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Particle size analysis — Small angle X-ray scattering (SAXS)

Analyse granulométrique — Diffusion des rayons X aux petits angles (SAXS)

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Contents

Page

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 24, *Particle characterization including sieving*, Subcommittee SC 4, *Particle characterization*.

This second edition cancels and replaces the first edition (ISO 17867:2015), which has been technically revised. The main changes compared to the previous edition are as follows:

- inclusion of various methods for the extraction of particle size distribution by using the SAXS method;
- correction of technical terms.

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

This document deals with small-angle X-ray scattering (SAXS), which is performed for particle size analysis in the 1 nm to 100 nm size range. Under certain conditions (narrow size distributions, appropriate instrumental configuration, and idealised shape) the limit of 100 nm can be significantly extended. In ideal circumstances, SAXS can determine the mean particle diameter and particle size distribution, surface area, and sometimes particle shape in a reasonably rapid measurement time. User-friendly commercial instruments are available worldwide from a number of manufacturers for both routine and more sophisticated analyses, and state-of-the-art research instruments are available at synchrotron radiation facilities.

As in all particle size measurement techniques, care is required in all aspects of the use of the instrument, collection of data, and further interpretation. Therefore, there is a need for an International Standard that allows users to obtain good interlaboratory agreement on the accuracy and reproducibility of the technique.

SAXS can be applied to any hetero-phase system, in which the two or more phases have a different electron density. In most cases, the electron density corresponds reasonably well to the mass density. SAXS is sensitive to the squared electron density difference. For fixed volume fractions, it does not matter whether the particles constitute the denser phase and the solvent (or matrix) is the less-dense phase or vice versa. Thus, pore size distributions can be measured with SAXS in the same way as size distributions of oil droplets in emulsions or solid particles in suspensions. Core-shell-nanoparticles can also be investigated, but low density (e.g. organic) shells are not detected if the core has a significantly higher density. To obtain the outer particle diameter including the shell, other methods should be used.

Although SAXS allows the determination of particle size, size distribution, surface area, and sometimes particle shape in concentrated solutions, in powders and in bulk materials, this document is limited to the description of particle sizes in dilute systems. A dilute system in the sense of SAXS means that particle interactions are absent. In case of long-range interactions (Coulomb forces between the particles), special care needs to be taken and a reduction of the concentration or the addition of salt can be necessary.

Since all illuminated particles present in the X-ray beam are measured simultaneously, SAXS results are ensemble and time averaged across all the particle orientations which are present in the sample.

The shape of the particles can be assigned to a basic geometry: spheroid, disk, or cylinder. This does not exclude more detailed information about the shape of the particle being obtained. However, the method of calculation for more detailed shape analysis is very complex to be included in an International Standard at this time. The sizes of irregularly shaped nanoparticles can be assessed by the radius of gyration (R_g) as obtained by classic Guinier analysis.

The size and size distribution of particles with basic shapes (sphere, disk, cylinder, core-shell, etc.) can be determined from curve fitting for relatively narrow size distributions. The reliability of the method of calculation for broader distributions depends on prior knowledge of the distribution.

This document assumes isotropically oriented nanoparticles of any shape in a test procedure. No dimension of the nanoparticle shall be larger than defined by the scattering accessible to the specific SAXS instrument. This generally limits the largest measurable particle size of the conventional technique to 100 nm, although this limit can be significantly extended in samples with a very narrow size distribution.

Small-angle neutron scattering is not described in this document but can be used without restriction because the theory and application are similar.

A list of suitable references for further reading is given in the Bibliography.

Particle size analysis — Small angle X-ray scattering (SAXS)

1 Scope

This document specifies a method for the application of small-angle X-ray scattering (SAXS) to the estimation of mean particle sizes in the 1 nm to 100 nm size range. It is applicable in dilute dispersions where the interaction and scattering effects between the particles are negligible. This document describes several data evaluation methods: the Guinier approximation, model-based data fitting, Monte-Carlo–based data fitting, the indirect Fourier transform method and the expectation maximization method. The most appropriate evaluation method is intended to be selected by the analyst and stated clearly in the report. While the Guinier approximation only provides an estimate for the mean particle diameter, the other methods also give insight in the particle size distribution.

