantity, by which the individual size fractions are weighted (see 5.2 and Annex A). The conversion of these quantities to fundamental ones (i.e. volume or number) can rely on an unbiased or biased linear scaling or can involve parametric models (e.g. for light obscuration).

5.2 Technical realisation of sedimentation-based measurement techniques

There is a considerable variety of analytical techniques, which characterise particle systems based on the sedimentation velocity (or equivalently the Stokes diameter). In general, they monitor the sedimentation induced separation of the disperse sample via the depletion of the dispersion or the growth of deposited particle layer (sediment or cream). Yet, they differ in several aspects.

At first, fundamental difference is the driving force. This document only covers sedimentation under gravity, while the techniques based on sedimentation in centrifugal fields are described within the ISO 13318 series. A further distinction refers to the type of the primary measurand: some techniques probe integral properties of the segregated particles (e.g. sediment mass or volume), others address an integral (cumulated) quantity of dispersed particles (e.g. via hydrostatic pressure) and a third group measures the local particle concentration within the dispersion (e.g. via X-ray attenuation or light extinction). With regard to data analysis, the two former types of measurement techniques are called integral (or cumulative) techniques, whereas the latter types are called incremental techniques (see Figure 2).

Integral sedimentation techniques comprise all techniques that monitor the growth of the sediment, such as sedimentation balances techniques (see ISO 13317-4) or sedimentations tubes (see ISO 6344-3 and ISO 8486-2). These techniques apply to all disperse systems of solid particles with a positive density contrast to the liquid phase. They measure mass, volume or height of the sediment as a function of time. Another group of integral techniques probe the total amount of (solid) particles, which is still suspended in the continuous phase, for which purpose they, for example, measure the hydrostatic pressure (manometric sedimentation techniques[46]) or the weight force of a diving body (diving balance techniques[47],[48]).

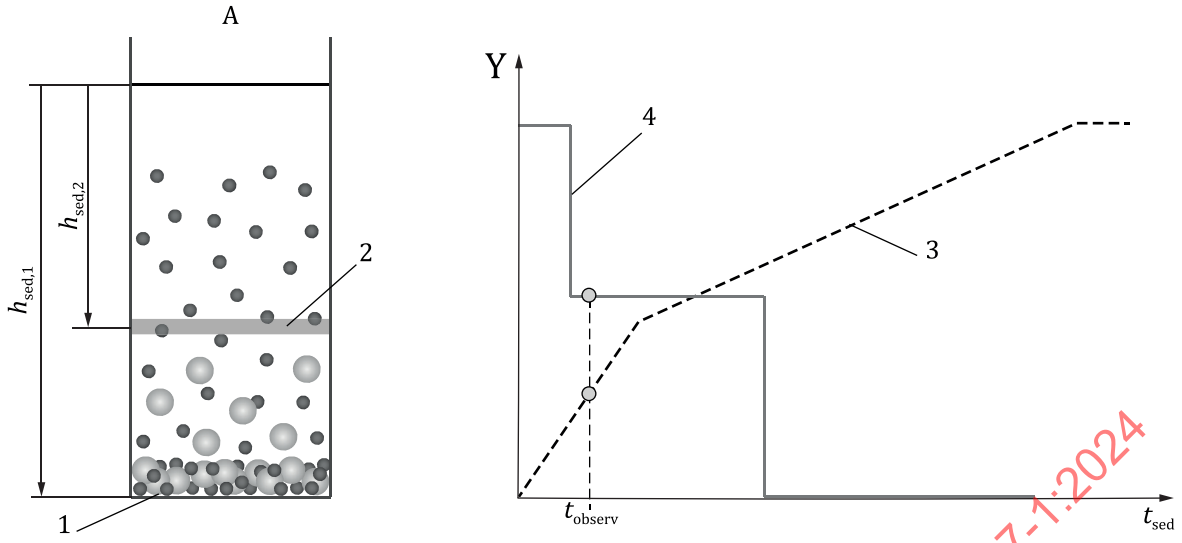
Incremental sedimentation techniques measure the local particle concentration. One way to accomplish this consists of periodic sampling with a pipette and subsequent quantification of dispersed material (pipette techniques, see ISO 13317-2). Alternatively, these techniques probe local, macroscopic properties of the sample, for example, dispersion density (with micro-diving bodies, i.e. small hydrometers, see ISO 17892-4, ISO 11277 and ASTM D7928-17), X-ray attenuation (X-ray sedimentometer, see ISO 13317-3), light extinction or scattering (photosedimentometer, see GB/T 6524, ANSI B74.20) or refractive index[49]. Pipette-based and hydrometric sedimentation techniques were rather popular in the past, whereas modern sedimentometers typically employ radiation-based sensing technologies, especially for fine particles $\ll 100$ µm.

Figure 2 illustrates the differences between integral and incremental sedimentation techniques through examples of monitoring the growth of sediment (integral) and the continuous observation of local particle concentration (incremental). Time curves of the corresponding measurement signals are shown for two modes of operation:

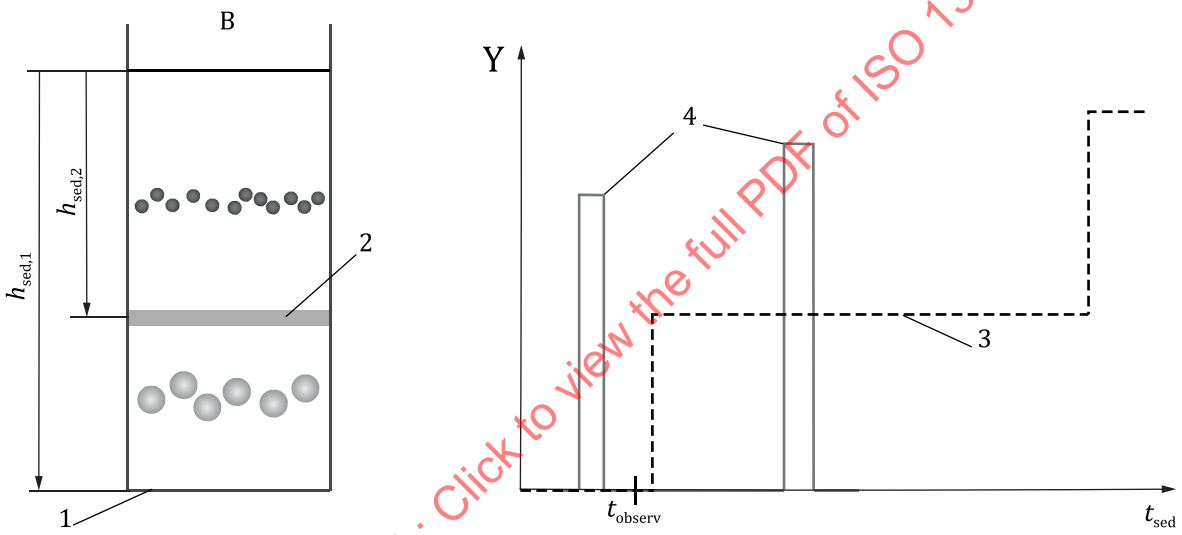
a) HSM (also suspension mode, situation A), and

b) LSM (situation B).

The former, which is preferably used in gravitational sedimentation analysis, starts with thoroughly mixed, homogeneous samples, whereas in case of the latter, the initial state is characterised by a thin layer of dispersion sample on top of a particle-free liquid. Although, the line-start method is prone to adverse hydrodynamic instabilities (e.g. density convections), it is still used for specific applications (e.g. ISO 6344-3) because it offers a few advantages such as the determination of the coarsest grain size. The two different operational modes coincide with different shapes of time-curves (see Figure 2) and require different procedures in data analysis (see 6.2.2).



a) Sedimentation for HSM used for incremental techniques and integral techniques



b) Sedimentation for LSM used for incremental techniques and integral techniques

Key

t_{sed}	time elapsed since starting the sedimentation experiment
Y	observed quantity (e.g. sediment mass or X-ray attenuation)
1	sediment layer [an example of measured object for integral (cumulative) techniques]
2	measurement zone for incremental (differential) techniques
3	time curve for sediment quantity (e.g. mass or volume)
4	time curve for local particle concentration at measurement zone
$h_{sed,1}$	sedimentation distance for 1, from which the sedimentation velocity at t_{sed} is calculated
$h_{sed,2}$	sedimentation distance for 2, from which the sedimentation velocity at t_{sed} is calculated
t_{observ}	time point of observation for situations on left-hand side

Figure 2 — Example of sedimentation growth monitoring using gravitational sedimentation techniques and corresponding time curves of observed quantities

Incremental techniques use different modes of sensing. Traditionally, the measurements are conducted at a fixed vertical position (see Figure 1) or are gradually changed over a vertical range (scanning mode, (see Reference [43], chapters 9.4.4 and 9.5]). The sedimentation distance refers either to the liquid surface (meniscus) for positive density contrast or to the bottom for a negative one. A recently introduced

sensing technology realises a time-resolved measurement of the complete concentration profile (STEP-Technology®[1)][50]), which considerably enhances the data analysis (see ISO 13318-2) and e.g. facilitate the distinction between settling and creaming phases.

Despite the significant differences among the various sedimentation techniques, they all directly measure the same particle property, the settling velocity or Stokes diameter and should therefore yield identical results for monodisperse particles of arbitrary shape. However, the instrument's response to polydisperse samples can substantially scatter because the various measurands (e.g. sediment height, X-ray attenuation, light scattering) are differently affected by the individual size fractions. Indeed, the experimental method or sensing technique employed for quantifying the amount of particles with a certain sedimentation velocity determine the intrinsic type of quantity, in which the originally measured distribution functions are weighted.

Annex A lists main characteristics and references for selected sedimentation techniques.

6 Measurement data and basic rules of data evaluation

6.1 Sedimentation velocity distribution

The primary result of sedimentation techniques is the distribution of the sedimentation velocity. In general, the observed sedimentation velocity is a collective property, which depends on particle interactions and the particle concentration, which allows for an evaluation of typical quality endpoints such as phase separation or flocculation. However, within the scope of this document (i.e. dilute particle systems), the sedimentation velocity constitutes a dispersity property, i.e. an individual property of the respective particles. It provides information about the particles that goes beyond particle size. For instance, it can be used to distinguish between creaming and settling constituents in complex formulations with multiple dispersed phases. Last but not least, velocity distributions allow an evaluation of polydispersity for particulate materials of unknown composition or in the event of lacking data needed for the transformation of sedimentation velocity into particle size.

Sedimentation techniques relate a property of the dispersion phase (zones 1 to 3 in Figure 1) or the sediment (zone 4 in Figure 1) to the time elapsed t_{sed} since starting the gravitational phase separation in a thoroughly mixed sample. Such properties are the local particle concentration, the total mass of dispersed matter above a probe or the height of a sediment layer. They are measured at a certain vertical position below the liquid surface, can be thus related to the maximum settling distance h_{sed} for all particles, which pass the measurement position at t_{sed} (see Figure 2). Elapsed time and settling distance define the sedimentation velocity as shown in Formula (3):

$$v_{sed} = \frac{h_{sed}}{t_{sed}} \tag{3}$$

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

The distribution of the sedimentation velocity can be described in analogy to particle size distributions, yet the possible occurrence of negative sedimentation velocities (i.e. counter-directed to gravitational acceleration) requires the pragmatic convention of only considering their absolute values:

$$Q_{toq}(v) = \int_0^v q_{toq}(v_{sed})\,\mathrm{d}|v_{sed}| \tag{4}$$

1) STEP-Technology® is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

$$q_{\mathrm{toq}}(v) = \left.\frac{\mathrm{d}Q_{\mathrm{toq}}(v_{\mathrm{sed}})}{|\mathrm{d}v_{\mathrm{sed}}|}\right|_{v} \tag{5}$$

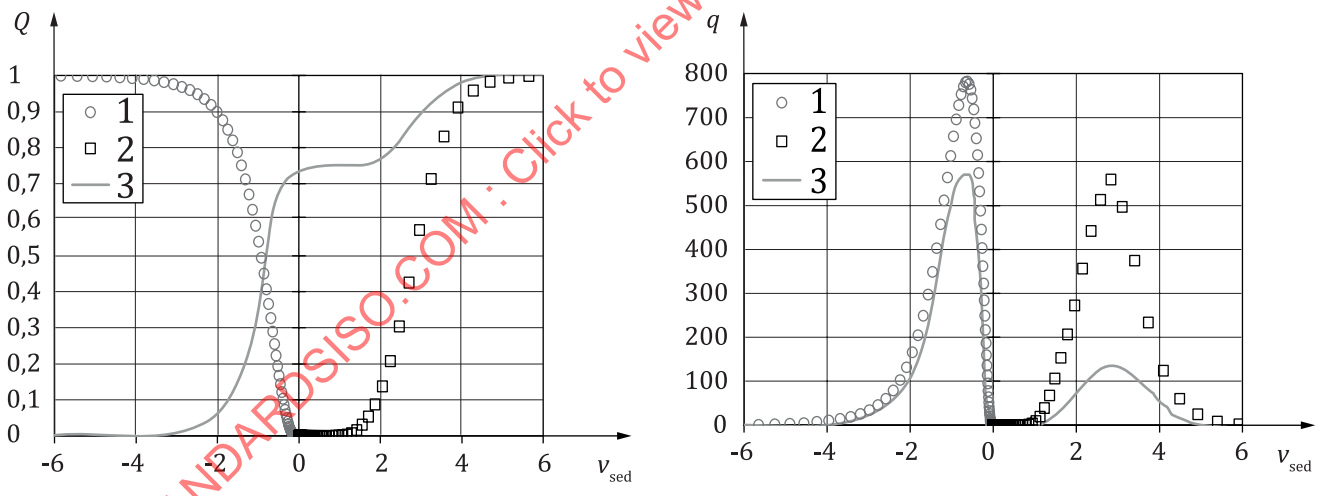
The functions Q_{toq} and q_{toq} are the cumulative and density function of the velocity distribution. The index "toq" denotes the type of quantity, in which the "amount of dispersed phase" is quantified. The introduction of the absolute values (| |) ensures that, for creaming particles, the cumulative function rises from zero at $v_{\mathrm{sed}} = 0$ to one at $v_{\mathrm{sed}} \to -\infty$. This typically coincides with mirroring the cumulative and density functions of creaming particles at the ordinate. However, if creaming and settling occurs simultaneously, Formulae (4) and (5) need to be replaced by expressions, that allow a variation in the sign of the velocity values:

$$Q_{\mathrm{toq}}(v) = \int_{-\infty}^{v} q_{\mathrm{toq}}(v_{\mathrm{sed}})\,\mathrm{d}v_{\mathrm{sed}} \tag{6}$$

$$q_{\mathrm{toq}}(v) = \left.\frac{\mathrm{d}Q_{\mathrm{toq}}(v_{\mathrm{sed}})}{\mathrm{d}v_{\mathrm{sed}}}\right|_{v} \tag{7}$$

These conventions are illustrated in Figure 3 for the sedimentation velocity of oil droplets and polystyrene particles in aqueous solution (for each material separately and for a mixture of both). While the polystyrene particles settle down to the bottom of the vessel, oil droplets rise up, i.e. they move against the direction of gravitational acceleration with a negative sedimentation velocity.

Velocity distributions can be similarly used as particle size distributions; modal values $v_{\mathrm{mod,toq}}$ localise the most frequent velocities and quantiles $v_{P,\mathrm{toq}}$ correspond to a value P (in percent) of the cumulative function. For instance, the main quartiles of the velocity distribution were successfully employed to quantify the polydispersity by the "sharpness" (which can be quantified by the ratio $v_{25,\mathrm{toq}}/v_{75,\mathrm{toq}}$) of the sedimentation front of concentrated suspensions[51]. Furthermore, velocity distributions indicate directly polydispersity and allow to rate the effectiveness of disruptive processing (see ISO/TS 22107).



a) Cumulative functions **b) Distribution density**

Key

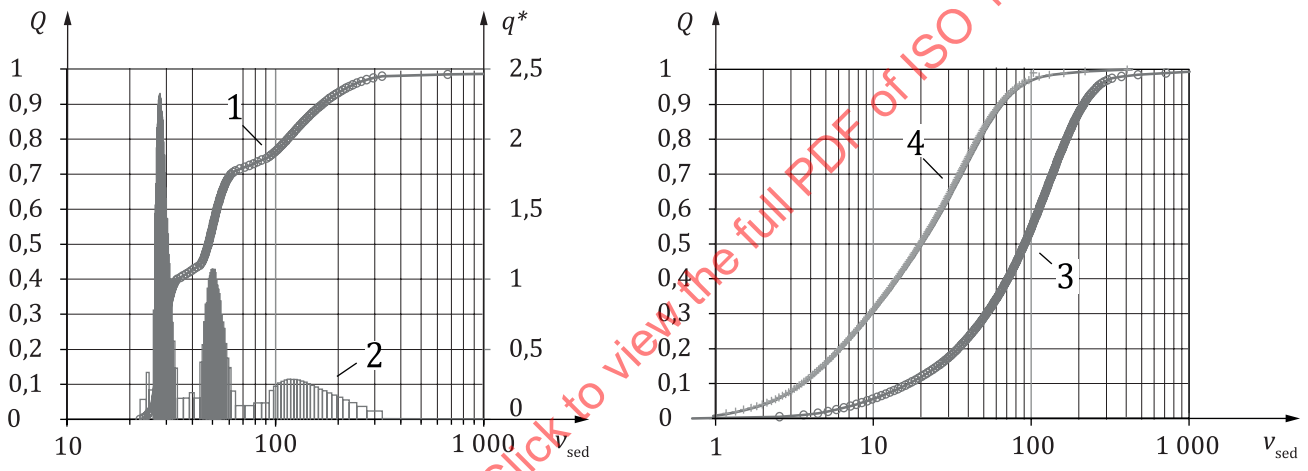
v_{sed} sedimentation velocity, in µm/s
Q cumulative function (extinction-weighted) of the velocity distribution
q density function (extinction-weighted) of the velocity distribution, in s/mm
1 oil-in-water emulsion (ρ_{oil} = 917 kg/m^3, $x_{50,3}$ = 7 µm)
2 polystyrene suspension (ρ_{PS} = 1 055 kg/m^3, $x_{50,3}$ = 9 µm)
3 mixture

Figure 3 — Sedimentation velocity distributions of an oil-in-water emulsion (negative velocities), a polystyrene suspension (positive velocities) and a mixture of both (1:1 by weight, continuous line)

Distributions of the sedimentation velocity reflect the state of dispersion (at least for sufficiently dilute samples). That means they can be used to assess polydispersity or multimodality [see Figure 4 a)], the presence of coarse contaminants or the dispersibility of a particulate material [see Figure 4 b)]. Their main advantage is that they do not require detailed knowledge of the material properties of the continuous and dispersed phases. Direction of particle motion for sedimenting or creaming particles results in "velocities" of different sign (falling is equivalent to positive velocity, creaming is equivalent to negative velocity) as shown in Figure 3 and allows an easy classification.

