



BSI Standards Publication

Determination of particle size distribution by centrifugal liquid sedimentation methods

Part 1: General principles, requirements and guidance

National foreword

This British Standard is the UK implementation of ISO 13318-1:2024. It supersedes BS ISO 13318-1:2001, which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee LBI/37, Particle characterization including sieving.

A list of organizations represented on this committee can be obtained on request to its committee manager.

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International
Standard

ISO 13318-1

**Determination of particle size
distribution by centrifugal liquid
sedimentation methods —**

**Part 1:
General principles, requirements
and guidance**

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

Partie 1: Principes généraux, exigences et orientation

**Second edition
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CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
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Foreword

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

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).

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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 13318-1:2001), which has been technically revised.

The main changes are as follows:

- revision of core terms ([3.3](#), [3.5](#), [3.10](#), [3.11](#), [3.16](#), [3.14](#)) and inclusion of further terms;
- revised and expanded explanation of measurement principle and techniques ([Clauses 5](#) and [6](#));
- inclusion of the terminal sedimentation velocity as a measurand;
- introduction of informative annexes that provide:
 - an overview of particle sizing techniques based on centrifugal liquid sedimentation ([Annex A](#));
 - remarks on particle density ([Annex B](#));
 - information regarding sedimentation beyond the validity of Stokes' law ([Annex C](#));
 - trueness, reproducibility and uncertainty determination for velocity and particle size ([Annex D](#));
 - an explanation on the multiwavelength approach ([Annex E](#));
 - a description of the spatial distribution of particles in centrifugal fields ([Annex F](#));
 - the use of CLS for particle characterization beyond the particle size and sedimentation velocity ([Annex G](#)).

A list of all parts in the ISO 13318 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

Particle size analysis by centrifugal liquid sedimentation (CLS) methods has been performed for several decades, and there are numerous national and international standards employed in various academic and industrial applications. Along with the development of manifold new measurement techniques during the last two decades, sedimentation methods are currently enjoying a renaissance due to technical progress (e.g. multiwavelength features) and the fact that most sedimentation techniques are based on the first-principle measurement of the directed motion (migration) of particles in gravitational or centrifugal fields. The rate of this motion is the particle sedimentation velocity, its acceleration-specific value is called "sedimentation coefficient". Both are individual particle properties, which are related to the particles' external dimensions, and can be considered as primary measurands of liquid sedimentation methods.

Analytical centrifuges determine distributions of these primary measurands from the variation of concentration-dependent signals over time and/or along the radial coordinate of the centrifugal field. This step does not require any pre-knowledge of the dispersed or liquid phase. Further, data processing allows for particle size distributions to be derived from sedimentation velocity and sedimentation coefficient. For this purpose, spherical particles and the applicability of Stokes' law are assumed; the equivalent particle diameter is called the Stokes diameter. The conversion requires knowledge of the relevant properties of the particles and liquids (e.g. particle shape, density or refractive index). In this regard, CLS resembles gravitational liquid sedimentation (see ISO 13317-1 for further information).

The ISO 13318 series covers methods for characterizing dispersed materials in liquids by centrifugation with respect to the particle size distribution and the related distributions of sedimentation velocity and sedimentation coefficient. Their common principle is allocating a particle quantity to the rate of migratory motion in the centrifugal field. They differ with respect to particle quantification, mode of operation and data analysis.

The measurement techniques described in the ISO 13318 series are applicable to liquid dispersions, like suspensions and emulsions, with the continuous phase being a Newtonian liquid. Particles and liquid should not undergo any interactions, which cause significant changes of the dispersed phase in the course of the measurement, such as swelling, shrinking, and dissolution. For some instrumentation, the density difference (also called density contrast) between the dispersed and continuous phase should be limited to positive values.

The measurable particle size range depends on the properties of the materials and typically reaches from a few nm to 100 μm for aqueous samples, whereas the migration velocity can be quantified for the range of 10 nm/s to 1 mm/s. Sedimentation analysis is conducted for low particle concentrations. The permissible range of concentration depends on the measurement technique and theory of analysis; with no correction, it is typically no higher than 0,5 vol%.

As a fractionating technique, sedimentation analysis allows for distinguishing between particle fractions of close sedimentation velocity and the corresponding equivalent Stokes diameter. Accordingly, particle size distributions can be finely resolved, which is an advantage compared to spectroscopic ensemble techniques.

Finally, CLS techniques principally offer the chance to characterize liquid dispersions beyond sedimentational particle properties (see [Annex G](#)). For instance, some CLS techniques facilitate the quantification of the total and fractional particle concentration. Moreover, if particles are very fine, i.e. in the case of nanoparticles such as protein aggregates or quantum dots, the diffusional flux of particles can be in the order of the sedimentation flux. Such a situation allows a multidimensional characterization of particle systems, i.e. the simultaneous determination of more than one distributed quantity (e.g. particle size and density or shape factor).

Determination of particle size distribution by centrifugal liquid sedimentation methods —

Part 1: General principles, requirements and guidance

1 Scope

This document specifies the principles of particle size analysis by centrifugal liquid sedimentation (CLS). It also:

- defines the relevant terms;
- describes the various measurement techniques;
- gives guidance for sample preparation, conducting measurements as well as data analysis;
- establishes rules for method validation, determination of the uncertainty budget as well as representation of results.

An important part of this document deals with the derivation of particle size distributions from CLS data, including discussions on:

- the impact of Brownian motion;
- the parallel determination of particle concentrations;
- the working range with respect to size and concentration;
- the handling of non-spherical and porous particles.

This document applies to samples composed of dispersions of low particle concentration, so that the particles' motion can be considered as that of fully isolated particles. This document does not cover particle migration by gravity, electric or magnetic forces. It also does not cover deriving particle properties other than size, sedimentation velocity and sedimentation coefficient.

NOTE This document can involve hazardous materials, operations and equipment. It does not purport to address all the safety problems associated with its use. Regulations regarding explosion-proof analysers can apply when examining volatile liquids with a low flash point. 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.

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* (3.18), sedimentation occurs in the direction of centrifugal acceleration; it is counter directed to this acceleration for a negative density contrast.

Note 2 to entry: An outward motion due to centrifugal force is also called "settling" or "falling".