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 26824, *Particle characterization of particulate systems — Vocabulary*

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

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 26824, ISO/TS 80004-2 and the following apply.

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

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

3.1
particle
minute piece of matter with defined physical boundaries

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

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

Note 3 to entry: This general particle definition applies to nano-objects.

[SOURCE: ISO 26824:2013, 1.1]

3.2
particle size
x
d
linear dimension of a particle determined by a specified measurement method and under specified measurement conditions

Note 1 to entry: Different methods of analysis are based on the measurement of different physical properties. Independent of the particle property actually measured, the particle size is reported as a linear dimension, e.g. as the equivalent spherical diameter.

Note 2 to entry: Examples of size descriptors are those based at the opening of a sieve or a statistical diameter, e.g. the Feret diameter, measured by image analysis.

Note 3 to entry: In ISO 9276-1:1998, the symbol x is used to denote the particle size. However, it is recognized that the symbol d is also widely used to designate these values. Therefore the symbol x may be replaced by d.

3.3
radius of gyration

R_g

square root of the ratio of the moment of inertia to the particle mass

Note 1 to entry: Guinier radius (i.e. radius of gyration) is expressed in nanometres. Typical average radii are in the range of 1 nm to 50 nm.

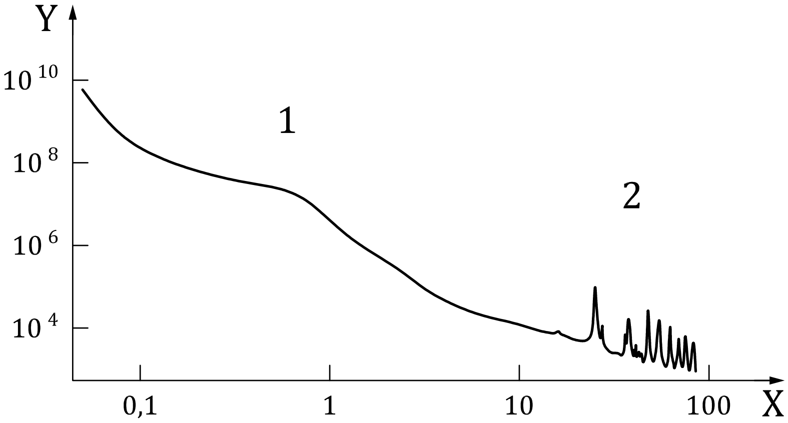
[SOURCE: ISO 26824:2013, 10.2]

4 Symbols

Symbol	Description	Unit
$\bar{d}_{\mathrm{vs}}$	Volume-squared-weighted mean particle diameter	nm
$\bar{d}_{\mathrm{num}}$	Number-weighted mean particle diameter	nm
$g_{\mathrm{int}}(r)$	Intensity-weighted particle size distribution	
$g_{\mathrm{num}}(r)$	Number-weighted particle size distribution	
$g_{\mathrm{vol}}(r)$	Volume-weighted particle size distribution	
I_{out}	Primary beam intensity with sample	
I_{in}	Primary beam intensity without sample	
$I(q)$	Scattered intensity (or scattering intensity)	
M	Number of degrees of freedom in fitting	
N	Number of particles	
$P(q, r)$	Particle form factor as functions of q-value and particle radius, r	
q	Momentum transfer or q-value, magnitude of the scattering vector given by $q = 4\pi/\lambda \sin(\theta)$	nm^{-1}
q_{min}	Small angle resolution, minimum accessible q-value	nm^{-1}
q_{max}	Maximum accessible q-value	nm^{-1}
r	Particle radius	nm
R_g	Radius of gyration (Guinier radius, see A.4)	nm
t_o	Optimum sample thickness	mm
T	Transmission	
V	Volume of particle	nm^3
2θ	Scattering angle	deg or rad
λ	Wavelength of the incident X-rays in vacuum	nm
μ	Linear absorption coefficient	mm^{-1}
$\rho(r)$	Electron density distribution	nm^3
σ	Standard deviation of size distribution	nm