Velocity distributions are plotted for the intrinsic type of quantity, by which the different particle fractions contribute to originally measured properties of the partly demixed dispersion or the separated particles (i.e. sediment or cream layer). For instance, X-ray and photometric transmission measurements of local particle concentrations lead to X-ray-absorption-weighted and (light) extinction-weighted distributions, respectively. A direct conversion with respect to the type of quantity is typically not possible because such a conversion relies on the relationship between quantity and particle size (see 6.2.2.6).

The disadvantage of sedimentation velocity is its dependency on the properties of the continuous phase (density, viscosity), which restricts its applicability and impedes its transferability to arbitrary situation of sedimentation-induced particle separation. Distributions of the sedimentation velocity are therefore transformed to ones of particle size (see 6.2) for most analytical purposes.



a) Velocity distribution of a multimodal suspension of PMMA particles

b) Velocity distribution of a silica suspension due to different dispersive processing

Key

v_{sed}	sedimentation velocity, in µm/min
Q	cumulative function (extinction-weighted) of the velocity distribution
q^*	transformed density function (extinction-weighted) of the velocity distribution
1	cumulative function
2	transformed density function (histogram)
3	feed
4	after milling

Figure 4 — Application examples of sedimentation velocity distribution

For the sake of completeness, it should be mentioned that sedimentation velocity is often replaced by the sedimentation coefficient in centrifugal sedimentation – especially in the ultracentrifugation community. This coefficient relates the particle velocity to the acceleration of the applied force field (i.e. gravitational or centrifugal acceleration) and is expressed in units of time (see ISO 13318-1). Unlike with sedimentation velocity data, sedimentation coefficient data facilitate a direct comparison of results from gravitational and centrifugal sedimentation.

6.2 Stokes-based analysis for obtaining particle size distributions

6.2.1 Particle size

The sedimentation of particles is induced by gravity and retarded by hydrodynamic resistance. The terminal sedimentation velocity is thus affected by their volume and hydrodynamic mobility. Both parameters are size-dependent which allows to calculate the particle size from the sedimentation velocity [see Formula (3)].

For small spherical particles of diameter *x*, Formula (8) applies[52]:

$$v_{\mathrm{sed}} = \frac{g\left(\rho_{\mathrm{p}} - \rho_{\mathrm{c}}\right)}{18\eta_{\mathrm{c}}} x^2 \tag{8}$$

where

g is the gravitational acceleration;

η_{c} is the dynamic viscosity of the continuous phase;

ρ_{c} is the density of the continuous phase;

ρ_{p} is the density of the particle.

The validity of Formula (8) relies on a series of assumptions, which are referred to as “standard theory” and comprised of the following.

a) The motion is slow, which means that creeping flow conditions applies (i.e. Stokes flow) and the hydrodynamic drag obeys Stokes' law for spherical objects (see also Clause C.1).

b) There are only three forces that act on the particles: gravity, buoyancy and viscous drag (see also Clause C.2).

c) Gravity and buoyancy can be calculated according to Newton’s law and Archimedes’ principle.

d) The liquid is incompressible and Newtonian (see also Clause C.3).

e) A particle’s sedimentation is not affected by the presence of other particles (see also Clause C.4).

f) The sphere is isotropic and has a smooth and rigid surface (see also Clauses C.5 and C.7).

g) The sedimentation is not affected by the walls of the vessel (see also Clause C.8).

h) The terminal sedimentation velocity is achieved instantaneously (see also Clause C.9).

i) The particles do not experience changes during the experiment (e.g. no dissolution, no swelling, no agglomeration).

Last but not least, the gravitational acceleration, g, is commonly regarded as a physical constant, but it is not. The standard value of 9,806 65 m/s^2 applies approximately to a latitude of 45°, whereas the equatorial value is 9,780 m/s^2 and the polar value amounts to 9,832 m/s^2 (i.e. the maximum deviation from the standard value is <0,3 %).

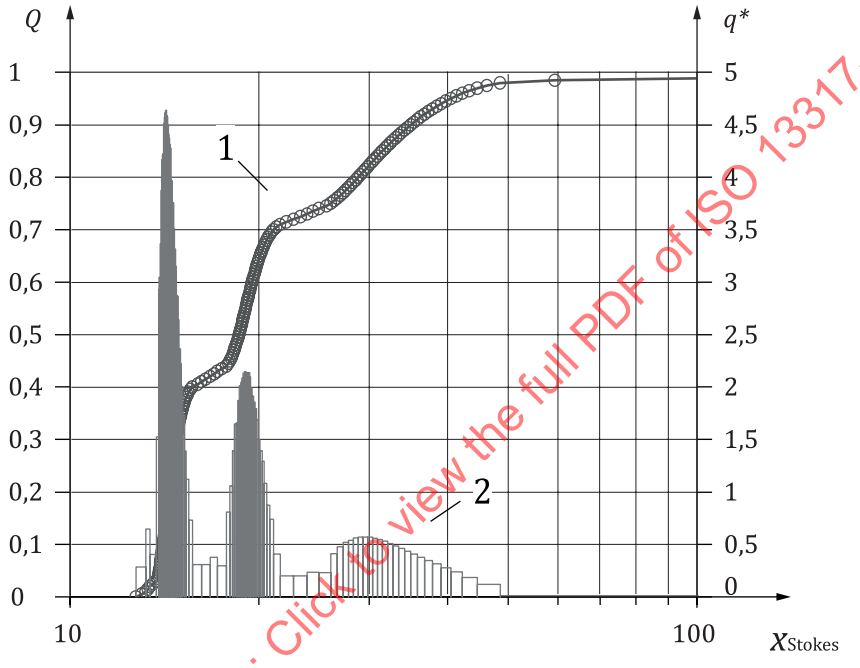
In practice, it is rather unlikely that the particles are spherical and that all assumptions listed above apply. In particular, particles of most real-world materials are commonly neither spherically shaped nor non-agglomerated. For that reason, one conventionally accepts the invalidity of all assumptions concerning the particulate phase, as long as the remaining assumptions are met by adequate sample preparation and proper measurement conditions. Measured sedimentation velocities are then transformed into particle size

as if the particles were non-porous, isotropic spheres with smooth surface. The equivalent diameter, the Stokes diameter, x_{Stokes}, is defined as given in Formula (9).

$$x_{Stokes} = \sqrt{\frac{18\eta_c v_{sed}}{g(\rho_p - \rho_c)}} \tag{9}$$

where the appropriate particle density ρ_p is the buoyant density for the general case and the apparent particle density (of the constituent particles) for the case of fine, open pores (see Annex B).

It should be mentioned that the size distribution mirrors the velocity distribution, yet on a nonlinearly rescaled abscissa [see also Formula (32)]. Figure 5 displays the corresponding particle size distribution, which corresponds to the velocity distribution given in Figure 4 a) employing the values g, η_c and the density contrast (ρ_p – ρ_c) as given in D.3.2. As the square root of sedimentation velocity has to be taken, relative distance between peaks is narrower than in Figure 4 a).



Key

x_{Stokes}	Stokes diameter, in µm
Q	cumulative function of the extinction-weighted particle size distribution
q^*	transformed density function of the extinction-weighted particle size distribution
1	cumulative function
2	transformed density function (histogram)

NOTE The wavelength is 870 nm, transformation of corresponding sedimentation velocities [see Figure 4 a)] to size distribution occurs with Formula (9).

Figure 5 — Distribution of the Stokes diameter of a multimodal mixture of PMMA reference particles

6.2.2 Quantification of size fractions

6.2.2.1 Variety of technical solutions

The various sedimentation techniques essentially use the same principle in their determination of sedimentation velocity, but they differ in the quantification of size fractions.

For instance, X-ray sedimentometers record changes over time, t, which result from the depletion of a given size fraction in the measurement zone. On the other hand, sedimentation balances attribute the increase in sediment mass to the continuing deposition of all size fractions except those that have already been completely segregated from the liquid phase before. For both examples, the sedimentation velocity is straightforwardly calculated from the maximum sedimentation distance and the elapsed time (see 6.1). Yet, the values of sedimentation velocity are differently attributed to the relative quantity of size fractions. X-ray sedimentometer probe the local concentration via X-ray attenuation, which is mass-proportional for a given material, whereas sedimentation balances measure a cumulated mass, which reflects the time course of deposition.

The broad variation of technical solutions for quantifying the size fractions cannot be comprehensively described in this document. Instead, subclauses 6.2.2.2 to 6.2.2.7 address the general principles and requirements, and ISO 13317-2, ISO 13317-3, ISO 13317-4, ISO 13317-5[2)] and Reference [43] can be referred to for more detailed information.

Nowadays, incremental or integral techniques of gravitational sedimentation are commonly operated in a homogeneous-start method (see 5.2).

6.2.2.2 General principles — Integral techniques in the homogeneous-start method

Integral techniques typically measure an extensive quantity M such as mass, volume, weight force or hydrostatic pressure. This quantity is recorded as function of sedimentation time (see Figure 2). The value of the quantity M at a certain time t depends on the current composition of suspension and for the HSM also on the past of the separation process. That is, the integral values M does not only reflect, which particle fractions have "survived" in suspension or emulsion, but also how much of the "surviving" fractions have been already separated. The measured values can be transformed into a cumulative function of the particle size distribution in dependence whether M refers to sediment or suspension properties:

$$\text{integral sediment properties: } 1-Q_{\mathrm{toq}}(x_{\mathrm{Stokes}})=\frac{M_{\mathrm{sed}}(t)}{M_{\mathrm{tot}}}\cdot\left(1-\frac{\mathrm{d}\ln M_{\mathrm{sed}}(t)}{\mathrm{d}\ln t}\right) \tag{10}$$

$$\text{integral suspension properties: } Q_{\mathrm{toq}}(x_{\mathrm{Stokes}})=\frac{M_{\mathrm{sus}}(t)}{M_{\mathrm{tot}}}\cdot\left(1-\frac{\mathrm{d}\ln M_{\mathrm{sus}}(t)}{\mathrm{d}\ln t}\right) \tag{11}$$

with $v_{\mathrm{sed}}(x_{\mathrm{Stokes}})=\frac{h_{\mathrm{sed}}}{t}$

where

M_{sed} is the time-dependent particle quantity M in sediment;

M_{sus} is the time-dependent particle quantity M in the observed zone of suspension phase;

M_{tot} is the total or maximum value of the observed quantity M;

Q_{toq} is the cumulative function of the particle size (or velocity) distribution with index "toq" indicating the intrinsic type of quantity defined by quantity M.

Formulae (10) and (11) define the relationship between cumulative functions and measurement signals, but the computation can be realised by different numerical schemes; the classical way of data treatment was purely graphically (see References [43] chapter 10.4, [53] and [54]).

6.2.2.3 General principles — Integral techniques in the line-start method

Despite the enormous experimental challenges, there are few applications where particle size analysis relies on gravitational sedimentation in LSM (e.g. ISO 8486-2). Employed techniques are merely integral; for instance, they record the sediment volume as a function of time [see Figure 2 b), Key 3]. The observed quantity is either rising from zero to a maximum value (sediment properties) or steadily decreasing to

2) Under preparation. Stage at the time of publication: ISO/DIS 13317-5:2024.

zero (suspension properties) and the signal increments solely represent a certain size fraction. Hence, the time curves can be considered as scaled cumulative functions of the particle size distribution, as given in Formulae (12) and (13):

$$\text{integral sediment properties: } 1-Q_{\text{toq}}(x_{\text{Stokes}})=\frac{M_{\text{sed}}(t)}{M_{\text{tot}}} \tag{12}$$

$$\text{integral suspension properties: } Q_{\text{toq}}(x_{\text{Stokes}})=\frac{M_{\text{sus}}(t)}{M_{\text{tot}}} \tag{13}$$

where

M_{sed} is the time-dependent particle quantity M in sediment;

M_{sus} is the time-dependent particle quantity M in observed zone of suspension phase;

M_{tot} is the total or maximum amount of the observed quantity M;

Q_{toq} is the cumulative function of the particle size (or velocity) distribution with index "toq" indicating the intrinsic type of quantity defined by quantity M.

In addition, gravitational LSM facilitates the visual identification and characterisation of the coarsest particles, i.e. the fastest moving particles (see ISO 6344-3).

6.2.2.4 General principles — Incremental techniques in the homogeneous-start method

Incremental techniques measure local properties of the suspension. These are intensive quantities such as mass fraction, suspension density, extinction coefficient, X-ray attenuation coefficient or refractive index increment, which can be presented as local concentration c_M (i.e. as extensive quantitative M per unit volume). For deriving particle size distributions, the local concentrations can be determined

— as a function of time for a fixed position or for a steady change of position (scan);

— as a function of position (profile) for a given sedimentation time;

— as a function of position and time (profile evolution).

The latter offers a chance to reduce noise and uncertainty.

Time curves, $c_M(t)$, and profiles, $c_M(z)$, can be both considered as scaled cumulative functions of the particle size distribution. For a time curve at sedimentation distance h_{sed}, one finds:

$$Q_{\text{toq}}(x_{\text{Stokes}})=\frac{c_M(t)}{c_{M,0}} \tag{14}$$

with x_{Stokes} derived from Formula (15):

$$v_{\text{sed}}(x_{\text{Stokes}})=\frac{h_{\text{sed}}}{t} \tag{15}$$

whereas the evaluation of a concentration profile measured at a sedimentation time, t_{sed}, leads to:

$$Q_{\text{toq}}(x_{\text{Stokes}})=\frac{c_M(z)}{c_{M,0}} \tag{16}$$

with x_{Stokes} derived from Formula (17):

$$v_{\text{sed}}(x_{\text{Stokes}})=\frac{\Delta z}{t_{\text{sed}}} \tag{17}$$

where

$c_{M,0}$ is the uniform initial concentration within the sample;

Δz is the vertical distance from liquid surface for density contrast $\Delta\rho > 0$ or from the bottom for $\Delta\rho < 0$.

Formulae (14) and (16) reveal that incremental measurement techniques directly yield the cumulative distribution function, without further data treatment. This holds true as long as the technique probes only one quantity. Data analysis becomes more complex in the event of multiparametric incremental analyses (i.e. simultaneous measurements of multiple quantities). Such kind of analyses are intended to widen the measurement range, to probe additional parameters or to reduce the bias on the particle system (e.g. on shape or optical properties). They are, for example, realised by spectral optical techniques.

6.2.2.5 Remarks on signal processing

In principle, sedimentation techniques facilitate a direct and simple derivation of the cumulative function without further data treatment. There is no need for numerically inverting smeared or spectral signals for techniques such as PTA and FBRMs, or DLS and ALS, respectively. Hence, the shape of the distributions can remain unbiased and does not require a general smoothing rule, which would reduce the resolution. However, smoothing of the original measurement data (time curves or concentration profiles) can be appropriate in order to cope with signal noise and to facilitate the derivation in Formulae (10) and (11) as well as the computation of the density function $q_{\mathrm{toq}}(x_{\mathrm{Stokes}})$ from the cumulative functions $Q_{\mathrm{toq}}(x_{\mathrm{Stokes}})$. Moreover, signal noise defines detection limits for size fractions of very low concentration and thus affects the reliability of minimum and maximum particle sizes measured by sedimentation techniques.

A special situation for data analysis arises when the sedimentation techniques perform several independent measurements made on the same sample (i.e. multiparametric analyses, see 6.2.2.4) or yield a sequence of concentration profiles. Though each of the measurement results can be evaluated separately with respect to size distribution, only their combined evaluation yields a real benefit for the characterisation (e.g. less influence of material properties or lower uncertainty due to noise subtraction). According data analysis relies on appropriate numerical schemes, where the attribution of time, position and signal to the cumulated frequency of sedimentation velocity or particle size is not obvious anymore.

