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Particle size analysis — Photon correlation spectroscopy

Analyse granulométrique — Spectroscopie par corrélation de photons

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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.

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.

International Standard ISO 13321 was prepared by Technical Committee ISO/TC 24, *Sieves, sieving and other sizing methods*, Subcommittee SC 4, *Sizing by methods other than sieving*.

Annex A forms an integral part of this International Standard. Annexes B to F are for information only.

Introduction

Particle sizing in the submicrometer size range is nowadays performed on a routine basis using photon correlation spectroscopy (PCS). The success of the technique is mainly based on the facts that it provides estimates of average particle size in measuring times of a few minutes and that user-friendly commercial equipment is available. Nevertheless, proper use of the instrument and interpretation of the results require certain precautions. Therefore there is a need for an International Standard for the determination of particle size by photon correlation spectroscopy, in order to provide a methodology that allows the users to obtain good interlaboratory agreement on accuracy and reproducibility.

Although PCS allows the determination of particle size distribution, this International Standard is limited to the description of size distribution by means of only two parameters: an average size and a polydispersity index, as obtained by so-called cumulants analysis (see annex A). This does not exclude more detailed information about particle size distributions being obtained. However, the reproducibility and reliability of the method of calculation for full distributions is, at the present state of the art, not good enough to include in an International Standard. Again, this does not exclude determination of acceptable size distributions in particular applications.

This International Standard recommends measurements at a single scattering angle of 90° using a He-Ne laser light source with a wavelength *in vacuo* of 632,8 nm. Since solid state laser sources operating at other wavelengths have become available and may be used in future instruments, this International Standard already includes recommendations for such instruments. Although the procedure given is limited to a single angle measurement, with some instruments additional measurements and valuable additional information can be obtained at other scattering angles or by simultaneous analysis of measurements performed at different angles.

This International Standard uses isotropic spherically shaped particles within a test procedure. Measurement of nonspherical and/or nonisotropic particles can be made by this technique where the size of such particles is reported by a spherical equivalence.

A list of suitable references for further reading is given in annex F.

Particle size analysis — Photon correlation spectroscopy

1 Scope

This International Standard describes the application of photon correlation spectroscopy (PCS) to the measurement of an average particle size and a measure of the broadness of the size distribution of particles dispersed in liquids. It is applicable to particle sizes ranging from a few nanometres to about 1 μm, or to the onset of sedimentation. In the data analysis procedure (see annexes A and C) it is assumed that the particles are isotropic and spherically shaped.

NOTE 1 — The technique is also known or referred to under other names, e.g. quasi-elastic light scattering (QELS) and dynamic light scattering (DLS).

2 Definitions

For the purposes of this International Standard, the following definitions apply.

2.1 average particle diameter, x_{PCS}**:** Harmonic intensity-averaged particle diameter, as determined by equation (C.10) of annex C.

It is expressed in nanometres (10^{-9} m).

2.2 polydispersity index, PI: Dimensionless measure of the broadness of the size distribution, as determined by equation (C.9) of annex C.

2.3 scattering volume, V**:** Section of the incident laser beam viewed by the collecting or detector optics.

Typical order of magnitude is 10^{-6} cm³.

3 Symbols

B value of the intercept of the intensity autocorrelation function [see equation (C.6) of annex C];

B_{max} maximum value of the intercept B for a given setting of the detection optics;

c concentration of particulate material, in moles per litre;

$G_2(\tau)$ intensity autocorrelation function;

n refractive index of the dispersion medium;

N_V number of particles in scattering volume V;

η viscosity of the dispersion medium;

Γ decay rate;

λ_0 laser wavelength *in vacuo* (632,8 nm for He-Ne laser);

ϕ particle volume fraction;

ρ particle density;

θ scattering angle;

μ_2 second cumulant.

4 Principle

A monochromatic and coherent laser light beam illuminates a representative sample for particle size analysis, dispersed at a suitable concentration in a liquid. The light scattered by the particles at an angle (typically 90°) is recorded by a detector whose output is fed to a correlator. The decay of the autocorrelation function of the scattered intensity is interpreted in terms of average particle size and polydispersity index by the so-called cumulants method.