5 Principle of the method

When electromagnetic radiation passes through matter, a small fraction of the radiation may be scattered due to electron density differences in the matter. The scattered radiation intensity profile (as a function of the scattering angle or momentum transfer, q), contains information that can be used to deduce morphological characteristics of the material. When X-rays are used to probe a geometrically ordered group of particles or molecules ("crystals"), the well-known X-ray diffraction pattern is obtained at wide scattering angles, which can be used to characterize the unit cell and lattice constants of such crystalline material. In the small-angle regime (typically $2\theta < 5$ °; wavelength dependent), information on the particle or pore dimensions within the material is available from the elastic scattering arising from the electron density contrast between the particles and the medium in which they reside. This is analogous to static light scattering and small-angle neutron scattering. A diagrammatic form of the angular dependence of the X-ray scattered intensity of a titanium dioxide mixture (rutile and anatase) is shown in Figure 1.



Key

X scattering angle 2θ (in degrees)

Y intensity

1 SAXS range

2 XRD range

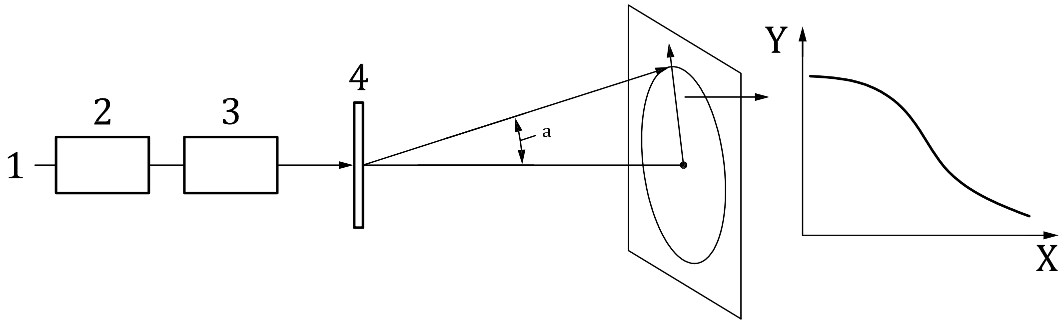
Figure 1 — X-ray scattering diagram illustrating the small-angle SAXS region (left hand side) and the wide-angle XRD (X-ray diffraction) region (right hand side) of a titanium dioxide powder

At low concentration, the small-angle scattering region contains information about the particle morphology, which may be evaluated to extract either the particle size (distribution), or particle shape. Only in very few cases is it possible to obtain both size and shape information. Different regions in q are dominated by signals from a particular length range, and so can contain distinct (exploitable) information aspects. In the low-q range, the Guinier approximation can be applied as an indicative method to get an intensity weighted mean size, provided the particles are smaller than $2\pi/q_{\mathrm{min}}$. Model fitting can be applied in the full range of q to compute a traceable particle size and size distribution with associated uncertainties. Both methods can fail depending on data quality and particle properties.

At increased concentrations, i.e. those higher than typically one volume %, particle-particle interactions and inter-particle interference can be relevant. Such interactions require sophisticated data modelling and expert knowledge for data interpretation, which is beyond the scope of the present document. In practice, a concentration ladder may be explored to determine the dependence of reported size on concentration. If available, each sample shall be measured twice: in its original concentration, and diluted 1:1 to allow identification of concentration artefacts. The result of both measurements shall be arithmetically averaged and the uncertainty enhanced by the variation. If dilution is not possible for technical reasons, this shall be stated in the report. In particular, the Guinier approximation is highly sensitive to concentration-induced scattering effects.