Note 3 to entry: An inward motion due to centrifugal force is also called "creaming" (e.g. droplets) or, more generally, "rising" and "floating".

[SOURCE: ISO 13317-1:2024, 3.1, modified — notes are adapted for centrifugal liquid sedimentation]

3.2 **migration**

directional motion of particles in a viscous liquid under the action of a force field

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

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

3.3 **terminal sedimentation velocity**

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

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

3.4 **sedimentation coefficient**

velocity of sedimentation divided by the acceleration of the force field (gravitation or centrifugation)

[SOURCE: IUPAC Gold book^[1]]

3.5 **Stokes diameter**

equivalent diameter of a sphere that has the same *buoyant density* (3.17) and *terminal sedimentation velocity* (3.3) as the real particle in the same liquid under *creeping flow* (3.20) conditions

Note 1 to entry: The general rule that the *buoyant density* is used for calculating the Stokes diameter also applies to coated particles or multiconstituent particles (such as droplets in multiple emulsions). The *buoyant density* can be approximated with the *skeleton density* (3.15) for monoconstituent particles.

Note 2 to entry: For porous particles, it is common use to compute particle size based on the *apparent particle density* (3.16). This approach considers the stagnant liquid in the *open pores* (3.10) as intrinsic constituent of the dispersed phase. Thus, the obtained size values are hydrodynamic equivalent diameters.

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

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

3.6

shape correction factor

ratio of the sedimentation velocity of a non-spherical particle to the one of a spherical particle of the same volume and *apparent particle density* (3.16)

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

3.7

hindrance function

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

[SOURCE: ISO 13317-1:2024, 3.6, modified "divided by" changed to "to" and "for" changed to "in".]

3.8

particle

minute piece of matter with defined physical boundaries

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

3.9

agglomerate

collection of weakly or medium-strongly bound *particles* (3.8) where the resulting external surface area is similar to the sum of the surface areas of the individual components

Note 1 to entry: The forces holding an agglomerate together are weak forces such as, for example, van der Waals forces or simple physical entanglement.

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

[SOURCE: ISO 26824:2022, 3.1.2]

3.10

open pore

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

[SOURCE: ISO 15901-1:2016, 3.11, modified — the word "fluid" is replaced by "liquid" and "surface" is changed to "particle surface".]

3.11

closed pore

pore that is totally enclosed by its walls and, hence not interconnecting with other pores and not accessible by liquids

[SOURCE: ISO 15901-1:2016, 3.10, modified— the word "fluids" is replaced by "by liquids".]

3.12

dynamic viscosity

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

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

3.13

apparent viscosity

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

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

3.14

true density of the dispersed phase

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

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

3.15

skeleton density

ratio of the sample mass to the volume of the sample, including the volume of *closed pores* (3.11) (if present) but excluding the volume of *open pores* (3.10)

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

[SOURCE: ISO 12154:2014, 3.3, modified — reference to the volume of void spaces between particles within the bulk sample is removed and Note 1 is added]

3.16

apparent particle density

effective particle density

ratio of mass to volume for a particle including particulate inclusions, entrapped stagnant liquid and gas in pores, voids and surface fissures as well as surface 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* (3.10) and the kinetics of wetting or the 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* (3.17). They deviate from each other for porous particles and particle agglomerates (3.8) in particular.

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

3.17

buoyant density

ratio of mass to volume for a particle (3.7) including particulate inclusions, liquid and gas in *closed pores* (3.11) and voids, as well as surface layers and coatings, but excluding the liquid continuous phase that penetrates *open pores* (3.10)

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 further information.

Note 3 to entry: The buoyant density of monoconstituent particles can be approximated with their *skeleton density* (3.15).

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* (3.16), particularly for porous particles and particle agglomerates.

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

3.18

density contrast

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

Note 1 to entry: For quantifying the density contrast, the *buoyant* (particle) *density* (3.17) is used, but for porous particles the *apparent particle density* (3.16) is more appropriate.

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

3.19

particle Reynolds number

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

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

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

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

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

3.20

creeping flow

type of flow solely governed by viscous forces and not affected by inertial forces

Note 1 to entry: For moving particles or for the flow past a particle, the creeping flow condition applies if the *particle Reynolds number* (3.19) is well below 0,25.

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

3.21

Brownian motion

random motion of particles caused by collisions with the molecules or atoms of the surrounding continuous phase

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

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

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

3.22

lower size limit

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

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

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

3.23

upper size limit

size of the largest particle that satisfies the condition of *creeping flow* (3.20) and of which the *terminal sedimentation velocity* (3.3) is detectable

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

3.24**type of quantity**

specification of the physical property employed to quantify the individual particle 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"

[SOURCE: ISO 9276-1:1998, 4.3, modified — the definition and notes are expanded to include frequently used, non-geometrical quantities.]

3.25**sensitivity**

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

Note 1 to entry: 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* (3.24).

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

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

3.26**limit of quantity detection**

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

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

Note 2 to entry: The limit of quantity detection affects the *lower* (3.22) and *upper size limit* (3.23).

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

3.27**measurement uncertainty****uncertainty of measurement**

parameter associated with the result of a measurement that characterizes 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]

3.28

homogeneous-start method

HSM

method characterized by measurement cell(s) filled with a homogeneously mixed dispersion

3.29

line-start method

LSM

method characterized by measurement cell(s) filled with a thin layer of the sample either on top or below a particle free (spin) liquid depending on the density contrast of the dispersed and continuous phase

4 Symbols and abbreviated terms

For the purposes of this document, the following symbols apply. In some cases, an alternative SI unit is given in parentheses in the right column.

