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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Foreword

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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, $k_B = 1{,}380\ 649 \times 10^{-23}\ J \cdot K^{-1}$	$J \cdot K^{-1}$
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}

$\tilde{q}_{toq}$	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	$m\cdot s^{-1}$ ($\mu m\cdot s^{-1}$)
v_{Stokes}	terminal sedimentation velocity for creeping flow (Stokes regime)	$m\cdot s^{-1}$ ($\mu m\cdot s^{-1}$)
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	$N\cdot s/m^2$ ($Pa\cdot s$)
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	$kg\cdot m^{-3}$ ($g\cdot cm^{-3}$)
ρ_p	particle density	$kg\cdot m^{-3}$ ($g\cdot cm^{-3}$)
τ_{sed}	sedimentation coefficient	s
φ_V	volume fraction of the dispersed phase	1
Ψ	sphericity	1
ω	angular frequency	$rad\cdot s^{-1}$

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