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Determination of the specific surface area of porous and particulate systems by small-angle X-ray scattering (SAXS)

Détermination de la surface spécifique pour des systèmes poreux et particulaires par diffusion des rayons X aux petits angles (SAXS)

Reference number
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Foreword

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

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

Small-angle X-ray scattering (SAXS) can be used to determine the specific surface area of nanoporous (presence of nanopores) and nanoparticulate systems which include mesoporous and partly macroporous materials. SAXS is a well-established method to obtain structural information on inhomogeneities in materials at the nanoscale, typically between 1 nm and 100 nm, and is thus perfectly suited for nanoporous, i.e. materials comprising nanopores and nanoparticulate systems which include mesoporous (presence of mesopores) and partly macroporous (presence of macropores) materials. With special instrumentation, and/or by using absolute-scale techniques, the limits can be significantly extended. 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 measurement techniques for surface area, 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. A 'phase' is in this context understood as a homogeneous electron density domain in the typical size range for SAXS between about 1 nm and 100 nm. State-of-the-art SAXS instruments and synchrotron SAXS beamlines allow significantly extending the limit of 100 nm to several hundred nanometres. Special instrumentation for ultra-small angle X-ray scattering (USAXS) pushes the upper size limit even up to the µm range. This document describes two different evaluation approaches for determining the specific surface area: The Invariant (K/Q) method has an upper size limit for the structure of up to several hundred nanometres, whereas for the absolute-scale method the size of the structure can even be in the µm range.

Because SAXS is sensitive to the squared electron density difference, it does not matter whether the scattering system is composed of pores or particles within a matrix, respectively.

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

Determination of the specific surface area of porous and particulate systems by small-angle X-ray scattering (SAXS)

1 Scope

This document specifies the application of small-angle X-ray scattering (SAXS) for the determination of specific surface area. Both the mass specific surface area in the order of 1 m^2g^{-1} to 2 000 m^2g^{-1} and the volume specific surface areas in the range from 0,01 m^2cm^{-3} to 1 000 m^2cm^{-3} can be obtained.

The method described is applicable to dilute and concentrated systems.

NOTE In ISO 17867:2020, the determination of the particle size by SAXS is limited to dilute systems.

The determination of surfaces with SAXS is straightforward for two-phase systems only. Surface determination in systems with more than two phases is beyond the scope of this document.

The term 'surface' refers to any interface between domains of different density (more precisely: electron density) and is not restricted to the external surface of particles. As any interfaces between areas with different electron density, not only to air or vacuum, can be probed, the method can be applied to any heterogeneous system.

SAXS measures not only the specific surface area of open pores but also of inaccessible, closed pores or inclusions.

NOTE This is in contrast to gas sorption methods which are described in ISO 9277:2010.

In addition to porous systems, there can be contributions of internal interfaces to the measured specific surface area of any heterogeneous compact solid system, such as between crystalline and amorphous phases, provided there is an electron density contrast. Although materials comprising micropores (pore width < 2 nm) can also be analysed with respect to their specific surface area with SAXS, this document does not cover these materials.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions 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
nanopore
pore with width of 100 nm or less

[SOURCE: ISO 15901-2:2021, 3.10]

3.2
macropore
pore with width greater than 50 nm

[SOURCE: ISO 15901-1:2016, 3.7]

3.3
mesopore
pore of internal width between 2 nm and 50 nm

[SOURCE: ISO 15901-1:2016, 3.8]

3.4
micropore
pore of internal width less than 2 nm

[SOURCE: ISO 15901-1:2016, 3.9]

3.5
surface area
extent of accessible surface area as determined by a given method under stated conditions

[SOURCE: ISO 15901-1:2016, 3.30]

3.6
mass specific surface area
surface area of the sample divided by sample mass

3.7
volume specific surface area
surface area of the sample divided by sample volume

3.8
external (outer) surface
envelope surface of particles in the micrometre and sub-micrometre range

3.9
internal (inner) surface
surface of pores, cavities, or any other heterogeneity within particles or bulk materials

3.10
closed pore
pore totally enclosed by its walls and hence not interconnecting with other pores and not accessible to fluids

[SOURCE: ISO 15901-1:2016, 3.10]

3.11
open pore
pore not totally enclosed by its walls and open to the surface either directly or by interconnecting with other pores and therefore accessible to fluid

[SOURCE: ISO 15901-1:2016, 3.11]

3.12
powder
porous or nonporous solid composed of discrete particles with maximum dimension less than about 1 mm, powders with a particle size below about 1 µm are often referred to as fine powders

[SOURCE: ISO 15901-1:2016, 3.4]

3.13
granules
granules (granular material) is a conglomeration of discrete solid, macroscopic particles

3.14
monolith
monolith is a single discrete, solid object

4 Symbols

Table 1 — Symbols

Symbol	Description	Unit
S	Total surface area	m^2
S_v	Volume specific surface area (surface to volume ratio)	$m^2\ cm^{-3}$
S_m	Mass specific surface area (surface to mass ratio)	$m^2\ g^{-1}$
m_s	Mass of the scattering sample	g
V	Volume of the scattering sample	cm^3
ρ_s	Density of the sample	$g\ cm^{-3}$
ρ_m	Density of the matrix	$g\ cm^{-3}$
ρ_p	Density of the pore phase or particle	$g\ cm^{-3}$
ρ_{bulk}	Bulk density	$g\ cm^{-3}$
ρ_{grain}	Grain density	$g\ cm^{-3}$
$\rho_{packed\text{-}bed}$	Density of packed beds of nanoparticles	$g\ cm^{-3}$
$\rho_{dispersion}$	Density of dispersion of nanoparticles	$g\ cm^{-3}$
ρ_1	Density of phase 1	$g\ cm^{-3}$
ρ_2	Density of phase 2	$g\ cm^{-3}$
ρ_e	Electron density	nm^{-3}
β	Mass concentration	$g\ cm^{-3}$
q	Momentum transfer, $(4\pi/\lambda)\sin\theta$, with scattering angle 2θ	nm^{-1}
φ_1	Volume fraction of phase 1	
φ_2	Volume fraction of phase 2	
φ_m	Volume fraction of the matrix	
φ_p	Volume fraction of the pore phase (or particle)	
V_p	Mass specific pore volume	cm^3g^{-1}
λ	Wavelength of the incident X-rays	nm
Ω	Solid angle	sr
$d\Sigma/d\Omega$	Macroscopic differential scattering cross-section	$m^{-1}sr^{-1}$
$I(q)$, $I(q)_s$	Scattered intensity of the sample	
$I(q)_{ref}$	Scattered intensity of the reference (standard)	
$\tilde{I}(q)$	Scattered intensity (line-smeared data)	
Q	Invariant	nm^{-3}
$\tilde{Q}$	Invariant (line-smeared data)	
K	Porod constant	
$\tilde{K}$	Porod constant (line-smeared data)	
K_{abs}	Absolute Porod constant	m^{-5}
A	Constant background term	
$\tilde{A}$	Constant background term (line-smeared data)	