6.2.2.6 Conversion with respect to the type of quantity

The technique-specific principle of quantifying the amount of particles for each size fraction defines the intrinsic type of quantity in which the distribution of the sedimentation velocity or Stokes diameter is described [see Formulae (4) to (7)]. These types of distribution functions can require a transformation with respect to the type of quantity before further use. For spherical particles, the transformation is conducted by means of

$$q_B(x) = \frac{f_B(x)}{f_A(x)} q_A(x) \Big/ \int \frac{f_B(x)}{f_A(x)} \mathrm{d}Q_A \tag{18}$$

where A and B are size dependent quantities:

$$A = f_A(x) \text{ and } B = f_B(x) \tag{19}$$

The corresponding functions frequently obey power-laws of particle size, for instance:

— weight of particles with uniform density: $f_{\mathrm{weight}}(x) \propto x^3 \rightarrow q_{\mathrm{weight}}(x) = q_3(x)$;

— X-ray attenuation at dispersed particles: $f_{\mathrm{Xray}}(x) \propto x^3 \rightarrow q_{\mathrm{Xray}}(x) = q_3(x)$;

— light extinction at opaque micrometre particles: $f_{\mathrm{ext}}(x) \propto x^2 \rightarrow q_{\mathrm{ext}}(x) = q_2(x)$ (yet in general, light extinction does not simply scale to a power of particle size).

Note that any conversion amplifies the uncertainties of the size distribution, in particular at the fringes of the distribution function. The integral effect of this error propagation can be quantified based on the original measurement data, which helps to qualify the meaningfulness of conversion[55].

For non-spherical particles, one commonly uses the same quantity functions as for spheres. This introduces an error, which is more pronounced when the deviation from spherical shape is larger.

6.2.2.7 Non-normalised particle size distributions

Particle size distributions are commonly presented as normalised functions, i.e. the total integral of the density function $q_{\mathrm{toq}}(x)$ amounts to 1 and the sum function $Q_{\mathrm{toq}}(x)$ varies between 0 and 1, because the detected signals cannot always be transformed in absolute quantities, such as mass concentration and because normalisation ensures the comparability of measured data.

However, most sedimentation techniques facilitate the direct measurement of the particle concentrations in the measurement zone – or at least their calculation from measured data. Hence, they offer a chance to derive a non-normalised size distribution which quantifies the particle concentration in the selected size fractions given in Formulae (20) and (21):

fractional concentration: $c_{\mathrm{toq},i} = c_{\mathrm{toq,tot}} \cdot \Delta Q_{\mathrm{toq},i}$ (20)

concentration density: $c_{\mathrm{toq}}(x) = c_{\mathrm{toq,tot}} \cdot q_{\mathrm{toq}}(x)$ (21)

where

$c_{\mathrm{toq}}(x)$ is the concentration density function with respect to the quantity indicated by the index toq;

$c_{\mathrm{toq},i}$ is the particle concentration of the i-th size fraction, the type of quantity is indicated by index toq;

$c_{\mathrm{toq,tot}}$ is the total particle concentration, the type of quantity being indicated by the index toq;

$q_{\mathrm{toq}}(x)$ is the density function of particle size distribution with respect to the quantity toq.

A non-normalised size distribution does not only reflect the state of dispersion, but also the amount of particle in the analysed sample, which is typically adjusted to match the working range of given instrument. This principally undermines the comparability of non-normalised size distributions. Yet, if the dilution factor of sample preparation is known, one can calculate the absolute quantity of specified size fractions of the original sample, e.g. the mass concentration (in g/ml) of all oversized particles >10 µm.

6.3 Deviations from Stokes-based analysis

6.3.1 General

The calculation of particle size from sedimentation velocity according to Formula (9) relies on a couple of assumptions, which relate to

— particle motion: steady-state, three forces, creeping flow, isolated particles;

— particle properties: spherical shape, smooth surface, homogeneous density, inert behaviour; and

— liquid properties: incompressible, Newtonian.

The individual effects are discussed in Annex C.

Some of the above-mentioned assumptions can be addressed by proper sample preparation (see 7.3 and 7.4). For instance, solvents should show Newtonian behaviour, must not promote dissolution or swelling and can contain dispersing agents that impede particle agglomeration[56].

Other assumptions set limits on the working range with regard to particle size and concentration or they have to be addressed by data analysis.

6.3.2 Upper limit for sedimentation velocity and particle size

The assumption of creeping flow (see 6.2.1) imposes general upper limits for particle size and sedimentation velocity, because it only holds true for small particle Reynolds numbers:

$$Re_p = \frac{\rho_c v_{sed} x}{\eta_c} \tag{22}$$

Conventionally, a threshold value of $Re_p = 0{,}25$ is used.

As the definition of Re_p is based on size and sedimentation velocity, it is more convenient to calculate the upper limits of size, x_{max}, and sedimentation velocity, v_{max}, from the corresponding thresholds of the dimensionless Archimedes and Ljaščenko numbers:

$$Ar_{cr} = \frac{g\Delta\rho\,\rho_c x_{max}^3}{\eta_c^2} = 4{,}68 \text{ and } Lj_{cr} = \frac{\rho_c^2 v_{max}^3}{g\Delta\rho\eta_c} = 0{,}003\,34 \tag{23}$$

Formula (23) shows to which degree the upper limits can be moved to higher values by adjusting the viscosity and density of the continuous phase.

In addition, there can be further, technique-specific restrictions on the maximum particle size or sedimentation velocity. For instance, the separation of the fastest settling particles should be slow enough to ensure

a) its time-resolved monitoring with the available instrument, and

b) that the period for moving the complete sedimentation distance (see Figure 2) is considerably larger than the transient time in that initial convective flows can fade away.

Another restriction can be that the stochastic number fluctuation of particles in the measurement zone does not exceed a critical value, above which this fluctuation conceals the effect of phase separation.

6.3.3 Lower limits for particle size

The lower size limit of gravitational sedimentation analysis is frequently related to the interfering effect of Brownian motion, which is the faster the finer the particles are. Brownian motion results in a diffusional flux, which superposes the migration in the gravitational field and essentially broadens the sedimentation front. The average Brownian displacement is proportional to the square root of time, unlike to a migratory displacement, which grows linearly with time. Hence, the impact of Brownian motion on the results of a sedimentation analysis becomes lower with progressing phase separation and increasing sedimentation distance.

The dimensionless Péclet number facilitates a general quantification of this effect:

$$Pe \overset{!}{=} \frac{v_{sed} h_{sed}}{D_p} = \frac{\pi g \Delta\rho x^3 h_{sed}}{6 k_B T} \tag{24}$$

where

D_p is the particle diffusion coefficient;

g is the gravitational acceleration;

h_{sed} is the sedimentation distance;

k_B is the Boltzmann's constant, $k_B \approx 1{,}381 \times 10^{-23}$ J/K;

T is the absolute temperature;

v_{sed} is the terminal sedimentation velocity;

x is the particle diameter;

$\Delta\rho$ is the density contrast between the dispersed and continuous phase.

As a rule of thumb, the impact of Brownian motion for a Pe < 200 can be neglected[57].

NOTE The critical Péclet number (Pe_{cr} = 200, see Reference [57]) allows an estimation of the smallest particle size, for which Brownian motion is negligible. For aqueous suspensions of quartz particles ($\Delta\rho$ = 1,65 g/cm^3) it yields lower size limits of 0,21 µm and 0,10 µm at sedimentation distances of 10 mm and 100 mm, respectively. These limits are shifted to finer sizes if the density contrast is larger than for quartz-water systems. They are raised for a lower density contrast (e.g. for 0,1 g/cm^3 to 0,54 µm and 0,25 µm, respectively).

6.3.4 Limits for particle concentration

Stokes developed Formula (8) for unhindered settling of a single particle in an infinite liquid. This assumption is practically only fulfilled for dilute (polydisperse) particle systems of volume fractions of the dispersed phase below 0,5 %. Under these conditions, individual particles settle essentially independent from each other.

The lower concentration limit results essentially from the limit of quantity detection. That means, it is defined by the need of sufficiently high signals for the quantification of particles (e.g. via weight increment for sedimentation balances or radiative attenuation for X-ray sedimentometer). Hence, these are specific limits for the various sedimentation techniques and can depend on the material (X-ray sedimentometer) and even particle size (e.g. photosedimentometer). They are discussed in the other parts of the ISO 13317 series.

6.3.5 Handling of porous and heterogeneous particles

The transformation of sedimentation velocity into particle size [see Formula (9)] relies on sound knowledge of the material properties, in particular of the particle density. For homogeneous liquids and solid particles, data is commonly available in textbooks or in material data sheets (e.g Reference [58]). However, quite a few particulate materials consist of inhomogeneous particles. That is, particles can have pores (open or closed), be coated or composed of multiple constituents. Since particle size analysis typically aims at the outer dimensions of moving entities, one employs the apparent particle density for calculating the particle size. The apparent particle density can be considered as the average density of the settling entity. It is identical to the buoyant density in the absence of open pores, e.g. for coated particles (core-shell particles), multiconstituent particles or solid particles with occluded voids (i.e. closed pores). This facilitates the experimental determination of the relevant particle density within the framework of sedimentation (refer to ISO 18747-1 and ISO 18747-2). In contrast, the apparent particle density differs from the buoyant density in case of open pores, for which the former needs to be computed from the particle's density and the specific pore volume.

NOTE The apparent density of porous particles is a function of pore filling by air and liquid. It depends on material properties, such as wettability or employed dispersants, and can be affected by the dispersing procedure (e.g. degassing, pre-wetting). Gravitational sedimentation analysis of porous particles thus relies on the quality of SOPs for sample preparation.

Close-packed aggregates and agglomerates, which are sometimes treated as porous particles, are discussed in 6.3.6.

6.3.6 Handling of non-spherical particles and particle agglomerates

In contrast to the assumption behind Formula (8), the majority of particle systems that are characterised by analytical sedimentation consists of non-spherical and even agglomerated or aggregated particles. Moreover, particle shape and agglomerate structure are typically distributed quantities, which are unknown to the operator. For the sake of feasibility, one therefore ignores all specific effects of non-sphericity (e.g. spatial alignment, particle rotation or lateral drift) and computes an equivalent diameter, the Stokes diameter, with Formula (9). This calculation uses the buoyant density of the particles and yields size values, which are smaller than, e.g. the hydrodynamic or volume equivalent diameters. For close-packed agglomerates, which are typically isometric and with uniform porosity, the buoyant density can be replaced by the apparent density, which refers to the constituent particles and the stagnant liquid in the voids. In this case, the

calculated size is a hydrodynamic equivalent diameter. For fractal-like agglomerates, with size-dependent, rather high porosity, this approach fails and only buoyant density should be employed.

7 Performing size analyses

7.1 General

The granulometric characterisation of particle systems comprises several steps, which all affect the outcome of the analysis. Hence, they need to be thoroughly planned and organised in advance. A starting point for each analysis is the definition of its objectives, which specify the relevant state of dispersion, the target measurands and their acceptable uncertainty. Target measurands in the context of sedimentation analysis can refer to the distribution of sedimentation velocity or the one of Stokes diameter; they can consist of selected distribution parameters (e.g. median, arithmetic mean or modal sizes) and they are specified with regard to the type of quantity. In addition, the analysts need to identify all data that ensure an adequate analysis of measurement, such as material properties. After having finished all pre-considerations, the granulometric analysis can start; it typically includes:

— sampling (7.2),

— primary sample preparation that yields a stock dispersion with a defined granulometric state (7.3),

— secondary sample preparation for feeding the instrument (7.4),

— instrument preparation (7.5),

— measurement (7.6),

— data analysis (7.7), and

— reporting (7.8).

The quality of an analysis depends on whether all of these steps are conducted in an adequate and careful manner. In addition, the quality is influenced by sample properties (e.g. polydispersity, particle concentration and density contrast), instrumentation (e.g. type of sedimentation technique and corresponding details, such as the wavelength of radiation) and measurement conditions (e.g. temperature, temporal resolution).

7.2 Sampling

The analysis starts with taking a representative sample from powder or liquid dispersion by using adequate techniques for sampling and sample splitting (see ISO 14488) and obeying constraints on sample mass or volume resulting from the demands of the measurement technique and necessary requirements on statistical uncertainty.

7.3 Dispersion process and primary sample preparation

Sample preparation constitutes a crucial step in granulometric analyses because it defines – or at least 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 of producing stock 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. For sedimentation analysis, it yields a master sample, which can be further divided to conduct multiple measurements with one instrument or comparative analyses with different granulometric techniques.

The primary sample preparation consists of various steps, which depend on the objectives of analysis and the type of the original material. Powders need to be suspended into an appropriate liquid (continuous phase) at first and then dispersed in it, which includes both distributive and disruptive processes (see ISO/TS 22107). The process of suspending can be supported by wetting agents and the liquid can contain dispersing agents,

which help to maintain colloidal stability. The liquid should primarily ensure the chemical stability of the dispersed phase (i.e. neither dissolution, nor chemical reaction) and of course its sedimentation (i.e. the density contrast must not vanish). In addition, the liquid should behave indifferent to the measurement cell. Reference [56] lists liquids and dispersing agents, which have proved successful for a couple of solid materials.

If the original material is a liquid dispersion, the original continuous phase (dispersion medium) is usually adhered to, although its replacement by a different solvent is in principle possible. In some situations, it can be helpful or necessary to adjust the density contrast by adding solutes to the original continuous phase.

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

In conclusion, a reproducible sample preparation for sedimentation analysis shall specify:

— continuous phase and possible additives (substances and concentration),

— particle concentration,

— technique(s) employed for dispersing the particles,

— if applicable, settings that correlate with the local stress intensity (e.g. rotational speed for given geometry or power densities),

— energy density (e.g. as determined by calorimetric analyses or calculated from pressure drop and flow rate),

— further conditions of the dispersion process (e.g. temperature, cooling systems), and

— if necessary relevant data on the vessel (beaker) containing the sample during dispersion (e.g. for indirect ultrasonication with ultrasonic baths or inverted up-horns).

7.4 Secondary sample preparation (sample conditioning)

The master samples of defined state of dispersion, which were produced at the primary sample preparation, 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

— sample splitting or aliquot production,

— dilution,

— adjustment of viscosity or density, and

— 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).

For sample splitting, refer to ISO 14488.

The most typical task is the adjustment of particle concentration via dilution, notably for avoiding mutual sedimentation hindrance and for adapting to the linear range of sensing techniques.

Adjustment of the continuous phase's viscosity and density can be meaningful for the analysis of heterogeneous dispersions with multiple dispersed phases.

7.5 Instrument preparation

Before starting an analysis, the instrument needs to be set ready for operation. The necessary procedures depend strongly on sedimentation technique and instrumentation; corresponding recommendations and instructions of the instrument producer should be obeyed. 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. Optimum measurement conditions depend on both, instrumentation and sample, for which reason their determination can require preliminary experiments.

In a broader sense, instrument preparation also includes the regular performance qualification (see 8.3) and fulfilment of quality rules of the corresponding organisation have to be obeyed. For advice, see the manual of the supplier.

7.6 Measurement

As mentioned in 5.2, gravitational sedimentation analysis should be and is most commonly performed in the HSM. Consequently, the measurements shall comply with the following, general scheme.

a) Distribute the particles homogeneously in the thermally equilibrated sample.

b) Stop homogenisation and immediately start measurement.

c) Observe the classification of the particle system under gravity in accordance with the principles of the respective sedimentation technique.

These steps can be completely or partly controlled by the instrument software, but they can be also left to the full responsibility of the operator. A reliable measurement requires:

— a homogeneous, mixing state right at the start of the observed sedimentation state;

— an undisturbed, purely sedimentational motion of the individual particles;

— an undisturbed measurement of sediment growth or change in concentration of dispersed particles (see 5.1);

— an observation and continuous recording of sample temperature during the measurement.

Failing these requirements leads to measurement errors, which are explained in detail in 8.4.

Regarding the current state-of-the-art instrumentation for gravitational sedimentation techniques, the temperature, measurement date and time as well as baseline values of the sensor system are favourably recorded and saved together with the measurement data of the separation by the instrument software. It is recommended to perform measurements of six samples and determine the arithmetic mean and standard deviation. Under routine conditions, three measurements are considered acceptable if the standard deviation for the average or median distribution parameters is less than 5 % for sedimentation velocity or less than 2,5 % for particle size. 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: should not change with time (e.g. due to evaporation) and correctly detected (if applicable);

— initial and final signals: signals can, for example, refer to the position interface between sediment and dispersion, the accumulated mass of the sediment or the attenuation of a radiation in the dispersion phase; usually the plausibility for the start of the measurement (zero deposition) and the finished sedimentation process (zero concentration) can be tested; additionally, requirements can be imposed on the range of signal values in order to ensure a linear instrument response;

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

— the shape of time curves or concentration profiles: time curves of local concentration, sediment mass, sediment height or amount 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.

7.7 Data analysis

Gravitational sedimentation techniques generally monitor the sedimentation-induced phase separation in an initially homogeneous liquid dispersion by measuring indicative properties of the dispersion phase or the deposited particle layer, i.e. the sediment or cream layer. Correspondingly, each data set of the measurement comprises at least three parameters: time elapsed after having stopped mixing, position of the measurement zone and value of the observed quantity (e.g. sediment mass or X-ray attenuation). The analysis of these data can be considered as a tiered process:

a) calculation of sedimentation velocities: from time and position of the data sets based on the 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: from the sedimentation velocity; typically, by assuming spherical particles (i.e. Stokes diameters), Newtonian liquid, creeping flow condition and absence of concentration effects; this transformation requires knowledge of the dynamic viscosity (η_c), density contrast ($\Delta\rho$) and gravitational acceleration (see 6.2.1);

c) computation of the distribution function with respect to the intrinsic type of quantity: from the observed quantity based on Formulae (10) and (11) (integral techniques) or Formulae (14) and (16) (incremental techniques); 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 Formulae (18) and (19)]; this computation frequently requires further model parameters (e.g. wavelength of radiation, refractive index, see 6.2.2.6).

