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Particle size analysis — Dynamic light scattering (DLS)

Analyse granulométrique — Dispersion lumineuse dynamique (DLD)

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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 documents 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 of ISO 22412 cancels and replaces ISO 22412:2008 and ISO 13321:1996.

Introduction

Particle size analysis in the submicrometre size range is performed on a routine basis using the dynamic light scattering (DLS) method, which probes the hydrodynamic mobility of the particles. The success of the technique is mainly based on the fact that it provides estimates of the average particle size and size distribution within a few minutes, and that user-friendly commercial instruments are available. Nevertheless, proper use of the instrument and interpretation of the result require certain precautions.

Several methods have been developed for DLS. These methods can be classified in several ways:

a) by the difference in raw data acquisition (autocorrelation, cross-correlation and frequency analysis);

b) by the difference in optical setup (homodyne versus heterodyne mode);

c) by the angle of observation.

In addition, instruments show differences with respect to the type of laser source and often allow application of different data analysis algorithms (e.g. cumulants, NNLS, CONTIN, etc.).

Particle size analysis — Dynamic light scattering (DLS)

1 Scope

This document specifies the application of dynamic light scattering (DLS) to the measurement of average hydrodynamic particle size and the measurement of the size distribution of mainly submicrometre-sized particles, emulsions or fine bubbles dispersed in liquids. DLS is also referred to as "quasi-elastic light scattering (QELS)" and "photon correlation spectroscopy (PCS)," although PCS actually is one of the measurement techniques.

This document is applicable to the measurement of a broad range of dilute and concentrated suspensions. The principle of dynamic light scattering for a concentrated suspension is the same as for a dilute suspension. However, specific requirements for the instrument setup and specification of test sample preparation are required for concentrated suspensions. At high concentrations, particle-particle interactions and multiple light scattering can become dominant and can result in apparent particle sizes that differ between concentrated and dilute suspensions.

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*

ISO 9276-2, *Representation of results of particle size analysis — Part 2: Calculation of average particle sizes/diameters and moments from particle size distributions*

3 Terms and definitions

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

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

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

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

3.1
particle
minute piece of matter with defined physical boundaries

Note 1 to entry: A physical boundary can also be described as an interface.

Note 2 to entry: A particle can move as a unit.

[SOURCE: ISO 26824:2013, 1.1, modified]

3.2
average hydrodynamic diameter
$\bar{x}_{DLS}$
hydrodynamic diameter that reflects the central value of the underlying particle size distribution

Note 1 to entry: The average particle diameter is either directly determined without calculation of the particle size distribution, or calculated from the computed intensity-, volume- or number-weighted particle size distribution or from its fitted (transformed) density function. The exact nature of the average particle diameter depends on the evaluation algorithm.

Note 2 to entry: The cumulants method yields a scattered light intensity-weighted harmonic mean particle diameter, which is sometimes also referred to as the "z-average diameter."

Note 3 to entry: Arithmetic, geometric and harmonic mean values can be calculated from the particle size distribution according to ISO 9276-2.

Note 4 to entry: Mean values calculated from density functions (linear abscissa) and transformed density functions (logarithmic abscissa) may significantly differ (ISO 9276-1).

Note 5 to entry: $\bar{x}_{DLS}$ also depends on the particle shape and the scattering vector (and thus on the angle of observation, laser wavelength and refractive index of the suspension medium).

3.3
polydispersity index
PI
dimensionless measure of the broadness of the size distribution

Note 1 to entry: The PI typically has values less than 0,07 for a monodisperse test sample of spherical particles.

3.4
scattering volume
volume defined by the intersection of the incident laser beam and the scattered light intercepted by the detector

3.5
scattered intensity
intensity of the light scattered by the particles in the scattering volume

3.6
count rate
photocurrent
I_S
number of photon pulses per unit time

Note 1 to entry: It is also a photodetector current which is proportional to the scattered intensity as measured by a detector.

3.7
validation
proof with reference material that a measurement procedure is acceptable for all elements of its scope

Note 1 to entry: Evaluation of trueness requires a certified reference material.