Ar	Archimedes number	1
a_c	centrifugal acceleration	$m \cdot s^{-2}$ ($cm \cdot s^{-2}$)
b	systematic deviation of measured value from true value	varying
C_D	drag coefficient	1
C_{rel}	relative centrifugal acceleration	1
C_{toq}	concentration density of particle size being indicated by the index "toq"	varying
$\tilde{C}_{toq}$	concentration density of the sedimentation coefficient with respect to the type of quantity being indicated by an index	varying
D_p	particle diffusion coefficient	$m^2 \cdot s^{-1}$ ($\mu m^2 \cdot s^{-1}$)
c_{toq}	particle concentration with respect to a specified index "toq"	varying
F_D	drag force (also known as "hydrodynamic resistance")	N
g	gravitational acceleration	$m \cdot s^{-2}$ ($cm \cdot s^{-2}$)
H	hindrance function	1
K_c	auxiliary coefficient of centrifugation	$m^2 \cdot s^{-1}$
k_B	Boltzmann's constant, $k_B = 1,380\,649 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$	$\text{J} \cdot \text{K}^{-1}$
k_{shape}	shape correction factor	1
Lj	Ljaščenko number	1
M_{disp}	is the amount of dispersed phase quantified by a specified property	varying
Pe	Péclet number	1
Q_{toq}	cumulative function of distributed quantity, index "toq" indicates which of the fractions are weighted	1
q_{toq}	density function of particle size, index "toq" indicates which of the fractions are weighted	m^{-1}

$\tilde{q}_{\text{toq}}$	density function of sedimentation coefficient, index “toq” indicates which of the fractions are weighted	s^{-1}
Re_p	particle Reynolds number	1
r	radial distance from rotor axis, radial coordinate	m
S	signal of CLS measurement, being proportional to particle concentration	varying
T	absolute temperature	K
t	time	
t_{sed}	sedimentation time	s
U	expanded uncertainty of a measurand	varying
u	uncertainty of a measurand	varying
v_{sed}	terminal sedimentation velocity	$\text{m}\cdot\text{s}^{-1}$ ($\mu\text{m}\cdot\text{s}^{-1}$)
v_{Stokes}	terminal sedimentation velocity for creeping flow (Stokes regime)	$\text{m}\cdot\text{s}^{-1}$ ($\mu\text{m}\cdot\text{s}^{-1}$)
x	particle size	m (μm , nm)
x_{Stokes}	Stokes diameter	m (μm , nm)
Δr	radial sedimentation distance	m
$\Delta\rho$	density contrast between the dispersed and continuous phase	
ε	porosity	1
η_c	viscosity of the continuous phase	$\text{N}\cdot\text{s}/\text{m}^2$ (Pa·s)
θ	volume fraction of open pores that is filled with liquid	1
$\tilde{\kappa}, \kappa$	kernel functions of Formulae (22) and (23) , respectively	1
ρ_c	density of the continuous phase	$\text{kg}\cdot\text{m}^{-3}$ ($\text{g}\cdot\text{cm}^{-3}$)
ρ_p	particle density	$\text{kg}\cdot\text{m}^{-3}$ ($\text{g}\cdot\text{cm}^{-3}$)
τ_{sed}	sedimentation coefficient	s
φ_V	volume fraction of the dispersed phase	1
ψ	sphericity	1
ω	angular frequency	$\text{rad}\cdot\text{s}^{-1}$

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

0	initial state, start position
aggl	agglomerate, aggregate
app	apparent
bias	bias, deviation from true value
bouy	bouyancy
c	continuous phase
cr	critical
d	dispersed phase
incl	inclusions
max	maximum
meas	measurement position
min	minimum
occl	occluded voids
ref	reference
rel	relative
rep	repeatability
RMS	root mean square, quadratic mean
Rw	reproducibility
sed	sedimentation
sk	skeleton
toq	type of quantity
tot	total

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

CLS	centrifugal liquid sedimentation
CRM	certified reference material
DBM	direct boundary method
HSM	homogeneous-start method
LSM	line-start method
QCM	quality control material
RCA	relative centrifugal acceleration
RM	reference material

5 Measurement principle and technical realisations

5.1 General measurement principle

Centrifugal liquid sedimentation (CLS) techniques¹⁾ quantify the separation of particles (dispersed phase) from a liquid (continuous phase) under the presence of a centrifugal force. This phase separation relies on the directional, migratory motion of each particle, which this document refers to as "sedimentation". Its rate is called the "sedimentation velocity", while the acceleration-specific rate is named the "sedimentation coefficient". Both depend on the particle size and, thus, offer a chance for the granulometric characterization of particle systems. Additional factors are particle shape and the particle density.

NOTE 1 CLS techniques are generally called "sedimentation techniques" in this document, irrespective of whether the particles move along or against a centrifugal force.

CLS occurs for any particle dispersed in a quiescent viscous liquid and exposed to a centrifugal field, as long as a density contrast exists. It is driven by centrifugal forces that act on the particle (weight) and the displaced liquid (buoyancy). The resulting net force (excess force) causes a migratory directed particle motion, which is retarded by a frictional force (also called the drag force). The drag force increases linearly with the migration velocity. If the excess force is positive (i.e. weight > buoyancy), the particle motion is called falling or settling. In the opposite case, it is called rising, creaming or floating. In contrast to gravitational sedimentation (see ISO 13317-1), particle motion never reaches a true steady state as the centrifugal force depends on the radial position (in relation to the centre of rotation) and thus changes in the course of sedimentation (see 6.1). Particles settling outwards are steadily accelerated whereas creaming, i.e. inwards moving, particles experience a gradual deceleration. Nevertheless, the time scale of this alteration is much larger than the time scale of viscous relaxation. Hence, the particles are considered to be in a quasi-steady state, which means that at each radial position, they move with the terminal sedimentation velocity [see [Formula \(4\)](#)] they would achieve if the local force field prevailed at all radial positions.

The main advantage of centrifugal versus gravitational liquid sedimentation is in the considerably higher and more variable driving force, which allows the characterization of nanosized particles and facilitates a broadening of the measurement range. Particle size analysis for CLS is typically conducted at centrifugal accelerations of $10 \times g$ to about $25\,000 \times g$. Yet some instruments (analytical ultracentrifugation) can even realise rotation speeds of up to 60 000 rpm corresponding to centrifugal accelerations considerably above $100\,000 \times g$, which facilitates an expanded characterization to very fine objects, such as macromolecules or quantum dots, and may include shape and material analyses.^[2] It is common to calculate the relative centrifugal acceleration (RCA) as a ratio of the centrifugal to gravitational acceleration. This dimensionless parameter relates the time scales of sedimentation phenomena under gravity to those in centrifugal fields.

