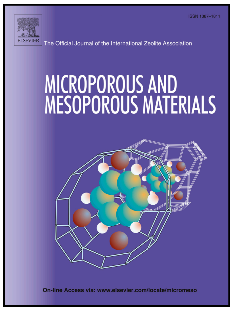

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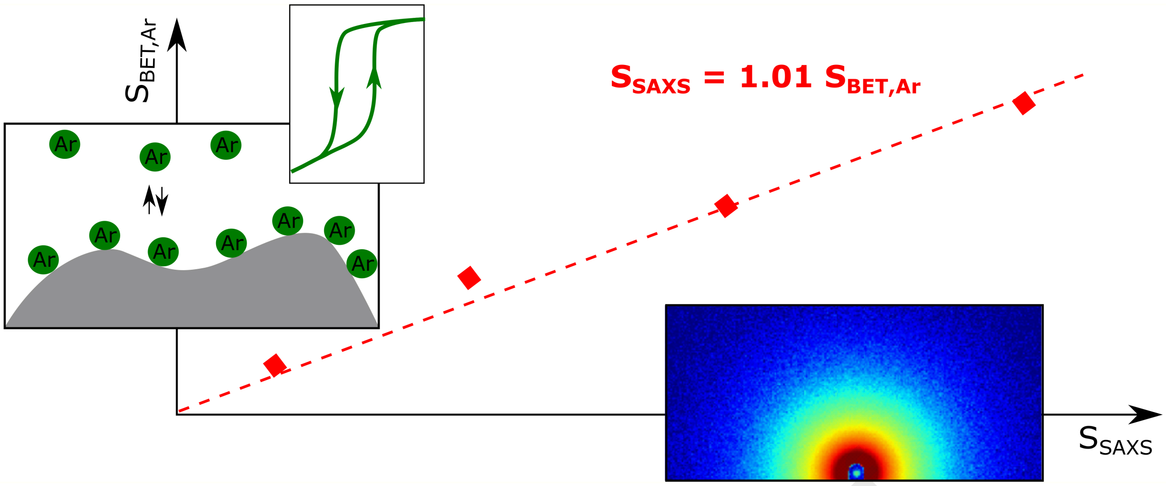
$S_{BET,Ar}$
Ar
$S_{SAXS} = 1.01\ S_{BET,Ar}$
S_{SAXS}

Reliable Surface Area Determination of Powders and Meso/Macroporous Materials: Small-Angle X-ray Scattering and Gas Physisorption

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Abstract

The specific surface area is key for various application fields of porous materials. Its reliable and fast determination is therefore crucial for materials development and product quality management. Surface area assessment is usually based on physical adsorption using the Brunauer-Emmett and Teller (BET) theory. However, the BET method/gas adsorption exhibits a number of limitations and challenges including (i) time consuming sample preparation and measurement time and (ii) the BET approach allows only for non-porous and meso-/macroporous materials to obtain reliable surface areas. In addition, the accuracy of the obtained surface area depends on the proper choice of adsorptive/probe.

Within this context, this work evaluates in a rigorous way *in-depth* Small Angle X-ray Scattering (SAXS) as an alternative and complimentary approach for reliable and fast surface area assessment. To our knowledge, this work can be considered the first systematic study where the surface areas from SAXS are compared and validated with true benchmark surface area data. We utilize silica-based nanoparticles as well as a well-defined mesoporous controlled pore glass for systematic SAXS and adsorption studies (argon and nitrogen at 87 K and 77 K, respectively). Owing to the lack of micro- and narrow mesopores of these model materials, the BET method based on argon 87 K adsorption can be applied to determine benchmark surface areas. Indeed, excellent agreement was found between surface areas derived from argon 87 K adsorption and SAXS. In fact, we demonstrate that the determination of specific surface area can be brought with SAXS to a new level, where parameters such as size of the probing adsorptive, its orientation and thus its effective cross-sectional area, (when adsorbed on the surface) are no longer affecting the value of the specific surface area determined. Furthermore, SAXS was shown to be significantly faster than gas adsorption. For the silica materials used, the study shows that SAXS does not require degassing and – along with analysis times of a only few minutes per sample – provides an accurate and extremely fast, high-throughput approach.

This fundamental study can be considered a major step in enabling SAXS for reliable surface area assessment for applications both in nanoporous materials development and quality control, thus boosting SAXS for surface area determination in general, but in particular also for materials, where the usage of gas adsorption is restricted or not possible at all.

