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Particle size analysis — Dynamic light scattering (DLS)

Analyse granulométrique — Dispersion lumineuse dynamique (DLD)

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 22412 was prepared by Technical Committee ISO/TC 24, *Particle characterization including sieving*, Subcommittee SC 4, *Sizing by methods other than sieving*.

Introduction

Particle[1)] sizing in the submicrometer size range is nowadays performed on a routine basis using the dynamic light scattering (DLS) method. The success of the technique is mainly based on the fact that it provides estimates of average size and its distribution in a measurement time of a few minutes, and user-friendly commercial instruments are available. Nevertheless, proper use of the instrument and interpretation of the result require certain precautions.

To this end, ISO 13321 was developed. ISO 13321 provides the procedures necessary to allow determination of the correct particle size using the photon correlation technique. The instruments specified in ISO 13321 are restricted to low particle concentrations in order to avoid disturbances due to multiple scattering. Instruments that seek to minimize this restriction are now available. Therefore, there is a need for an International Standard for the determination of particle size by DLS suitable for a wide concentration range of dispersions that will enable users to obtain good interlaboratory agreement on accuracy and reproducibility.

Several techniques have been developed for DLS[2)]. These techniques can be classified in two ways:

a) by the difference in data analysis (correlation method and frequency analysis method);

b) by the difference in optical set-up (homodyne and heterodyne detection optics).

Instruments are now available with a range of fixed and movable cell options.

Although DLS allows the determination of particle-size distribution, this International Standard is limited to the description of size distribution by means of only two robust descriptors: an average size and a polydispersity index. Many different methods for the calculation of full size distributions are used. However, reproducibility of the different methods of calculation for full distributions is, at present, not good enough to include in an International Standard. Therefore, today, there is no standardized algorithm that may be included in an International Standard.

1) The NIST definition of a particle is: “Any condensed-phase tridimensional discontinuity in a dispersed system may generally be considered a particle” (Reference [19]).

2) DLS probes the dynamics of time-dependent phenomena such as particle motions. DLS combined with the correlation method of data analysis is often referred to as photon correlation spectroscopy.

Particle size analysis — Dynamic light scattering (DLS)

1 Scope

This International Standard specifies a method for the application of dynamic light scattering (DLS) to the estimation of an average particle size and the measurement of the broadness of the size distribution of mainly submicrometre-sized particles or droplets dispersed in liquids.

This International Standard is applicable to the measurement of a broad range of dilute and concentrated suspensions. The principle of DLS is the same as for a dilute dispersion. However, specific requirements for the instrument set-up and specification of test sample preparation, as well as some advice on the correct interpretation of the results of measurements for concentrated dispersions, are required.

NOTE A photon correlation spectroscopy method for dilute dispersions is specified in ISO 13321.

2 Normative references

The following referenced documents are indispensable for the application 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 13321:1996, *Particle size analysis — Photon correlation spectroscopy*

3 Terms and definitions

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

3.1
average particle diameter
$\bar{x}_{DLS}$
⟨dynamic light scattering⟩ harmonic intensity-weighted arithmetic average particle diameter

NOTE Average particle diameter is expressed in nanometres. Typical average particle diameters are in the range 1 nm to about 1 000 nm.

3.2
polydispersity index
PI
dimensionless measure of the broadness of the size distribution

NOTE 1 Adapted from ISO 13321:1996, 2.2.

NOTE 2 The PI typically has values less than 0,1 for a monodisperse test sample.

3.3
scattering volume
V
section of the incident laser beam viewed by the detector optics

NOTE Adapted from ISO 13321:1996, 2.3.

3.4
scattered intensity
count rate
photocurrent
I_s
intensity of the light scattered by the particles in the scattering volume; in practice, a number of photon pulses per unit time or a photodetector current which is proportional to the scattered intensity as measured by a detector

3.5
qualification
⟨dynamic light scattering⟩ proof with reference material that an instrument is operating in agreement with its specifications

3.6
validation
⟨dynamic light scattering⟩ proof with reference material that a procedure is acceptable for all elements of its scope

4 Symbols, abbreviated terms and units

$C(\Gamma)$	distribution function of decay rates or inverse characteristic frequencies	arbitrary units	
D	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
$g^{(1)}(\tau)$	normalized electric field correlation function	arbitrary units	
$G^{(2)}(\tau)$	intensity correlation function	arbitrary units	
I_s	scattered intensity, count rate, photocurrent		
n	refractive index of the dispersion medium	dimensionless	
$P(\omega)$	power spectrum	arbitrary units	
PI	polydispersity index		
$\Delta Q_{\text{int},i}$	intensity-weighted amount of particles with size x_i	arbitrary units	
V	scattering volume		
x	diameter of a spherical particle	nanometres	nm
$\bar{x}_{\text{DLS}}$	average particle diameter	nanometres	nm
Γ	decay rate and characteristic frequency	reciprocal seconds	s^{-1}
$\bar{\Gamma}$	intensity-weighted average value of the decay rate	reciprocal seconds	s^{-1}
η	viscosity of the dispersion medium	millipascal seconds	mPa·s
θ	scattering angle	degrees	°
λ_0	wavelength of the laser in a vacuum	nanometres	nm

μ_2	second cumulant of the intensity-weighted size distribution	arbitrary units	
ρ	particle density	grams per cubic centimeter	g/cm^3
τ	correlation time	seconds	s
φ	particle volume fraction	arbitrary units	
ω	angular frequency	reciprocal seconds	Hz

5 Principle

5.1 General

Submicrometre-sized particles suspended in a fluid are in constant random Brownian motion as the result of the interaction with the molecules of the suspending fluid. In the Stokes-Einstein theory of Brownian motion (Reference [16]), particle motion at very low concentration is determined by the suspending fluid viscosity and temperature, and the size of the particle. From a measurement of the particle motion in a fluid of known temperature and viscosity, the particle size can be determined. At low particle concentrations, this is a hydrodynamic particle size (see ISO 13321). At increased concentrations, multiple scattering and particle-particle interactions are relevant. The influence of multiple scattering can be suppressed by the measurement setup. Particle-particle interactions mean that only an apparent particle size can be measured (see Annex B). The DLS technique (References [15], [17], [18]) probes the motion optically. The suspended particles are illuminated with a coherent 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.

