TECHNICAL SPECIFICATION

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First edition

Nanotechnologies — Evaluation of the mean size of nano-objects in liquid dispersions by static multiple light scattering (SMLS)

Nanotechnologies — Evaluation de la taille moyenne des nano-objets dans les dispersions liquides par diffusion statique multiple de la lumière (SMLS)

Member bodies are requested to consult relevant national interests in IEC/TC 113 before casting their ballot to the e-Balloting application.

PROOF/ÉPREUVE

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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This document was prepared by Technical Committee ISO/TC 229 *Nanotechnologies*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Dispersions of nanoparticles in liquids are widely used in industry. Nanoparticles dispersed in liquids interact via a variety of weak and strong forces, which can lead to aggregation or agglomeration of objects (primary particles, agglomerates, aggregates, etc.). As a result, the dispersion state and the apparent mean particle size and size distribution can differ from those determined during product manufacturing, storage, and processing, particularly when using measurements requiring sample dilution or extensive preparation. Sample preparation can result in breaking or formation of aggregates or agglomerates and in some cases can also affect morphology of primary particles. Industrial stakeholders require analytical methods that are applicable to dispersions in their native state for reasons of product development, quality control and regulatory compliance.

While many methods exist for characterization of nanoparticle properties, in particular their size and size distribution, these methods typically require a specific and frequently complex sample preparation (e.g. dilution, stirring, shearing or pumping) and, therefore, do not yield characteristics specific to as-received dispersions. In addition, some experiments do not require measurement of a full particle size distribution with the mean particle size being the main measurand. Using the mean particle size measurement, it is possible to monitor other dispersion parameters of the system such as the state of agglomeration, aggregation or dissolution.

Static multiple light scattering (SMLS) based methods do not require sample preparation allowing, within limitations outlined in this document, direct measurement of the mean equivalent particle diameter in the native (as-received) state of dispersion. In addition, and beyond the scope of this document, SMLS is capable in some cases of monitoring in real time the temporal evolution of mean equivalent particle diameter due to agglomeration or aggregation processes.

This document describes a standardized method for evaluating the mean equivalent particle diameter in various sample types (including as-received samples) having a wide range of concentrations using the SMLS based method.

Nanotechnologies — Evaluation of the mean size of nano-objects in liquid dispersions by static multiple light scattering (SMLS)

1 Scope

This document provides guidance and requirements for the determination of the mean (spherical) equivalent diameter of nano-objects (i.e. particles, droplets or bubbles) dispersed in liquids using the static multiple light scattering (SMLS) technique. The technique is applicable to a wide range of materials and does not require dilution of concentrated samples.

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/TS 80004-1, *Nanotechnologies — Vocabulary — Part 1: Core terms*

ISO/TS 80004-2, *Nanotechnologies — Vocabulary — Part 2: Nano-objects*

ISO/TS 80004-4, *Nanotechnologies — Vocabulary — Part 4: Nanostructured materials*

ISO/TS 80004-6, *Nanotechnologies — Vocabulary — Part 6: Nano-object characterization*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 80004-1, ISO/TS 80004-2, ISO/TS 80004-4, ISO/TS 80004-6 and the following apply.

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

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

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

3.1
static multiple light scattering
SMLS
technique in which transmitted or backscattered light intensity is measured after multiple successive scattering events of incident light in a random scattering medium

3.2
transport mean free path
average distance that a photon travels before its direction vector in its initial direction of motion is reduced to 1/e of its initial magnitude by elastic scattering alone

[SOURCE: ISO 18115-1:2013, 4.299, modified — "an energetic particle" has been changed to "a photon"; "momentum" has been changed to "direction vector"; "initial value" has been changed to "initial magnitude"; notes to entry have been deleted.]

3.3
mean free path
mean distance between photon scattering events in a dispersion

[SOURCE: ISO 22493:2014, 3.2.4, modified — "electron" has been changed to "photon".]

3.4
volume fraction
quotient of the volume of a specified component and the total sample volume

3.5
refractive index
ratio of the speed of light (more exactly, the phase velocity) in a vacuum to the speed of that same light in a material

[SOURCE: ISO 18369-1:2017, 3.1.6.3, modified — "(more exactly, the phase velocity)" has been added; the alternative preferred term "index of regraction" and note 1 to enty have been deleted.]