Table 1 *(continued)*

Symbol	Description	Unit
A_{abs}	Absolute constant background term	m^{-1}
T_s	Transmission of the sample	
T_{ref}	Transmission of the reference (standard)	
t_s	Thickness of the sample	mm
t_o	Optimum thickness of the sample	mm
t_{ref}	Thickness of the reference (standard)	mm
μ_{tot}	Linear attenuation coefficient (including coherent scattering)	m^{-1}
r_e	Classical electron radius	m
Z	Number of protons	
M_v	Molar mass	$g\,mol^{-1}$
N_A	Avogadro constant	mol^{-1}
$C_{1,2}$	Conversion factors between mass densities and electron densities	g^{-1}
$C_{m,p}$	Conversion factors between mass densities and electron densities	g^{-1}
C_m	Conversion factor (for SiO_2)	

Table 2 — Overview of sample density ρ_s

		Solid samples with defined sample thickness			Solid samples with unknown thickness			Liquid-suspended particles	
Method	**Eq.**	porous monolith	mesoporous powder/ granules	non-porous particles (packed bed)	dispersed nanoparticles	mesoporous powder/ granules	non-porous particles (packed bed)	referred to whole mass of dispersion	referred to particle phase only[a]
K/Q method	10	ρ_{bulk}	ρ_{grain}	n.a.	ρ_{bulk}	ρ_{grain}	n.a.	$\rho_{dispersion}$	β
	11							n.a.	n.a.
	12							$\rho_{dispersion}$	β
Absolute-scale method	14	ρ_{bulk}	$\rho_{packed\text{-}bed}$	$\rho_{packed\text{-}bed}$	ρ^*	ρ^*	ρ^*	n.a.	n.a.
	15							$\rho_{dispersion}$	β
	18							n.a.	n.a.
	19		ρ_{grain}	n.a.	n.a.	n.a.	n.a.	$\rho_{dispersion}$	β

[a] Equivalent to dry powder.

* Equivalent values for irregular particles, e.g. unknown thickness and/or sample density (see 9.2)

n.a. not applicable

5 Principle of the method

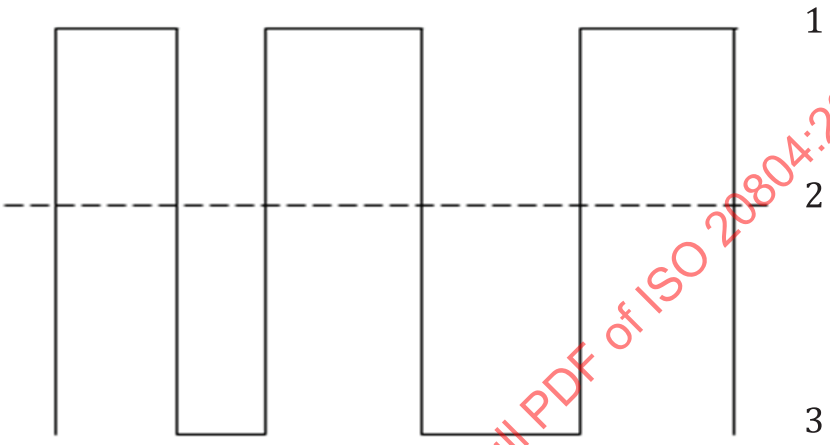
5.1 General

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. In the small-angle regime (typically $2\theta < 5°$; wavelength dependent), information on the particle or pore dimensions within a 2-phase material is available from the elastic scattering arising from the electron density contrast between the particles or pores and the medium or matrix in which they reside. This is analogous to static light scattering and

small-angle neutron scattering. The measured scattering profile is used for determining the specific surface area of porous materials using two approaches described in this document.

5.2 Ideal two-phase model

For the purposes of this document, the term 'phase' shall refer to any domain, within the mentioned limits of resolution within which the electron density is constant and which is confined by a sharp boundary. It is also assumed that there is no long-range order or orientation, such that the system as a whole is isotropic. A schematic density profile is shown in Figure 1.