Hence, the distribution of sedimentation velocity (weighted by the intrinsic type of quantity) 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. Nowadays, users find many required parameters in databases of the instrument software. In addition, there are several books with tabulated values of material properties (e.g References [58] and [59]). Last but not least, parameters like particle density, liquid density, liquid viscosity or refractive index can be measured by means of established and standardised techniques (e.g. ISO 18747-1, ISO 18747-2, ISO 15212-1, ISO 2555, ISO 3219-1, ISO 3219-2, ISO 280).

The data analysis also includes a calculation of the different measures of uncertainty as described in 8.5.

7.8 Reporting

Documentation of all steps and results is indispensable for a good laboratory practice. Measurement reports shall

— allow a reproduction of the analysis,

— visually emphasize the most important results, and

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

The document should address the following points, while referring to ISO/IEC 17025:

a) test report title;

b) file name of measurement/report;

c) name and contact information of the customer;

d) name and address of testing laboratory;

e) 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) standard applied for testing and any other operation not specified in this document or other applied parts of the ISO 13317 series which can influence the result;

k) instrument type and identifier as well as software version used;

l) sampling place and conditions (if applicable);

m) sample preparation:

— dispersion medium and/or dilutant: composition (solvent as well as wetting and dispersing agents) and relevant properties (density, viscosity, refractive index),

— dispersion and/or homogenisation process and instrumentation,

— condition [e.g. temperature, energy, time, volume, (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; indication of the type of quantity, e.g. weighted by extinction, X-ray attenuation, intensity, volume, mass, 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 have to be indicated for the lowest concentration or the value extrapolated to infinite dilution;

q) principle of used algorithms (including references) for calculation of the distribution function;

r) conditions of measurement:

— particle concentration, if known,

— sedimentation time,

— temperature of sample during measurement,

— measurement cells and sample volume;

s) date of report;

t) name, position of the person releasing the report;

u) any deviations from the procedure;

v) any unusual features observed.

8 System qualification and quality control

8.1 General remarks

The measurement of the particle velocity by means of sedimentation methods is based on first principles and does not require calibration by the user with a RM of specified velocity or size. Obtained sedimentation velocity can be transformed into particle size according to Formula (9) by relying on the input quantities gravitational acceleration, g, density contrast, $\Delta\rho$, and liquid viscosity, η_c.

However, measured values of particle velocity deviate from the true value due to errors that are related to sample preparation (see 7.2 to 7.4), instrument design and status quo, measurement procedure, operator skill and environment conditions. The sources of uncertainty can be of a random or systematic nature (see Figure 6). Correspondingly, a distinguishment is made between precision and trueness when assessing the performance of a sedimentation method. Trueness can be estimated via the systematic deviations of measured size values from the true ones (e.g. known for CRM), whereas precision can be quantified from the variation among repeated measurements of a sufficiently stable QCM (i.e. RMs with proven homogeneity and stability, can be a CRM). Trueness and precision determine the accuracy of a method. Quantitative expressions of instrument performance characteristics (performance validation) are the measurement uncertainty estimate based on bias and standard deviation of measurement results according to Reference [60]. In some respect, it is the quantitative expression of measurement accuracy.

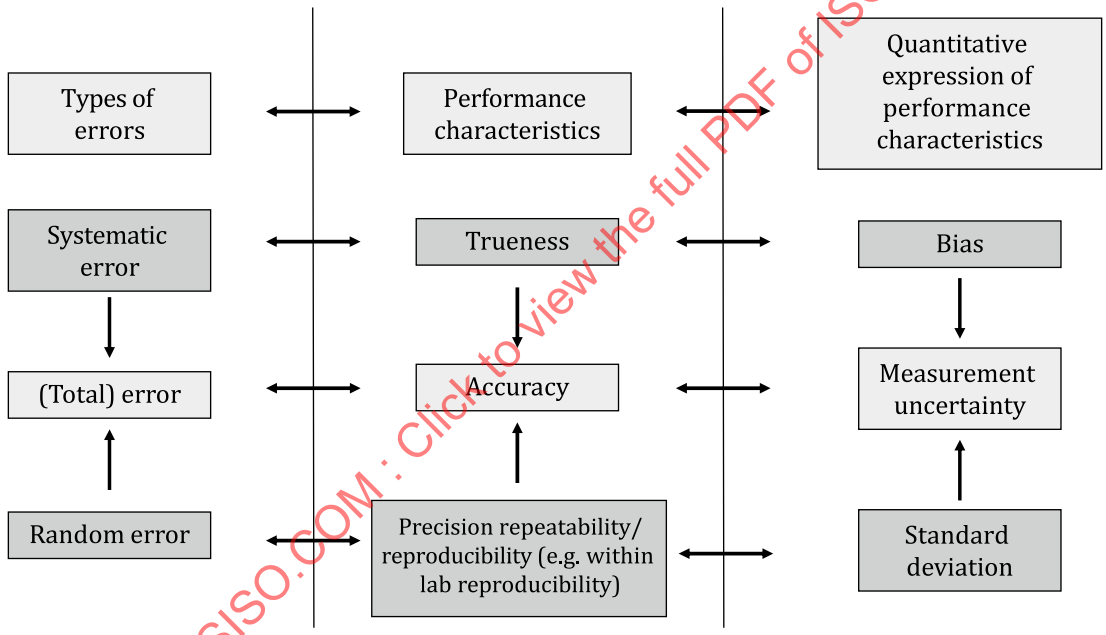


Figure 6 — Interrelations between error types, performance characteristics used to estimate them and expressions of quantitative estimates[60]

Trueness is a necessary qualifying attribute for a sedimentation measuring technique. Yet from a practical viewpoint of end-user, especially in the industry, reproducibility and robustness can be even more important. On the other hand, metrological traceability of analytical methods is often demanded by regulatory administration bodies.

8.2 Reference materials

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. When used for gravitational sedimentation, RMs should meet a few minimum requirements for a given instrumental configuration. These are the negligibility of

Brownian motion (see 6.3.3) and hydrodynamic wall effects (see Clause C.8) as well as the absecence of wall adhesion. In case of CRMs, the certificate should

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

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) list the uncertainty and coverage factor,

d) indicate the material properties used for data analysis (e.g. particle density),

e) reveal the type of sedimentation technique used in the certification process, and

f) specify the procedures of sample preparation.

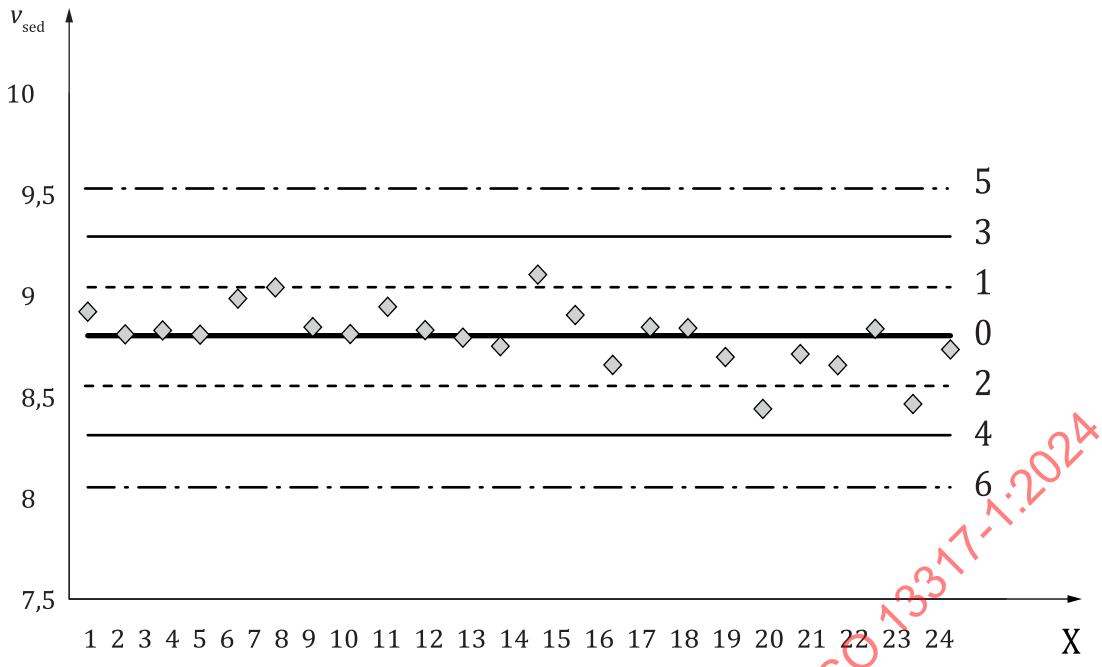
The comparison among different sedimentation techniques and the conversion of a measured distribution function to a different type of quantity can require additional material properties (e.g. the attenuation coefficient or refractive index (see ISO 13317-3 and ISO 13317-5) and be restricted to spherical 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 case of powder) and they shall preserve the state of dispersion during the time of use, i.e. no swelling, shrinking, dissolution, flocculation or agglomeration, see ISO 14887). Some RMs are available as ready-to-use suspensions, which only require a slight re-dispersion of deposited particles before being directly analysed. They avoid, for example, the risk of destabilisation by dilution or segregation due to sampling. If RMs are used to test the instrument performance for specific materials, they should match the expected size range and resemble the material properties (i.e. particle density, if relevant, also refractive index and X-ray absorbance).

8.3 Performance qualification

Performance qualification of a sedimentation method shall be implemented on a regular basis and shall be performed in accordance to the manufacturer's recommendations. Time intervals should reflect quality requirements of the organisation, where the sedimentation method is employed.

NOTE National regulations can apply.



Key

X	consecutive performance measurement identifier	3	upper warning
v_{sed}	sedimentation velocity, in µm/min	4	lower warning
0	arithmetic mean value	5	upper control limit
1	mean value + standard deviation	6	lower control limit
2	mean value – standard deviation		

Figure 7 — Shewhart control chart of the performance velocity data accessed periodically for a quality control material (nominal velocity 8,84 µm/min)

Beside a general careful visual inspection, performance qualification should cover the full range of equipment capabilities like, the positioning of the sedimentation cell, constancy of distance between sensor system and cell bottom, precision of time clock and temperature measurement as well as the sensor system to quantify the concentration changes during sedimentation. Experimentally, CRMs or QCMs can be employed to verify different aspects of performance test. Qualification shall be performed at a sufficiently high frequency – at least once a year – and after each major change of the instrument (such as repairs, change of location) or in case of doubt about the validity of measurement results. The results shall be completely documented. It is recommended to graphically present the performance data in time order (e.g. Shewhart control chart, see Figure 7), as to facilitate an identification of any trend in the instrument performance.

Tests of performance qualification can also serve for an estimation of the intralaboratory reproducibility. This is possible, as they typically involve independent sample preparations and a variation of "environmental" conditions (e.g. room temperature). However, the determination of intralaboratory reproducibility requires a deliberate random variation of all laboratory-specific factors that can influence the analytical results (e.g. operators, batches of dispersants).

Moreover, qualification tests with CRMs allow 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 (see Reference [61] and Clause D.4).

Performance qualification is conducted by the users of an analytical instrument. In contrast, installation and operational qualification is part of the manufacturer's responsibility.

8.4 Sources of measurement uncertainty

The general requirements for accurate sedimentation velocity measurements by any method are: constant temperature of the measurement cell (temporal variation should be at least less than 1,0 K) and even lower horizontal and vertical temperature gradients, perfect vertical alignment of the sedimentation cell and an absence of vibration for the equipment. The calculation of particle size distribution further requires compliance with "standard theory" (see 6.2.1). Under these conditions, systematic deviations should be at a low level.

Beyond issues of sample preparation, one can identify different sources of systematic and random errors, which lead to a loss of accuracy and an increase of measurement uncertainty as quantitative expression of known method performance characteristics are the following.

— Technical uncertainties to determine sedimentation time and sedimentation distance: These are the basic measurands for sedimentation velocity and conversion into particle size determination [see Formula (3)]. In this context, the determination of meniscus position, if necessary, is an important factor for measurement uncertainty (see 8.5).

— Non-homogeneous mixing state at the start of sedimentation: There are different strategies to achieve homogeneity (e.g. stirring, manual turning of the cell, constant flow just before starting the measurement); however, there can be a finite time lag between mixing and the start of observation, which affects the upper limit of the measurement range.

— Convective flow: It can be due to temperature gradients, non-vertical alignment of the cell or vibrations from environment. The occurrence of convective flow can be avoided by controlling the temperature of the sample, blocking thermal radiation (e.g. sunlight), ensuring a perfect vertical alignment (refer to advice in manuals), placing the instrument on a stable, vibration-damped ground.

— Signal noise: Signal noise refers to the quantification of size fractions and can be relevant for integral as well as incremental sedimentation techniques. It hampers the differentiation of the original signal curves (time curves or vertical profiles), defines the limits of detection and thus affects the minimum and maximum detectable particle size.

— Adhesion of particles at walls: Particle adhering at the walls of a measurement cell affect the quantification of dispersed particles by sensing techniques based on radiation and thus systematically distort the distribution function; the occurrence of this effect can be checked via visual inspection after the sedimentation process. Wall adhesion depends on the properties of the particles, the wall material and the dispersion medium; it can be, for example, influenced via solvent properties (e.g. pH) and dispersing agents.

— Air bubbles at walls and tubing: These present a general or sudden disturbance of creep flow.

— Air bubbles adhering to particles: The buoyant particle density is reduced, there is a broadening of size distribution, especially in direction of fine particles.

— Disturbance induced by sampling in sedimentation zone (pipette technique): Such disturbances are minimised by keeping the withdrawn volume small and the flow rate low. In addition, the sampling procedure should be standardised (see ISO 13317-2).

Uncertainty sources are related to specific sedimentation techniques.

8.5 Accuracy and measurement of uncertainty of particle velocity

Accuracy of the primary measurand – sedimentation velocity – depends predominately on the measurement precision of sedimentation time, t_{sed}, and sedimentation distance, h_{sed}, according to Formula (3). These quantities are metrologically straightforward to determine and can be very truly and precisely experimentally obtained. In addition, no calibration and no assumptions or simulations are necessary.

Absolute time uncertainties are, generally today, below 10 ms. Relative uncertainties are, therefore, even for very short sedimentation times of about 60 s, below 0,1 %. Uncertainty regarding the sedimentation distance, h_{sed}, depends on the technical realisation of the sedimentation method, the implemented distance measurement technique and even data analysis. Its relevance depends on the absolute value of h_{sed} and on

the vertical breadth of the measuring zone (see Annex E). The former varies from tens of millimetres (i.e. for photosedimentometer, see ISO 13317-5) to tens of centimetres (i.e. for pipette techniques, see ISO 13317-2; for sedimentation tubes, see ISO 8486-2; or for detector tray, see ISO 13317-4). The latter covers a range from a few millimetres (pipette method) down to a few micrometres (photo- and X-ray sedimentometer). However, the most critical contribution to the uncertainty in h_{sed} commonly results from the lack to exactly define the spatial and temporal start of the sedimentation experiment.

The ideal start position of phase separation can be the bottom of vessel (for negative density contrast) or the upper interface of the dispersion sample (positive density contrast). This position is associated with the instant, at which the homogeneous mixing ends and phase separation starts. Yet in practice, a time gap can be encountered between mixing and starting the clock, which means that at the "official" time zero, phase separation has already started, which is equivalent with a shift of the start position. In addition, the exact position of air-liquid interfaces (menisci) is difficult to determine due to the curvature of the liquid surface. In the case of creaming, a deviation can result, if the cell bottom is not perfectly flat. Uncertainty in start position has a relatively high impact on the uncertainty in sedimentation velocity and particle size, if the sedimentation distance is short and the process is monitored at just one position, for example, for balance techniques or fixed-sensor techniques [see Figure 2 a) and b), respectively].

As described in 8.4, numerous circumstances can cause a variation of measured sedimentation velocity. A general roadmap to quantify it can consist in, firstly, converting all (or most) uncertainty components into random variables by multiple measurements over a longer time span (intermediate precision) or by interlaboratory comparison. And secondly, in estimating a combined uncertainty of velocity based on repeatability, quantitative comparison of analysing CRMs or interlaboratory test results as well as between different devices and laboratories.

This combined uncertainty of the sedimentation velocity can be used to estimate the uncertainty of measured particle size, for which purpose the uncertainty of the transformation from velocity to particle size needs to be known (see 8.7).

Random uncertainties can be experimentally estimated by repeating n-times ($n \geq 6$) the velocity determination of a given prepared stable sample under otherwise same measurement conditions within a short time interval of experiments. The individual results v_j ($j = 1...n$) yield an arithmetic mean velocity, v_{mean}, and a standard deviation, s_v, under this measurement conditions. The latter constitutes an estimate of the repeatability uncertainty, u_{rep}, [see Formula (25)] also called short-term precision (see Annex D). Systematic errors shall be separately estimated.

$$u_{rep} = s_v = \sqrt{\frac{1}{n-1}\sum_{j=1}^{n}\left(v_j - v_{mean}\right)^2} \tag{25}$$

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 variation of the measurand obtained under less defined conditions (eg. different operators, larger time differences between measurements, different batches of chemicals) but the same methodology.

NT TR 537 and 8.6 proposes to estimate the reproducibility – more specifically, the intralaboratory reproducibility of measurement method – by performing experiments with stable QCMs over a longer time. The individual results v_k ($k = 1...m$) yield an arithmetic mean velocity of all determinations for a given QCM (v_{mean}) and a standard deviation (s_v), which equals the standard uncertainty or reproducibility uncertainty u_{Rw} [see Formula (26)]. This deviation is also often called intermediate precision or long-term precision. Data obtained in the course of performance qualification can be used to estimate reproducibility uncertainty u_{Rw}.

$$u_{Rw} = s_v = \sqrt{\frac{1}{m-1}\sum_{k=1}^{m}\left(v_k - v_{mean}\right)^2} \tag{26}$$

Due to the long period (6 months to one year), this performance test also covers unintended 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. Yet, when assessing the performance characteristics of sedimentation techniques, it is tested

at stable aliquots of an identical stable master sample, which are ready-to-use or solely require secondary sample preparation (see 7.4) by each laboratory.