6 Apparatus and procedure

A diagrammatic form of a SAXS instrument is shown in Figure 2.



Key

X	2θ or q
Y	scattered intensity
1	X-ray source
2	optics
3	collimation system
4	sample
a	2θ.

Figure 2 — Diagrammatic form of a SAXS instrument, consisting of X-ray source, optics, collimation system, sample holder, beam stop, and X-ray detector

The SAXS set-up consists of X-ray source, optics, collimation system, sample holder, beam stop, and detector. In order to extract meaningful information from the measurement, the following key parameters define the capability of the system:

— q-range: q_{min} and q_{max}; number of sampled points in the Guinier region for Guinier approximation;

— detector sensitivity and system background noise.

Most available X-ray sources produce divergent beams which shall be collimated for SAXS measurements. With laboratory X-ray sources, multilayer optics are commonly used but basic SAXS measurements can also be achieved with slit collimation. The X-ray flux on the sample is generally higher when optics is used. Furthermore, multilayer coated optics can be used to generate a monochromatic X-ray beam.

The greatest challenge in SAXS is to separate the unscattered, transmitted beam (“direct beam”) from the scattered radiation at small angles (around 0,1°). The direct beam is normally blocked by a beam stop and parasitic scattering should be eliminated. The need for separation of primary and scattered beam makes collimation of the primary beam mandatory.

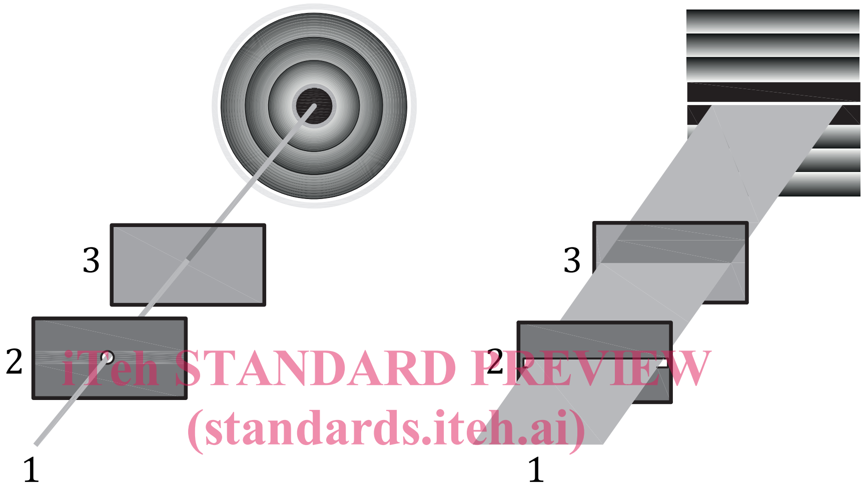
There are two main options to collimate an X-ray beam (see Figure 3).

— Point collimation systems have multiple pinholes or crossed slits that limit the shape of the X-ray beam to a low divergence and a small dimension (typically, the beam spot on the sample is less than 0.8 mm in diameter). The scattering is normally centro-symmetrically distributed around the primary X-ray beam. For isotropic samples, the scattering pattern in the detection plane perpendicular to the X-ray beam exhibits circular contour lines around the point of incidence of the primary beam. The illuminated sample volume is smaller than in line-collimation. Point collimation allows the study of isotropic and anisotropic systems.

— Line-collimation instruments confine the beam in one dimension so that the beam profile is a long and narrow line. The beam dimensions can be adapted to accommodate a given sample geometry. Typical dimensions are 20 mm × 0,3 mm. The illuminated sample volume is larger compared to point-collimation and the scattered intensity at the same flux density is proportionally larger. If the system is isotropic, the resulting smearing can be reverted using a deconvolution procedure, albeit at the cost of magnified uncertainties of the observed intensities. The investigation of anisotropic nanostructure with such line-collimated instruments is not as straightforward as for point collimation.