Key

1 ρ_1

2 ρ_s ($\rho_s = \varphi_1 \cdot \rho_1 + \varphi_2 \cdot \rho_2$)

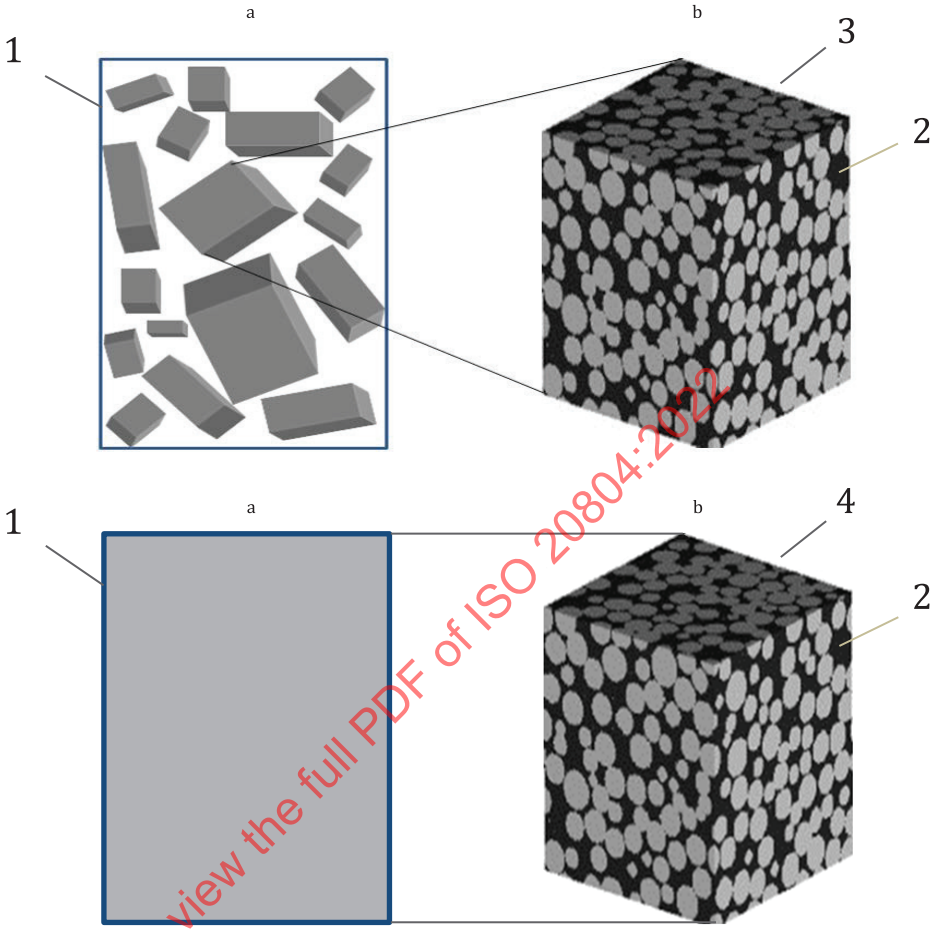
3 ρ_2

Figure 1 — Density profile in an ideal two-phase model

Such an idealized system is defined by two parameters, the volume fractions of the two phases φ_1 and φ_2 (= 1 – φ_1), and the volume specific surface area S_V of the interface between the phases. In general, a combination of scattering by inner and outer surfaces is measured. However, for porous or heterogeneous particles larger than 10 µm the contribution of outer surface is very small.

In practice, different sample types can be distinguished: porous monolithic samples, porous irregular monolithic samples such as powders and fragments (see Figure 2), packed beds of nanoparticles or nanoparticles in liquid suspension.

There are different terms for the density commonly used in the field of porous materials (see Table 2 and Figure 2). For reasons of simplification, this document uses mainly the density of the sample ρ_s and the density of the matrix ρ_m for calculating the mass specific surface area. The density of the matrix ρ_m is the true solid-state density in case of porous materials, and the density of the suspending medium in case of nanoparticles in liquid suspension. Depending on the studied sample material (e.g. monolith, powder, particle) and the used evaluation method (K/Q method, absolute-scale method) the correct density of the sample ρ_s shall be calculated or used in the relevant formulae (see Table 2).



a) Porous powder

b) Monolith

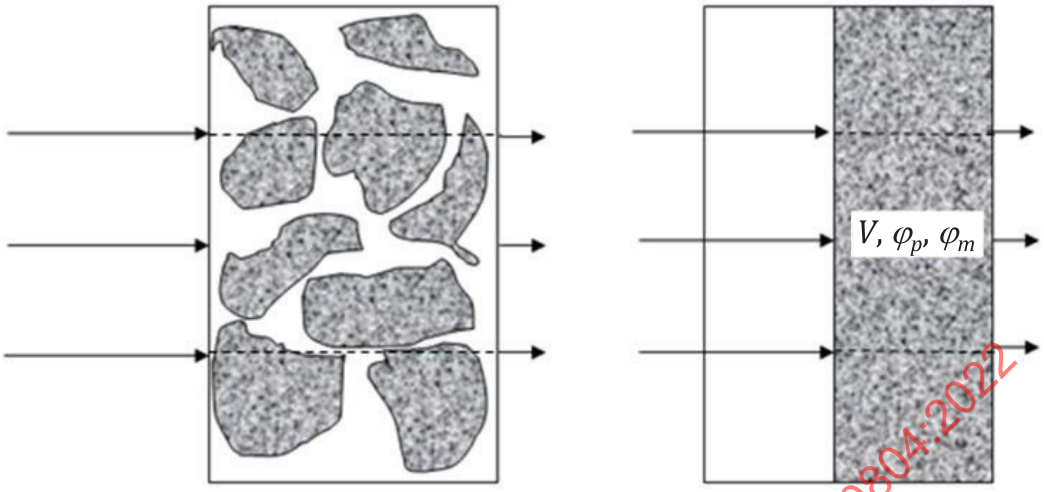
Key

1 ρ_s (density of the sample)
2 ρ_m (density of the matrix)
3 ρ_{grain} (grain density)
4 ρ_{bulk} (bulk density)
a Outer surface – particle envelope
b Inner surface – pores (microphase separation)

NOTE The outer surface area of particles usually is very small as compared to the inner surface area, if the particle sizes are in the 10 µm range and above.

Figure 2 — Schematic view of outer and inner surfaces in a system of porous particles or grains

The situation within a bed of coarse grain powder (granules consisting of porous entities) or in a system of liquid-suspended particles, with its equivalent volume fractions is schematically shown in Figure 3.



NOTE SAXS 'sees' the internal structure at the scale below several hundred nm within the porous powder grains. The volume V of the scattering sample in a system of porous particles, with volume fractions φ_1, φ_2 can be imagined as one continuous block.