A so-called interlaboratory test combines intralaboratory and intra-instrument variation of a given sedimentation method. The mean particle velocity is calculated from all reported velocities and the standard uncertainty estimated in analogy to Formula (26).

8.6 Combined and expanded uncertainty of velocity measurement

The basic uncertainty estimation is given in detail in ISO/IEC Guide 98-3. Several documents build on the GUM with the aim to simplify the calculations by not quantifying all uncertainty components separately. This is achieved by using long-term reproducibility measurements to estimate combined uncertainties (see Reference [62] and ISO 21748). In this subclause, the approach developed by NT TR 537 is used, but other approaches like in ISO 21748 are also valid.

Figure 6 depicts that measurements are affected by a certain error. The uncertainty of a measurement indicates the possible extent of the measurement error. It quantifies an interval associated with the measured value that characterises the deviation from the true value and where the true value lies with some high probability (see Figure D.1). The measurement difference between the true and the mean measured value is the measurement error. Uncertainty comprises, in general, many components. Some can be evaluated from the statistical distribution of the results of series of measurements [experimental (standard) uncertainty, often called standard deviation] as described in 8.5. The other components (often called systematic effects), which also can be characterised by standard uncertainties, are evaluated from assumed probability distributions based on experience or other information.

According to NT TR 537, the full uncertainty budget can be experimentally determined based on the concept of reproducibility (intermediate precision) measurement [see Formula (26)] and the bias quantification of a specific sedimentation method. Bias can be estimated from repeated velocity determination of one or better several CRM samples. The number of measurements performed on the CRM needs to be sufficiently high in order to ensure that the observed bias is not dominated by random uncertainties, u_{rep}. Sources of bias uncertainty, u_b, are the average root mean square bias of reproducibility results (b_{RMS}) obtained for the CRMs and the average uncertainty of the reference values, u_{ref}:

$$u_b = \sqrt{{b_{\mathrm{RMS}}}^2 + u_{\mathrm{ref}}^2} \tag{27}$$

where b_{RMS} is the average bias of the different CRMs and is calculated as follows:

$$b_{\mathrm{RMS}} = \sqrt{\frac{1}{m}\sum_{i}^{m} b_i^2} \tag{28}$$

$$b_i = v_{\mathrm{lab},i} - v_{\mathrm{ref},i} \tag{29}$$

where

b_i is the bias for the i-th bias determination with i-th CRM;

m is the number of bias determinations carried out for different CRMs;

$v_{\mathrm{lab},i}$ is the measured value of v for the i-th bias determination; it is the average of all determinations for a given CRM;

$v_{\mathrm{ref},i}$ is the reference value of v for the i-th bias determination.

The average standard uncertainty of the reference values of the reference samples, u_{ref}, is found as follows:

$$u_{\mathrm{ref}} = \sqrt{\frac{1}{m}\sum_{i}^{m} u_{\mathrm{ref},i}^{2}} \tag{30}$$

where

m is the number of bias determinations carried out for different CRMs;

$u_{\mathrm{ref},i}$ is the standard uncertainty of the i-th reference value.

In the context of a performance evaluation with respect to sedimentation velocity, one should use one CRM with certified velocity values in the centre of the specified velocity range and another two CRMs with average sedimentation velocities that are twice as high as the lower velocity limit and about half the upper velocity limit, respectively. These velocity recommendations have to be evaluated in relation to the real-world particle properties, as detectable velocity ranges can be smaller under practical circumstances. For instance, the working range of photosedimentometers depends on the optical properties of the particles.

The combined standard measurement uncertainty taking into account the reproducibility determination and the possible bias is given in Formula (31).

$$u_{\mathrm{c}} = \sqrt{u_{\mathrm{Rw}}^{2} + u_{b}^{2}} \tag{31}$$

The calculated combined uncertainty u_{c} spans a range around the arithmetic mean, which covers 68,3 % of all measurement results, if normally distributed (see Figure D.1). To increase the probability, a numerical factor k (coverage factor) as multiplier of u_{c} is used to estimate the expanded combined uncertainty U_{c} [see Formula (32)].

$$U_{\mathrm{c}} = k \cdot u_{\mathrm{c}} = k \cdot \sqrt{u_{\mathrm{Rw}}^{2} + u_{b}^{2}} \tag{32}$$

For the sedimentation velocity, usually a coverage factor k = 2 can be proposed (probability 95 %, normal distribution) to calculate the expanded uncertainty U_{c}.

The expanded uncertainty describes the half-width of the uncertainty range of a measured sedimentation velocity, $v_{\mathrm{sed,meas}}$. The true sedimentation velocity v_{sed} lies to 95 % probability within the range of $v_{\mathrm{sed,meas}} \cdot (1 \pm U_{\mathrm{rel,c}})$ (see Figure D.1). If the number of performed measurements is below 30 then a Student's t-distribution should be assumed resulting in a reduction of the probability (see D.4.5). If values of expanded combined uncertainty are communicated, coverage factor and assumed distribution should be indicated.

If corresponding CRM samples are not available, inter-laboratory comparison measurements can be used to estimate the combined uncertainty. A practicable way is to calculate the uncertainty of the mean (standard deviation) of all participants of the interlaboratory test. In general, this approach leads to an overestimation of u_b.

The combined sedimentation velocity uncertainty summarises the different relative standard uncertainties and is an expression for the performance characteristic of the employed sedimentation method. It can also serve as a first step in quantifying the uncertainty with respect to particle size (stokes diameter).

8.7 Combined and expanded uncertainty of particle size (Stokes diameter)

The combined and expanded uncertainty of particle size values can be computed in analogy to the procedure described in 8.6. In other words, one has to conduct performance tests over a sufficiently long period in order to specify the reproducibility and the bias of particle size measurements. These tests employ CRMs

with certified values of the Stokes diameter. Formulae (27) to (32) can be used as before with u_{Rw} referring to the variation in measured particle size Formula (29) being replaced by Formula (33):

$$b_i = x_{lab,i} - x_{ref,i} \tag{33}$$

where

$x_{lab,i}$ is the measured size value for the i-th bias determination; it is the average of all determinations for a given CRM;

$x_{ref,i}$ is the reference size value of v for the i-th bias determination.

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 (9). Provided that the experimental conditions ensure the applicability of this formula, the uncertainty in transforming the measurand can be attributed to the uncertainty of the input quantities, which are the density contrast, the viscosity of continuous phase and the gravitational acceleration. Their impact can be consolidated into a transformation factor C [see Formula (34)]:

$$C = \sqrt{\frac{18\eta_c}{g(\rho_p - \rho_c)}} \text{ with } x_{Stokes} = C \cdot \sqrt{v_{sed}} \tag{34}$$

The relative uncertainty of the multiplication factor, C, reads:

$$\frac{u(C)}{C} = \sqrt{\frac{u(\eta_c)^2}{4\eta_c^2} + \frac{u(g)^2}{4g^2} + \frac{u(\Delta\rho)^2}{4\Delta\rho^2}} \tag{35}$$

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 $u_c(v_{sed})$ [see Formula (31)]. The following formula for the relative combined uncertainty of the Stokes diameter can be derived:

$$\frac{u_c(x_{Stokes})}{x_{Stokes}} = \sqrt{\frac{u(C)^2}{C^2} + \frac{u_c(v_{sed})^2}{4v_{sed}^2}} \tag{36}$$

By multiplying the combined uncertainty, u_c, by the coverage factor, k, the expanded combined size uncertainty is obtained [see Formula (35)]:

$$U_c(x_{Stokes}) = k \cdot u_c(x_{Stokes}) \tag{37}$$

Annex D exemplarily shows the application of the uncertainty calculations described in 8.5 to 8.7 for real measurement data obtained for silica particles analysed by means of photosedimentation.

Strictly speaking, the full uncertainty budget is underestimated by Formula (37) because sampling and sample preparation of real-world materials can affect the analytical results the more strongly than the learning experienced in the experiments with QCM or CRM.

Annex A
(informative)

List of gravitational sedimentation-based particle sizing techniques

	References	Detected quantity	Detection method	Detection mode(s)	Sample supply	Quantification	Intrinsic result	Special features
Pipette technique	ISO 13317-2, ISO 11277, ISO 17892-4, ASTM F1632-03, References [63], [64], [65], [66]	particle mass concentration at fixed position	incremental	fixed position	homogeneous start	gravimetric (on dried samples)	$Q_3(x_{Stokes})$	—
X-ray sedimentometer	ISO 13317-3, ASTM B761-17, ASTM C958-92, ASTM C1730-17, References [67], [68]	X-ray extinction at defined position(s)	incremental	fixed position, scanning position, complete profile	homogeneous start	X-ray extinction	$Q_3(x_{Stokes})$	selection of spectral range
Photo-sedimentometer	ISO 13317-5, GB/T 6524, ANSI B74.20, References [43], [50], [69]	optical particle concentration at defined position(s)	incremental	fixed position, scanning position, complete profile	homogeneous start	photometric (extinction), nephelometric (scattering)	$Q_{ext}(x_{Stokes})$ $Q_{int}(x_{Stokes})$	multiple wavelengths
Sedimentation balance	ISO 13317-4, References [53], [54], [70], [71]	mass of sediment	integral	fixed position	homogeneous start	gravimetric	$Q_3(x_{Stokes})$	—
Sedimentation tube	ISO 6344-3, ISO 8486-2, FEPA 42-2, FEPA 43-2	volume or height of sediment	integral	fixed position	line-start	visual, photometric, via beta radiation	$Q_3(x_{Stokes})$	—
Manometric sedimentation	References [46], [72], [73]	density of suspension phase	integral	fixed position	homogeneous start	manometric	$Q_3(x_{Stokes})$	—
Aerometric analysis	ISO 17892-4, ISO 11277, ASTM D7928-17, References [47], [48], [74]	density of suspension phase	integral or incremental	—	homogeneous start	position(s) of a hydrometer or several micro-hydrometers	$Q_3(x_{Stokes})$	—

Annex B
(informative)

Remarks on particle density

B.1 Particle density and particle size in sedimentation analysis

The transformation of sedimentation velocity into a particle size (Stokes diameter) according to Formula (9) requires solid knowledge on the density contrast between the particle and continuous phase. In general, particle density is a well-defined quantity, computed as a ratio of particle mass to particle volume. However, in practical applications there can be some confusion when particles are heterogeneous; that is, they are composed of different internal and external phases. This confusion mainly results from the question, which volume should be attributed to the particle.

From the perspective of an observer of sedimentation experiments, the question has at first a simple answer. The complete migrating entity is considered as a particle. This entity has a sedimentation velocity (the measurand of analysis) and contributes to the observed quantity (e.g. sediment weight or light extinction). The density of this entity is a weighted average of all its constituents. This average is commonly called apparent particle density or effective particle density and can be calculated if according structural details are known – e.g. the thickness of a coating or the specific pore volume. Frequently, this density is identical to the buoyant density, which can be experimentally determined via sedimentation (refer to ISO 18747-1 and ISO 18747-2) or pycnometry (see ISO 787-10 and ISO 8130-2). However, some types of particulate materials need further considerations:

— porous particles: open pores, which are filled with continuous phase in sedimentation or pycnometry, do not contribute to buoyancy; yet pore liquid is stagnant during sedimentation and is thus part of the migrating entity;

— agglomerates and aggregates: interstitial voids are filled with the continuous phase and do not contribute to buoyancy; the void liquid is not necessarily stagnant; in addition, the specific void volume is frequently size-depending; for small numbers of constituent particles or fractal dimensions below 2, it is not meaningful to define a void volume;

— particles with, for example, adsorbed layers of surfactants, polyelectrolytes, polymers: these layers are added to the original material in order to tune product functionality, ensure wettability, dispersibility, stability during application or just during measurement; though moving with the migrating particle, they are commonly not considered being part of the particle; a solvate shell, especially in case of nanoparticles, has to be considered as well.

Table B.1 discusses examples of experimental practice with information on the buoyant density and the apparent particle density.

NOTE The buoyant density can be understood as the (hypothetical) density of a continuous phase for which the gravitational force acting on the immersed particle is counterbalanced by buoyancy. Whereas the apparent particle density is the mass-to-volume ratio for the migrating particle, including all entrapped stagnant liquid and gas.

B.2 Selected cases of particle structure with corresponding remarks on the buoyant density and the apparent particle density

Table B.1 — Selected cases of particle structure with corresponding remarks on the buoyant density and the apparent particle density

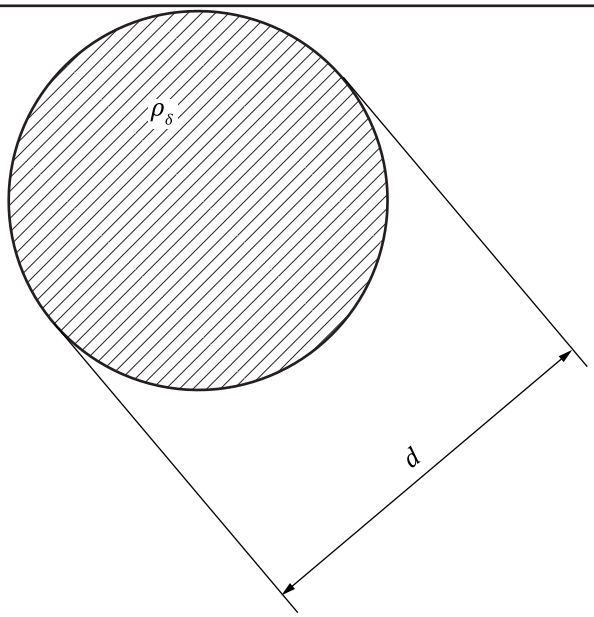
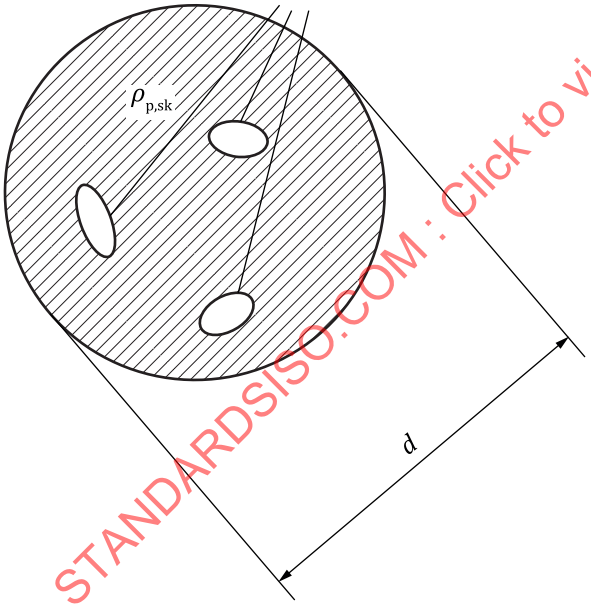
Configuration	Density and size
	Homogeneous particle without inclusions and pores buoyant density: $\rho_{p,buoy} = \rho_d$ apparent particle density: $\rho_{p,app} = \rho_d$ where ρ_d denotes the true density of the dispersed phase, which is also known as true particle density (see ISO 18747-1:2018, 3.4) size: $d^2 = x_{Stokes}^2 = \frac{18\eta_c v_{sed}}{g(\rho_d - \rho_c)}$
OV (ρ = 0) 	Particle with OVs buoyant density: $\rho_{p,buoy} = \rho_{p,sk} = (1-\varepsilon_{occl}) \cdot \rho_d$ apparent particle density: $\rho_{p,app} = \rho_{p,buoy}$ where $\rho_{p,sk}$ is the skeleton density, which is also known as skeletal density (see ASTM D3766) size: $d^2 = x_{Stokes}^2 = \frac{18\eta_c v_{sed}}{g(\rho_{p,sk} - \rho_c)}$
SOURCE: Reproduced with the permission of Frank Babick.	

