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Particle size analysis — Small-angle X-ray scattering

Analyse granulométrique — Diffusion des rayons X aux petits angles

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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.

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword — Supplementary information.

The committee responsible for this document is ISO/TC 24, *Particle characterization including sieving*, Subcommittee SC 4, *Particle characterization*.

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Introduction

This International Standard deals with Small-Angle X-ray Scattering (SAXS), which is performed for particle size analysis in the 1 nm to 100 nm size range. In ideal circumstances, it can provide an estimate of particle size, average size and its 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 inter-laboratory 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. The so-called 'particle' is always the phase with the smaller volume fraction. Because SAXS is sensitive to the squared electron density difference, 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.

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 International Standard 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 has to be taken and a reduction of the concentration or the addition of salt might 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 International Standard 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 measureable 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 International Standard, 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.

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Particle size analysis — Small-angle X-ray scattering

1 Scope

Small-angle X-ray scattering (SAXS) is a well-established technique that allows structural information to be obtained about inhomogeneities in materials with a characteristic length from 1 nm to 100 nm. Under certain conditions (narrow size distributions, appropriate instrumental configuration, and idealised shape) the limit of 100 nm can be significantly extended. This International Standard specifies a method for the application of SAXS to the estimation of mean particle sizes in dilute dispersions where the interaction between the particles is negligible. This International Standard allows two complementary data evaluation methods to be performed, model fitting and Guinier approximation. The most appropriate evaluation method shall be selected by the analyst and stated clearly in the report. SAXS is sensitive to electron density fluctuations. Therefore, particles in solution and pores in a matrix can be studied in same way.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 9276-1, Representation of results of particle size analysis — Part 1: Graphical representation

ISO/TS 27687, Nanotechnologies — Terminology and definitions for nano-objects — Nanoparticle, nanofibre and nanoplate

3 Symbols and abbreviations

Symbol	Name	Unit
$\overline{d}_{\rm vs}$	Volume-squared-weighted mean particle diameter	nm
\overline{d}_{num}	Number-weighted mean particle diameter	nm
Iout	Primary beam intensity with sample	
I _{in}	Primary beam intensity without sample	
<i>I(q)</i>	Scattered intensity (or scattering intensity)	
q	Momentum transfer or q -value, magnitude of the scattering vector given by $q=(4\pi \ /\lambda){\sin \theta}$	nm ⁻¹
r	Particle radius	nm
Rg	Radius of gyration (Guinier radius, see <u>A.4</u>)	nm
to	Optimum sample thickness	mm
Т	Transmission	

Table 1 — Symbols

Symbol	Name	Unit
V	Volume of particle	nm ³
λ	Wavelength of the incident X-rays in vacuum	nm
20	Scattering angle	deg or rad
μ	Linear absorption coefficient	mm ⁻¹
σ	Standard deviation of size distribution	

 Table 1 (continued)

4 Principle of the method

When electromagnetic radiation impinges on matter, a small fraction of the radiation is scattered. As a function of the scattering angle or momentum transfer, *q*-value, the scattered radiation intensity profile contains information that can be used to obtain various characteristics of the material. In particular, when X-rays impinge on a geometrically ordered group of particles or molecules, this gives rise to the well-known X-ray diffraction pattern at wide scattering angles which is used to characterize the unit cell and lattice constants of the material. In the small-angle regime (typically $2\theta < 5^{\circ}$; wavelength dependent), information on the size of particles or pores within the material is available from the elastic (no change in wavelength) scattering arising from the electron density contrast between the particles and the medium in which they reside. This is analogous to static light 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.



Кеу

- 1 SAXS range
- 2 XRD range
- X scattering angle $2\theta/\deg$
- Y intensity

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

At low concentration, the small-angle scattering region contains information about particle size, size distribution, and particle shape, for which different ranges of *q* are evaluated. The Guinier approximation

can be applied in the low-q range to get an intensity weighted mean size, when the particles are smaller than $2\pi/q_{min}$. Model fitting can be applied in the full range of q to compute traceable particle size and size distribution with associated uncertainties. Porod's law can be applied to the high-q range to get an indication of the particle shape. This last method does not provide particle size and is therefore outside the scope of this International Standard. Note that all three 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 standard. In practice, a concentration ladder may be explored in order 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 exclude 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 and the uncertainty shall be marked. Note that the radius of gyration is more affected by concentration than model fitting.