Figure 3 — Internal structure at within the powder grains

5.3 Porod law - Specific surface area

The general basis for surface area determination by SAXS is the Porod law which states that the scattering intensity $I(q)$, where $q = \frac{4\pi}{\lambda} \cdot \sin\theta$, with 2θ the scattering angle, decays towards large angles asymptotically with the inverse fourth power of the scattering vector q; hereby, the total surface area S within the irradiated volume is a proportionality factor as given in Formula (1):

$$\lim_{q\to\infty} I(q) \propto S \cdot q^{-4} \tag{1}$$

In practice, the following master formula is found to apply for the tail of the scattering curve towards large q values:

$$\lim_{q\to\infty} I(q) = A + K \cdot q^{-4} \tag{2}$$

where A denotes a constant background term for the short-range atomic structure and K contains the surface area information. Using a double-log plot according to Formula (2) the q-range for the Porod extrapolation can be determined. A and K are derived directly via a non-linear fit according to Formula (2) in this plot.

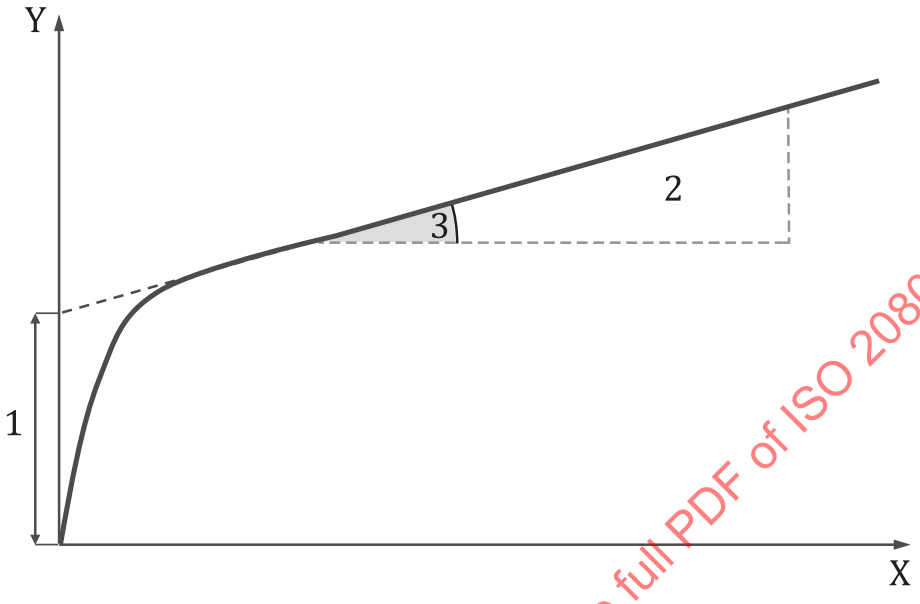
As an alternate procedure, A and K can be determined from the 'Porod plot' (see Figure 4) according to Formula (3), which is a linearization of Formula (2).

$$I(q) \cdot q^4 = K + A \cdot q^4 \tag{3}$$

This can be done by performing a linear least-squares fit according to this linearized equation. For the search of the linear region in the Porod plot either the transition zone between the Porod slope and flattening towards larger q values is used or the q-range is taken from the double-log plot as described above.

In the case of infinite line-smearing, e.g. with Kratky optics (see Figure 6 - right), the Porod slope becomes proportional to q^{-3} instead of q^{-4}. Line-collimation instruments confine the beam in one dimension so that the beam profile is a long and narrow line.

$$\lim_{q\to\infty} \tilde{I}(q) = \tilde{A} + \tilde{K}\cdot q^{-3} \tag{4}$$



Key

X q^4
Y $I(q)\cdot q^4$
1 K
2 A ($\tan\alpha = A$)
3 α

Figure 4 — 'Porod plot', from which the parameters *A* and *K* can be determined.

The Porod law is found to hold in many cases. Therefore, the volume specific surface area can be straightforwardly determined by SAXS. In practice however, in complex systems or fractal materials the scattering intensity frequently deviates from the Porod law, q^{-4}, which could be caused by a transition layer between the two phases, or a high degree of rugosity (surface roughness). These cases are not described in this document.

To arrive at the mass specific or volume specific surface area (S_m or S_V) the following two methods find widespread use in practice:

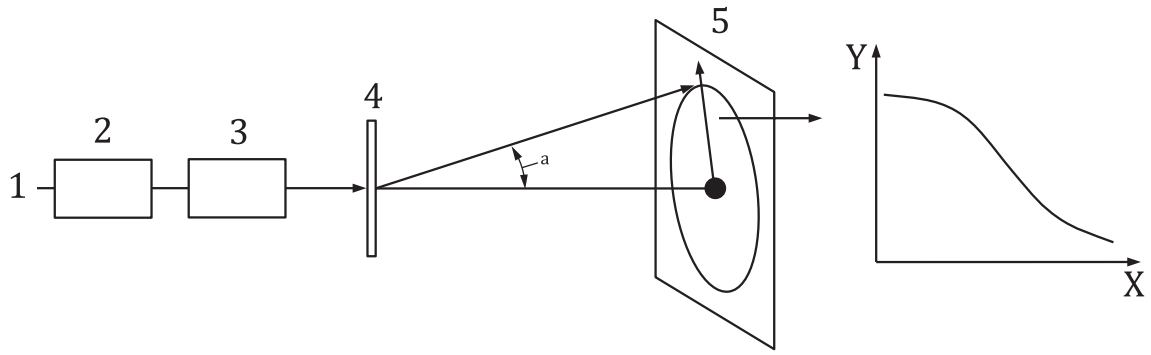
— K/Q ('Invariant') method

— Absolute-scale method

6 Apparatus

6.1 Optics - Focusing - Collimation – Resolution

The general design of a SAXS instrument is shown in Figure 5.

