TECHNICAL SPECIFICATION

ISO/TS 13762

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Particle size analysis — Small angle X-ray scattering method

Analyse granulométrique — Méthode de dispersion par rayons X sous angle faible

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.ch
Web www.iso.ch

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of normative document:

— an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;

— an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

An ISO/PAS or ISO/TS is reviewed every three years with a view to deciding whether it can be transformed into an International Standard.

Attention is drawn to the possibility that some of the elements of this Technical Specification ISO/TS 13762 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TS 13762 was prepared by Technical Committee ISO/TC 24, *Sieves, sieving and other sizing methods*, Subcommittee SC 4, *Sizing by methods other than sieving*.

Annexes A and B form a normative part of this Technical Specification. Annexes C to E are for information only.

Introduction

The size range for which the small angle X-ray scattering (SAXS) method is applicable is approximately in the range of 1 nm to 300 nm. The success of the technique is mainly based on the fact that SAXS effect results from the difference of electron density between particles and their surroundings so that size X_{SAXS} always indicates the size of a primary particle rather than the internal crystallite or external agglomerate size; in other words, the requirement of particle dispersion of a sample for SAXS analysis is not as strict as that for other methods.

However, the SAXS method has its limitations: firstly, it cannot distinguish pores from particles; secondly, the interference effect between particles will arise as the sample is available only in concentrated form.

SAXS measurements and the interpretation of the data are currently not uniform. The purpose of this Technical Specification is to facilitate comparisons of size analysis made in different laboratories.

It is well known that X-rays can kill human tissue. However, this Technical Specification does not purport to address all the safety problems associated with the use of the SAXS method; it is the responsibility of the user to establish appropriate safety and health practices prior to its use.

Particle size analysis — Small angle X-ray scattering method

1 Scope

This Technical Specification specifies the method for determining particle size distribution of ultra-fine powders by the small angle X-ray scattering technique. It is applicable to particle sizes ranging from 1 nm to 300 nm. In the data analysis, it is assumed that particles are isotropic and spherically shaped.

The method described in this Technical Specification is also applicable to particle suspensions.

This Technical Specification does not apply to:

a) powders containing particles whose morphology is far from spherical, except by special agreement;

b) powders consisting of porous particles;

c) mixtures of powders.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this Technical Specification. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this Technical Specification are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 9276-1, *Representation of results of particle size analysis — Part 1: Graphical representation*.

ISO 9276-2:—[1)], *Representation of results of particle size analysis — Part 2: Calculation of average particle sizes/diameters and moments from particle size distributions.*

1) To be published.

3 Symbols and abbreviations

SAXS	small angle X-ray scattering
x	particle size, diameter of a sphere
Δx_i	length of particle size interval, $\Delta x_i = x_i - x_{i-1}$
n	total number of size classes
$\overline{q}_{3,i}$	average density distribution of the class Δx_i by volume or mass
$\overline{q}_{3,i'}$	average density distribution in a representation with logarithmic abscissa
$Q_{3,i}$	cumulative volume fraction of particle sizes $x \leqslant x_i$
ε	scattering angle
$\Delta Q_{3,i}$	volume fraction within the class Δx_i, $\Delta Q_{3,i} = \overline{q}_{3,i \cdot \Delta x_i}$
$\Phi(\zeta)$	scattering function of a spherical particle: $\Phi(\zeta) = 3(\sin\zeta - \zeta\cos\zeta)/\zeta^3$, $\zeta = \frac{\pi x}{\lambda}(\varepsilon^2 + t^2)^{1/2}$
λ	wavelength of incident X-ray beam
t	angle variable along the slit-height direction
$F(t)$	slit-weighting function along the slit-height direction

4 Principle

As a narrow beam of X-ray passes through a powder layer containing ultra-fine particles, it will be dispersed around the incident beam at a small angle range resulting from the electron scattering in the particles. The distribution of scattered intensity is closely related to the particle size distribution.

The scattered intensity $I(\varepsilon)$ from a dilute spherical particle system can be expressed by the integral equation:

$$I(\varepsilon) = c \int_{-\infty}^{+\infty} F(t)\mathrm{d}t \int_{x_0}^{x_n} \omega(x) x^3 \Phi^2(\zeta)\mathrm{d}x \qquad (1)$$

where

x_0 is the size below which there are no particles;

x_n is the size above which there are no particles;

$\omega(x)$ is the size distribution function by volume (without normalization);

c is a synthetic constant.