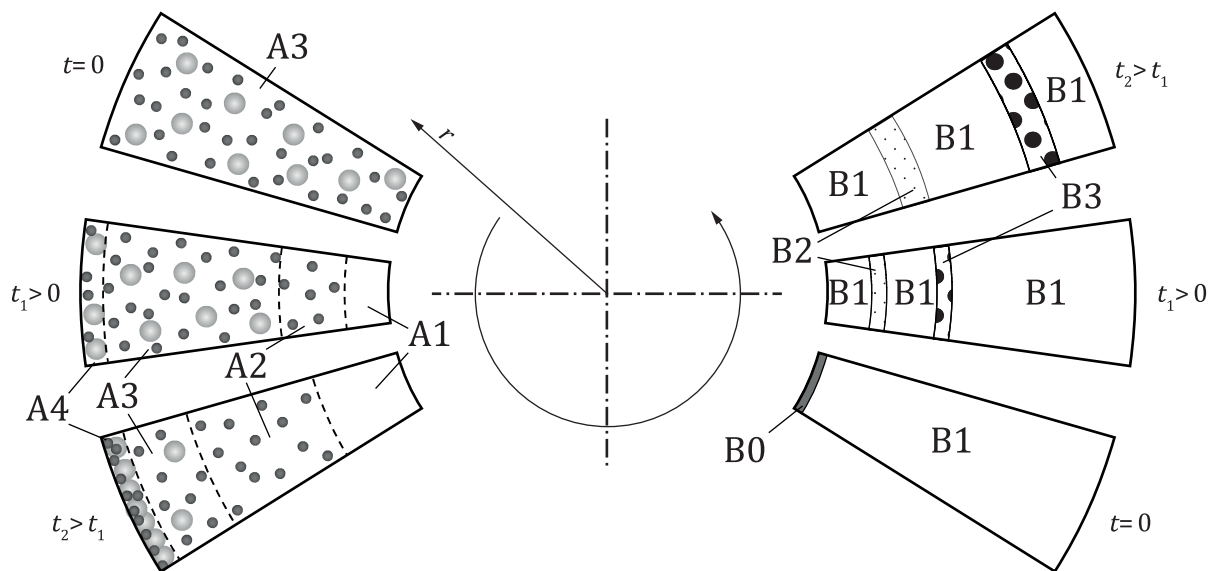
Sedimentation results in a size-dependent separation of dispersed particles from the liquid, which coincides with classification in the case of polydisperse materials. These effects can be employed to measure the particle size distribution. In CLS there are two principal approaches (see [Figure 1](#)).

- One approach is a gradual demixing of a homogeneously mixed dispersion [i.e. the homogeneous-start method (HSM)], which consists of the following:
 - an initially homogenous sample undergoes a gradual depletion of the dispersed phase which leads to the formation of a particle layer at the outermost or innermost cell position for settling and creaming, respectively;
 - in HSM, depletion occurs as successive separation of the respective largest particles at a given position and time;

1) CLS techniques are also referred to as analytical centrifugation. Instruments are called analytical centrifuges.

- within the dispersed phase, a concentration gradient is observed, which is directed to the aforementioned particle layer.
- The other approach is a chromatography-like separation in a particle-free medium (i.e LSM), which consists of the following:
 - a thin layer of the particle sample is placed on the top of a particle-free liquid (supernatant or spin liquid);
 - particles move through this “stationary phase” according to their size and density;
 - polydisperse materials are split into separate bands, which contain all particles of a certain size and density fraction;
 - this kind of separation requires density gradients within the supernatant or spin liquid in order to avoid instabilities and attain a high size resolution.

Particle motion in centrifugal fields occurs along radial trajectories at a steadily increasing or decreasing velocity resulting in a change of the particle concentration, which is independent from the separation between fine and coarse particles. A radial dilution is observed for settling particles (i.e. for positive density contrast), which is due to the divergence of the trajectories and to the acceleration along the sedimentation path. The effect is particularly comprehensible for the LSM. Radial acceleration broadens the chromatographic band, while radial divergence widens its perimeter. As the total amount of particles within the band remains constant, their concentration becomes reduced.



Key

- r radial coordinate, starting at the axis of rotation
- t sedimentation time
- $t_{1/2}$ two successive time points
- A1 particle-free supernatant
- A2 depleted dispersion phase (due to loss of coarse particles)
- A3 original dispersion phase
- A4 sediment
- B0 initial layer with the bi-disperse particle sample

- B1 particle-free zones
- B2 band with fine particle fraction
- B3 band with coarse particle fraction

NOTE This figure shows spatial distribution of fine and coarse particles at the start ($t=0$) and at two later instances ($t_2 > t_1 > 0$ for HSM on the left and LSM on the right).

Figure 1 — Illustration of phase separation due to sedimentation in a centrifugal field for a bimodal sample with a positive density contrast

The principal effects of CLS are illustrated in [Figure 1](#), which depicts the spatial distribution of settling particles for a bi-disperse system at the start of centrifugation and two subsequent instances. The illustration refers to both modes of operation, the HSM and the LSM. In either case, a classification of the particle system is observed, as coarse particles move faster in the centrifugal field than fine ones.

The formation of four zones along the radial coordinate is observed in case of the HSM (see [Figure 1](#)). The innermost layer, the supernatant (zone A1), has become free of all particles. In the subsequent layer (zone A2), there are only particles from the fine fraction, whereas the next layer (zone A3) contains particles of both fine and coarse size fractions. The particles from zones A2 and A3 migrate outwards due to a centrifugal force and eventually deposit as a sediment (zone A4). As a result, a step-like concentration profile is seen at each instance. However, while the particle concentrations in zones A2 and A3 are invariant with respect to space, they steadily decrease with time as the zones move to the outermost part of the cell. This is due to the increasing centrifugal acceleration along the radial coordinate and, on the other hand, the divergence of particle trajectories (that is, radial dilution). The effect also concerns the composition of zone A3 because coarse particles leave zone A3 faster than fine ones. Consequently, the size distribution of zone A3 becomes gradually dominated by fine particles.

NOTE 2 In the general case of polydisperse materials, zone A3 is composed of all the size fractions that were originally present and experiences a gradual shift in size distribution towards the fine edge. Zone A2 can be considered as a blurred sedimentation front, which is partly depleted of coarse particles (with the coarsest particles at the border to A3, and all but the finest ones at the border to A2).