3.8
reference material
RM
material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process

[SOURCE: ISO Guide 30:2015, 2.1.1, modified]

3.9
certified reference material
CRM
reference material characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability

[SOURCE: ISO Guide 30:2015, 2.1.2, modified]

3.10
qualification
proof with reference material that an instrument is operating in agreement with its specifications

4 Symbols and units

$C(\Gamma)$	normalized distribution function of decay rates or characteristic frequencies	dimensionless	
D_T	translational diffusion coefficient	metres squared per second	m^2/s
D_c	collective diffusion coefficient	metres squared per second	m^2/s
D_s	self-diffusion coefficient	metres squared per second	m^2/s
f	frequency, $f = \omega/(2\,\pi)$	hertz	Hz
$g^{(1)}(\tau)$	normalized electric field correlation function	dimensionless	
$G^{(2)}(\tau)$	scattered intensity correlation function	arbitrary units	
$G(\Gamma_j)$	normalized distribution function of the individual decay rate Γ_j	arbitrary units	
I_s	scattered intensity, count rate, photocurrent	arbitrary units	
I_0	intensity of the incident light	arbitrary units	
M	number of steps in the histogram	dimensionless	
n	refractive index of the suspension medium	dimensionless	
$P(\omega)$	power spectrum	arbitrary units	
PI	polydispersity index	dimensionless	
$\Delta Q_{\text{int},i}$	scattered light intensity-weighted amount of particles in size fraction i, i.e. $x_{i-1} < x < = x_i$	dimensionless	
x	within this document: hydrodynamic diameter of a particle	nanometres	nm
$\bar{x}_{\text{DLS}}$	average hydrodynamic diameter	nanometres	nm

$\bar{\Gamma}$	scattered light intensity-weighted average value of the distribution function of the decay rate or characteristic frequency	reciprocal seconds	s^{-1}
Γ_{max}	maximum decay rate (histogram method)	reciprocal seconds	s^{-1}
Γ_{min}	minimum decay rate (histogram method)	reciprocal seconds	s^{-1}
η	viscosity of the suspension medium	millipascal seconds	mPa·s
θ	scattering angle	degrees	°
λ_0	wavelength of the laser light in vacuum	nanometres	nm
μ_2	second cumulant of the distribution function of decay rates or characteristic frequencies	reciprocal square seconds	s^{-2}
ρ	particle density	grams per cubic centimetre	g/cm^3
τ	correlation time	seconds	s
q	modulus of the scattering vector	reciprocal nanometres	nm^{-1}
φ	particle volume fraction	dimensionless	
ω	angular frequency	radian per seconds	rad/s

5 Principle

Particles suspended in a fluid are in constant Brownian motion as the result of the interaction with the molecules of the suspending fluid. In the Stokes-Einstein theory of Brownian motion[1], particle motion of smooth spheres at very low concentration is determined by the suspending fluid viscosity and temperature, as well as the size of the particles. Thus, from a measurement of the particle motion in a fluid of known temperature and viscosity, the particle size can be determined.

The DLS technique[2][3][4][5][6] probes the particle motion optically. The suspended particles are illuminated with a coherent monochromatic light source. The light scattered from the moving suspended particles has a time-dependent phase imparted to it from the time-dependent position. The time-dependent phase of the scattered light can be considered as either a time-dependent phase shift or as a spectral frequency shift from the central frequency of the light source. Measured over time, random particle motion forms a distribution of optical phase shifts or spectral frequency shifts. These shifts are determined by comparison either with all scattered light (homodyne or self-beating mode) or by using a portion of the incident light as reference (heterodyne mode). Regardless of the setup, the optical signals received from the particles are related to the scattering efficiency of the particles and are thus scattered intensity-weighted.

Sedimentation of particles, dependent on their density, sets an upper limit to the particle size that can be assessed by the technique; typically, the upper limit is much less than 10 µm.

DLS was developed for static suspensions. Provided that orthogonal flow and observation axes are adopted, flowing samples may, under some circumstances, be measured if the procedure is properly validated (see Annex C).

Different modes of diffusion, particle-particle interaction, multiple scattering and fluorescence can significantly influence the apparent particle diameter calculated from a DLS experiment. Annex B should be consulted.