Table B.1 *(continued)*

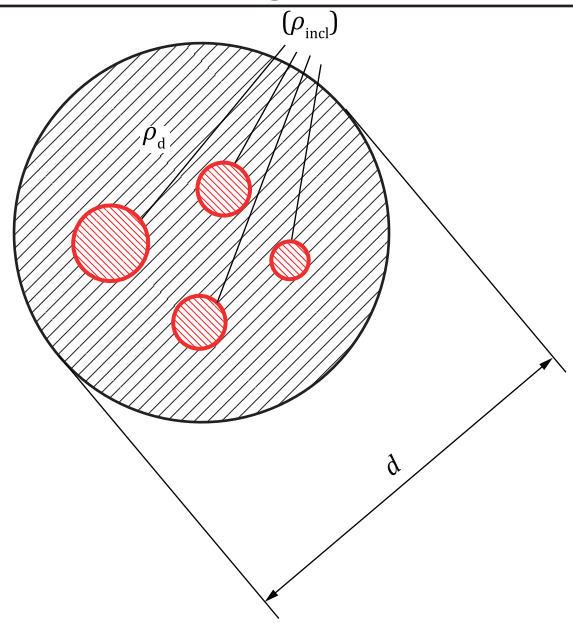
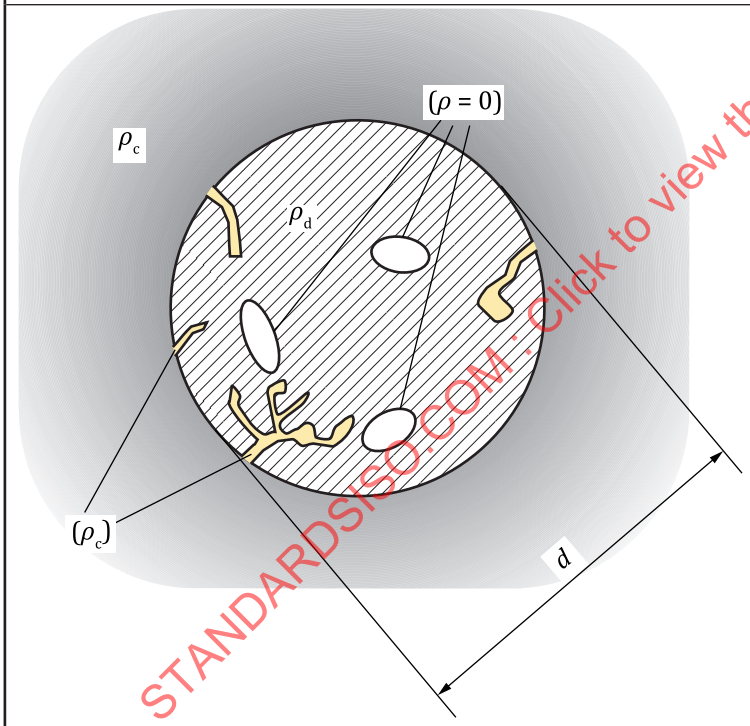
Configuration	Density and size
 EXAMPLE Droplets of a W/O/W-emulsion, debris particles from a composite material or coating.	Particle with particulate inclusions buoyant density: $\rho_{p,buoy} = (1-\varphi_{V,incl}) \cdot \rho_d + \varphi_{V,incl} \cdot \rho_{incl}$ apparent particle density: $\rho_{p,app} = \rho_{p,buoy}$ size: $d^2 = x_{Stokes}^2 = \frac{18\eta_c v_{sed}}{g(\rho_{p,bouy} - \rho_c)}$
	Particle with occluded voids and open, completely filled pores buoyant density: $\rho_{p,buoy} = \rho_{p,sk} = (1-\varepsilon_{occl}) \cdot \rho_d$ apparent particle density: $\rho_{p,app} = (1-\varepsilon_{tot}) \cdot \rho_d + \varepsilon_{open} \cdot \rho_c$ size: $d^2 = x_{Stokes}^2 = \frac{18\eta_c v_{sed}}{g(\rho_{p,app} - \rho_c)}$
SOURCE: Reproduced with the permission of Frank Babick.	

Table B.1 *(continued)*

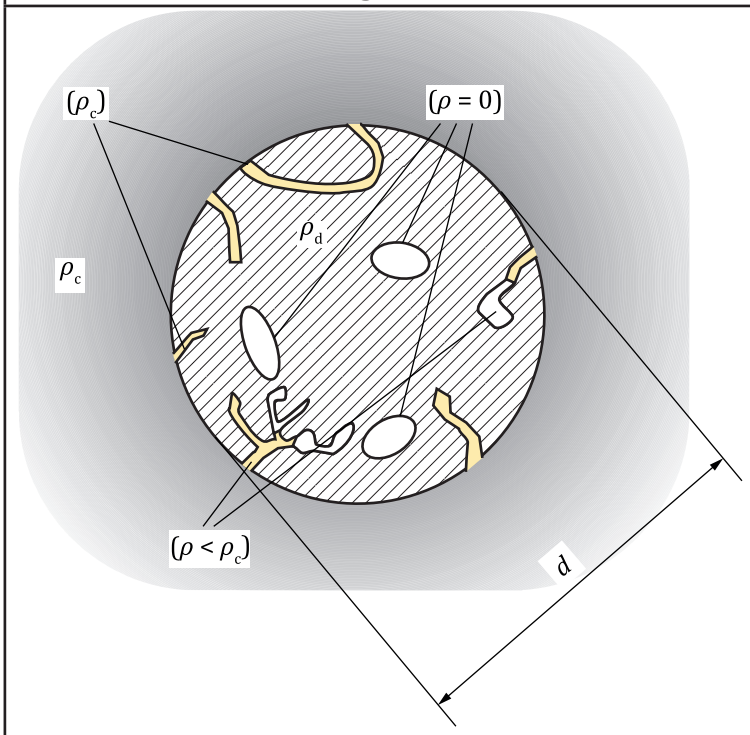
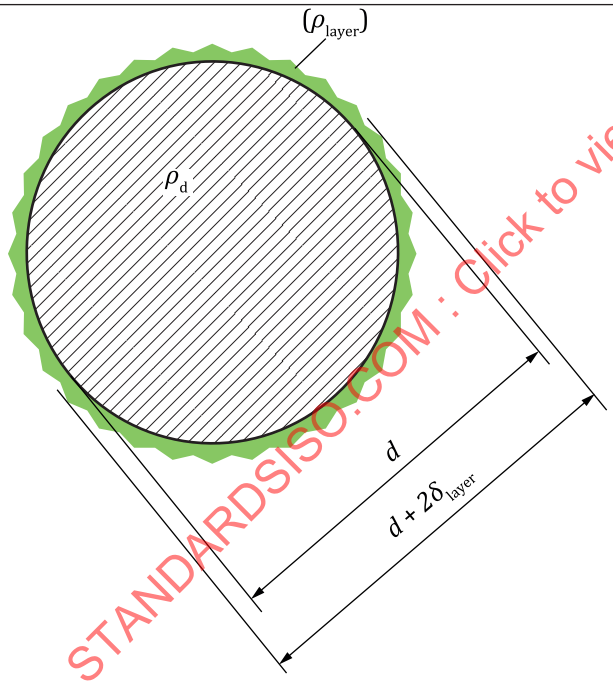
Configuration	Density and size
	Particle with occluded voids as well as open and partly filled pores buoyant density: $\rho_{p,buoy} = \left(1 - \varepsilon_{tot} + S \cdot \varepsilon_{open}\right) \cdot \rho_d$ where S is the volume fraction of liquid in the open pores apparent particle density: $\rho_{p,app} = (1 - \varepsilon_{total}) \cdot \rho_d + S \cdot \varepsilon_{open} \cdot \rho_c$ size: $d^2 = x_{Stokes}^2 = \frac{18\eta_c v_{sed}}{g\left(\rho_{p,app} - \rho_c\right)}$
	Homogeneous particle with an adsorbed layer buoyant density: $\rho_{p,buoy} = \left(1 + 2\frac{\delta_{layer}}{d}\right)^{-3} \cdot \left(\rho_d - \rho_{layer}\right) + \rho_{layer}$ apparent particle density: $\rho_{p,app} = \rho_{p,buoy}$ size: $\left(d + 2\delta_{layer}\right)^2 = \frac{18\eta_c v_{sed}}{g\left(\rho_{p,buoy} - \rho_c\right)}$ sedimentation only yields outer dimension, i.e. $d + 2\delta_{layer}$.
SOURCE: Reproduced with the permission of Frank Babick.	

Table B.1 *(continued)*

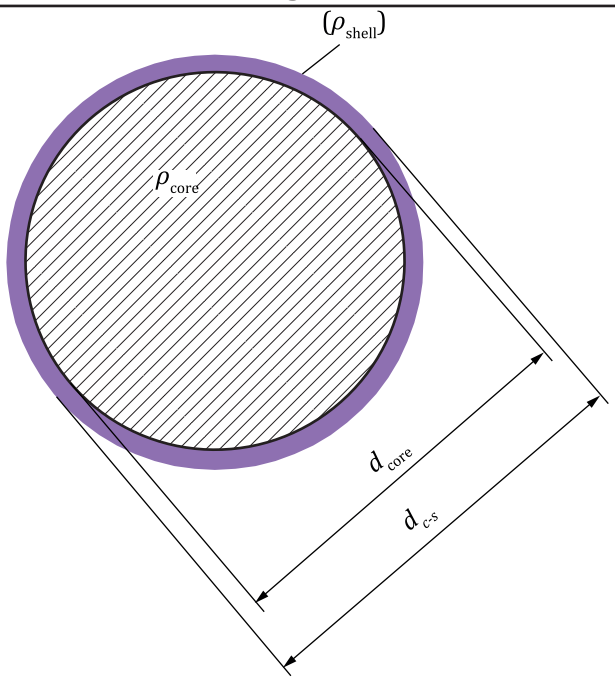
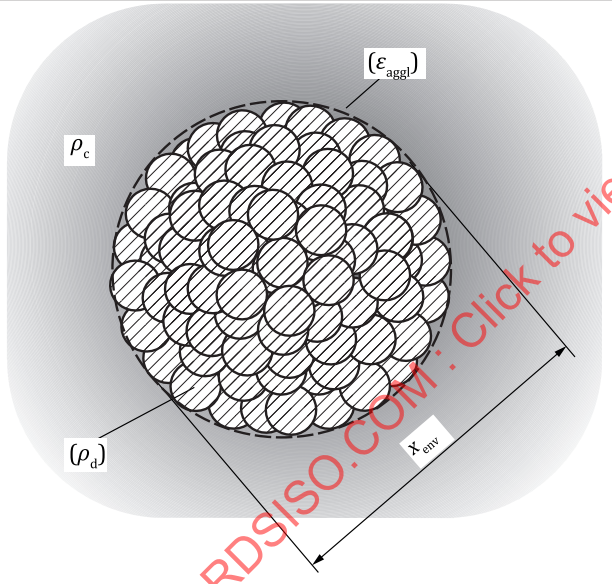
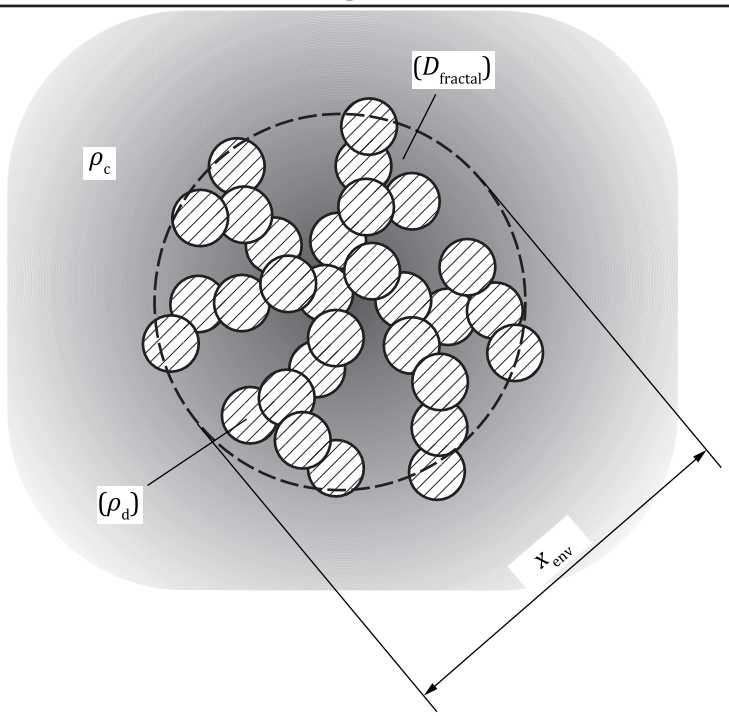
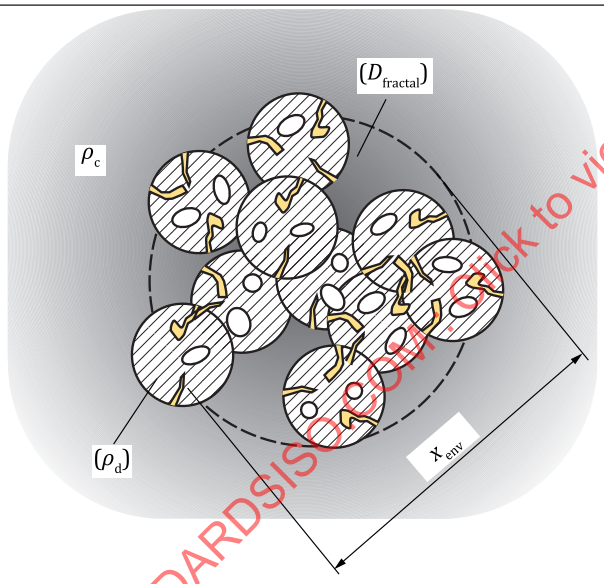
Configuration	Density and size
	Homogeneous particle with a fixed shell/coating buoyant density: $\rho_{p,buoy} = \left(1+2\frac{\delta_{shell}}{d_{core}}\right)^{-3} \cdot (\rho_d - \rho_{shell}) + \rho_{shell}$ apparent particle density: $\rho_{p,app} = \rho_{p,buoy}$ size: $d_{c\text{-}s}^2 = \frac{18\eta_c v_{sed}}{g(\rho_{p,buoy} - \rho_c)}$ sedimentation only yields outer dimension, i.e. $d_{c\text{-}s}$
	Close-packed agglomerate of homogeneous particles buoyant density: $\rho_{aggl,buoy} = \rho_d$ apparent agglomerate density: $\rho_{aggl,app} = (1-\varepsilon_{aggl}) \cdot \rho_d + \varepsilon_{aggl} \cdot \rho_c$ size: a) if ε_{aggl} is known, the approximate diameter of the convex hull can be calculated, which is very close to the hydrodynamic diameter: with: $x_{env}^2 \approx x_{hd}^2 \approx \frac{18\eta_c v_{sed}}{g(\rho_{aggl,app} - \rho_c)}$ b) typically, ε_{aggl} is not known, hence ρ_d is used: $x_{Stokes}^2 = \frac{18\eta_c v_{sed}}{g(\rho_d - \rho_c)} < x_{env}^2$
SOURCE: Reproduced with the permission of Frank Babick.	

Table B.1 *(continued)*

Configuration	Density and size
	Fractal-like agglomerate of homogeneous particles buoyant density: $\rho_{aggl,buoy} = \rho_d$ apparent agglomerate density: not meaningful, fractal aggregates defy any attempt to define and measure ε_{aggl} size: $x^2_{Stokes} = \frac{18\eta_c v_{sed}}{g(\rho_d - \rho_c)} < x^2_{hd} < x^2_{env}$
	Fractal-like agglomerate of porous particles buoyant density: $\rho_{aggl,buoy} = \rho_{p,sk}$ apparent agglomerate density: not meaningful, fractal aggregates defy any attempt to define and measure ε_{aggl} For porous constituents, size can be calculated based on: a) the skeleton density, $\rho_{p,sk}$: $x^2_{Stokes} = \frac{18\eta_c v_{sed}}{g(\rho_{p,sk} - \rho_c)}$, or b) the apparent density of the constituent particles, $\rho_{p,app}$: $\tilde{x}^2_{Stokes} = \frac{18\eta_c v_{sed}}{g(\rho_{p,app} - \rho_c)}$ NOTE The second approach requires knowledge of the specific pore volume of the constituent particles; in practice, one stays with the first approach.
SOURCE: Reproduced with the permission of Frank Babick.	

The buoyant density can be measured within the framework of sedimentation, for which reason it can be considered as the most appropriate particle density for computing the Stokes diameter. Only in case of particles with open porosity, we need to replace it by the apparent particle density.

Moreover, the buoyant density can be 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. Typically, there is a lack of relevant data (layer thickness and composition) as the structures of adsorbate layers depend on the environment.

Annex C
(informative)

Sedimentation beyond the validity of Stokes' law

C.1 Settling beyond creeping flow

Stokes' law of flow resistance [see Formula (C.1)] was derived for single spherical objects in an unconfined Newtonian fluid (see Clause C.8) under the condition of creeping flow. For particle sedimentation in quiescent liquids, the Stokes' law of flow resistance is:

$$F_D = 3\pi\eta_c x v_{sed} \text{ or } C_D \overset{!}{=} \frac{F_D}{\frac{1}{2}\rho_c v_{sed}^2} = \frac{24\cdot\eta_c}{\rho_c x v_{sed}} \quad \text{(C.1)}$$

where

C_D is the drag coefficient;

F_D is the drag force;

v_{sed} is the terminal sedimentation velocity;

x is the particle diameter;

η_c is the dynamic viscosity of the continuous phase;

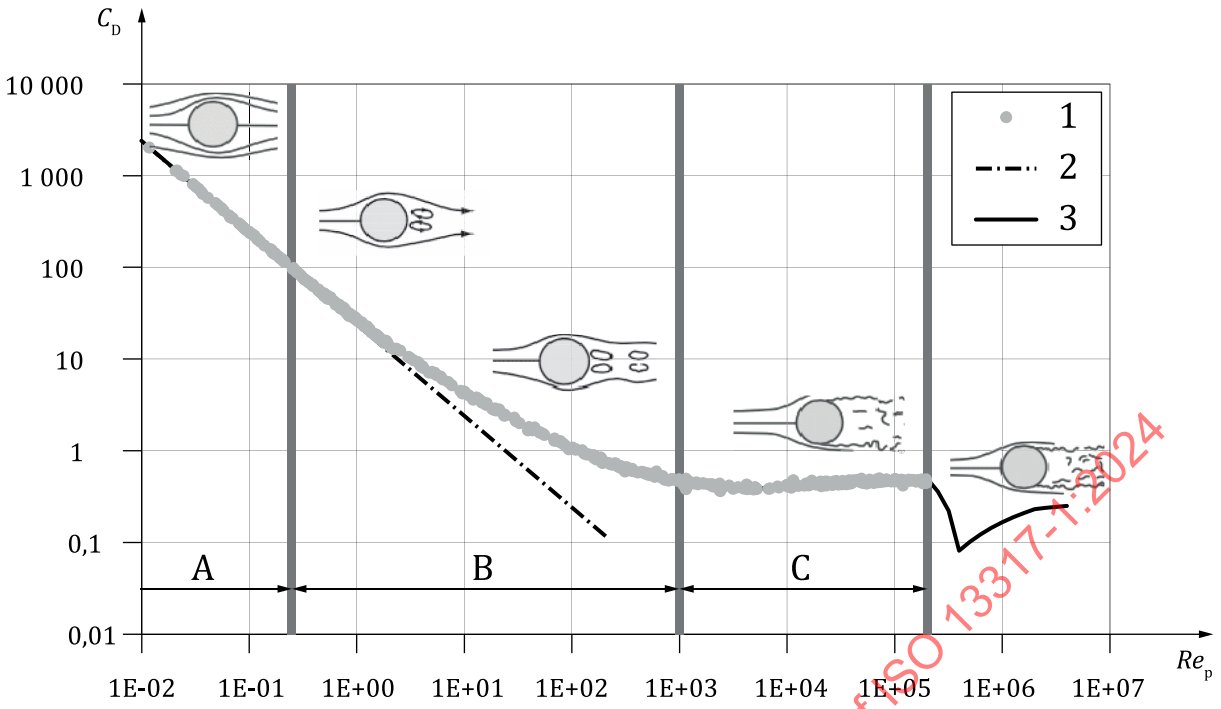
ρ_c is the density of the continuous phase.