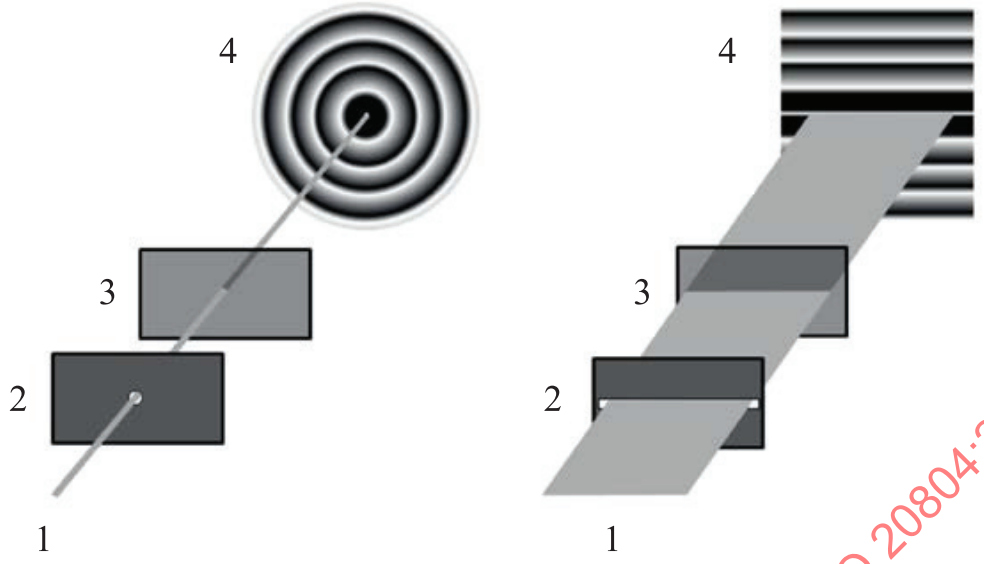


Key

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

Figure 5 — Schematic design of a SAXS instrument, consisting of X-ray source, optics, collimation system, sample holder, and X-ray detector

The above outlined principles strictly apply only for scattering patterns obtained with ideal point-collimation optics, i.e. point-shaped X-ray beam cross-section and monochromatic radiation. However, a widely used instrument design (e.g. Kratky camera) uses line collimation, i.e. the probing X-ray beam is confined in one dimension so that the beam profile is a long and narrow line. This has the advantage of producing higher intensities in the weak outer part of the scattering curve (towards large q), but generally requires numerical corrections (desmearing). The two principles are shown in Figure 6.



Key

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

Figure 6 — Schematic view of point- (left) and line-collimation (right) optics

6.2 Additional requirements for the absolute-scale method

The technical requirements for the absolute-scale method with respect to the SAXS-instrument are:

a) A **stable X-ray source**, i.e. a constant photon rate over time. After switching on the SAXS-instrument (X-ray source and detector), it takes some time until a stable photon/time rate is reached (usually several hours). The stability of X-ray source and detector also depend on the temperature of the instrument's environment; therefore, an actively temperature-controlled room is favourable. All samples as well as the primary/secondary standard shall be measured in one "run" as a change of the instrument's set-up or switching off devices of the SAXS-instrument usually changes the photon/time rate.

b) The **transmission** T_s of a sample shall be determined. It can, e.g. be derived by recording the intensity of the primary beam with and without sample by a photodiode or the detector itself. If the detector is used, the detector-response shall be linear in the appropriate range.

c) The sample, standard (if used), and empty beam scattering measurements shall be made under identical conditions. If this is not the case, then this will invalidate the transmission and calibration measurements.

With certain solid-state pixel detectors that have a large linear dynamic range, it has become possible to measure the intensity of the direct, un-attenuated (or attenuated by calibrated filter, if monochromatic X-rays are used) beam, which then makes the procedure of absolute-scale method very simple.

7 Preliminary procedures and instrument set-up

Generally, it is of greatest importance to ensure that the instrument background (from optics, detector, and sample windows, air) be strictly minimized, since the validity of Porod's law extends into the low-intensity outer (large-q) parts of the scattering curve. On the other hand, however, the typical samples for specific surface area determination are solids (powders, pastes, bulk materials) with strong SAXS

intensity, so that the background may become uncritical. In any case, this shall be verified by control measurements. Apart from this, there are no particular requirements for the instrument set-up, except of choosing a sufficiently large q-range for the measurement of K and/or Q according to Formula (2) and (4). For all measurements requiring background subtraction, the stability of the X-ray source, optics, and detector is of paramount importance.

8 Sample preparation

8.1 General

Sample preparation is simple and fast for SAXS measurements. The required sample quantity is generally small: for powder samples less than 1 g is required, in the case of solid sample slices an area of (1 × 1) mm^2 to (1 × 20) mm^2 is sufficient. 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.

NOTE According to ISO 17867:2020, the ideal specimen transmits about 37 % of the incident radiation. The specimen thickness can be adjusted accordingly to optimize transmission.

The samples are usually filled in sample holders (cuvettes/capillaries, sandwich-type holders comprising windows) which shall be transparent to X-rays and exhibit little scattering themselves. Frequently used window materials include polyimide films, mica or silicon nitride. Care should be taken that the scattering from the window material does not affect the result of the measurement and can be appropriately subtracted.

Solid sample slices can be clamped onto frames with or without additional window foils for protection against the vacuum. Powder samples shall be prepared in a way that the powder is fixed properly and therefore cannot move or sediment during the measurement.

8.2 Degassing

For many mesoporous materials degassing has no significant impact on the specific surface area determined by SAXS. However, in order to exclude any impact caused by adsorbed gases and vapours it is recommended to compare measurements with and without degassing (see Reference [12]).

The degassing temperature should be chosen as high as possible without altering the sample. Degassing may be performed outside or within the SAXS instrument; however, it shall be ensured that handling of the sample between degassing and analysis does not result in a significant uptake of adsorbate or absorbed species.