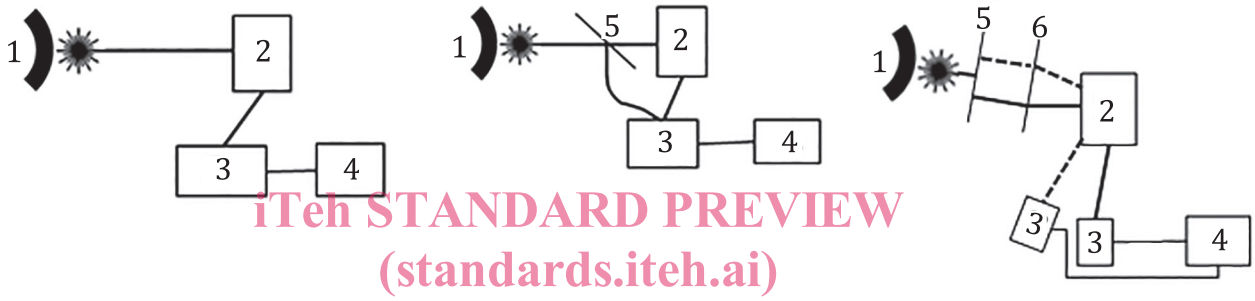
6 Apparatus

A typical apparatus consists of the following components:

6.1 Laser, emitting coherent monochromatic light, polarized with its electric field component perpendicular to the plane formed by the incident and detected rays (vertical polarization). Any kind of lasers may be used, e.g. gas lasers (He-Ne laser, Ar-ion laser), solid-state lasers, diode-pumped solid-state lasers and laser diodes.

6.2 Optics, lenses and equipment used to focus the incident laser light into a scattering volume and to detect scattered light. Optical fibres are often used as a part of the detection system and for light-delivering optics.

The use of a coherent optical reference allows using interference between the scattered light and the reference to measure the frequency shift of the scattered light. Two methods of referencing are commonly used and are illustrated in Figures 1 a) and b).



a) Homodyne **b) Heterodyne** **c) Cross-correlation (= two simultaneous homodyne experiments)**

Key

1 laser
2 sample
3 detector
4 correlator or spectrum analyser
5 beam splitter
6 lens

Figure 1 — Typical optical arrangement for DLS

— In homodyne detection (also referred to as "self-beating detection") [Figure 1 a)], the mixing at the optical detector of all of the collected scattered light provides the reference for frequency- or phase-difference measurement.

— In heterodyne detection [Figure 1 b)], the scattered light is mixed with a portion of the incident light. The unshifted incident light provides the reference for the frequency- or phase-difference measurement.

NOTE In DLS, "heterodyne" is understood as mixing of scattered light with unscattered light from the same source. This convention differs from, for example, the use in optical interferometry.

— In a cross-correlation setup [Figure 1 c)], two homodyne scattering measurements are performed simultaneously in such a way that the two scattering vectors and scattering volumes are the same, but the corresponding wave vectors are not coincident. These two laser beams produce two correlated fluctuation patterns. The correlation is not perfect, since on the one hand, both detectors collect

light from the other scattering experiment, and on the other hand, multiply scattered light of the incoming laser beams is totally uncorrelated. The two contributions of the multiply scattered light to the detector signal, however, do not contribute to the time-dependent signal but to an enhanced background.

6.3 Test sample holder, allowing fluctuations of the sample temperature to be controlled to within ±0,3 °C. While precise knowledge of the sample temperature is required for evaluation, it is not necessary to regulate the temperature to any defined value.

6.4 Photodetector, with an output that is proportionally related to the intensity of the collected scattered light. A photomultiplier tube or an (avalanche) photodiode is typically used. Detectors can be placed at any angle. Data collection can be performed in a linear or logarithmic manner.

6.5 Signal processing unit, capable of taking the time-dependent scattered light intensity signal and outputting the autocorrelation function, cross-correlation function or power spectrum of the input signal. This correlation can be performed by hardware and/or software correlators, operating linearly, logarithmically or in a mixed mode.