The formulae are valid when inertia effects of the liquid flow field are negligible, which holds true for fine particles and low sedimentation velocities. A similar criterion is the particle Reynolds number, Re_p, for sedimenting particles [see Formula (22)].

The Stokes' law applies to creeping laminar flow, where $Re_p < 0{,}25$ and the drag force is entirely due to viscous friction within the liquid (Stokes regime). The flow field is axisymmetric and the drag coefficient inversely proportional to the particle Reynolds number ($C_D = 24/Re_p$). As the Reynolds number increases, the flow field becomes steadily deformed and eventually loses its axial symmetry due to flow separation and eddy formation (see Figure C.1). At large Reynolds numbers, the flow field in the wake region becomes turbulent and the drag coefficient is approximately constant (Newton regime).

Beyond the Stokes regime, Formula (C.1) underestimates the hydrodynamic drag of spherical particles. Accordingly, a calculation of Stokes diameter from measured velocity based on Formula (9) would underestimate the particle size (see Figure C.2).

NOTE For a particle Reynolds number of $Re_p = 0{,}25$, Stokes' law for the drag force fails by 3,9 % and the attendant error from the calculation of the particle size from a measured sedimentation velocity [see Formula (9)] amounts to 2,0 %. The critical Reynolds number of $Re_p = 0{,}25$ defines the upper limits for the sedimentation velocity and particle size, which depend on the examined materials. For aqueous dispersions at 25° C, these limits are 7,8 mm/s and 61,3 µm for a density contrast $\Delta\rho$ of 1,65 g/cm^3 (e.g. quartz); they amount to 3,1 mm/s and 156 µm for density contrast $\Delta\rho$ of 0,1 g/cm^3, while for gold particle ($\Delta\rho$ = 18,3 g/cm^3), 17,5 mm/s and 27,5 µm is found.



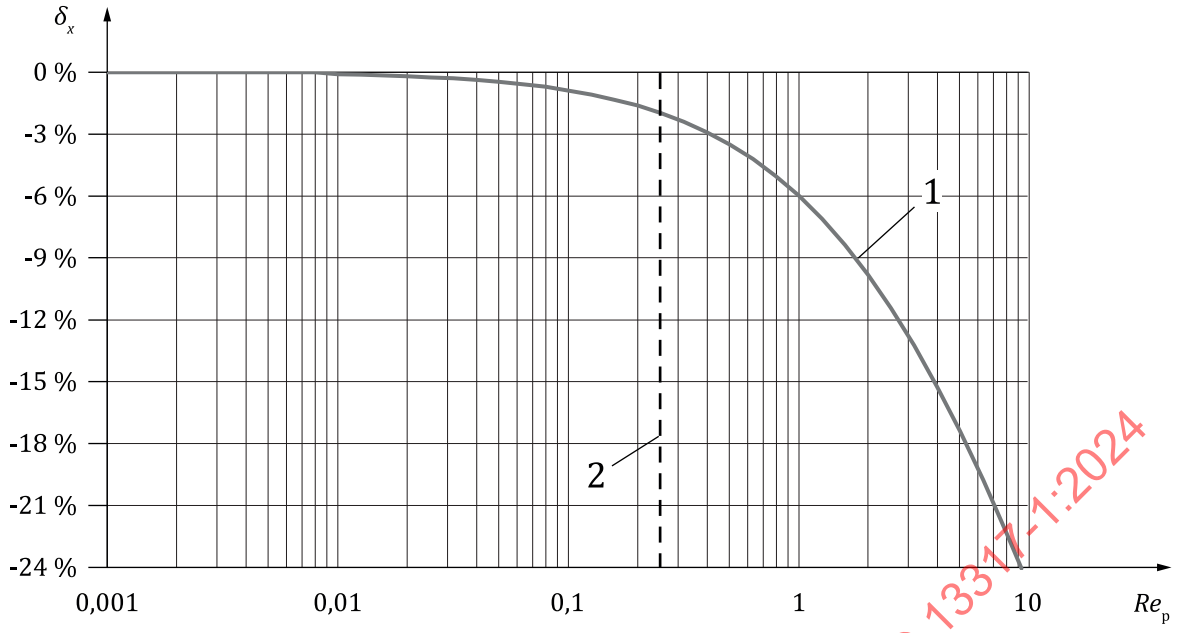
Key

Re_p	particle Reynolds number
C_D	drag coefficient
A	Stokes regime
B	intermediate regime
C	Newton regime
1	experimental data, collected and revised by Brown and Lawler[75]
2	solution for Stokes regime, Formula (C.1)
3	regression according to Reference [78]

Streamline images for each flow regime.

Figure C.1 — Drag coefficient of spheres, experimental data[75], corresponding regression[78] and Stokes solution [see Formula (C.1)]

In order to avoid errors in particle size determination for large Reynolds numbers, i.e. rather coarse particles, one can adopt two different strategies. One strategy applies correction functions based on established models for the hydrodynamic drag at moderate and high Reynolds numbers. The other strategy, which is preferred, modifies the sedimentation conditions so that the creeping flow condition ($Re_p \leq 0{,}25$) is satisfied for the largest particles of the sample.



Key

Re_p	particle Reynolds number
δ_x	relative error of calculated particle size
1	relative error
2	conventional threshold for the applicability of Formula (9), i.e. $Re_p = 0,25$

NOTE The transition from Stokes regime to intermediate flow regime is marked by the dashed line (at $Re_p = 0,25$).

Figure C.2 — Underestimation of the size of spherical particles when derived from sedimentation velocity with Formula (9)

The drag of non-isotropic and/or non-spherical particles is not only a function of Reynolds number, but also depends on the particles' alignment in the flow field. Similarly, their sedimentation velocity is affected by the particle orientation with regard to the gravity vector [43],[79],[80].

C.2 Superposition with Brownian motion

Sedimentation-based measurement techniques derive the distribution of particle size or sedimentation velocity by either monitoring the concentration changes in the dispersion phase or by monitoring the growth of the sediment or cream layer (see Figure 2). They all rely on the assumption that these changes are solely due to sedimentation, i.e. the steady migratory motion induced by gravity and retarded by buoyancy and viscous drag. However, particles also experience undirected Brownian motion, which results in a diffusive flux, which smears concentration steps and gradients that are related to sedimentation (e.g. in Figure 1 between the supernatant – zone 1 – and depleted dispersion phase – zone 2). Consequently, measured distribution functions appear broader and smoother than real particle size distribution (see Reference [81] and ISO 13318-1). In practice, this effect is only relevant for fine particles as the particle diffusion coefficient is inversely proportional to particle size. The dimensionless Péclet number, *Pe*, which expresses the ratio between migratory and diffusional particle flux, helps to estimate the additional effect of Brownian diffusion [see Formula (24)].

The number should be larger than unity. For gravitational sedimentation, this criterion is typically met for micrometre particles. However, Brownian motion can significantly affect the sedimentation of submicrometre particles.

The overall impact of Brownian motion on the measured particle size distributions depends on particle system (average particle size, degree of polydispersity, density contrast) and on the measurement set-up (sedimentation distance, fixed or scanning measurement position, incremental or integral sedimentation

technique). It is particularly pronounced for the fine fractions of a particle system, materials with low density contrast and very small sedimentation distances. The effect can be reduced by lowering the temperature and by conducting the measurements at large sedimentation distances or long sedimentation times. Brownian motion is one criterion for the lower size limit of gravitational sedimentation techniques. Reference [57] derived from experimental data that for Péclet numbers [see Formula (24)] above 200, Brownian motion is irrelevant for gravitational sedimentation. More elaborate estimations by Chung and Hogg[81] indicated that its impact is negligible when the Péclet number of the volume-weighted median, $x_{50,3}$, exceeds 100 and Bernhardt (see chapter 3.2 of Reference [82]) concludes that the impact of Brownian motion "becomes critical at particle sizes under 0,1 µm in the gravity field".

The importance of Brownian diffusion is much higher for centrifugal sedimentation techniques than for gravitational sedimentation techniques; it is described in more detail in ISO 13318-1 and ISO 13318-2.

C.3 Non-Newtonian continuous phase

Pure liquids and highly diluted solutions and dispersions frequently obey Newton's law of (dynamic) viscosity, η_c, which display a linear relationship between shear stress and strain rate. Under this condition, frictional force by Stokes can be derived [see Formula (C.1)]. In practice, some continuous phases can behave clearly non-Newtonian (e.g. polymer solutions). In that event, dynamic viscosity depends on shear stress and most often shows so-called shear thinning behaviour, i.e. viscosity decreases when shear rates increase. The average shear rate at the surface of migrating particles is a function of particle size, shape and velocity. For sedimentation, it correlates positively with particle size and sedimentation velocity.

Analytical solutions for the drag and sedimentation in non-Newtonian liquids exist only in selected cases.[76],[77],[78] A pragmatic approach is therefore to replace the dynamic viscosity η_c in Formula (C.1) by the apparent viscosity, η_{app}, which corresponds to the average shear rate at the particle surface. An estimate of the maximum shear rate in the vicinity of a migrating particle under creeping-flow condition is provided by Formula (C.2)[83].

$$\dot{\gamma}_{max} = \frac{3}{2}\frac{v_{sed}}{x} \tag{C.2}$$

Although this relation was successfully employed to explain particle sedimentation in shear-thinning solutions[50], it has not yet been comprehensively explored for the purpose of particle size analysis. It is therefore recommended to conduct sedimentation-based particle size analysis with Newtonian liquids only, which can require appropriate dilution of the original dispersion medium with a Newtonian solvent.

C.4 Effects of hydrodynamic particle interaction, hindrance

Stokes developed Formula (C.1) for an unhindered single particle settling in an infinite liquid. This assumption of an unhindered settling [see Formula (8)] is practically only fulfilled for dilute particle systems of volume fractions of the dispersed phase below 0,5 %. Under these conditions, individual particles settle sufficiently independent from each other.

If more particles are dispersed in a liquid, different particle-particle interactions take place due to the finite separation distances. Such interactions can lead to structured arrangements of particles having its origin in steric and osmotic or long-ranging and short-ranging non-viscous forces. All effects related with increased particle concentration affect viscous interaction among particles (e.g. via structure). They create an additional hydrodynamic hindrance and thus reduce the sedimentation velocity. Particle sizes, which are derived by referring to Stokes velocity [see Formula (8)] are therefore underestimated. In addition, hindrance depends on particle size distribution at a given volume concentration, because the mean distance between two particles narrows with decreasing size of the dispersed phase. The lessening of the sedimentation velocity can be quantified by the so-called hindrance function $H(\varphi_V)$, which is defined as the ratio of sedimentation velocity at given volume fraction, $v_{sed}(\varphi_V)$, to the Stokes velocity of an isolated particle, $v_{sed,0}$, under otherwise identical settling conditions.[84],[85] The hindrance function has been investigated in

experimental studies[86] as well as by theoretical analyses[87],[88],[89]. A generic hindrance function $H(\varphi_V)$ is frequently used as proposed by Kynch[90]:

$$H(\varphi_V) \overset{!}{=} \frac{v_{\text{sed}}(\varphi_V)}{v_{\text{sed},0}} = \frac{(1-\varphi_V)^2}{\eta_{\text{rel}}(\varphi_V)} \tag{C.3}$$

where

φ_V is the volume fraction of the dispersed phase;

η_{rel} is the relative apparent viscosity of the liquid dispersion.

Numerous empirical, semi-empirical and analytical one-to-multiparameter models have been proposed since the pioneering work of Kynch. Approaches allow taking into account any viscosity-concentration relationship $\eta_{\text{rel}}(\varphi_V)$ for dispersions[91],[92],[93].

There are numerous articles, giving evidence that concentration effects can be accounted for up to volume concentrations of about 5 % to 10 %[85]. For a polydisperse particle system, concentration effects are more complex, as swarm sedimentation pass over into zone sedimentation and finally all particles separate with the same velocity independent on the particle size. Determination of particle size distribution is not possible anymore.

It should be noted that beside the phenomena described above, multiple particles in the measuring volume can also affect the concentration determination by the measuring techniques (e.g. light intensity) due to obscuration, interference of scattering of different particles or structured systems.

As a practical approach to determine the necessary dilution of a dispersion, experiments with decreasing volume concentrations can be performed. If sedimentation velocity does not increase further, hydrodynamic hindrance practically can be neglected.

C.5 Non-spherical particles and particle agglomerates

The geometry of particles has relevance for particle motion and, in the concept of this document, has to be discussed under two aspects:

— the spatial alignment of non-spherical particles and agglomerates, and

— the hydrodynamic friction due to gravity settling.

The sedimentation velocity of non-isotropic, non-spherical particles clearly depends on their orientation with regard to the gravity vector[43],[79],[80]. Most literature opinions assume that in Stokes regime symmetrical particles are randomly oriented and they migrate due to gravity in any (stable) orientation. Orientation effects due to migration develop only for moderate and high particle Reynolds numbers, Re_p. Nonetheless, monodisperse non-isotropic shaped homogeneous particles of the same mass, exhibit different sedimentation velocities according to their orientation. In general, the velocity scatter for non-spherical particles with aspect ratios smaller than 10 is rather small. Experimentally, it manifests itself in a larger standard uncertainty of the average size.

As any non-spherical shaped particle has a larger surface area than a sphere with the same volume, frictional force [see Formula (C.1)] will consequently differ along with its terminal sedimentation velocity. This effect can be taken into account by a so-called sphericity Ψ, which is defined as the ratio between the surface area of a sphere having the same volume or mass and the one of the non-spherical particle[43],[94]. By definition, it is smaller than one. If particles are randomly aligned, the measured velocity based on local concentration change during sedimentation will be an average of the sedimentation velocities of the differently oriented particles and smaller than the sedimentation velocity of volume equivalent spherical particles. The ratio

between the two velocities is called shape correction factor and is tabulated for various shapes (see Table C.1). For Stokes regime, it can be approximated[95]:

$$k_{\text{shape}} = 0{,}843 \lg \frac{\Psi}{0{,}065} \tag{C.4}$$

If the sedimentation velocity would be measured for single particles, it would be distributed due to the varying orientation and thus mimic an artificial polydispersity. The shape of particles can also affect the signals used for the quantification of size fractions, which becomes relevant when the measured quantities are converted in volume or number. This is particularly relevant for photosedimentation; for sedimentation techniques based on a mass-proportional detection (e.g. X-ray attenuation), it becomes important for samples of fractal-like agglomerates only.

Agglomerates and fractals can be characterised based on a Stokes velocity for an equivalent spherical diameter. To get a size estimate, the apparent density of these objects has to be available. In some cases, like close-packed agglomerates, they can be treated similar to porous particles (see Clause C.6).

Table C.1 — Volume-equivalent diameter, sphericity, shape correction factors for regular bodies[96] and approximation according to Reference [95] (Formula (C.4))

Shape	Volume-equivalent diameter	Sphericity	Shape correction for Stokes	Approximation with Formula (C.4)
spheroids with equator diameter d and polar diameter L				
$L = 0{,}1d$	$0{,}464d$	0,418	0,686	0,681
$L = 0{,}5d$	$0{,}794d$	0,913	0,96	0,967
$L = 2d$	$1{,}260d$	0,929	0,958	0,974
$L = 10d$	$2{,}154d$	0,588	0,648	0,806
polyhedrons with edge length a				
cuboctahedron	$1{,}651a$	0,905	0,952	0,964
octahedron	$0{,}966a$	0,846	0,92	0,939
cube	$1{,}241a$	0,806	0,92	0,922
tetrahedron	$0{,}608a$	0,671	0,819	0,855
rectangular cuboid with edge length a				
$a \cdot a \cdot 2a$	$1{,}563a$	0,768	0,9	0,904
$a \cdot 2a \cdot 2a$	$1{,}969a$	0,762	0,89	0,901
$a \cdot 2a \cdot 3a$	$2{,}255a$	0,726	0,88	0,883
$a \cdot a \cdot 0{,}1a$	$0{,}576a$	0,434	0,7	0,695
$a \cdot a \cdot 0{,}01a$	$0{,}267a$	0,110	0,19	0,193
cylinder with diameter D and length L				
$L = 2D$	$1{,}442D$	0,832	0,93	0,933
$L = D$	$1{,}145D$	0,874	0,95	0,951
$L = 0{,}5D$	$0{,}909D$	0,825	0,93	0,930
$L = 0{,}15D$	$0{,}608D$	0,569	0,79	0,794
$L = 0{,}01D$	$0{,}247D$	0,119	0,22	0,222
straight chains of N spheres with diameter d				
$N = 2$	$1{,}260d$	0,794	0,905	0,916
$N = 5$	$1{,}710d$	0,585	0,736	0,804
$N = 10$	$2{,}154d$	0,464	0,597	0,720

C.6 Density of porous particles or particles with any kind of internal structure

The calculation of particle size from the sedimentation velocity [see Formula (9)] relies on the knowledge of the density contrast between particles and continuous phase. The density of most common liquids is temperature dependent and well tabulated in several handbooks. Such data are also available for crystalline or amorphous solid particles without any internal structure. However, there are many particulate materials that are composed of porous particles, coated particles or agglomerated particles. Moreover, when dispersed in solvents the employed dispersing, emulsifying or stabilising agents (e.g. polyelectrolytes, polymers and surfactants) can adhere as fixed layer on the particle surface. Hence, migrating entities of sedimentation experiments are frequently not monoconstituent – e.g. porous particles with stagnant liquid in the open pores, emulsion droplets with a stabilising polymer film or particle layer on their surface, pigments with an inorganic coating or plastic particles with included pigments. Their density differs from the one of the respective main constituent (e.g. solid skeleton, droplet liquid, pigment core or pure polymer; see consideration in Annex B).