9 Determination of the specific surface area

9.1 K/Q ('Invariant') method

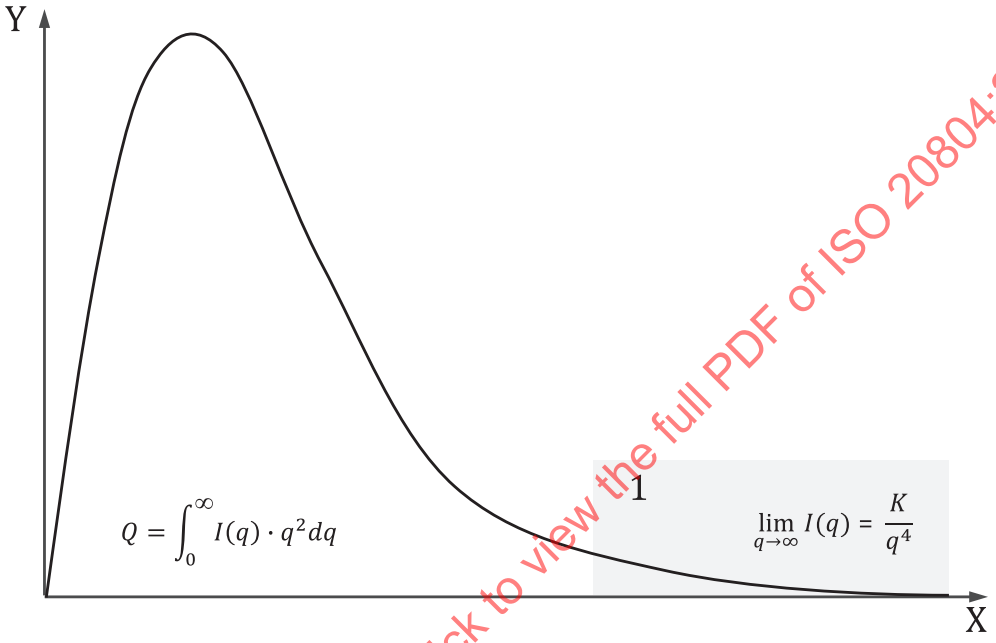
The K/Q or Invariant method is only applicable for mesoporous materials, where the dimensions of both phases are completely within the q-limits or for highly diluted systems like dispersions, where the dimension of the liquid phase is several orders larger than the size of the particles. It cannot be applied to particulate materials, e.g. *Stöber* particles, fumed silica, since the specific pore volume and consequently the volume fractions cannot be determined by this method.

The method is based on the determination of the integral second moment of the scattering curve Q, called the 'Invariant', (since it is independent of shape and form of the scattering entities) which is proportional to the inspected system volume, according to Formula (5):

$$Q = \int_0^\infty I(q) \cdot q^2 \cdot dq \propto V \cdot (\Delta\rho_e)^2 \cdot \varphi_1 \cdot \varphi_2 \cdot 2\pi^2 \tag{5}$$

The integral second moment of the entire scattering curve shall be used i.e. including the extrapolated parts at low (Guinier extrapolation) and high q (Porod extrapolation).

NOTE 1 In ISO 17867:2020, the Guinier extrapolation is explained in detail.



Key

X q/nm^{-1}

Y $I(q) \cdot q^2/\mathrm{nm}^{-2}$

1 Porod region

NOTE 2 The Invariant Q (integral of the scattering curve) is proportional to the volume and the Porod constant K (final slope) is proportional to the surface.

Figure 7 — Schematic view of specific surface area determination by the K/Q method

For samples held in sample cuvettes (e.g. capillaries, polyimide windows) the scattering from the cell windows (corrected for the sample transmission) shall be determined and subtracted:

Combination with Formula (1) leads to the desired formula for the volume specific-surface area:

$$S_V = \pi \cdot \varphi_1 \varphi_2 \cdot \frac{K}{Q} \tag{6}$$

with K available from the Porod plot (see Figure 4) and Q from the integral in Formula (5).

In the case of infinite line smearing, Formula (6) changes to Formula (7)

$$S_V = 4 \cdot \varphi_1 \varphi_2 \cdot \frac{\tilde{K}}{\tilde{Q}} \tag{7}$$

with Formula (8)

$$\tilde{Q} = \int_0^\infty \tilde{I}(q) q \cdot dq \tag{8}$$

For porous materials the pore and matrix volume fractions φ_p and φ_m, respectively, can be calculated from the specific pore volume V_p according to Formula (9)

$$\varphi_p = \frac{V_p \cdot \rho_m}{1 + V_p \cdot \rho_m} \tag{9}$$

with $\varphi_m = 1 - \varphi_p$.

For mesoporous solids and powders, the specific pore volume V_p of the sample is accessible from other methods (e.g. mercury porosimetry or gas adsorption) and shall be determined separately. For liquid particle suspensions, the volumetric phase fractions of the particles and the solvent, respectively shall be determined.

The volume specific surface area S_V – calculated using Formula (6) – can be converted into the customary mass specific surface area given in Formula (10):

$$S_m = S_v \cdot \rho_s^{-1} \tag{10}$$

The determination of S_m requires knowledge of the density ρ_s. Depending on the studied sample, the correct density of the material needs to be used (see Table 2 and Figure 2).

For porous monolithic solids the relevant sample density can be derived from the specific pore volume V_p by Formula (11)

$$\rho_s = \frac{\rho_m}{(1 + \rho_m \cdot V_p)} \tag{11}$$

Formula (8) holds for porous systems, where the pores are void, with zero density. The mass specific surface area is then obtained by Formula (12)

$$S_m = \frac{K}{Q} \cdot \pi \cdot \frac{1}{\rho_m} \cdot \left(1 - \frac{\rho_s}{\rho_m}\right) \tag{12}$$

A typical experimental protocol of using the K/Q method on the example of the CPG (controlled pore glass) sample BAM ERM-FD121 is shown in Annex A.