3.6
equivalent particle diameter
diameter of the sphere with defined characteristics which behaves under defined conditions in exactly the same way as the particle being described

[SOURCE: ISO 21501-1:2009, 2.4]

3.7
absorption
reduction of intensity of a light beam not due to scattering

[SOURCE: ISO 13320:2020, 3.1.1]

4 Symbols and abbreviated terms

I_{BS}	backscattered light intensity
I_T	transmitted light intensity
l^*	transport mean free path
l	mean free path
g	asymmetry factor
Q_e	extinction efficiency factor
φ	volume fraction
D	mean equivalent particle diameter
λ	wavelength of the incident light (in vacuum)
R	sample half thickness
n	refractive index
T_0	light flux transmitted by the continuous phase
TEM	transmission electron microscopy
CCD	charge-coupled device

CMOS	complementary metal–oxide–semiconductor
ILC	interlaboratory comparison
RM	reference material
VAMAS	Versailles Project on Advanced Materials and Standards

5 Principles

5.1 Relevant theory

The SMLS technique is based on the principle of elastic light scattering from dispersed objects in a liquid. Incident light is scattered multiple times successively, which results in a loss of correlation of the incident light direction. The I_{BS} or I_T light depends on the incident light wavelength, particle concentration, particle size and shape, optical properties (n and absorption of both the continuous and dispersed phases), and the measurement geometry.

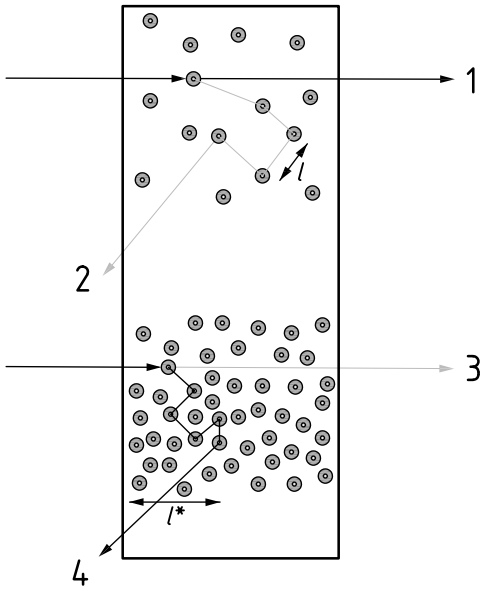
Light propagation in concentrated dispersions (Figure 1) can be characterised by two parameters: the mean free path (Formula (1)), l, and the transport mean free path, l^* [8],[9],[11]. The mean free path characterizes scattering phenomena at the microscopic level, while l^* describes multiple scattering at a macroscopic level as the penetration depth of radiation in a random medium (i.e. no significant correlation between scattering objects). Both parameters l and l^* are related by the Mie theory[14] under the hypothesis where $l > \lambda$ [11]:

$$l = \frac{2D}{3\varphi Q_e} \tag{1}$$

where D is the mean equivalent particle diameter, φ is the volume fraction of the material and Q_e is the extinction efficiency factor.

$$l^* = \frac{l}{(1-g)} \tag{2}$$

NOTE 1 The anisotropic scattering of light by an object can be characterized by the asymmetry factor g, which is the average cosine ($\cos\theta$) of the scattering angles weighted by the phase function or scattering diagram of the scatterer (e.g. $g = 0$ for isotropic Rayleigh scatterers and $0 < g < 1$ for Mie scatterers)[14]. Q_e takes into account scattering efficiency and light absorption phenomena.



Key

1	high I_T signal	2	low I_{BS} signal
3	low I_T signal	4	high I_{BS} signal

NOTE The I_{BS} dependence on the volume fraction is depicted.

Figure 1 — Schematic representation of the I_{BS}, I_T, l and l^*

Both Q_e and g are described by the Mie theory[8],[14] and depend on optical properties of the particles and the medium, particle size and wavelength of light.

The Mie theory is then used to determine either equivalent particle diameter or volume fraction, provided that the other is known, from I_T or I_{BS}. This is accomplished by comparing the experimental values of l or l^* with the values determined from the Mie theory.

For measuring (for instance) I_{BS} from the incident light, it is possible to derive an approximate[13]:

$$I_{BS} = \sqrt{\frac{\alpha^2}{l^*} + \beta} = \left[\alpha^2 \frac{3\varphi(1-g)Q_e}{2D}\right]^{1/2} + \beta \tag{3}$$

Due to the influence of experimental geometry and the optical detector, an output calibration to convert the raw I_{BS} and the raw I_T (e.g. voltage signal) into an exploitable unit is used. The gain α and offset β in Formula (3) are determined with a set of samples of different volume fraction with known l^* (calculated theoretically with the Mie theory).