If an isolated particle without porosity or very fine porosity is looked at (i.e. the pore size is much smaller than the particle size), the outer dimensions of the moving entity can be derived by employing the apparent particle density for calculating particle size. The apparent density can be calculated if the internal composition and the density values of all constituents are known. In the absence of open pores, it can be identified with the buoyant density, which is accessible by experiment (refer to ISO 18747-1 and ISO 18747-2).

The situation is different for aggregates and agglomerates because of several reasons:

a) the interstitial distance is in the order of the constituent particles and included liquid is not necessarily stagnant,

b) the surface that separates the continuous phase from the moving entity is ill-defined,

c) the structure can be fractal-like, i.e. the porosity depends on agglomerate size,

d) relevant details on the morphology are typically not known.

Hence, the apparent particle density is typically meaningless for such particles and defies its computation (exception: close-packings with large number of constituent particles). Therefore, sedimentational size determination of aggregates and agglomerates relies on the buoyant density.

In conclusion, the buoyant density is the appropriate density value in sedimentational size analysis for most types of materials and frequently is equal/resembles the apparent particle density. Only for particles with fine open pores, the buoyant density by the apparent particle density can be replaced.

C.7 Liquid and gaseous particles (droplets, bubbles)

In principle, the sedimentation of droplets and bubbles differs from the one of solid particles in three aspects. The hydrodynamic forces acting on the particle surface

a) can induce internal flow,

b) provoke a motion of possible layers at the interface, and

c) can result in particle deformation.

Particle deformation is only relevant for rising bubbles larger than 1 mm, which is beyond the scope of this document. Similarly, the flow inside droplets and bubbles is the more pronounced the larger such particles are. Interfacial energy as well as adsorbed layers of dissolved species (e.g. surfactants) significantly affect the momentum transfer from the outer to the internal flow field. In general, interfacial tension, interfacial viscosity and viscosity ratio (of dispersed to continuous phase) constitute essential factors that determine the sedimentation behaviour of liquid and gaseous particles. However, in sedimentation practice, they behave as solid particles for a particle Reynolds number <0,4[78], i.e. within the applicability of this document.

Bubbles and frequently droplets rise during sedimentation analysis which restricts the number of applicable sedimentation techniques. This has to be accounted for during signal analysis. Precaution shall be taken

to provide well-mixed sample at the start of measurement and to precisely determine the start position. Moreover, the samples should be properly stabilised in order to avoid coalescence of colliding particles as well as Ostwald ripening during the sedimentation analysis.

C.8 Wall effects

The impact of walls and bottom on particles moving very close to them disturb viscous-flow conditions (see Clause C.1) and therefore the sedimentation velocity reduces. Wall effects can be handled (e.g. as correction for ball viscometers[97]), if the minimum wall distance, L_{min}, is much larger than particle size ($x_p/L_{min} < 0{,}01$). In this case, the error amounts up to 2 %[50],[98],[99],[100]. Regarding the influence of the bottom, the measurement position should be 50 particle diameters above the bottom to account for a friction error of less than 1 %[43]. Sedimentation cell geometry and sensor position (see Figure 1) shall be estimated based on the size of the expected coarsest particles.

C.9 Miscellaneous effects

One assumption behind the data analysis for gravitational sedimentation techniques is that the particle motion achieves steady-state quasi-instantaneously (see 6.2.1). A rough approximation based on the equation of motion shows that the relaxation time of the transient phase is $\propto v_{sed}/g$ and that the ratio of the acceleration distance to particle size amounts to approximately $\frac{1}{81} Ar \cdot \rho'_p/\rho_c$ (with ρ'_p being the virtual particle density that also comprises the accelerated liquid). Within Stokes regime, which defines the principal range of application for sedimentation analysis, this ratio is in the order of 1 or smaller ($Ar_{cr} = 4{,}7$, $Re_{p,cr} = 0{,}25$). The transient time is thus negligibly small.

A further effect of minor relevance in most applications of gravitational sedimentation techniques is related to the electrical double layer, which form around charged particles. The DORN effect[101] describes a lowering of sedimentation velocity due to the sedimentation-induced polarisation of the double layer. When moving, the charged particle runs ahead the liquid layer containing the oppositely charged ions. Hence, sedimentation induces an electric dipole and according ionic flux to neutralise it. The retarding DORN effect is a second order effect, which is only relevant for highly charged particles and very thick double layers. It is practically irrelevant for the particle size range addressed by gravitational sedimentation.

Annex D
(informative)

Example for the determination of the uncertainty of velocity and particle size

D.1 General

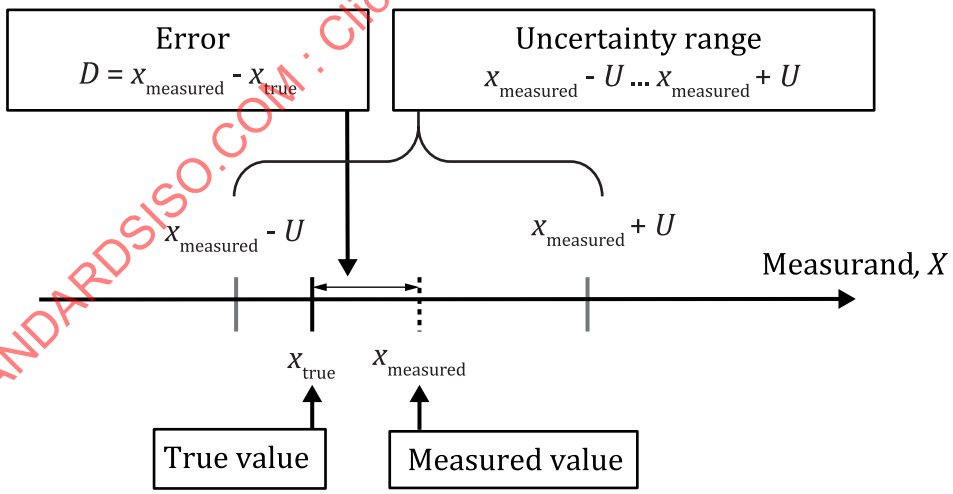
This annex describes an exemplary procedure for computing the full combined uncertainty of results from gravitational sedimentation techniques[102]. This annex discusses the uncertainty in both measurands, sedimentation velocity and particle size, and their individual contributions. As it only illustrates how to perform an uncertainty analysis, it should not be taken as indicative of actual experimental values.

The presented data refer to measurements collected with photosedimentation; modifications to the details of the procedure can be required when other measurement techniques are employed (such as X-ray sedimentometer or sedimentation balances; see ISO 13317-3 and ISO 13317-4, respectively). The description is restricted to the uncertainty of mean values in velocity or size; uncertainty with respect to the measured quantities of each particle fraction is not considered.

D.2 Preliminary remarks on uncertainty in sedimentation experiments

D.2.1 Relationships between different terms describing the uncertainty of a measurement

Figure D.1 gives a short overview regarding the different terms used to describe the relation between the true value and the measured value of a measurand as well as the formulae for the measurement error and uncertainty range[62]. In addition, Figure D.1 presents the notation regarding different types of error, performance and expression of performance.



Key

x_{true}	true value of the measurand	U	uncertainty
$x_{measured}$	measured value of the measurand	X	measurand
D	measurement error		

SOURCE: Reference [62]. Reproduced with permission of the authors.

Figure D.1 — Overview of the measured value, true value, error and uncertainty range for particle sizing

D.2.2 Relationship between uncertainties in sedimentation velocity and particle size

The direct results of sedimentation analysis are the relative quantities of particles in narrow fractions of sedimentation velocity or corresponding particle size (Stokes diameter). The latter is computed from the former by assuming the validity of Formula (8) and that the used values of the model parameters are correct. This introduces a type of uncertainty to the measured size value, which is typically not present for sedimentation velocity, because the uncertainties in sedimentation distance and time are commonly very small.

D.3 Experiments for deriving precision and trueness

D.3.1 General

Clause D.3 describes measurements that aimed at the determination of performance characteristics and quantitative expressions of uncertainty for gravitational photosedimentation (see Figure 6 for types of errors and performance characterisation). The intention was to quantify the precision under repeatability and reproducibility conditions as well as trueness and combined uncertainty of measured sedimentation velocity and particle size (median values). The analyses used a CRM with certified values for the sedimentation velocity and the Stokes diameter:

— material: aqueous suspension of spherical, quasi-monodisperse silica particles,

— certified values: extinction-weighted medians of sedimentation velocity (8,837 µm/min ± 0,568 µm/min at 25 °C) and Stokes diameter (490,0 nm ± 20,0 nm); indicated uncertainty with a coverage factor of 2.

The measured data are interpreted in the framework of Figure D.1 and the Nordtest approach (NT TR 537).

D.3.2 Determination of method precision and trueness

The precision under repeatability conditions of a measurement system refers to the closeness of results from replicate measurement, i.e. which are repeated under the same conditions. It is often called repeatability. In this example, the data refer to the determination of sedimentation velocity and particle size within 10 consecutive measurements (i.e. without significant time delays between measurements) by the same operator and with the same device (photosedimentometer LUMiReader 452, LUM GmbH[3)]). All the measurements were conducted at at 25 °C with uniform settings for wavelength (470 nm) and measurement cell (2 mm polycarbonate).

The calculation of Stokes diameters from sedimentation velocity employed the following values of the model parameters:

— gravitational acceleration, g = 9,81 m/s^2;

— dynamic viscosity of the continuous phase, η_c = 0,891 mPa·s;

— density of the continuous phase, ρ_c = 997,3 kg·m^{-3};

— buoyant density of the particle, ρ_p = 2 000 kg·m^{-3};

— silica (SiO_2) particle concentration mass fraction, c = 0,1 %.

Densities and liquid viscosity were obtained from literature for the set temperature of 25 °C ± 1 °C.

Table D.1 presents the results of individual measurements as well as the mean values and standard deviations. The latter quantifies the precision or short-term repeatability and amounts to 1,57 % for velocity and 0,78 % for size.

3) LUMiReader 452 is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO this product.

Table D.1 — Measured velocity and calculated particle size (median values of the extinction-weighted size distribution) under repeatability conditions

Sample	v_{sed} µm/min	x_{Stokes} nm
Mass fraction 0,10 % SiO_2 – 1	8,837	492,3
Mass fraction 0,10 % SiO_2 – 2	8,694	488,3
Mass fraction 0,10 % SiO_2 – 3	8,437	481,0
Mass fraction 0,10 % SiO_2 – 4	8,708	488,7
Mass fraction 0,10 % SiO_2 – 5	8,653	487,1
Mass fraction 0,10 % SiO_2 – 6	8,833	492,2
Mass fraction 0,10 % SiO_2 – 7	8,462	481,7
Mass fraction 0,10 % SiO_2 – 8	8,731	489,3
Mass fraction 0,10 % SiO_2 – 9	8,607	485,8
Mass fraction 0,10 % SiO_2 – 10	8,732	489,4
Mean value	8,669	487,6
Standard deviation	0,136	3,8
Relative standard deviation	1,57 %	0,78 %

The differences between mean experimental values in Table D.1 and the certified values of the reference particle (CRM) are the measurement errors (see Figure 6 and Figure D.1). The smaller these differences are, the better is the instrument (method) trueness. For the certified values, 8,837 µm/s and 490,0 nm, the measurement errors amount to −0,17 µm/s and −2,4 nm or −1,9 % and −0,5 %, respectively.

D.3.3 Reproducibility of the particle velocity methods

Reproducibility, besides repeatability, is another aspect of the precision of a measurement or test method. Similar to repeatability, reproducibility is quantified and reported as a standard deviation (standard uncertainty). This kind of uncertainty covers deviations due to precision of the measurement technique under very defined measurement conditions and deviations due to a much broader budget of factors influencing the measurement results compared to short-term precision. Experiments are intentionally performed over a longer period of many months, ideally up to a year. Instead of reproducibility, it is sometimes also called intermediate precision or within-lab precision. Besides the random errors, the measurement uncertainty also includes some systematic errors.

Table D.2 lists measurement results of the CRM (spherical silica particles) that were obtained over a period of six months for measurement conditions as employed in the precision analysis (see D.3.2). Due to the rather long period for running gravitational sedimentation analysis of the CRM, each data set represents only one measurement. The data refers to

a) several operators, and

b) different photosedimentometers, which were operated at different wavelengths (470 nm and 870 nm) and different cell types (optical pathlength).

The data also reflects unintended variations in sample preparation (e.g. induced by different batches of chemicals). The measurement cell itself was thermostatically controlled at 25 °C, but temperature in the laboratory varied between 22 °C and 28 °C. Overall, the observed variation in measured values reflect typical day-to-day variations in the corresponding laboratory.

Table D.2 — Measured velocity and calculated particle size under reproducibility conditions

Sample	WL nm	Operator initials	Device	Date	Cell type mm	v_{sed} µm/min	x_{Stokes} nm
SiO_2 – 1	470	LR	LR1	21 Oct	2	9,195	502,2
SiO_2 – 2	470	KB	LR3	25 Oct	2	8,610	485,9
SiO_2 – 3	470	PD	LR1	29 Oct	2	8,689	488,2
SiO_2 – 4	470	KB	LR2	02 Nov	2	8,721	489,0
SiO_2 – 5	470	LR	LR3	06 Nov	2	8,619	486,2
SiO_2 – 6	470	PD	LR3	10 Nov	2	8,501	482,8
SiO_2 – 7	470	PD	LR1	14 Nov	2	8,612	486,0
SiO_2 – 8	470	KB	LR2	18 Nov	2	8,034	469,4
SiO_2 – 9	470	LR	LR1	22 Nov	2	8,730	489,3
SiO_2 – 10	470	KB	LR2	26 Nov	2	8,730	489,3
SiO_2 – 11	470	KB	LR1	30 Nov	2	9,138	500,6
SiO_2 – 12	870	KB	LR2	04 Dec	10	8,979	496,2
SiO_2 – 13	470	LR	LR3	08 Dec	2	8,773	490,5
SiO_2 – 14	470	KB	LR2	12 Dec	2	8,779	490,7
SiO_2 – 15	470	LR	LR1	16 Dec	2	8,917	494,5
SiO_2 – 16	470	KB	LR2	20 Dec	2	8,806	491,4
SiO_2 – 17	470	LR	LR3	24 Dec	2	8,825	492,0
SiO_2 – 18	470	PD	LR1	28 Dec	2	8,804	491,4
SiO_2 – 19	470	PD	LR1	01 Jan	2	8,982	496,3
SiO_2 – 20	470	KB	LR2	05 Jan	2	9,037	497,8
SiO_2 – 21	470	PD	LR3	09 Jan	2	8,842	492,4
SiO_2 – 22	470	LR	LR1	13 Jan	2	8,808	491,5
SiO_2 – 23	870	KB	LR2	17 Jan	10	8,941	495,2
SiO_2 – 24	470	LR	LR3	21 Jan	2	8,827	492,0
SiO_2 – 25	870	PD	LR3	25 Jan	10	8,790	491,0
SiO_2 – 26	870	KB	LR1	29 Jan	10	8,748	489,8
SiO_2 – 27	470	LR	LR3	02 Feb	2	9,100	499,6
SiO_2 – 28	470	LR	LR2	06 Feb	2	8,901	494,1
SiO_2 – 29	470	LR	LR2	10 Feb	2	8,655	487,2
SiO_2 – 30	470	KB	LR1	14 Feb	2	8,842	492,4
Mean value						8,798	491,2
Standard deviation						0,217	6,1
Relative standard deviation						2,47 %	1,24 %

The average values of sedimentation velocity and particle size amount to 8,80 µm/min and 491 nm, respectively. The corresponding standard deviations are 0,22 µm/min (2,5 %) and 6,1 nm (1,2 %), respectively. These values refer to the uncertainty of an individual measurement result. The uncertainty with respect to the mean value gradually decreases with the number of measurements conducted. For the 30 measurements of Table D.2, the uncertainty of the average values is reduced by a factor of $\sqrt{30} = 5,5$ when compared to the indicated values (i.e. the relative uncertainty of averages amounts to 0,4 % and 0,2 %). However, regarding the uncertainty of an individual measurement, a higher standard deviation is clearly observed under reproducibility conditions than under repeatability ones (see D.3.2).