9.2 Absolute-scale method

The term 'absolute scale' refers to the absolute calibration of the scattered intensity *I(q)* thus providing the differential scattering cross-section $\frac{d\Sigma}{d\Omega}(q)$. The differential scattering cross-section is a measure for the probability of an incident X-ray to be scattered into a solid angle unit. For the absolute-scale method, a stable X-ray source and an option to determine the transmission of the sample are required.

The absolute intensity calibration can be carried out by direct methods if the dynamic range of the detector is high enough or if the incident photon flux and the efficiency of the detector are known. Otherwise, primary or secondary standards can be used. Primary standards are materials for which

the scattering cross-section $\frac{d\Sigma}{d\Omega}(q)$ can be calculated independently from scattering measurements. Common standards are water or other pure liquids; for these standards, information about compressibility, density and composition are required as well as the detector efficiency. Since scattering of these liquids is often very weak, thus requiring long analysis time, other certified reference materials (CRMs) are often used for absolute calibration. These CRMs are materials with a well-known scattering cross-section that does not change with time. They are calibrated with the above-mentioned liquids. A typically used CRM for absolute intensity calibration is NIST SRM 3600 'glassy carbon' (see Reference [14]).

The background-corrected experimental scattering data $I(q)_s$ can be converted into absolute-scale data [i.e. the scattering cross-section $(d\Sigma/d\Omega)$], by comparing to the scattered intensity $I(q)_{ref}$ for the reference material measured with the same SAXS instrument configuration. Using the transmission T_s and thickness t_s of the sample as well as the respective information of the primary or secondary reference material, T_{ref} and t_{ref}., the absolute scattering cross-section of the sample can be calculated as given in Formula (13):

$$\left(\frac{d\Sigma}{d\Omega}(q)\right) = \frac{\left(\frac{d\Sigma}{d\Omega}(q)\right)_{ref}}{I(q)_{ref}} \cdot \frac{T_{ref}}{T_s} \cdot \frac{t_{ref}}{t_s} \cdot I(q)_s \tag{13}$$

Additionally, the mass density "seen by the X-ray", i.e. the mass in the sample volume penetrated by the radiation is required for the absolute-scale method. Depending on the sample type, one of the two following approaches shall be used:

a) For monolithic plane-parallel slices the required input parameters are:

   — Thickness of the sample t_s

   — Transmission of the sample T_s

   — Mass density of the sample ρ_s

b) If the mass density "seen by the X-ray" is not known, e.g. in case of powders, fragments, irregular monoliths, it shall be calculated. For this, knowledge is required of:

   — Thickness of the sample t_s (in case of cuvettes d_s is the distance between the windows/inner walls of the cuvette)

   — Transmission of the sample T_s

   — Matrix density ρ_m which can be determined by, e.g. gas pycnometry

   — Total attenuation coefficient (including coherent scattering) μ_{tot} at the applied X-ray energy, which can be derived from literature by knowledge of the elemental composition (see Reference [15]).

The mass density of the sample "seen by the X-ray", ρ_s is then calculated by Formula (14):

$$\rho_s = -\frac{\ln T_s}{t_s} \cdot \frac{\rho_m}{\mu_{tot}} \tag{14}$$

In case of powders filling the gap in between the windows of the sample holder (distance between windows equivalent to sample thickness t_s) the calculated sample density ρ_s is equal to the packed-bed density $\rho_{packed\text{-}bed}$ of the powder between the windows.

If the sample thickness and/or sample density is not known (e.g. for irregular monoliths, powders) equivalent values d^*, ρ^*, $(d\Sigma/d\Omega)$, K^*_{abs} can be used in Formulae (14) and (15). Then, the calculated mass density ρ^* and the scattering cross-section $(d\Sigma/d\Omega)$ are equivalent values without distinct physical meaning. However, the relevant physical parameter is the areal density ("mass seen by the X-ray", i.e.

the product $t_s \cdot \rho_s$) which is not affected by these virtual values resulting in the correct scattering cross-section.

Eventually, the mass specific surface area can be calculated from Formula (15):

$$S_m = \frac{K_{abs}}{2\pi \cdot \rho_s \cdot r_e^2 \cdot \Delta\rho_e^2} \tag{15}$$

with r_e the classical electron radius (2,82 10^{-15} m), K_{abs} the Porod constant on absolute scale derived from Formula (2) (see Figure 4) and $\Delta\rho_e^2$ the square of the electron density difference between the two phases.

The electron density difference between the two phases can be calculated by Formula (16):

$$\Delta\rho_e^2 = (\rho_{e1} - \rho_{e2})^2 = (C_1 \cdot \rho_1 - C_2 \cdot \rho_2)^2 \tag{16}$$

where

$$C_{1,2} = \left(\frac{Z}{M_\upsilon}\right)_{1,2} \cdot N_A \tag{17}$$

Formula (17) connects the mass densities with the electron densities of the two phases. N_A is the Avogadro's constant (6,022 10^{23} mol^{-1}), Z the proton number and M_υ the molar mass of the respective phase (element, compound or mixture). For light elements ($Z/M_\upsilon \approx 0{,}5$ except of hydrogen) $C_{1,2}$ can be considered as a constant ($C \approx 3{,}0\ 10^{23}\ g^{-1}$).

If phase 2 is vacuum (or dry air, to a good approximation), i.e. $\rho_p \cong 0$, Formula (15) simplifies to Formula (18):

$$S_m = \frac{K_{abs} \cdot \rho_s^{-1}}{2\pi \cdot r_e^2 \cdot (C_m \cdot \rho_m)^2} \tag{18}$$

The volume specific surface area S_V is then calculated by Formula (19):

$$S_V = S_m \cdot \rho_s \tag{19}$$

where ρ_s is the mass density of the sample. Depending on the studied sample the correct density of the materials shall be used (see Table 2 and Figure 2, respectively).

A typical experimental protocol of using the absolute-scale method on the example of the CPG (controlled pore glass) sample BAM ERM-FD121 is shown in Annex A.