The resulting output from either mode contains a distribution of characteristic frequencies or time-dependent phases representative of the particle size of the suspended particles. Photon detection has a probability distribution of photon arrival times, which means that a fluctuating signal is obtained even if the intensity of the incident light is constant. The intensity of the photons arriving at varying time intervals is superimposed on this already fluctuating signal. In correlation analysis, the uncorrelated signal is constant, whereas the signal associated with the diffusing particles decays exponentially. In spectrum analysis, the uncorrelated signal is akin to a DC or zero frequency term which is not recorded. The time-dependent component is analysed to determine the particle-size distribution using the theory of DLS.

6.6 Computation unit, capable of signal processing to obtain the particle size and/or particle size distribution. Some computation units also function as the signal processing unit.

— Evaluation via the autocorrelation function allows determination of a mean diameter without determination of the particle size distribution, but determination of the distribution is also possible.

— Evaluation via the frequency distribution determines the particle size distribution using the power spectrum of the signal.

— Evaluation via photon cross-correlation allows quantification/minimization of the effects of multiple scattering, thus extending the useful concentration range towards higher concentrations (however, the effect of particle-particle interaction cannot be eliminated). The disadvantage of this method is that it requires a more complex optical setup.

6.7 Instrument location, placed in a clean environment, free from excessive electrical noise and mechanical vibration and out of direct sunlight. If organic liquids are used as the suspension medium, there shall be due regard to local health and safety requirements, and the area shall be well ventilated. The instrument shall be placed on a rigid table or bench to avoid the necessity for frequent realignment of the optical system.

WARNING — DLS instruments are equipped with a low- or medium-power laser whose radiation can cause permanent eye damage. Never look into the direct path of the laser beam or its reflections. Ensure highly reflecting surfaces are not in the path of the laser beam when the laser is on. Observe local regulations for laser radiation safety.

7 Test sample preparation

7.1 General

Test samples should consist of well-dispersed particles in a liquid medium. Dispersion procedures like sonication, filtration, etc. may influence the result and therefore have to be reported. The suspension liquid shall

a) be sufficiently transparent (non-absorbing) and non-fluorescent at the laser wavelength,

b) be free of particulate contamination,

c) not dissolve, swell or coagulate the particulate material,

d) have a known refractive index that is sufficiently different from that of the particulate materials,

e) have a known value of viscosity within ±2 % over the operational range of temperature to be used, and

NOTE As $\bar{x}_{\mathrm{DLS}}$ is directly proportional to η, the uncertainty of $\bar{x}_{\mathrm{DLS}}$ will always be larger than the uncertainty of η.

f) meet the guidelines of the instrument for low background scattering.

(This can be checked by measuring the count rate for the suspending medium alone and the dark count with no sample or solvent present. The former should be at least one order of magnitude lower than the sample, and the latter should be within the recommended range for the instrument.)

Inadequate suppression of the double layer can have a significant influence on the hydrodynamic diameter. A medium with ionic strength high enough to suppress the electric or diffuse double layer can improve agreement between results obtained by DLS and electron microscopy. A conductivity of 1 mS/cm is usually sufficient to achieve this between the hydrodynamic diameter and that obtained by microscopy techniques, especially for small particles.

Water is often used as a suspension medium. The use of freshly deionised and filtered (pore size 0,2 µm) water is recommended. A trace of ionic additive (e.g. NaCl at a concentration of 10 mmol/l = 0,6 g/l) may be added to such samples to reduce the double-layer thickness. However, precaution has to be made that such ionic strength adjustment will not make sample unstable or that the additive does not react with the sample (e.g. Cl with Ag ions).

7.2 Concentration limits

The lower concentration limit of the working range of DLS is determined, amongst other factors like particle size, detector sensitivity, etc., by the number of particles that are present in the scattering volume.

The scattered light intensity (e.g. expressed as count rate or I_S) of the sample containing the dispersed particles should ideally be ≥10 times the signal obtained by the suspension medium alone. Scattered intensity ratios below 10, either caused by low particle mass fractions or by very broad particle size distributions, will result in higher variation of results and poorer precision.

The maximum concentration of dispersed particles that can be measured without the concentration influencing the particle size reported is determined by particle-particle interaction and multiple scattering. This concentration limit should be determined empirically by dilution (see Annex B).

7.3 Checks for concentration suitability

Different instruments adopt differing optical observation angles and optical arrangements. The observations and checks given are for the general case, but the specific instrument operational advice should also be considered.