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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)

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<u>ISO 20804:2022</u> https://standards.iteh.ai/catalog/standards/sist/a22d518e-1fab-486c-9c19-75f1c4354bba/iso-20804-2022



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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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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 <u>www.iso.org/members.html</u>.

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 μ m 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 μ m 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.

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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 $1 \text{ m}^2\text{g}^{-1}$ to $2\ 000 \text{ m}^2\text{g}^{-1}$ and the volume specific surface areas in the range from 0,01 m²cm⁻³ to $1\ 000 \text{ m}^2\text{cm}^{-3}$ 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 <u>https://www.iso.org/obp</u>
- IEC Electropedia: available at <u>https://www.electropedia.org/</u>

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 ARD PREVIEW

3.7

volume specific surface area

surface area of the sample divided by sample volume

3.8

external (outer) surface itch.ai/catalog/standards/sist/a22d518c-1fab-486c-9c19-75flc4354bba/iso-

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 μ m 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

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
$ ho_{\rm m}$	Density of the matrix	g cm ⁻³
$\rho_{\rm p}$	Density of the pore phase or particle	g cm ⁻³
$\rho_{\rm bulk}$	Bulk density ANDARD PKEVIEW	g cm ⁻³
$ ho_{ m grain}$	Grain density	g cm ⁻³
$ ho_{ m packed-bed}$	Density of packed beds of nanoparticles	g cm ⁻³
$ ho_{ m dispersion}$	Density of dispersion of nanoparticles	g cm ⁻³
ρ_1	Density of phase 1 ISO 20804:2022	g cm ⁻³
ρ_2 https://standard	Density of phase 2 ndards/sist/a22d518e-1fab-486c-9c19-75f1c4354bba	g cm ⁻³
$ ho_{ m e}$	Electron density 20804-2022	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 ³ g ⁻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	
$I(q)_{\rm ref}$	Scattered intensity of the reference (standard)	
$\tilde{I}(q)$	Scattered intensity (line-smeared data)	
Q	Invariant	nm ⁻³
Q	Invariant (line-smeared data)	
K	Porod constant	
<i>Ř</i>	Porod constant (line-smeared data)	
K _{abs}	Absolute Porod constant	m ⁻⁵
A	Constant background term	
Ã	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)	
ts	Thickness of the sample	mm
t _o	Optimum thickness of the sample	mm
t _{ref}	Thickness of the reference (standard)	mm
$\mu_{ m tot}$	Linear attenuation coefficient (including coherent scattering)	m ⁻¹
r _e	Classical electron radius	m
Ζ	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

		So defin	Solid samples with defined sample thickness		Solid samples with unknown thickness			Liquid-suspended particles	
Method	Eq.	porous monolith	mesoporo- us powder/ granules	non-porous particles (packed bed)	dis- persed na- no-parti- cles	meso-po- rous powder/ granules	non-porous particles (packed bed)	referred to whole mass of dispersion	referred to particle phase only ^a
po	10	nupsi/stai	idards.iten.a	rcatalog/stan	1arus/sist/ 2080	1220318e 4 2022	n.a.	$\rho_{\rm dispersion}$	$\beta^{400a/80}$
Q ethi	11	$ ho_{ m bulk}$	$ ho_{ m grain}$	n.a.	$\rho_{\rm bulk}^{2080}$	$\rho_{\rm grain}$		n.a.	n.a.
K/m	12							$ ho_{ m dispersion}$	β
ıle	14	- - ρ _{bulk}						n.a.	n.a.
e-SC	15		$ ho_{ m packed-bed}$	$ ho_{ m packed-bed}$	$ ho^*$	$ ho^*$	$ ho^*$	$ ho_{ m dispersion}$	β
Absolut method	18							n.a.	n.a.
	19		$ ho_{ m grain}$	n.a.	n.a.	n.a.	n.a.	$ ho_{ m dispersion}$	β
a E	^a Equivalent to dry powder.								
* E	* Equivalent values for irregular particles, e.g. unknown thickness and/or sample density (see <u>9.2</u>)								
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 $2\theta < 5^\circ$; 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.



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).



Key

- https://standards.iteh.ai/catalog/standards/sist/a22d518e-1fab-486c-9c19-75f1c4354bba/iso- ρ_s (density of the sample)
- 1
- 2 $\rho_{\rm m}$ (density of the matrix)
- 3 $\rho_{\rm grain}$ (grain density)
- $ho_{
 m bulk}$ (bulk density) 4
- Outer surface particle envelope а
- b Inner surface - pores (microphase separation)

The outer surface area of particles usually is very small as compared to the inner surface area, if the NOTE 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.

2

2