The light-flux transmitted through a sample can be expressed as[15]:

$$I_T(l,R) = T_0 e^{\left[-\frac{2R}{l}\right]} = T_0 e^{\left[-\frac{3R\varphi Q_e}{D}\right]} \tag{4}$$

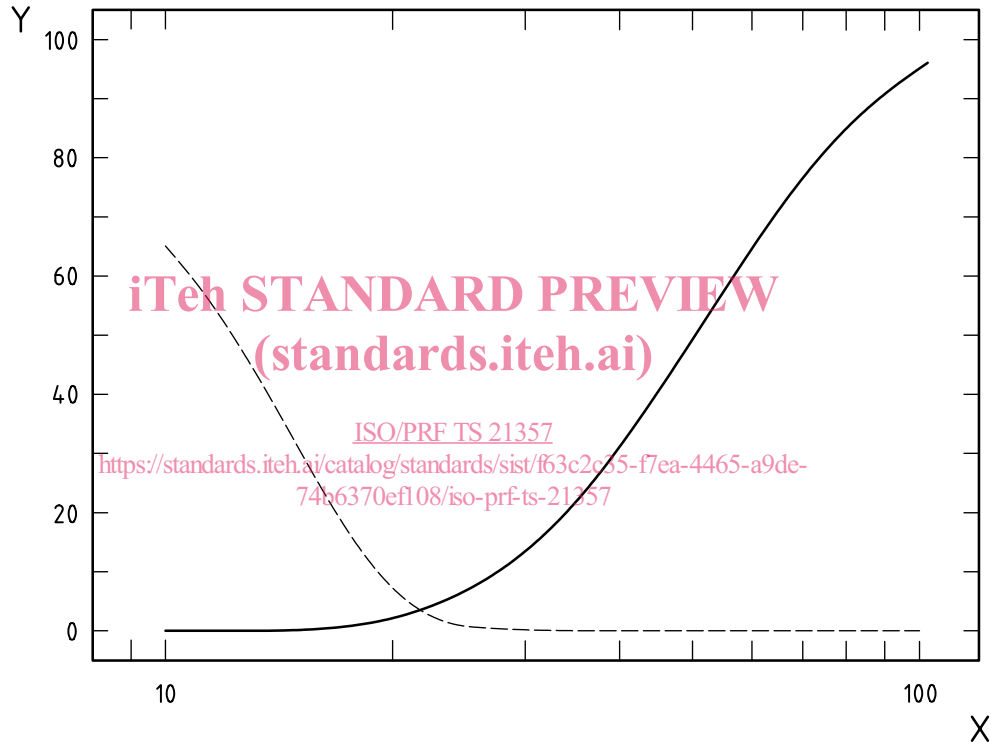
NOTE 2 Variations of I_{BS} and I_T as a function of l^* and l respectively are illustrated in Annex A. Variations of I_{BS} and I_T on mean equivalent particle diameter D for TiO_2 and melamine resin nanoparticles are illustrated in Annex B.

5.2 Key measurands

The measurand used in SMLS is a volume weighted mean equivalent (spherical) particle diameter. For a polydisperse suspension case, an effective I^* is defined that takes into account contributions to the signal from individual particles of various sizes (as described in 5.1). The diameter corresponding to the effective I^* is called the mean equivalent (spherical) particle diameter, also see Formula (2).

It can be shown that for particles smaller than the wavelength of light, the measured mean equivalent particle diameter linearly correlates with the mean volume diameter, D[10],[11]. In this case, backscattered light intensity scales approximately as D^3, meaning that "larger" (but still smaller than λ) particles contribute more to the signal.

The dependence of I_{BS} and I_T on the mean equivalent particle diameter is shown in Figure 2 by way of example. It is the calculated I_{BS} and I_T as a function of mean equivalent particle diameter in a 5 % volume fraction titanium dioxide aqueous dispersion.



Key

X D [nm]

Y intensity of light [%]

——— I_{BS}

– – – – I_T

Figure 2 — Calculated I_{BS} and I_T as a function of particle diameter for an aqueous dispersion (n = 1,33) of titanium dioxide (n = 2,50, φ = 5 %, λ = 880 nm)

The I_T and I_{BS} signals are instrument and sample dependent. Thus, as a rule of thumb, mean equivalent particle diameter estimation is obtained from I_T signal provided that it is not null and I_{BS} signal when I_T is null.