KEYWORDS: Specific Surface Area, Gas Adsorption, BET Method, Small-Angle X-Ray Scattering, Absolute Calibration

1 Introduction

The widely spread standard methodology for surface area assessment is traditionally based on the analysis of nitrogen gas adsorption with the Brunauer-Emmett-Teller (BET) method [1–3], with the original paper being one of the 100 most cited papers [4]. This clearly indicates the high relevance of surface area determination. The BET method is used as standard methodology not only in science but also particularly in the area of R&D, quality control and for the determination of parameters for technical data sheets of commercial products.

The BET method allows one to determine reliable surface areas of non-porous, macroporous (pores > 50 nm) and most mesoporous (2 nm ≤ pores ≤ 50 nm) materials, giving rise to well defined type II and type IV(a) adsorption isotherms according to the IUPAC recommendation [2]. However, various limitations of this methodology are known [5,6]. For example, only an apparent surface area can be determined for materials containing micropores (pores < 2 nm) or small mesopores (pores < 4 nm). Furthermore, a straightforward application of the BET method is not possible for materials, which change their structure during adsorption experiments, e.g. soft polymers, certain MOFs, or materials showing absorption effects. Another major practical limitation of surface area analysis by physisorption is that the experiments require relatively long measurement times, mainly due to the requirement of outgassing the samples prior to analysis, which is a limiting factor for many application areas, e.g., in the pharmaceutical industry. Furthermore, it has to be emphasized that a proper choice of adsorptive is essential for a reliable surface area determination as its molecular size and interaction with the sample`s surface functionalities may influence the outcome of the analysis. Within this context it has been shown that contrary to nitrogen adsorption (at 77 K), where uncertainties in the BET surface area determination in the order of 20-30 % occur, with argon at 87 K a reliable surface area assessment is possible (see also section 1.1)

To overcome the mentioned challenges associated with the BET method, surface area determination using Small-Angle X-ray Scattering (SAXS) has been proposed [7,8]. This method has been applied and compared to results from gas adsorption by many groups earlier, both to porous silica (e.g. [9–15]), as well as microporous carbons (e.g. [12,13,16,17]), however, never in a sufficient depth of methodology. Problematic here is also the lack of benchmark surface area data for comparison and validation. In fact, as already indicated the BET method cannot provide reliable surface area data for microporous materials. In addition, surface area data from adsorption were essentially always based on data from nitrogen adsorption, where however at least for surfaces with polar surface functionality, due the uncertainty in the cross-sectional area and overestimation of the surface area up to 20-25 % can occur. For instance, Tolami [12] investigated commercially available silica-gels, silica-aluminas and aluminium oxide. The determination of the specific surface area from SAXS was performed using the invariant method that does not require absolute calibration of the scattering data. However, the invariant method is strongly limited by the size of the structures to which it can be applied. Smarsly at al. [10] analyzed two mesoporous silicas and calculated the specific surface area from the correlation length determined from the scattering data without absolute calibration. The results were 10 to 30 % lower than from N_2-adsorption. Potential contributions due to microporosity could not be clarified. Szekeres et al. [11] studied silica Stöber particles and commercial fumed silica and claimed reasonable good agreement with gas adsorption for the deduced specific surface area in case of the fumed silica while the comparison completely failed for the Stöber particles. The authors discuss the discrepancies in terms of microporosity and surface inaccessible to N_2. Unfortunately, no information is given on the details of the SAXS data evaluation

Hence, in order to address the mentioned question and challenges we focus in this paper on a comparison of surface area assessment using both, gas adsorption and SAXS on non-porous particles and mesoporous silica model materials, where the BET method can be applied in a straightforward way and true benchmark surface area data based on argon 87 K adsorption can be obtained. This allows us to rigorously validate in-depth SAXS surface area analysis for the first time and to suggest a complementary or alternative, non-invasive method for reliable surface area assessment based on Small Angle X-Ray Scattering (SAXS),

1.1 Background on Gas Adsorption

Under certain, carefully controlled conditions, the specific BET surface area of non-porous, macroporous or mesoporous materials can be regarded as the probed accessible surface area. For surface area assessment, the determined isotherm is converted to the linear ‘BET plot’. The value of the BET monolayer capacity n_m is calculated using the BET equation:

$$\frac{\frac{p}{p_0}}{n(1-\frac{p}{p_0})} = \frac{1}{n_m C} + \frac{C-1}{n_m C}\left(\frac{p}{p_0}\right) \tag{1}$$