Annex C provides some theoretical background for particle sizing by PCS.

5 Apparatus

The main components of a typical photon correlation spectrometer are listed below.

NOTE 2 — Commercial or "home-made" instruments that meet the requirements of this International Standard may be used. There are several significant differences, both in hardware and software, not only between instruments from different manufacturers but also between different types from one manufacturer. The instrument specifications do not always give adequate information for proper assessment of its specific features. Therefore, annex D has been provided to recommend specifications for PCS instruments.

5.1 Laser, monochromatic, emitting light polarized with its electric field component perpendicular to the plane formed by the incident and detected rays (vertical polarization), e.g. a He-Ne laser capable of 2 mW to 5 mW power output.

5.2 Sample holder, allowing control and measurement of the temperature to within ± 0,3 °C.

5.3 Primary beam stop.

5.4 Optics and detector, to collect and digitize the radiation scattered by the sample at an angle of, e.g., 90°. If a polarization analyzer is included, it shall be positioned in the vertical position, i.e. with a maximum transmission for light polarized with its electrical field perpendicular to the plane of incident and scattered beams.

5.5 Correlator.

5.6 Computation unit.

6 Preliminary procedures

6.1 Instrument location

The instrument shall be placed in a clean environment, free from excessive electrical noise and mechanical vibration and out of direct sunlight. If organic liquids are used (e.g. as an index-matched liquid and/or 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 necessity for frequent realignment of the optical system.

NOTE 3 — Alternatively, it may incorporate a rigid optical bench internally.

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

6.2 Sample preparation and inspection

6.2.1 Samples shall consist of well-dispersed particles in a liquid medium. The dispersion liquid shall fulfil following requirements:

a) it shall be transparent (non-absorbing) at the laser wavelength;

b) it shall be compatible with the materials used in the instrument;

c) it shall not dissolve, swell or coagulate the particulate material;

d) it shall have a refractive index different from that of the particulate material;

e) its refractive index and viscosity shall be known with an accuracy better than 0,5 %;

f) it shall be well filtered.

Water is often used as a dispersion medium. The use of freshly distilled water (the still shall be built from quartz glassware) or of deionized and filtered (pore size 0,2 μm) water is recommended. Since long-range particle interaction may affect the results for strongly charge-stabilized dispersions, a trace of salt [c(NaCl) about 10^{-3} mol/l] may be added to such samples to reduce the range of particle interaction.

Large fluctuations in recorded scattered time-averaged signals (count rate) on short time scales (e.g. 0,1 s intervals) with bursts of high count rates indicate the presence of contaminating dust. The appearance of sparkling centres in the beam also usually indicates a dusty sample. Such liquids shall be further cleaned (by filtration and/or distillation) before use.

Detailed recommendations for sample preparation are given in annex E.

The dispersion liquid alone shall give no (or very low) scattered signal when checked in the instrument for dust or contaminants.

6.2.2 The concentration of particulate material shall be above some minimum level and shall not exceed a maximum level. The minimum level is determined by the following two requirements:

1) The scattered intensity (count rate) of the sample containing the dispersed particles shall be at least 10 times higher than the signal scattered by the dispersion medium alone.

2) The number N_V of particles in the scattering volume shall be at least about 1 000 (any number in the range 500-1 000 is acceptable).

NOTE 4 — This number can be estimated from the average PCS diameter x_{PCS}, from the particle volume fraction ϕ and from the value V of the measuring volume by

$$N_V = 6\phi V/\pi x_{PCS}^3$$

A typical order of magnitude of V is 10^{-6} cm^3 (its value can be found in the specifications provided by the instrument manufacturer). This equation relates to monosized materials only; for polydisperse samples the actual number of particles in the scattering volume may be much larger than predicted by this equation. If this larger number density compromises the single-scattering criteria 3) to 5), it may be that further dilution is necessary, leading to a requirement that either the coherence aperture in the receiver be increased or the incident laser beam made larger to increase the measurement volume. A subsequent reduction in measured intercept will then be incurred. This compromise is not permitted for the purposes of calibration and verification.