NOTE Although outside the scope of the document, for particles larger than λ, the measured mean equivalent particle diameter correlates with the mean surface diameter D[9],[10]. In this case, the I_{BS} signal scales as D^{-1}, meaning that "smaller" (but still larger than λ) particles contribute more to the backscattered intensity.

5.3 Method applicability and limitations

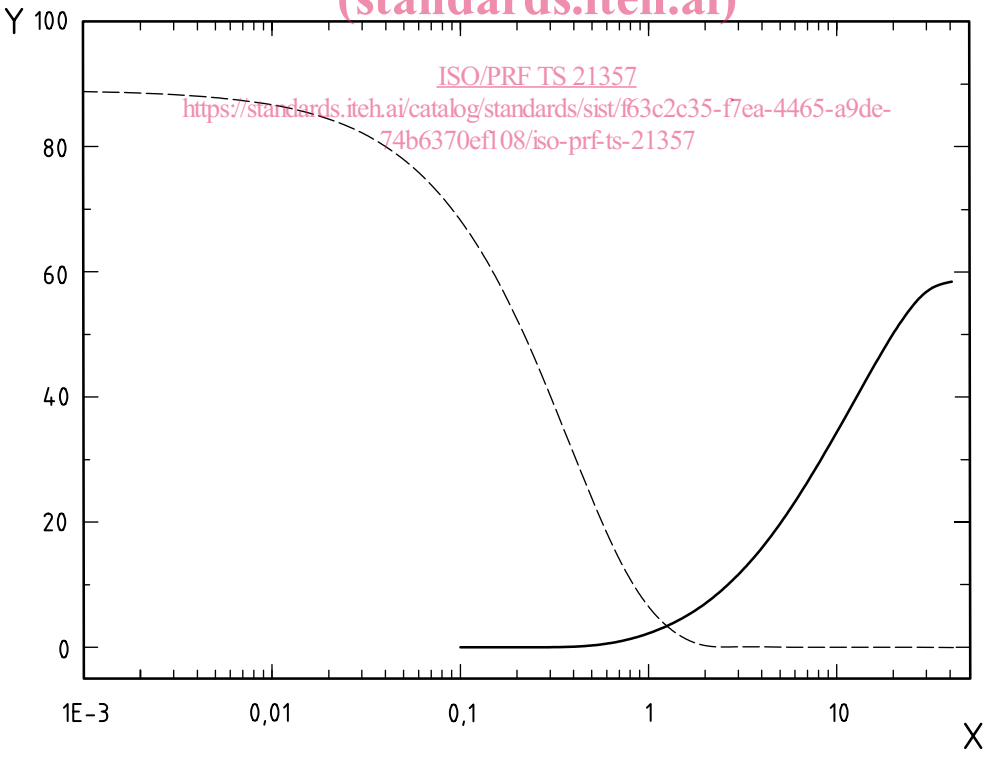
5.3.1 General

The SMLS technique can determine the mean equivalent particle diameter of nano-objects in concentrated dispersions as well as monitor stability of dispersions over time on the very same sample as it is a non-destructive method. It should be noted that this technique may be used for dispersions of solid particles in liquids (i.e. suspensions), liquid-in-liquid emulsions and bubble dispersions in liquids.

The SMLS technique does not allow for the analysis of particle size distributions. It yields a single parameter based on the I_{BS} or I_T measurement, which is converted into a mean equivalent particle diameter (when the particle concentration and n are known). This limits the applicability of the measurement technique to dynamic systems where at least one parameter (equivalent particle diameter or volume fraction) remains constant during the measurement. For mean equivalent particle diameter measurement, material n and volume fraction shall be known independently. The method has been successfully applied to measurements of metal oxides, metals, ceramics, emulsions and ultrafine bubble dispersions in water.

5.3.2 Sample concentration

The ability to analyse undiluted (as-received) samples that have not been modified by sample preparation is one of the main strengths of the SMLS method. Another feature of the method is the ability to measure mean equivalent particle diameter for a broad range of concentrations (from very low to very high concentration). 5.1 describes how I_T and I_{BS} relate to system parameters and the equivalent particle diameter and concentration. Using the Mie theory, I_{BS} and I_T can be calculated for a given material (such as 100 nm diameter silica beads in water). Figure 3 shows these data.



Key

X φ [%]
Y intensity of light [%]
I_{BS}
I_T

Figure 3 — Variation of I_T and I_{BS} with particle volume fraction for silica beads (n = 1,46) in water (n = 1,33) with D = 100 nm and λ = 880 nm