NOTE 3 In systems with a negative density contrast, i.e. for floating particles, the order of the four zones along the radial coordinate is reversed. In addition, the effect of radial dilution causes thickening and coarsening of the size distribution in zone A3.

When LSM is applied to materials with a positive density contrast (see [Figure 1](#)), a very thin layer (zone B0) of the original sample is, at first, placed “on the top” (i.e. close to the rotor) of a particle free spin liquid (zone B1). During centrifugation, all particles of a given size fraction move together at the same velocity at a given radial position through the spin liquid to “the bottom” (i.e. the outermost wall of the cell). A polydisperse system is thus split into size-specific yet generally coherent bands, with the coarsest, i.e. fastest settling, particles leading the particle sedimentation front and the finest, i.e. slowest settling, particles following behind. For a bi-disperse system as shown in [Figure 1](#), two distinct bands are observed for each size fraction. The separation of the bands and their broadening increases with centrifugation time.

The rate of phase separation for CLS, e.g. quantified by the sedimentation velocity or sedimentation coefficient, depends on the properties of the continuous phase (such as density and rheological behaviour) and on characteristics of the particles (i.e. size, density and shape) in HSM as well as in LSM. This allows its conversion into particle size based on Stokes’ law and its corresponding presumptions (see [6.1](#)). This (indirect) quantification yields an equivalent diameter with respect to sedimentation velocity, called the 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 for a given particle. According to Leschonski,^[3] [Formula \(1\)](#) applies:

$$x_{\text{Stokes}} < x_V < x_S = x_{\text{proj,m}} < x_{\text{proj,st}} \quad (1)$$

where

- x_V is the volume equivalent diameter;
- x_S is the surface equivalent diameter;
- $x_{proj,m}$ is the projected area equivalent diameter for mean orientation;
- $x_{proj,st}$ is the projected area equivalent diameter for stable orientation.

The difference between these equivalent diameters is particularly pronounced for particle aggregates and agglomerates, where the following relationship applies^[4]:

$$x_{Stokes} \ll x_{hd} < x_{gyr} < x_{Feret,max} \quad (2)$$

where

- x_{hd} hydrodynamic equivalent diameter
- x_{gyr} diameter of gyration
- $x_{Feret,max}$ maximum Feret diameter

NOTE 4 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. $0,5 \times x_{gyr}$).

Particle size analysis by means of CLS relies on the assumption that centrifugal sedimentation completely explains the observed phase separation. This holds true for the vast majority of practical applications. However, in the event of extremely low sedimentation velocities, e.g. for fine nanoparticles (< 100 nm), sedimentation can be superposed by the diffusion fluxes due to Brownian motion.^{[5],[6]} Diffusion causes a smoothing of concentration gradients, thus broadening the measured distribution function. This effect is well-understood and described by quantitative models, which can be used to correct the impact of broadening due to diffusion.^{[2],[6],[7]} A more sophisticated method (Lamm equation) is described in [6.3.7](#).^[8]

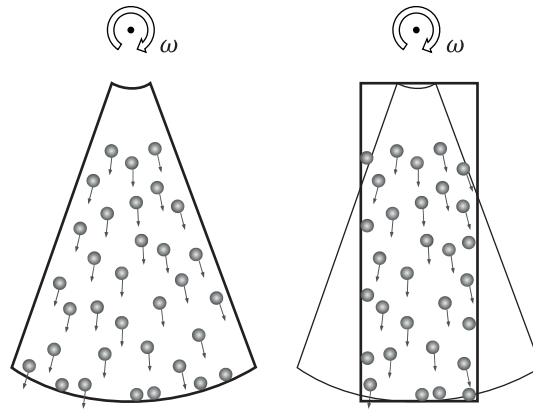
An essential feature of each sedimentation technique is the way of quantifying the particles and thus the particle size fractions. It occurs separately from the physical process of particle classification via sedimentation and can employ very different measurands (e.g. local mass concentration, local X-ray attenuation or light obscuration, hydrostatic pressure, sediment height). The quantification defines 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 either rely on an unbiased or biased linear scaling or involve parametric models (e.g. for light obscuration).

5.2 Technical realisation of sedimentation-based centrifugal measurement techniques

There is considerable variety in analytical instrumentation for particle characterization based on CLS (refer to [Tables A.1](#) and [A.2](#)). All types of CLS instruments probe the Stokes diameter of dispersed particles by either monitoring the depletion of the dispersion phase or observing the growth of the deposited particle layer (sediment or cream). However, these techniques differ in several aspects which can significantly affect data interpretation and comparability.^{[9],[10]}

Geometry of the measurement cell:

The most popular criteria to distinguish an analytical centrifuge refers to the cell-type, in which the dispersion samples are exposed to a centrifugal field. This cell can be either a cuvette, or a hollow, cylindrical disc. Accordingly, the instruments are called disc-type centrifuge or cuvette-type centrifuge.

**Key**

ω angular frequency

NOTE This figure shows a sector-shaped cuvette which mimics disc cells on the left, and a rectangular cuvette on the right.

Figure 2 — Schematic representation of CLS in regards to the sample cell geometry

Cuvettes for CLS have either a sector-like or rectangular shape in the centrifugal plane ([Figure 2](#)). The former can be considered as a representative part of a disc-cell, in which particle trajectories cannot meet the sidewalls, which ensures a uniform particle concentration along the tangential coordinate. In contrast, rectangular cells inevitably cause the deposition or an increase of concentration of particles at the sidewalls, which can promote convective flow due to temperature gradients or density gradients.^[11] However, rectangular cells are acceptable for most applications if the ratio of the distance between rotational centre and position of the particle sensor to the sedimentation path is larger than 5 (based on observations documented in Reference [\[12\]](#)). Disc-like measurement cells possess the advantage of a uniform particle distribution along the tangential coordinate and, additionally, facilitate the operation with the LSM (see [5.1](#)).

While the difference between disc-type and cuvette-type centrifugation is probably the most evident one in centrifugal instrumentation, it is not the most fundamental one.

Detection and quantification of particles:

A further distinction refers to the detection of temporal and/or spatial variation in the particle concentration within the centrifugal field. While centrifugation time and radial position determine the sedimentation velocity and thus the particle size, further techniques for detecting concentration shifts and/or gradients as prerequisite must be used for weighing the individual size fractions of polydisperse systems. Techniques can:

- probe integral properties of segregated particles (e.g. sediment mass);
- address the integral (cumulated) quantity of dispersed particles (e.g. via hydrostatic pressure);
- measure the local concentration of the dispersed phase (e.g. via X-ray attenuation, light extinction, interferometric or Schlieren optics).