In addition, both the point and line collimation systems can use either a parallel or focused beam (see Figure 4).

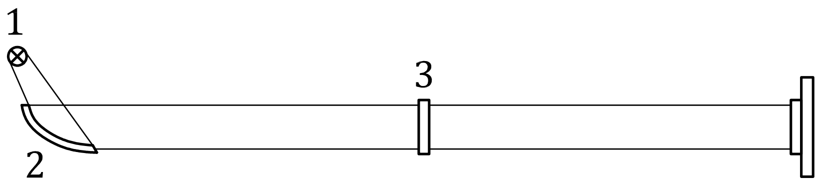
The scattered radiation (containing the morphological information, as described in Clause 5) forms a pattern that contains the information on the size and structure of the sample. This pattern is detected typically by a 1-dimensional or 2-dimensional flat X-ray detector situated behind the sample and perpendicular to the direction of the primary beam. Some multipurpose diffractometers that combine SAXS and diffraction use a scanning point (0-dimensional) detector. Detector classes commonly used include photon-counting and integration type detectors, although in practice, the least problematic/distorted measurements come from high-dynamic range, direct-detection, photon-counting detectors.



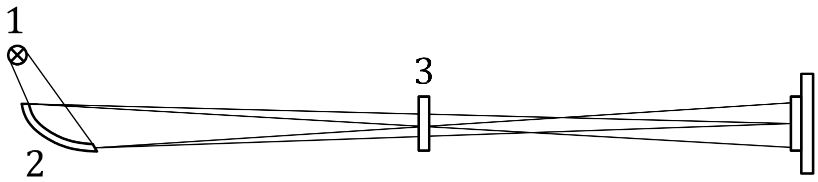
Key

1 X-ray source
2 collimation system
3 sample

Figure 3 — Point and line collimation types used in SAXS



a) Parallel beam



b) Point (2D) or line (1D) focused beam

Key

1 X-ray source

2 mirror

3 sample

Figure 4 — Focused and parallel beam set-up

7 Preliminary procedures and instrument set-up

Wavelength calibration (see Annex B) can be performed before conducting an experiment and thus would be classified as a preliminary procedure, but this is only required for polychromatic sources. If characteristic X-ray emission lines (e.g. copper Kα or molybdenum Kα lines) are used, a suitable absorber can be used to check that the right emission line has been selected correctly (Nickel for Cu Kα, Zirconium for Mo Kα). Utilization of a calibration material, such as silver behenate, should form part of a full system qualification and fit-for-purpose specification as noted in Annex B.

Only if, in addition to the mean particle diameter and the particle size distribution, the (absolute) concentration or volume fraction of scatterers is to be determined, the intensity shall be scaled to absolute units. For this purpose, a variety of auxiliary calibration materials are available, including water and glassy carbon. Alternatively, some instruments can determine this directly by means of calibrated detectors, or measurement of the unattenuated primary beam intensity on the SAXS detector. The use of semi-transparent beamstops to measure the beam intensity is not recommended due to the radiation hardening effects of such, which can lead to inaccurate values.

All calibrations should be described in the analysis report.

8 Sample preparation

Sample preparation is simple and fast for SAXS measurements. The required sample volumes are small, typically in a range of 5 µl to 50 µl for liquids and pastes, if copper radiation is used. Solid samples require an area of (1 × 1) mm^2 to (1 × 20) mm^2. The sample thickness is typically smaller than 1 mm and can be tuned to optimize the scattering and limit the X-ray absorption, depending on the composition of the sample.

Liquid samples are usually measured inside a thin-walled capillary, the diameter of which is typically between 0,5 mm to 2 mm when the liquid primarily contains water or hydrocarbons. Solvents that