The maximum level is mainly determined by the condition that only single scattering shall be observed, i.e. no multiple scattering. The absence of significant contributions from multiple scattering shall be determined by the three following checks.

3) The samples shall not look opaque but shall look clear, or only slightly cloudy or turbid. This shall always be verified before putting the sample into the instrument.

4) The ratio of the measured intercept (see annex A for its determination) to its maximal value (see the specifications of the manufacturer or clause 8 for its determination) shall be at least 0,8.

5) If the instrument allows the laser beam passing through the sample to be viewed indirectly, a sharp parallel beam shall be observed; a spreading halo around the beam or any apparent absorbance shall not be present.

NOTE 5 — If possible, the following additional check is recommended. If a spectrophotometer is available, the optical density (O.D.) of the sample at the laser wavelength used for a 1-cm path length can be used as an indicator for multiple scattering: for O.D. values larger than 0,04, multiple scattering effects are to be expected.

In many applications a volume fraction (ϕ) of dispersed particulate material in the range 10^{-5} to 10^{-4} fulfils the requirements for particle sizes below about 500 nm. [In order to obtain the concentration range (c) in mass of dispersed material per unit volume, multiply the volume fraction by the particle density ρ ($c = \rho\phi$).] For polydisperse and/or larger particles, it may not be possible to find a concentration that satisfies requirements 2), 3) and 4) without either increasing the coherence aperture of the receiver or increasing the diameter of the incident laser beam in order to increase the measurement volume. If this is so, then the intercept values obtained may not meet the criterion set out in 4). For particle sizes above 1 μm, the

requirements 2), 3) and 4) can only be fulfilled in exceptional cases.

7 Measurement procedure

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

7.1 Switch the instrument on and allow it to warm up.

Typically about 0,5 h is required to stabilize the laser intensity and to bring the sample holder to the desired temperature.

7.2 Check the dispersion medium and record the average count rate scattered by a blank sample of it.

7.3 Place a sample of the dispersion (dispersion medium + particulate sample) in the instrument and allow temperature equilibrium to be established between sample and sample holder. The temperature shall be controlled and measured with an accuracy of 0,3 °C.

NOTE 6 — It can take about 10 min for the liquid in the measurement volume of a 1-cm measuring cell to equilibrate by thermal diffusion for a temperature change of only 3 °C. Errors in particle-size determined from aqueous dispersions will be recorded at the rate of 2 % per °C if the temperature of the sample does not reach equilibrium.

A possible alternative method is to measure the room temperature and then set the instrument to control the sample holder temperature to within 0,3 °C of the room temperature. Samples can then equilibrate at room temperature and be measured immediately after insertion in the sample holder. Alternatively, samples can be equilibrated in a thermostatted bath whose temperature is within 0,3 °C of that of the instrument sample holder. In this case, remove the water from the cell before it contaminates the index-matching fluid.

7.4 The following data shall be recorded: sample identification, laser wavelength and scattering angle if necessary, measuring temperature, refractive index and viscosity of the dispersion medium, particle concentration and any other relevant details.

7.5 Perform a preliminary measurement on the dispersion to check that the particle concentration is not too low [less than about 1 000 particles in the scattering volume, see 6.2.2 check 2)] or too high [see 6.2.2, check 4)]. Check that the average scattered intensity (count rate) is in the range 5 kcounts/s to 1 000 kcounts/s (5 000 counts/s to 1 000 000 counts/s). If these criteria are not met, repeat a measurement on a sample with a different concen-

tration of particulate material, or use another laser power level if possible.

7.6 For each sample, at least six duplicate measurements of at least 60 s duration shall be performed and results stored. For sample count rates below 20 000 counts/s (20 kcounts/s), the duration in seconds shall be equivalent to at least 1 200 000 counts divided by the count rate in counts per second, or 1 200 kilocounts divided by the count rate in kilocounts per second.