5.2 DLS optical detection

5.2.1 The use of a coherent optical reference allows, through optical wave interference, the conversion from spectral central frequencies to the difference between light frequencies (the shift frequencies). For DLS the shift frequencies are on the scale 1 Hz to 100 kHz, readily detected by modest frequency electronics. Two methods of referencing are commonly used and are illustrated in Figure 1.

a) homodyne **b) heterodyne**

Key

1 scattered light
2 portion of unscattered beam
3 detector
4 autocorrelator or spectrum analyser

Figure 1 — Optical arrangement for DLS

5.2.2 Homodyne detection [see Figure 1 a)] is also referred to as self-referencing or self-beating detection. The mixing at the optical detector of all of the collected scattered light provides the reference for frequency- or phase-difference measurement.

5.2.3 Heterodyne detection [see Figure 1 b)] is also referred to as reference beating or controlled reference detection. 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.

5.2.4 The resulting detector output from either mode contains a distribution of frequencies or time-dependent phases representative of the particle size of the suspended particles. The detector output has two components; a constant level, representing the average intensity of the collected light and a time-varying component, representing the DLS effect. The time-dependent component is analyzed to determine the particle-size distribution using the theory of DLS.

The time-dependent signal is generally processed by one of two methods: time-based correlation function or frequency-based power spectrum. The two methods are mathematically related. The time-based correlation function is the Fourier transform of the frequency-based power spectrum. The two techniques of DLS analysis are presented in Annex A.

6 Calculation of mean particle size and PI

The signals captured by the detector can be processed and analyzed by correlation function analysis and frequency analysis. A short description of these methods is given in Annex A. Note that correlation functions and frequency power spectra are Fourier transform pairs. In both methods, the size distributions may be obtained as a discrete set of diameters, x_i, and corresponding intensity-weighted amounts $\{\Delta Q_{\text{int},i}, x_i, i = 1 \ldots N\}$.

From this set, the (intensity-weighted) average diameter, $\bar{x}_{\text{DLS}}$, is estimated from Equation (1):

$$\bar{x}_{\text{DLS}} = \frac{\sum_{i=1}^{N} \Delta Q_{\text{int},i}}{\sum_{i=1}^{N} \frac{\Delta Q_{\text{int},i}}{x_i}} \tag{1}$$

and a PI (a measure of the broadness of the distribution), is estimated from Equation (2):

$$\text{PI} = 2\bar{x}_{\text{DLS}}^2 \frac{\sum_{i=1}^{N} \Delta Q_{\text{int},i} (1/x_i^2 - 1/\bar{x}_{\text{DLS}}^2)}{\sum_{i=1}^{N} \Delta Q_{\text{int},i}} \tag{2}$$

Alternatively, correlation function data can be analysed by the cumulants method presented in A.1.3.2, yielding also an intensity-weighted average diameter, $\bar{x}_{\text{DLS}}$, and PI. Note that, in practice, the PI obtained from the cumulant analysis may be different from the one estimated by Equation (2).

7 Apparatus

Usual laboratory apparatus and in particular the following.

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

7.2 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.

7.3 Test sample holder, enabling the control and measurement of the temperature to within ±0,3 °C.

7.4 Photon detector, with an output proportional to the intensity of the scattered light. A photomultiplier tube, an avalanche photodiode or a photodiode is typically used.

7.5 Signal processing unit, capable of taking the time-dependent intensity signal and outputting the autocorrelation function, cross-correlation function or power spectrum of the input signal.

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

8 Preliminary procedures

8.1 Instrument location

Place the instrument in a clean environment, free from excessive electrical noise and mechanical vibration and out of direct sunlight.

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.

8.2 Test sample preparation

Test samples shall consist of well-dispersed particles in a liquid medium. The dispersion liquid shall:

a) not dissolve, swell or coagulate the particulate material;

b) have a refractive index different from that of the particulate materials;

c) have a refractive index and viscosity known to within ± 0,5 %;

d) give a very low intensity signal when checked in the instrument for contamination;

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

9 Measurement procedure

The measurement procedure assumes a properly installed and aligned instrument and an operator familiar with the instrument and its manual.

9.1 Switch the instrument on and allow it to warm up. Typically about 15 min to 30 min is required to stabilize the laser intensity and to bring the sample holder to the desired temperature.

9.2 Check the dispersion medium for background scattering; ensure that it is at least within the instrument guidelines and record its average scattered intensity.

9.3 Place the test sample (8.2) in the instrument and allow temperature equilibrium to be established between test sample and test sample holder. The temperature shall be controlled and measured to within ±0,3 °C.

Uncertainties in particle size determined in aqueous dispersions will be approximately 2 % per degree Celsius at ambient temperature if the test sample has not reached temperature equilibrium.

Ensure that no air bubbles are entrapped in the test sample.