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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 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.

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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.

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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
$\overline{x}_{DLS}$
⟨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		
$\Delta Q_{\mathrm{int},i}$	intensity-weighted amount of particles with size x_i	arbitrary units	
V	scattering volume		
x	diameter of a spherical particle	nanometres	nm
$\bar{x}_{\mathrm{DLS}}$	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):

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

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

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

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.

9.4   Record: test sample identification, actual local measurement time and measurement duration, measurement temperature, refractive index and viscosity of the dispersion medium, particle concentration, wavelength of laser and scattering angle if these parameters are selectable.

9.5   Check the average scattered intensity of the sample. The scattered intensity shall be greater than that of the dispersion medium on its own. For each sample, perform at least three measurements and record the results.

9.6   Record the average particle diameter, $\bar{x}_{DLS}$, and PI for each of the measurements.

9.7   Check at the end of the measurement that no significant sedimentation has occurred in the test sample. If sedimentation is found, then either the test sample may have aggregated and precipitated or the material may be fundamentally unsuitable for measurement.

10 System qualification

Instrument performance can be qualified using a dispersion of particles of certified size after the first installation of the instrument and at regular time intervals thereafter.

Failure of the qualification indicates a problem with this particle dispersion, the preparation of the test sample (8.2) or the instrument.

Dispersions of polystyrene latex with narrow size distribution with average particle diameter as measured by DLS of about 100 nm shall be used. For such dispersions, the measured average particle size shall be within ±2 % of the stated size and the repeatability shall be better than 2 %; the PI shall be smaller than 0,1.

11 Repeatability

For dispersions different from the one used for the qualification (Clause 10), the repeatability of the determination of average particle size shall be better than 5 %.

12 Test report

The test report shall contain at least the following information:

a)   average particle size, $\bar{x}_{DLS}$, being the mean and standard deviation of at least three repeat measurements[3];

b)   the PI, being the mean and standard deviation of at least three repeat measurements[3];

c)   if the mean values of $\bar{x}_{DLS}$ and PI are concentration dependent, their values extrapolated to infinite dilution or the value obtained at the lowest concentration;

d)   all the information required for the complete identification of the sample, including details of particle shape and homogeneity;

e)   the sampling method used, if known;

f)   the test method used, together with reference to this International Standard;

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3)   ISO 13321:1996 specifies six repeat measurements. Experience with the method specified in this International Standard indicates that three repeat measurements are sufficient.

g) the instrument type and number;

h) the dispersion conditions:

    1) dispersing liquid and its cleaning procedure,

    2) concentration of particulate material,

    3) dispersing agents and their concentration,

    4) dispersing procedure,

    5) sonication conditions: frequency and applied power (if necessary);

i) the measurement conditions:

    1) actual concentrations investigated,

    2) viscosity and refractive index of the dispersion liquid,

    3) temperature of the sample;

j) analyst identification:

    1) name and place of laboratory,

    2) operator's name or initials,

    3) date;

k) all operating details not specified in this International Standard, or regarded as optional, together with details of any incident that may have influenced the result(s).

Annex A
(informative)