7.7 Record the average particle diameter x_{PCS} and polydispersity index PI for each of the measurements. Calculate the mean:

$$\langle x \rangle = \frac{1}{N} \sum_{i=1}^{N} x_i$$

and the estimated standard deviation:

$$s_{N-1} = \frac{1}{N-1} \sqrt{\sum_{i=1}^{N} (x_i - \langle x \rangle)^2}$$

where N is the number of measurements x_i ($i = 1 \ldots N$) of x_{PCS} and of PI.

7.8 If a systematic concentration dependence of average particle size is observed, the results of an extrapolation to infinite dilution (or the results obtained at the lowest acceptable concentration) shall be reported.

NOTE 7 — Although checks 3) to 5) of 6.2.2 will exclude biasing effects due to multiple scattering, particle interactions may, in particular for smaller particles ($x_{PCS} \leqslant 100$ nm) at volume fractions above 0,01, bias the estimation of the average PCS diameter via equation (C.5) of annex C. Therefore for unknown dispersed systems it is recommended that steps in 7.5 to 7.7 are repeated for several concentrations in a range of a factor of at least 2.

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

8 Calibration and validation

Since particle size determination by PCS is an absolute method based upon first principles, calibration as such is unnecessary. However, verification of the instrument's performance should be performed with dispersions of particles of certified size after the first

installation of the instrument and at time intervals thereafter or in case of doubt.

Dispersions of polystyrene latex with narrow size distribution with average particle diameter as measured by PCS 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, defined as $100 s_{N-1}/\langle x \rangle$, shall be better than 2 %; the polydispersity index shall be smaller than 0,1.

NOTE 8 — Several suppliers provide traceable latices. A polystyrene latex (catalogue No. 1963) with a certified diameter of 100,7 nm can be obtained from the National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA. Annex E provides guidelines for the preparation of a suitable sample.

The maximal value of the intercept of the autocorrelation function can be determined as follows:

a) select a collecting aperture for which a value of B_{max} is available;

b) determine the intercept B (see annex A) with dispersions of polystyrene latex (diameter about 100 nm) with at least two different concentrations meeting requirements 1), 2), 3) and 5) of 6.2.2;

c) if B depends in a systematic way on particle concentration, extrapolate the results to infinite dilution.

9 Repeatability

The repeatability of the determination of average particle size, defined as $100 s_{N-1}/\langle x \rangle$, shall be better than 5 %.

10 Test report

The average particle size x_{PCS} and polydispersity index PI shall be reported. These data shall be the mean and standard deviation of at least six repeated measurements on a sample and shall be calculated according to the method given in annex A. If the mean values of x_{PCS} and PI are concentration-dependent, their values extrapolated to infinite dilution, or the value obtained at the lowest concentration, shall be reported.

The following details shall also be provided:

a) complete sample identification, including available information about particle shape and homogeneity;

b) instrument type and number, or its detailed description if a "homemade" instrument;

NOTE 9 — The following laser source details should also be provided: type, wavelength, power and that it was vertically polarized;

c) dispersion conditions:

— dispersing liquid and its cleaning/filtering procedure,

— concentration of particulate material,

— dispersing agents and their concentration,

— dispersing procedure,

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

d) measurement conditions:

— number of concentrations investigated,

— number of particles in the measuring volume, as estimated from particle concentration and average particle size x_{PCS},

— maximum value of the intercept B_{max} of the autocorrelation function attainable for the given optical arrangement of the instrument.

NOTE 10 — This value can be determined with a known material (see clause 8 and annex A).

— value of the intercept B of the autocorrelation function and value of the ratio B/B_{max},

— count rate observed for the dispersion medium,

— viscosity and refractive index of the dispersion liquid,

— temperature of the sample,

— average count rate observed for the sample,

— number of analyses and their duration,

— the variance of the fit [see annex A, equation (A.6)];

e) if available, any other useful results or comments obtained at other scattering angles or from multi-angle results. If available, results obtained by other data analysis methods and results from other particle sizing methods;

f) analyst identification:

— name and location of laboratory,

— operator's name or initials,

— date.