5 Apparatus and procedure

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



Кеу

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

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 incoming primary beam from the scattered radiation at small angles (around 0.1°). The direct beam should be 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 pinholes or crossed slits that shape the X-ray beam to a small dimension (typically, the beam spot on the sample is less than 0,8 mm in diameter) that illuminates the sample. The scattering is centro-symmetrically distributed around the primary X-ray beam. For isotropic samples, the scattering pattern in the detection plane consists of circles around 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 dimension can be adjusted according to the type of sample for studies. Typical dimensions are 20 mm \times 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 removed using deconvolution. The investigation of anisotropic systems is not as straightforward as for point collimation.

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

The majority of the generated X-rays will simply transmit through the diluted sample without interacting with the particles. The X-rays scattered by the particles form a scattering 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 detector. There are a number of types of detector routinely employed, for instance, photon-counting and integration type detectors. The scattering pattern contains the information on the structure of the sample.



Кеу

- 1 X-ray source
- 2 collimation system
- 3 sample

Figure 3 — Point and line collimation types used in SAXS



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



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- 1 X-ray source
- 2 mirror

Kev

3 sample

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Figure 4 — Focused and parallel beam set-up

6 Preliminary procedures and instrument set-up

Wavelength calibration (see Annex C) can be performed before conducting an experiment and thus would be classified as a preliminary procedure, but this is not routinely done in the laboratory. If characteristic X-rays of copper are used, a nickel absorber can be used to check that Cu K α radiation has been selected correctly. Utilization of calibration materials, for example, silver behenate, should form part of a full system qualification and fit-for-purpose specification as noted in Annex C.

7 Sample preparation

Sample preparation is simple and fast for SAXS measurements. The required sample volumes are small, typically in a range of 5 μ L to 50 μ L for liquids and pastes, if copper radiation is used. Solid samples require an area of (1 × 1) mm² to (1 × 20) mm². The sample thickness is typically smaller than 1 mm.

Liquid samples are usually measured inside a thin-walled capillary, the diameter of which is around 1 mm to 2 mm when the liquid primarily contains water or hydrocarbons. Solvents that contain heavy atoms, for example, chlorine in chloroform, should be measured in smaller diameter capillaries as the atoms strongly absorb the incident radiation. Viscous samples can be measured better in a paste cell.

Pastes, powders, and vacuum sensitive materials can be mounted into a sample holder with windows, which shall be transparent to X-rays and exhibit little scattering themselves. Frequently used window materials include polyimide foils. Care should be taken that the scattering from the window material

does not affect the result of the measurement. Polyimide films exhibit a broad small-angle diffraction peak in the vicinity of q approximately 0,7 nm⁻¹, which has to be taken into account in data interpretation.

Solids can be clamped onto frames with or without additional window foils for protection against the vacuum. The sample thickness shall be chosen in line with the respective absorption of the material.^[14] The optimum thickness, t_0 , is given by

$$t_{\rm o} = 1/\mu \tag{1}$$

where μ is the linear absorption coefficient of the material. The optimum specimen thickness corresponds to a ratio of the primary beam intensity with and without sample, I_{out} and I_{in} , of:

$$I_{\rm out} / I_{\rm in} = e^{-\mu t} = e^{-1} \sim 37\%$$
⁽²⁾

Thus, the ideal specimen will transmit about 37 % of the incident radiation, and the specimen thickness can be adjusted accordingly to optimize transmission. Any sample treatment (for example, dilution, sonication, or centrifugation) may affect the particle size distribution and should be described in the analysis report.

8 Measurement procedure

Every SAXS particle-sizing experiment consists of at least two measurements using the same sample holder and the same acquisition time:

a) sample scattering;

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b) solvent/matrix scattering, the so-called blank or background experiment.

This is the minimum requirement for determining the scattering of the particles, which is the difference between the two scattering measurements. A typical example for this procedure is given in Figure 5. Care has to be taken that the scattering of the window material of the sample cell, the parasitic scattering of the SAXS instrument, and the dark count rate of the detector are removed. The transmission from the sample and background/matrix material and efficiency variation over the detector shall be taken into account.