Correlation function and frequency analysis

A.1 Correlation function analysis

A.1.1 Autocorrelation

A monochromatic and coherent laser light beam illuminates a test sample of small volume in a cell. The light scattered by the particles in the test sample is measured by a detector. The scattered light at the detector at a given time is the sum of the scattered light radiated from all of the particles in the illuminated volume in the direction of the detector. The scattered light intensity is correlated with a delayed value of itself (see A.1.3 for further details). In Figure A.1 an example of autocorrelation functions is shown.
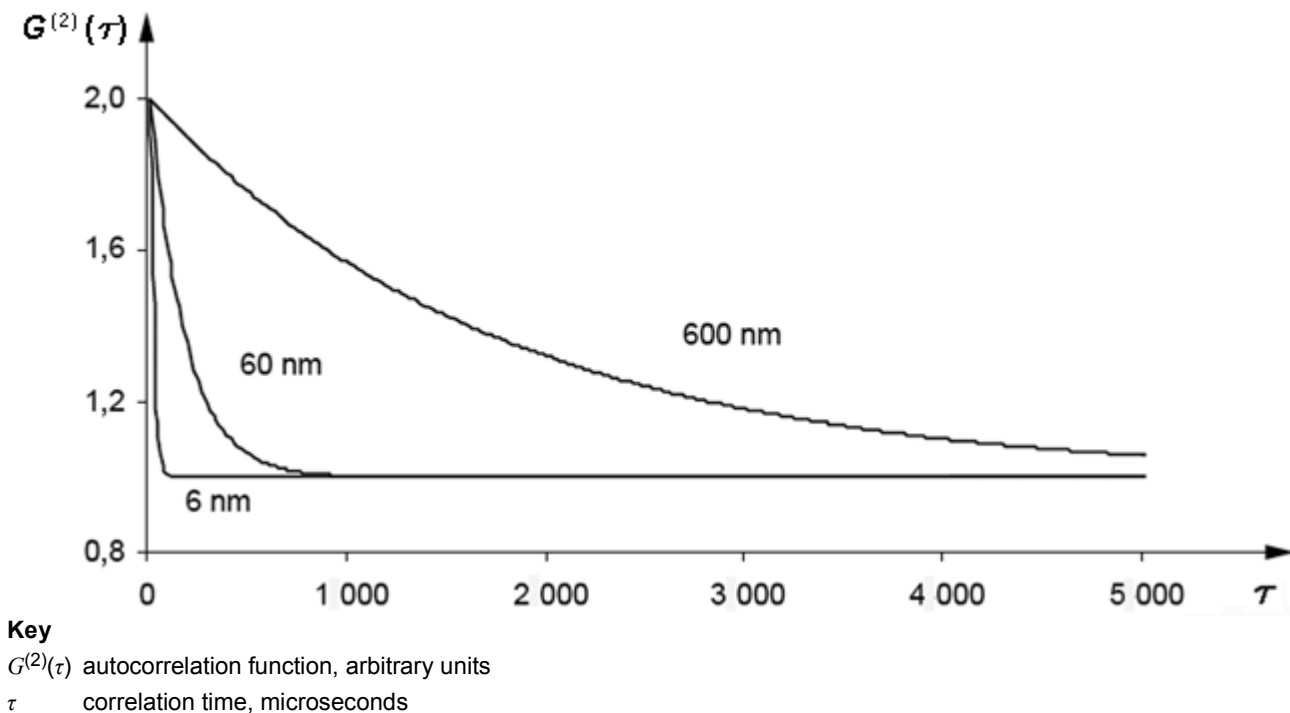

Key

$G^{(2)}(\tau)$ autocorrelation function, arbitrary units

τ correlation time, microseconds

Figure A.1 — Autocorrelation functions (normalized)

ISO 13321 provides the necessary procedures to allow determination of the correct particle size with the autocorrelation method. It is, however, restricted to dilute samples.

A.1.2 Cross-correlation

Two monochromatic and coherent laser light beams are focused in a test sample. The two light beams cross each other within the test sample. The overlap of the two laser beams forms the measurement volume. Light scattered by the particles is detected under the scattering angle by two detectors. Thus, two independent scattering measurements are performed at the same measurement volume. This reduces the effect of multiple scattering on the measurement result (see Annex B).

Measured cross-correlation functions look like the autocorrelation functions of Figure A.1.

A.1.3 Data analysis

A.1.3.1 Function analysis

Autocorrelation or cross-correlation function analysis is applied to the statistical fluctuations of the scattered intensity (see ISO 13321 for more details).

In general, the correlation function, $G^{(2)}(\tau)$, is defined by Equation (A.1):

$$G^{(2)}(\tau) = \langle I_{sA}(t)\, I_{sB}(t + \tau)\rangle \tag{A.1}$$

where

  $I_{sA}(t)$ is the scattered intensity of beam A at time t;

  $I_{sB}(t + \tau)$ is the scattered intensity of beam B at time $t + \tau$.