A model test report form is given in annex B.

Annex A

(normative)

Computation of the average particle diameter and polydispersity index

In this International Standard the two parameters describing particle size distribution, i.e. the average PCS diameter x_{PCS} and the polydispersity index PI, are determined by a variant of the so-called cumulants method[3].

The basis for this analysis is that the experimentally recorded intensity autocorrelation function $G_2(\tau)$ is approached by equation (C.12) of annex C. In order to obtain a linear regression, this equation is transformed as follows:

$$y(\tau) = \frac{1}{2}\ln\left[G_2(\tau) - A\right] \cong \frac{1}{2}\ln AB - \langle\Gamma\rangle\tau + \frac{\mu_2}{2}\tau^2$$

or

$$y(\tau_j) = a_0 - a_1\tau_j + a_2\tau_j^2 \qquad (j = 1, 2, 3 \ldots m) \quad \ldots \text{(A.1)}$$

where j is the number of the delay channel of the correlator.

The baseline or far point A can be determined in two ways: by the total number of photon counts in a total time duration of the considered experiment, or from an estimate of $G_2(\tau)$ for delay times $\tau \gg 25/\langle\Gamma\rangle$. It is recommended that both estimates of the baseline A are determined and that the largest of both is retained. However, for relative differences between the two estimates of the baseline larger than 10^{-3} times the smallest value, measurement shall be discarded for further analysis.

The range of values to be retained for $y_j = y(\tau_j)$ shall correspond to a range in $\left[G_2(\tau_j) - A\right]$ of $\left[G_2(\tau_1) - A\right] > \left[G_2(\tau_j) - A\right] > \left\{\left[G_2(\tau_1) - A\right]/100\right\}$ with at least one value smaller than $\left\{\left[G_2(\tau_1) - A\right]/50\right\}$. All values of $\left[G_2(\tau_j) - A\right]$ in this range must be positive, otherwise the measurement shall be discarded for further analysis.

Finally, the number m of values of y_j in the acceptable range shall be at least 20.

The parameters a_0, a_1 and a_2 are determined by least squares fitting of the experimental estimates of $y(\tau_j)$ to equation (C.12) whereby the following function is minimized:

$$s(a_0, a_1, a_2) = \sum_{j=1}^{m} w_j\left(y_j - a_0 + a_1\tau - a_2\tau_j^2\right)^2 \quad \ldots \text{(A.2)}$$

In equation (A.2) the normalized weighting factor

$$w_j = \frac{m\left[G_2(\tau_j) - A\right]^2}{\sum_{j=1}^{m}\left[G_2(\tau_j) - A\right]^2}$$

accounts for the nonlinear transformation of the raw data G_2 into the values for $y(\tau_j)$.

The average PCS diameter x_{PCS} is calculated from a_1 by

$$x_{PCS} = \frac{1}{a_1}\frac{kT}{3\pi\eta}\left[\frac{4\pi n\sin(\theta/2)}{\lambda_0}\right]^2 \qquad \ldots \text{(A.3)}$$

where

k is the Boltzmann constant;

T is the absolute temperature;

η is the viscosity of the dispersion medium;

n is the refractive index of the dispersion medium;

θ is the scattering angle;

λ_0 is the laser wavelength *in vacuo*.

The polydispersity index PI is related to a_2 and a_1 by

$$\text{PI} = 2a_2/a_1^2 \qquad \ldots \text{(A.4)}$$

The actual value of the intercept B is computed from a_0 and A by

$$B = \left[\exp(2a_0) \right] / A \qquad \ldots \text{(A.5)}$$

and is to be compared to the maximum value obtainable in the given experimental conditions, B_{max}.

Measurements for which the ratio $B/B_{max} < 0,8$ shall be discarded.

The variance, equal to

$$s/(m - 4) \qquad \ldots \text{(A.6)}$$

can be used as a criterion of goodness of the fit.