The size range of x_0 to x_n can be divided into n intervals and the lengths of the intervals, Δx, increase with x increasing. Let ω_j represent the average distribution function of the class Δx_j, and then measure scattering intensities at a series of chosen angles to obtain n values of $I(\varepsilon)$. The angles are specified by the equation:

$$\varepsilon_i = 2\sqrt{5}\ \lambda / \pi(x_{i-1} + x_i) \qquad (i = 1, 2, 3, ..., n) \tag{2}$$

Approximately, the integral equation (1) is transformed into a set of a linear equations:

$$l(\varepsilon_i) = \sum_{j=1}^{n} a_{ij}\omega_j \qquad (i = 1, 2, 3, ..., n) \tag{3}$$

where

$$a_{ij} = \int_{-\infty}^{+\infty} F(t)\mathrm{d}t \int_{x_{j-1}}^{x_j} x^3 \Phi^2(\zeta)\mathrm{d}x \tag{4}$$

All the coefficients, a_{ij}, in the set of linear equations are a group of constants for given λ, collimation geometry, classes and specific angles. We may calculate them one by one by using a numerical integration method as long as the slit-height weighting function, $F(t)$, has been measured (annex B). Thus, the values of distribution function corresponding to each class can be obtained from solving equation (3). Based on the solutions, the average density distribution, volume fractions, cumulative volume fractions and the mean size $\overline{x}$ of the particles can be calculated as follows:

$$\overline{q}_{3,j} = \omega_j / \sum_{k=1}^{n} \omega_k \Delta x_k \qquad (j = 1, 2, ..., n) \tag{5}$$

$$\Delta Q_{3,j} = \overline{q}_{3,j}\Delta x_j \times 100\,\% \qquad (j = 1, 2, ..., n) \tag{6}$$

$$Q_{3,j} = \sum_{k=0}^{j} \Delta Q_{3,k} \qquad (j = 1, 2, ..., n) \tag{7}$$

$$\overline{x} = \sum_{j=1}^{n} \Delta Q_{3,j}(x_{j-1} + x_j)/2 \qquad (j = 1, 2, ..., n) \tag{8}$$

The solution of equation (3) involves the inversions of an ill-conditioned problem but it can be improved through optimizing the coefficient matrix and introducing a diagonal matrix B and a stabilizer η. In matrix form, equation (3) can be modified as:

$$[A + \eta B]\,\omega = I \tag{9}$$

where

$A = (a_{ij})_{n \times n}$;

$B = \mathrm{diag}(a_{11}, a_{22}, ..., a_{nn})$;

$0 < \eta < 0{,}3$

$\omega = (\omega_1, \omega_2, ..., \omega_n)$

$I = (I_1, I_2, ..., I_n)$

5 Sample preparation and requirement

5.1 Preparation of collodion solution

The analytically pure acetone and collodion without small-angle scattering should be used to prepare the solution. In general, the concentration of the solution may be approximately 5 % to 10 %.

5.2 Requirements and preparation of the sample plate

5.2.1 Requirements of the sample plate

The sample plate used for scattering measurement should meet the following requirements:

a) the volume concentration of the test powder in the plate should be less than 1 %;

b) to achieve maximum scattering intensity, the thickness of the sample plate shall be chosen to an optimum value where the monochromatic X-ray beam will be attenuated to 37 %;

c) the sample plate should be uniform, flat, crack free and should ensure that the powder particles are separated as well as possible;

d) the sample plate should have suitable dimensions, for example a length of 20 mm and a width of 10 mm.

5.2.2 Preparation of the sample plate

Weigh out a given mass of test powder and pour onto it an appropriate volume of collodion solution. The quantities requested for the powder and solution may be estimated from the density of each and from their X-ray absorption coefficient, in order to meet the requirements in 5.2.1.

Stir the suspension in a small cup. A drop of wetting agent shall be added to the suspension if the solution does not readily wet the powder.

The dispersion of the powder in the suspension shall be made by the addition of dispersing agent and/or an ultrasonic treatment.

Place the cup containing the suspension into an oven at the temperature of 20 °C to 50 °C and with a relative humidity of below 50 %, until a dry sample plate has formed.

5.3 Preparation of dry powder sample

Place the dry powder in a special sample holder with a slot. If the requirements in 5.2.1 are met in this way, it shall be directly used for SAXS measurement.

5.4 Preparation of colloidal solution

The concentration of the colloidal solution should be less than 1 %. An appropriate surfactant may be added to prevent the colloids from agglomerating.

When preparing the sample for measurement, the method chosen should not affect the particle morphology.

6 Apparatus

The apparatus consists of:

— an X-ray generator combined with electronic circuit panel, detector and recording;

— a system, with synthetic stability superior to 1 %;

— a small angle scattering goniometer;

— a computation unit;

— an ordinary laboratory apparatus, such as an analytical balance, ultrasonator and oven.

See also annex C.

7 Procedure

7.1 Switch the X-ray diffractometer on and allow it to warm up.

7.2 Adjust or check the small angle scattering goniometer according to the manual.

7.3 Once the conditions of the instrument are stable, adjust the goniometer according to the instruction manual. Insert an appropriate number of absorber plates in front of the detector then set the goniometer at 0 scale of the angle. Register the intensity of the primary X-ray beam as an intensity of the goniometer's 0 degree.