The angular brackets indicate the ensemble mean of their contents. If only one detector is used, intensities $I_{sA}(t)$ and $I_{sB}(t)$ are identical and the intensity autocorrelation function, $G^{(2)}(\tau)$, is given by Equation (A.2):

$$G^{(2)}(\tau) = \langle I_s(t)\, I_s(t + \tau)\rangle \tag{A.2}$$

where

  $I_s(t)$ is the scattered intensity at time t;

  $I_s(t + \tau)$ is the scattered intensity at time $t + \tau$.

In homodyne detection mode, the correlation function of the scattered intensity, $G^{(2)}(\tau)$, is related to the electric-field correlation function, $g^{(1)}(\tau)$, by Equation (A.3) (the Siegert equation):

$$G^{(2)}(\tau) = A[1 + B\,|g^{(1)}(\tau)|^2] \tag{A.3}$$

where

  A is a normalization factor;

  B is an instrumental factor.

For polydisperse samples, $g^{(1)}(\tau)$ is related to the normalized distribution function of decay rates, $C(\Gamma)$ by Equation (A.4):

$$g^{(1)}(\tau) = \int_0^\infty C(\Gamma)\exp(-\Gamma\tau)\,\mathrm{d}\Gamma \tag{A.4}$$

with

$$\int_0^\infty C(\Gamma)\,\mathrm{d}\Gamma = 1 \tag{A.5}$$

The decay rates, Γ, are related to the translational diffusion coefficients of spherical particles by Equation (A.6):

$$\Gamma = Dq^2 \tag{A.6}$$

where

D is the translational diffusion coefficient of the set of illuminated particles;

q is the modulus of the scattering vector, given by Equation (A.7):

$$q = 4\pi n \sin(\theta/2)/\lambda_0 \tag{A.7}$$

in which

n is the refractive index of the dispersion medium;

λ_0 is the wavelength of the laser in a vacuum.

The particle diameter, x, is calculated by rearranging the Stokes-Einstein equation to give Equation (A.8) (Reference [16]), assuming that the sample being investigated consists of a set of non-interacting spherically shaped particles:

$$x = \frac{k_B T}{3\pi \eta D} \tag{A.8}$$

where

D is the translational diffusion coefficient of the set of illuminated particles;

k_B is the Boltzmann constant;

T is absolute temperature;

η is the viscosity of the dispersing medium.

There are two methods of calculating mean particle size and PI.

A.1.3.2   The cumulants method

In the cumulants method, the intensity correlation function, $G^{(2)}(\tau)$, is expanded around the average value, $\bar{\Gamma}$, yielding a polynomial series, which is normally truncated after the quadratic term in the series for the sake of practicability [see Equation (A.9)]:

$$G^{(2)}(\tau) \approx A\left[1 + B \exp\left(-2\bar{\Gamma}\tau + \mu_2 \tau^2\right)\right] \tag{A.9}$$

where $\mu_2 = \overline{\left(\Gamma - \bar{\Gamma}\right)^2}$.

The calculated cumulants are related to the intensity-weighted particle-size distribution.

The average particle size, $\bar{x}_{DLS}$, is calculated using Equations (A.6) to (A.8) with the average decay rate, $\bar{\Gamma}$.

The PI is defined as

$$PI = \frac{2\mu_2}{\bar{\Gamma}^2}$$ (A.10)

Note that, in practice, the PI obtained from the cumulant analysis may be different from the one estimated by Equation (2).

A.1.3.3 Laplace inversion for particle-size distribution

In these methods, Equation (A.4) is solved for the distribution of decay rates, $C(\Gamma)$. The decay rates, Γ, are linked to the particle sizes by Equations (A.6) to (A.8). Several methods are used to solve this non-linear equation. The first step consists of linearizing Equation (A.4) by fixing a particle-size range and dividing the range into a discrete set of fixed particle sizes $\{x_i, i = 1...N\}$. In a second step the intensity-weighted fraction of particles $\{\Delta Q_{int,i}, i = 1...N\}$ with sizes x_i is determined. The size distribution, $\Delta Q_{int,i}(x_i)$, is reported as a discrete set of diameters, x_i, and corresponding intensity-weighted fractions $\Delta Q_{int,i}$: $\{\Delta Q_{int,i}, x_i, i = 1...N\}$.