10 Documentation and test report

10.1 Test report

Test reports should be prepared in line with ISO 9276-1,ISO 9276-2, and ISO/IEC 17025. The report shall contain at least the following information:

a) A reference to this document, i.e. ISO ISO 20804:2022.

b) The specific surface area S_m or S_v and its uncertainty. In the absence of a full uncertainty evaluation, the standard deviation from several repeated measurements on the same aliquot of the sample should be provided as estimate of the repeatability. ISO/IEC Guide 98-3 can assist here, but expert judgment may have to be employed.

c) The complete sample identification, including available information on homogeneity. Electron micrographs, where relevant and informative, can be included in order to convey information on particle size, degree of dispersion, and other visual indicators that are not easily conveyed in graphical or tabular data.

d) Applied data evaluation method (K/Q ('Invariant') method or absolute-scale method).

e) Range of q selected for data evaluation.

f) Applied method for determination of Porod constant K.

10.2 Technical records

In addition to the information given in the test report, the following information on the measurements should be documented in line with the provisions on technical records as stated in ISO/IEC 17025. These records shall be readily retrievable and should be provided to the customer on request:

a) Instrument type and serial number;

b) Applied sample treatment procedures, e.g. homogenization;

c) Measurement conditions, e.g. exposure time, sample-to-detector distance, wavelength or photon energy, q-range, temperature;

e) Analyst identification (name or initials).

Annex A
(informative)

Example of a typical experimental protocol

A.1 General

This annex describes a typical experimental protocol in its essential details on the example of the CPG (controlled pore glass) sample BAM ERM-FD121. The results are compared to values that were obtained with Ar (87K) BET measurements of this material as reported in Reference [17]. The Ar (87K) BET results perfectly agree with the results derived from SAXS measurements using the Absolute scale method.

Note that the specific surface area obtained by using the Invariant (K/Q) method is in some cases found to be up to 10 % higher in comparison to the Absolute scale method. It is therefore recommended to use – if possible – both methods on the same sample material and to compare the obtained results.

With respect to the overall uncertainty of the SAXS method for determining the specific surface area it can be stated that it has comparable measurement uncertainties as the results obtained with the gas adsorption (BET) method (see Reference [17]).

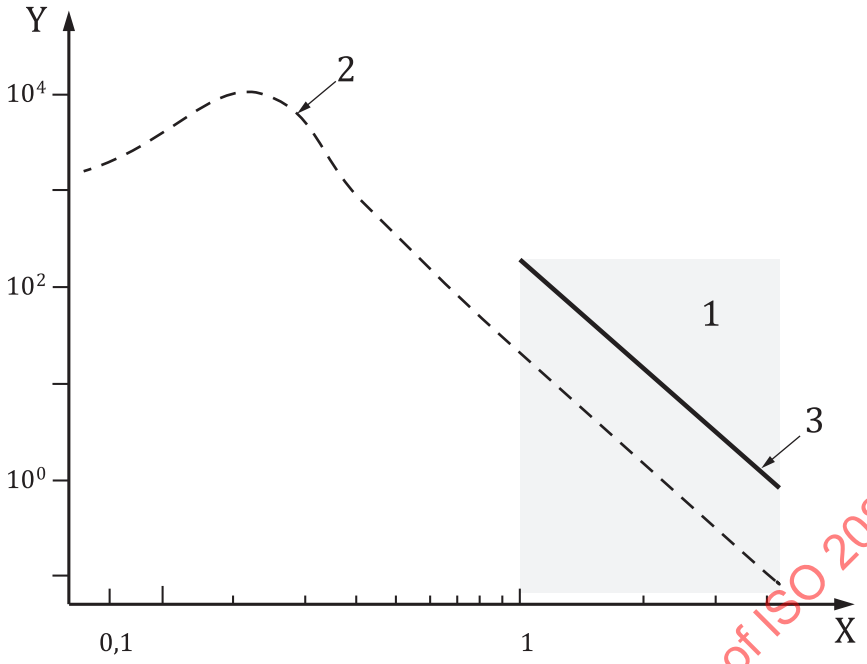
A.2 Invariant (K/Q) method

A.2.1 General information

The practical advantage of the Invariant method is that it does not require any absolute scaling of intensity measurement, and that the electron density difference does not need to be known. Its disadvantage lies in the fact, that the scattering of the structures of both phases shall be within the q-limits of the measurement or one highly diluted phase (e.g. dispersions) are needed. In addition, Q [see Formula (5)] can only be determined within the experimental q-limits of the SAXS measurement, and not completely from 0 to ∞ for which extrapolations are needed.

A.2.2 Check of q^{-4} – range

The range of validity of the q^{-4} condition (Porod's law) can be checked by inspecting the background-corrected scattering curve plotted in a double-logarithmic plot *log I vs log q* (see Figure A.1). The Porod constant K was determined by a linear least-square fit.



Key

X q on logarithmic scale/nm^{-1}

Y $I(q)$ on logarithmic scale [a.u.]

1 Porod region

dotted ERM-FD121

solid slope; −4

NOTE The double-logarithmic plot is used to define the range indicated by the shaded area, where Porod's law applies (slope −4). Within the limits shown, the slope is −4, hence the analysis in terms of the theory outlined in 9.1 is justified.

Figure A.1 — Double-logarithmic plot for ERM-FD121

A.2.3 Determination of the invariant *Q*

The scattering curve *I(q)* is only accessible between the limits of resolution q_{min} and q_{max}, respectively. Both, towards zero and infinite angles [as required for the integration according to Formula (2)] the values shall be found by extrapolation. Towards $q = 0$ this is typically done by the Guinier approximation (in many cases there is no linear Guinier range), and by the q^{-4} condition (Porod 's law) for the outer part (towards large q).

The total invariant Q is hence obtained from the sum of the experimental function (after subtraction of the empty sample cell/holder and the constant background A) and of the two extrapolated portions.