7.4 Fix the sample plate onto the sample holder, or inject the colloidal suspension sample into a special cell and then insert the holder with the sample into the shaft hole of the goniometer. Pull out the absorber plates.

7.5 Measure the scattering intensities, $I_a(\varepsilon_i)$, at the angles specified by equation (2). The total pulse counts measured should reach at least 5 000 at each angle. The measured intensity, $I_a(\varepsilon_i)$, is composed of the small-angle scattering from the sample as well as the scattering background.

7.6 Take out the sample. Reinsert the absorber plates, reset the goniometer to 0° and then measure the intensity of the primary beam. The relative deviation between this value and the intensity registered in 7.3 shall be less then 15 %; if this is not the case, repeat the procedures starting from 7.2.

7.7 Place the sample between the X-ray window and the first slits of the goniometer. Measure the scattering background, $I_b(\varepsilon_i)$, under the same instrumental conditions and at the same angles as in 7.5. However, the pulse counts for $I_b(\varepsilon_i)$ need not be specified.

7.8 Subtract the intensity measured in 7.7 from that measured in 7.5, i.e. the small-angle scattering intensity, $I(\varepsilon_i) = I_a(\varepsilon_i) - I_b(\varepsilon_i)$.

8 Calculation and expression of results

8.1 Calculation

8.1.1 Evaluation of equation (3)

Substitute the values obtained in 7.8 and 7.9 in equation (3); each ω_i can be calculated by means of a microprocessor. If the solution is not stable or reasonable enough, the equation (9) shall be used.

8.1.2 Calculation of average density distribution and volume fraction

The average densities distribution, q_{3j}, and the volume fractions, $\Delta Q_{3,j}$, for each class shall be calculated from the values of ω according to equation (5) and equation (6) respectively.

8.1.3 Calculation of mean particle size

The mean particle size shall be calculated from the volume fractions according to equation (8).

8.2 Expression of results

The data may be presented in tabular and/or graphical form, see ISO 9276-1.

8.2.1 Tabular form

The report shall be made in accordance with Table 1.

Table 1

Class (nm)	$x_0 \sim x_1$	$x_1 \sim x_2$	..... $x_{j-1} \sim x_j$	.....	$x_{n-1} \sim x_n$
Density distribution $\bar{q}_3$ (nm^{-1})	$\bar{q}_{3,1}$	$\bar{q}_{3,2}$	..... $\bar{q}_{3,j}$		$\bar{q}_{3,n}$
Volume fraction ΔQ_3 (%)	$\Delta Q_{3,1}$	$\Delta Q_{3,2}$	..... $\Delta Q_{3,j}$	.....	$\Delta Q_{3,n}$
Cumulative percentage (%)	$\Delta Q_{3,1}$	$\Delta Q_{3,1} + \Delta Q_{3,2}$	..... $\sum_{k=1}^{j} \Delta Q_{3,k}$	.....	100

The mean particle size, $\bar{x}$, is expressed in nanometres.

8.2.2 Graphical representation

8.2.2.1 Histogram, $\bar{q}_3(x)$

In some cases, the results are presented as a histogram by using the data in the first and second rows of Table 1 in 8.2.1. A schematic normalized histogram is shown in Figure 1.

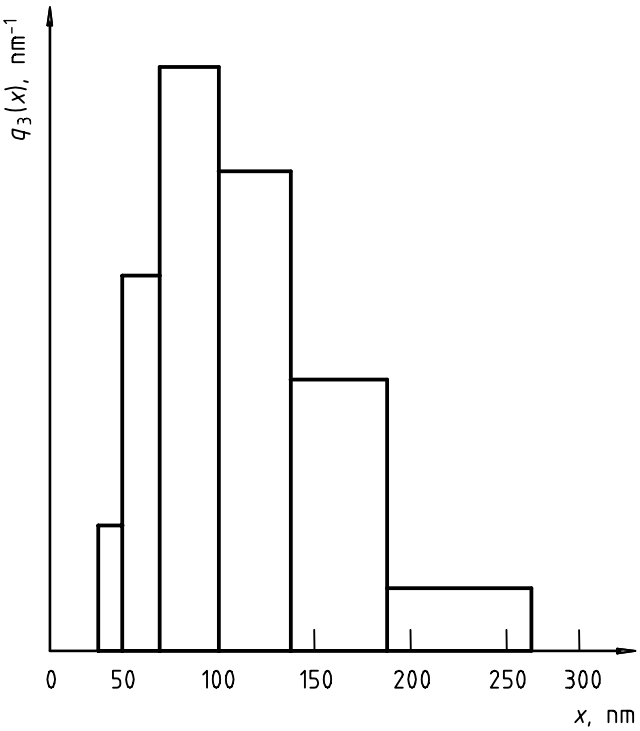

Figure 1 — Histogram of a density distribution function $\bar{q}_3(x)$