If the refractive indices for both the particles and the suspending medium are known, then distributions by a volume or number basis may be obtained. Many different methods are used. At the time of publication, there is no standardized algorithm that can be included in this International Standard.

A.2 Frequency analysis

For a monodisperse system, the forms of the power spectrum, $P(\omega)$, are given by Equation (A.11) for homodyne detection and Equation (A.12) for heterodyne detection (see Reference [2], section 5.4):

$$P(\omega) = \langle I_s \rangle^2 \frac{2\Gamma}{\omega^2 + (2\Gamma)^2}$$ (A.11)

$$P(\omega) = I_0 \langle I_s \rangle \frac{\Gamma}{\omega^2 + \Gamma^2}$$ (A.12)

where

I_0 is the intensity of the incident radiation;

I_s is the scattered intensity;

Γ is the characteristic frequency;

ω is the angular frequency.

Hence, the characteristic frequency, Γ, is related to the particle size, $\bar{x}_{DLS}$, by Equations (A.6) to (A.8).

In the homodyne mode, the amplitude of the power spectrum is proportional to the square of the scattered intensity, $\langle I_s \rangle^2$, which is proportional to the sample concentration. In this mode, it is assumed that no unscattered primary beam is mixed with the scattered light. It is assumed that the condition $I_0 << \langle I_s \rangle$ is met. This insures that the mode is purely homodyne with no mixture of heterodyne.

In the heterodyne mode, a reference component of the laser input is mixed with the collected scattered light. The power spectrum in the heterodyne mode will always have a component of the homodyne mode. In order to treat the power spectrum as pure heterodyne, the homodyne component has to be arranged to be very small compared with the heterodyne component. This can be met if $I_0 >> \langle I_s \rangle$. At high concentrations, and thus high $\langle I_s \rangle$, caution must be observed to insure that $I_0 >> \langle I_s \rangle$ is met. Mixing of the modes combines power spectra with different characteristic frequencies, Γ, in the heterodyne mode and 2Γ in the homodyne mode.

Numerous arrangements have been utilized to produce instruments operating in either the homodyne or the heterodyne mode.

The power spectrum is a Lorentzian function given by Equations (A.11) and (A.12). The characteristic frequency, Γ, is inversely proportional to the particle size and represents the half power point of the heterodyne spectrum (2Γ in the homodyne mode). Figure A.2 plots the power spectrum for different particle sizes in the heterodyne mode. The inverse relationship of the characteristic frequency with particle size is evident.

For a polydisperse system, the normalized power spectra are related to the distribution of characteristic frequencies or inverse decay rates, $C(2\Gamma)$, for homodyne and heterodyne, by Equations (A.13) and (A.14), respectively (see e.g. Reference [6]):

$$P_1(\omega) = \int_0^\infty C(\Gamma) \frac{2\Gamma}{\omega^2 + (2\Gamma)^2} \, \mathrm{d}\Gamma \tag{A.13}$$

$$P_1(\omega) = \int_0^\infty C(\Gamma) \frac{\Gamma}{\omega^2 + \Gamma^2} \, \mathrm{d}\Gamma \tag{A.14}$$