With regard to data analysis, the first two types of detection techniques are named integral or cumulative techniques, whereas the third type is an incremental technique. In addition, there are even different modes of detection at fixed position or scanning over a radial range, observing the evolution of complete concentration profiles ([Figure 3](#)). The detection technique affects the working range of analytical centrifuges and determines the intrinsic type of quantity, in which the measured distribution functions are weighted (see [Tables A.1](#) and [A.2](#)).

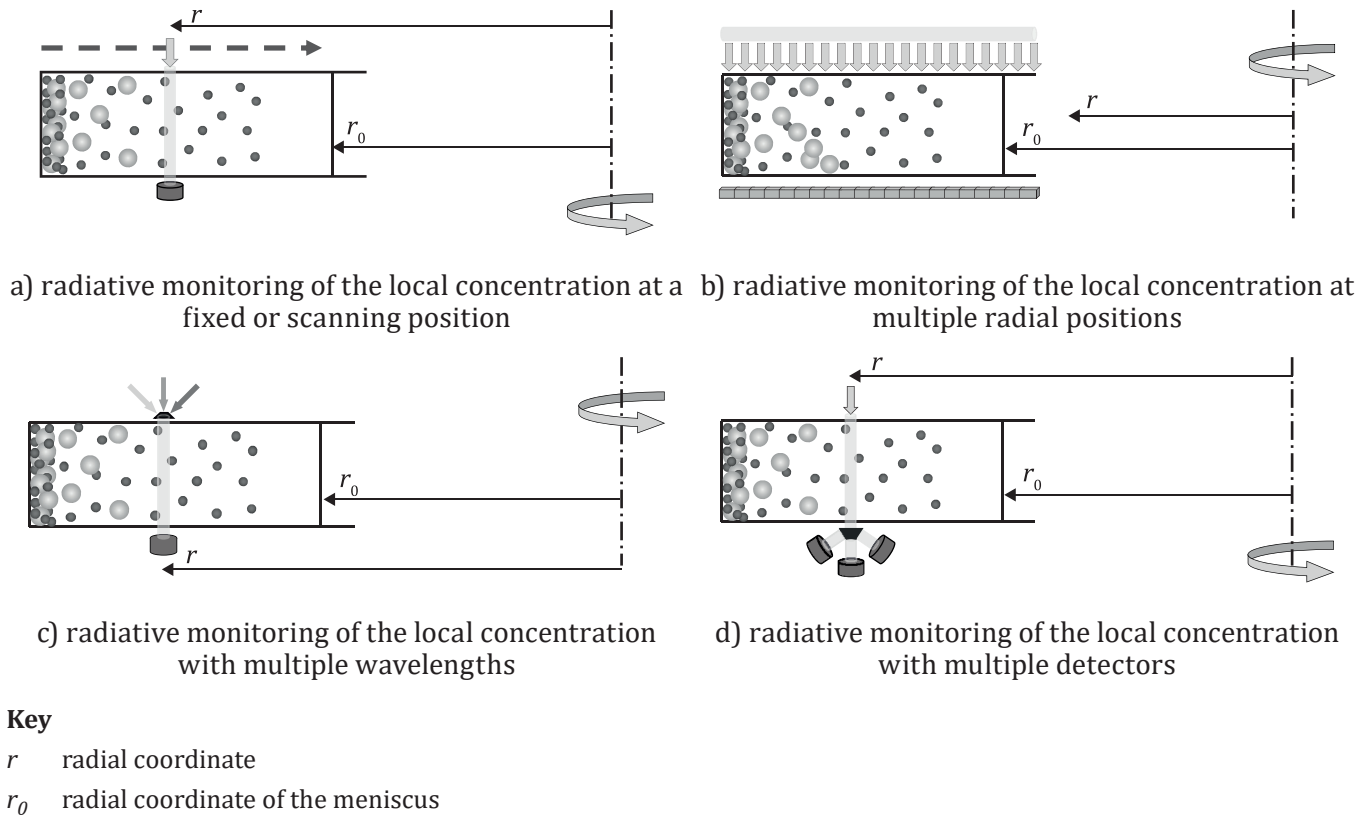


Figure 3 — Important measurement principles of CLS techniques

Figure 3 indicates the principles of common measuring techniques using CLS analysis, however there are other techniques, mainly realised in historical instrumentation or for academic purposes; [9], [10] an overview is provided in Annex A.

6 Measurement data and basic rules of data evaluation

6.1 Primary and derived measurands in centrifugal liquid sedimentation

The primary measurand of CLS is the sedimentation velocity of the particles. It can be derived either from changes in the local or integral concentration or from the formation of a sediment or cream layer. Sedimentation velocity is the rate of particle displacement in the centrifugal field. The driving force of this migratory motion, the centrifugal excess force, changes along with the particles' radial trajectories (see 5.1), for which reason the sedimentation velocity v_{sed} is also a function of the radial coordinate r as shown in Formula (3):

$$v_{\text{sed}} = \frac{\partial r}{\partial t} = f(r) \quad (3)$$

This is a principal difference to gravitational liquid sedimentation (ISO 13317-1) and affects the evolution of particle concentration (e.g. Figure 1) as well as the analysis of measurement results. Indeed, the functional relationship between the sedimentation velocity and the radial position is not conventionally derived from the measurement, rather it is supposed to obey the law of creeping flow (Stokes regime) which leads to Formula (4):

$$v_{\text{sed}}(r) = v_{\text{Stokes}}(r) = \frac{a_c(r) \Delta \rho}{18 \eta_c} x_{\text{Stokes}}^2 = a_c(r) \cdot \tau_{\text{Sed}}, \text{ with } \Delta \rho = \rho_p - \rho_c \quad (4)$$

$$\text{and } a_c(r) = \omega^2 r = C_{\text{rel}}(r) \cdot g \quad (5)$$

where

a_c	centrifugal acceleration
C_{rel}	relative centrifugal acceleration (RCA)
g	gravitational acceleration
r	radial coordinate
v_{Stokes}	terminal sedimentation velocity for small particle Reynolds numbers (Stokes regime)
$\Delta\rho$	difference between particle density (ρ_p) and density of the continuous phase (ρ_c)
η_c	dynamic viscosity of the continuous phase
ω	angular frequency
τ_{sed}	sedimentation coefficient