Equations (A.13) and (A.14) are solved for size distributions in a similar way to that used in correlation function analysis. Other techniques are also employed. First, a set of particle sizes $\{x_i, i = 1 \ldots N\}$ is fixed and, secondly, the intensity-weighted fraction of particles $\{\Delta Q_{\mathrm{int},i}, i = 1 \ldots N\}$ of each size x_i is determined.
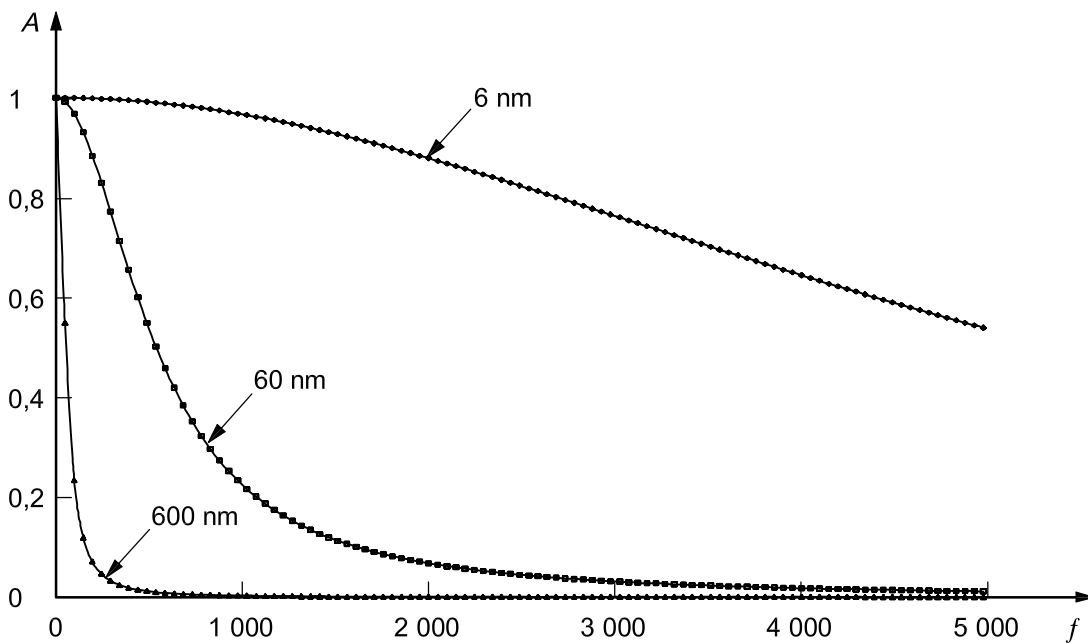
Key

A amplitude, arbitrary units

f frequency, hertz

Figure A.2 — Power spectrum in heterodyne mode (normalized)

If the refractive indices for both the particles and the suspending medium are known, then distributions by a volume or number basis may be obtained. Many different methods are used. At the time of publication, there is no standardized algorithm that can be included in this International Standard.

Annex B
(informative)

Concentration effects

B.1 General

DLS probes the random Brownian motion of the particles. Only for very dilute dispersions of spherical particles can the measured diffusion coefficient be related to particle size by the Stokes-Einstein equation. For more concentrated dispersions several limitations arise.

The main problems arise from multiple scattering, collective and self-diffusion and particle-particle interactions.

B.2 Multiple scattering limitations

DLS analysis assumes that only single scattered light is collected. As sample concentration increases, the probability increases that the scattered light is rescattered by further interaction with the suspension along the path the light takes to the detector. The experimental correlation function or power spectrum is not represented well by Equations (A.4), (A.13) or (A.14).

Several strategies are used to minimize the effect of multiple scattering.

One technique utilizes an optical system which minimizes the optical path in and out of the test sample. There are a number of means of accomplishing a minimum optical path in the test sample, including the use of backscatter optics. Backscatter optics allows a short pathlength to be designed. Even if the test sample is optically opaque for long pathlengths, multiple scattering over short pathlengths may be negligible. In one implementation, the measurement position within the cell is changed by moving the cell assembly. Thus for high concentration test samples, the measuring volume is located close to the cell wall. In another implementation, the maximum optical intensity of the incident beam is located at the interface of the suspension and the optical window into the sample. The sample volume in this case is located at the interface and requires a minimum pathlength for light to enter and backscattered light to be collected.

Another way is to use the cross-correlation method of A.1.2.

The idea is to perform simultaneously two scattering measurements in a three-dimensional geometry in such a way that the two scattering vectors and scattering volumes are the same, but the corresponding wave vectors are not coincident. On a screen in the far field, these two laser beams produce two speckle patterns which are also shifted with respect to each other. It is obvious that the signals of two detectors placed at the position of equivalent speckles are correlated. However, the correlation is not perfect, since on the one hand both detectors see 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.

In principle, this eliminates the contributions from multiple scattering. In practice, multiple scattering effects are minimized. The upper concentration limit for dispersed material is reached when scattered light can no longer be observed. Similar to the backscatter optics, higher concentrations can be achieved by reduced optical pathlengths.

B.3 Particle-particle interaction limitations

DLS theory assumes that the suspended particles interact only with the molecules of the suspending medium. As suspension concentration increases, the average particle to particle spacing decreases and the interaction between particles increases.

For concentrated samples, DLS probes the diffusion of an ensemble of many particles rather than measuring a single particle diffusion coefficient. Depending on particle size, concentration, scattering angle, and laser wavelength, two different diffusion coefficients can be distinguished. The ratio of the average interparticle distance, h, to the inverse of the modulus of the scattering vector q^{-1} will determine which of the following situations occurs (see Figure B.1).

If $q^{-1} < h/2\pi$, self-diffusion of single particles in the presence of many others is observed by DLS.

If $q^{-1} > h/2\pi$, the collective diffusion of an ensemble of particles is observed.
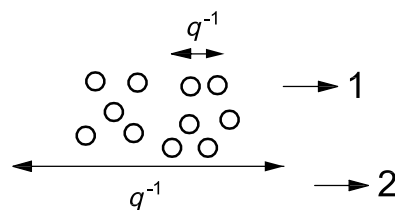
Key

1   self-diffusion

2   collective diffusion

**Figure B.1 — Effect of the ratio of mean interparticle distance
and inverse scattering vector modulus on diffusion**

Both modes can be described by a different diffusion coefficient, namely that of self-diffusion, D_s, and that of collective diffusion, D_c. Both diffusion coefficients are concentration dependent, but in different ways.

When measuring a dilute dispersion of relatively large particles in the test sample, the inverse modulus of the scattering vector, q^{-1} [Equation (A.7)], is smaller than the mean interparticle spacing.

$$\frac{h}{2\pi} = \frac{x}{2\left(6\pi^2\varphi\right)^{1/3}}$$

(B.1)

where

   x is particle size;

   φ is particulate volume fraction.

Therefore, the self-diffusion coefficient of each particle is observed. However, when the particle concentration is increased and/or for relatively smaller particles, the mean interparticle spacing becomes smaller than the scattering vector; the collective diffusion of particles is observed instead of self-diffusion.

As a result, the apparent particle size computed with the Stokes-Einstein equation from the measured diffusion coefficient can increase or decrease with particle concentration.

Note that the above discussion, and in particular the Stokes-Einstein equation for the translational diffusion coefficient, holds only for spherical particles. For an anisometric particle, the measured diffusion coefficient is a superposition of translational and rotational diffusion coefficients.

Finally, interparticle interactions have an important influence on the measured particle diffusion. There are several types of interactions, ranging from purely hydrodynamic hindering, to electrostatic repulsions caused by the existence of a surface potential of the particles, to van der Waals attraction. They can also all occur simultaneously. Due to the presence of particle interactions, the measured diffusion coefficients are no longer individual particle properties, but properties of the whole particle suspension.

B.4 Measurements of high concentration suspensions

For an unknown sample, it is not possible to predict at what concentration the limitations noted above will begin to affect the apparent size of the particles. Therefore, it is advised to perform a series of measurements over several decades of concentration. At higher concentrations, multiple scattering, particle-particle interaction and other effects (e.g. non-spherical geometry) may affect the measured size. In this case, extrapolation of the apparent measured size to zero concentration is necessary in order to obtain an unbiased particle size. Quality procedures should determine the maximum concentration allowed for measurement of a particular material-dispersant combination. This means that a validation procedure has to be executed for measurement of a given type of sample in a given instrument. Keep in mind that by diluting a sample, the particle size may change because of changes in the chemistry of the sample or the extent of the electrical double layer. However, the apparent particle size computed with the Stokes-Einstein equation for a fixed finite particle concentration can be used for quality control purposes even though this apparent size may not be the same as that measured by diluting the sample to the concentration recommended in ISO 13321.

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