In practice, the sedimentation velocity is compared to a certain reference point (r_{ref}) such as meniscus position or outermost cell wall:

$$v_{\text{sed,ref}} = \frac{r_{\text{ref}}}{r} \cdot \frac{\partial r}{\partial t} \neq \text{funct.}(r) \quad (6)$$

This quantity should be always reported together with the centrifugal acceleration at the reference point. It facilitates the comparison among different samples and measurements and can be easily transformed to gravitational sedimentation velocity. Alternatively, the sedimentation coefficient τ_{sed} can be used as the primary measurand.^{[6],[7]}

$$\tau_{\text{sed}} = \frac{1}{\omega^2 r} \cdot \frac{\partial r}{\partial t} \quad (7)$$

It can be considered as an acceleration-specific sedimentation velocity or as a characteristic time, which refers to the particles' viscous relaxation. Unlike the sedimentation velocity, the sedimentation coefficient can facilitate a direct comparison of results from gravitational and centrifugal sedimentation velocity. In addition, the parameter remains constant in speed ramp experiments (see [F.4](#)), whereas the velocity does not. However, for many (non-academic) users, it is less comprehensible than a velocity value.

Both the sedimentation velocity and sedimentation coefficient depend on the physical properties of the continuous phase (density and viscosity). This dependency is irrelevant for particulate objects whose morphology and density are bound to a specific liquid (e.g. micelles or proteins). However, in many situations a pure particle property representing the sedimentation behaviour is the Stokes diameter, which is specified by [Formula \(8\)](#):

$$x_{\text{Stokes}} = \sqrt{\frac{18\eta_c}{\Delta\rho} \cdot \frac{v_{\text{sed,ref}}}{\omega^2 r_{\text{ref}}}} = \sqrt{\frac{18\eta_c}{\Delta\rho} \cdot \tau_{\text{sed}}} \quad (8)$$

The Stokes diameter is the equivalent diameter for particle migration in gravitational or centrifugal fields. It is affected by the particle's inertia and drag coefficient under creeping flow conditions. Within this document, this is the measurand of the greatest interest.

Under certain conditions, additional measurands can be obtained from CLS that are not related to sedimentation. A first group of such measurands quantify the particle concentration in the original sample (see [6.3.6](#)). The signals of particle detection systems must reflect the total amount of particles in the detection zone. This applies, for instance, to the attenuation or phase shift of an electromagnetic radiation. The detection technique determines the CLS-type of quantity of concentration (e.g. volume for X-ray attenuation), which can require elaborate models for conversion in number or volume concentration (e.g. Mie theory for light extinction by spherical particles). Analytical sedimentation also offers an opportunity

to measure particle density (see the ISO 18747 series for methods on how to measure particle density). Another group of supplementary measurands can be derived for fine nanoparticles ($< 0,1 \mu\text{m}$) if Brownian motion significantly influences the spatial distribution of particles in the centrifugal field (see 6.3.7). In this event, the particle diffusion coefficient can be computed and so too the hydrodynamic or mobility equivalent particle diameter, which further offers a chance to extract particle density and shape parameters.^{[8],[15],[16]} The shell-thickness of core-shell particles is reported based on this approach.^[11]

6.2 Spatial distribution of particles in centrifugal fields

The characterization of a material's dispersity by CLS relies on the evaluation of time curves for the local or cumulated particle concentration, concentration profiles for defined sedimentation times or the evolution of these profiles over time. It thus relies on a clear understanding of the spatial distribution of particles in the centrifugal field, which is governed by phase separation and radial dilution (see 5.1).

[Annex F](#) provides a detailed derivation of the evolution of concentration profiles in centrifugal experiments. The solution depends on the initial conditions, i.e. whether the measurements were performed with homogeneous-start method (HSM) or line-start method (LSM). In the former case, the spatial and temporal distribution of particle concentration, c , can be expressed with [Formula \(9\)](#):

$$c_{\text{toq}}(r, t) = c_{\text{toq}}^0 \int_0^{x_{\text{cr}}(r, t)} q_{\text{toq}}(x) \cdot \left(\frac{r}{r_0} \right)^{-2x^2/x_{\text{cr}}^2} dx \quad (9)$$

$$\text{with } x_{\text{cr}}(r, t) = \sqrt{\frac{\ln(r/r_0)}{K_c \cdot t}} \quad (10)$$

$$\text{and } K_c = \frac{\omega^2 \Delta \rho}{18 \eta_c} \quad (11)$$

where

c_{toq}	particle concentration with respect to the type of quantity defined by index "toq"
c_{toq}^0	initial, uniformly distributed particle concentration with respect to the type of quantity defined by index "toq"
K_c	auxiliary variable
$q_{\text{toq}}(x)$	density function of particle size; the type of quantity being indicated by toq
r	radial coordinate
r_0	radial coordinate of meniscus ($\Delta \rho > 0$) or bottom ($\Delta \rho < 0$)
t	time
x	particle size (more precisely, the Stokes diameter)
x_{cr}	critical particle size
$\Delta \rho$	density contrast
η_c	dynamic viscosity of the continuous phase
ω	angular frequency

In case of the LSMs, the sample is uniformly distributed on an extremely thin layer at position r_0 over a particle-free spin liquid. Centrifugation causes a separation of all particle fractions from each other, so that at a certain radial position, r , infinitesimal narrow particle fractions can be observed passing by consecutively, with the fastest particles appearing first. In practice, the observation is performed over a

small radial distance, δr , which means that a measurement at instance t captures all particles in the size range $x_{cr} \dots x_{cr} + \delta x_{cr}$. The observed local concentration then reads:

$$\delta c_{toq}(r, t) = c_{toq}^0 \cdot \left(\frac{r_0}{r} \right)^2 \cdot \frac{\delta r}{2r \ln(r/r_0)} \cdot x_{cr} q_{toq}(x_{cr}) \quad \text{with } x \cdot \tilde{q}_{toq}(x) = \tilde{q}_{toq}^*(x) \quad (12)$$

where $q_{toq}^*(x)$ is the transformed density function of the particle size.

Hence, the time curves at certain measurement positions can be considered as scaled, transformed density functions for the distribution of sedimentation coefficient and particle size.

6.3 Determination of distribution functions

6.3.1 General remarks

Within the context of this document, there are three interrelated characteristics of a particle's sedimentation behaviour:

$$\text{sedimentation velocity: } v_{sed,ref} = \frac{r_{ref}}{r} \cdot \frac{\partial r}{\partial t} \quad (13)$$

$$\text{sedimentation coefficient: } \tau_{sed} = \frac{1}{\omega^2 r} \cdot \frac{\partial r}{\partial t} \quad (14)$$

$$\text{Stokes diameter: } x_{Stokes} = \sqrt{\frac{18\eta_c}{\omega^2 r \Delta \rho} \cdot \frac{\partial r}{\partial t}} \quad (15)$$

[Formula \(4\)](#) reveals the interrelation between these characteristics. Although the definition of sedimentation velocity and sedimentation coefficient does not rely on a specific model for particle sedimentation, data analysis assumes sedimentation under creeping flow conditions when computing distribution functions. This is in order to ease the correction for radial dilution, which is virtually always met by experimental conditions in CLS.

In real particle systems, these quantities are distributed and it is therefore insufficient to describe the sedimentation behaviour with just one value. Instead, distribution functions are required. They are typically defined for a property z as:

$$\text{cumulative distribution function: } Q_{toq}(Z) = \frac{M_{disp}(z \leq Z)}{M_{disp,tot}} = \int_0^Z q_{toq}(z) dz \quad (16)$$

$$\text{distribution density function: } q_{toq}(Z) = \left. \frac{dQ_{toq}(z)}{dz} \right|_Z \quad (17)$$

$$\text{transformed density function: } q_{toq}^*(Z) = \left. \frac{dQ_{toq}(z)}{dz/z} \right|_Z \quad (18)$$

where

M_{disp} is the amount of dispersed phase with a specified property, e.g. $z \leq Z$

$M_{disp,tot}$ is the total amount of dispersed phase

and where index "toq" denotes the type of quantity, in which the "amount of dispersed phase" is quantified.

Sedimentation velocity and sedimentation coefficient possess negative signs for negative density contrast, as their motion is then counter-directed to the centrifugal acceleration. In this event, the definitions of cumulative function and density function refer to the absolute values of the two quantities, for pragmatic

convenience. However, if creaming and settling occurs simultaneously, [Formulae \(16\)](#) and [\(17\)](#) need to be replaced by the more general [Formulae \(19\)](#) and [\(20\)](#), respectively:

$$Q_{\text{toq}}(v) = \frac{M_{\text{disp}}(v_{\text{sed}} \leq v)}{M_{\text{disp,tot}}} = \int_{-\infty}^v q_{\text{toq}}(v_{\text{sed}}) dv_{\text{sed}} \quad (19)$$

$$q_{\text{toq}}(v) = \left. \frac{dQ_{\text{toq}}(v_{\text{sed}})}{dv_{\text{sed}}} \right|_v \quad (20)$$

Most analytical centrifuges now employ an incremental type of quantification (see [5.2](#)). This means that the distributions of dispersity characteristics are calculated from either the spatial or local variation, or both, of particle concentration (beyond sediment or cream layer), that is:

- 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).

Each sedimentation technique can be attributed an intrinsic type of quantity, in which the separate particle fractions contribute to the measured signal. These contributions are considered to superpose linearly so that the measurement signal $S_{\text{toq}}(x)$ can be related to the local concentration of the different particle fractions:

$$S_{\text{toq}}(r, t) \propto c_{\text{toq}}(r, t) \text{ or } S_{\text{toq}}(r, t) \propto \delta c_{\text{toq}}(r, t) \quad (21)$$

The two relationships constitute the basis for computing particle size distributions from the measured signals.

6.3.2 Distribution analysis for incremental techniques —homogeneous-start method (HSM)

[Formulae \(12\)](#) and [\(14\)](#) describe the dependence of concentration on time and radial position for the HSM. Elapsed time and measurement position define the critical sedimentation properties, which refer to the progressing sedimentation front [see [Formulae \(13\)](#) and [\(15\)](#), respectively]. A reformulation of the two equations yields:

$$c_{\text{toq}}(\tau_{\text{cr}})/c_{\text{toq}}^0 = \int_0^{\tau_{\text{cr}}} \tilde{\kappa}(\tau_{\text{cr}}, \tau) \tilde{q}_{\text{toq}}(\tau) d\tau \text{ or} \quad (22)$$

$$c_{\text{toq}}(x_{\text{cr}})/c_{\text{toq}}^0 = \int_0^{x_{\text{cr}}} \kappa(x_{\text{cr}}, x) q_{\text{toq}}(x) dx \quad (23)$$

where $\tilde{q}_{\text{toq}}(\tau)$ and $q_{\text{toq}}(x)$ represent the target of analytical investigation. As concentration profiles are measured at discrete positions and time-curves are recorded at defined time intervals, these equations are commonly discretised for computing the distribution functions:

$$C_{\text{rel},k} = \sum_{\ell=1}^k \kappa_{k,\ell} \Delta Q_{\text{toq},\ell} \text{ or } \mathbf{C}_{\text{rel}} = \mathbf{K} \cdot \Delta \mathbf{Q}_{\text{tot}} \quad (24)$$

$$\text{with: } \kappa_{k,\ell} \approx \kappa(x_k, x_\ell) \approx \tilde{\kappa}(\tau_k, \tau_\ell) \quad (25)$$

The coefficients $\kappa_{k,\ell}$ vanish for $k < \ell$, for which reason the mathematical solution is a well-posed problem and the distribution function (ΔQ_{toq}) can be directly calculated from [Formula \(24\)](#) without the need for regularisation, e.g. by Reference [\[17\]](#).

If the measurement yields only one profile or one time-curve, the elements $C_{\text{rel},k}$ should monotonically increase or decrease for an ideal measurement. In practice, however, noisy signals are observed. The noise sets a limit for the achievable resolution of the distribution function. In order to avoid noisy distribution