The constant C is related to the energy of monolayer adsorption and hence, is a measure for the strength of interactions between adsorptive and adsorbent. In case of type II and IV(a) isotherms according to the IUPAC classification of isotherm types [2], linear BET plots can be found at relative pressures $p/p_0 = 0.05$-0.3. The surface area S can be calculated using the following equation with the Avogadro number N_A and the cross-sectional area σ of the adsorptive on the material's surface:

$$\mathrm{S} = \mathrm{n_m} \cdot N_A \cdot \sigma \tag{2}$$

However, some intrinsic factors limit a reliable surface area assessment using the BET method. In the presence of micropores, i.e. materials with pores smaller than 2 nm exhibiting type I isotherms or combinations with type I isotherms, only an apparent surface area can be determined with the BET method [2,18]. This is correlated with the fact that monolayer-multilayer adsorption cannot be separated from micropore filling which makes the BET theory inapplicable [2,5]. The BET method is also inaccurate for mesoporous materials exhibiting type IV(b) isotherms (with pores smaller than 4 nm) as the pore condensation pressure is very close to the pressure range where monolayer-multilayer formation occurs. This can cause significant overestimation of the monolayer capacity during BET analysis [2]. Moreover, as indicated the BET theory is not applicable for materials showing structural changes during adsorption.

It needs to be stressed that the choice of adsorptive is essential for reliable surface area assessment. Nitrogen (N_2) adsorption at 77 K has been the standard procedure for surface area assessment for many years. Usually, a cross-sectional area of 0.162 nm^2 is used for calculating the specific surface area. This value is based on the assumption that the nitrogen monolayer is in a close-packed liquid-like state at 77 K. This is true for hydrocarbon surfaces and in fact, the surface area of carbons can be determined accurately using nitrogen (77 K) adsorption [19]. However, nitrogen's quadrupole moment causes specific interactions with polar surface functional groups and exposed ions on the material surface. These interactions affect the orientation of the adsorbed nitrogen molecules and hence, the effective cross-sectional area of nitrogen strongly depends on the surface chemistry of the material under study. In case of highly polar surfaces, the cross-sectional area can be smaller than the usually assumed value of 0.162 nm^2 [2,19]. This was indicated before, but could not be addressed in a rigorous way [20,21]. For instance, experimental studies using ordered mesoporous silica materials such as MCM-41[22] and silica spheres of known diameter [23] further indicated the change of the cross-sectional area depending on the surface chemistry. It was demonstrated, that this can lead to an overestimation of the surface area of up to 20 - 25 % [22- 24]. Hence, the use of nitrogen as adsorptive is questionable if the surface chemistry is not exactly known, as a reliable cross-sectional area is not available in this case, as already mentioned in the IUPAC technical report [2] and in recent reviews, e.g. [25–28]. Argon adsorption at 87 K has been proposed as an alternative. In contrast to nitrogen, the monoatomic argon does not exhibit specific interactions with surface-functional groups due to the absence of a quadrupole moment. Consequently, the cross-sectional area of argon (0.142 nm^2 is usually assumed at 87K) does not change depending on the surface chemistry and argon can be used for reliable surface area determination for all material classes. Therefore, argon adsorption at 87 K is recommended for surface area assessment by IUPAC [2].

1.2 Background on Small Angle X-ray scattering

SAXS is a non-invasive technique that evaluates scattering of X-rays by quasi-free electrons in the system under investigation. The scattering pattern recorded is the Fourier Transform of the electron-density fluctuations (e.g. solid and pore phase) in the system. State-of-the-art lab-scale SAXS instruments cover a length scale from about 0.1 to 300 nm. With respect to the specific surface area, the technique probes the geometric interface between two phases with different electron densities (constant within each phase) and is thus not sensitive to the surface chemistry. Typical sample volumes necessary for analysis are in the range > 1 mm^3. The time required for the measurement of an individual sample with a lab-scale instrument is in the order of some minutes, depending on the X-ray source, the detector sensitivity and the material's properties (chemical composition, contrast, structure, transmission).

To calculate the specific surface area from SAXS, we used the scattered intensity on an absolute scale i.e. calibrated to yield the mass specific scattering cross section $1/m\cdot d\sigma/d\Omega$ [29]. In combination with Porod's law [30], this method can be applied to determine the specific surface area of meso- as well as macroporous samples and nano- to micron-sized particles. The only assumption entering the data evaluation is, that the sample exhibits a smooth solid/pore interface between the two phases and thus shows a decay of the scattering cross section $d\sigma/d\Omega$ per sample mass m towards large scattering vectors q with a power law dependence $\sim q^{-4}$:

$$\frac{1}{m}\cdot\frac{d\sigma}{d\Omega} = K\cdot q^{-4} \qquad (3)$$

With the prefactor K, i.e. the so-called Porod's constant, the specific surface area S for a porous solid or a bed of particles is calculated by:

$$S = \frac{K}{2\pi\cdot r_e^2\cdot\left(N_A\cdot\frac{Z}{M_v}\cdot\rho_{sk}\right)^2} \qquad (4)$$

Hereby the classical electron radius ($r_e = 2.82\cdot10^{-15}$ m) and Avogadro's number ($N_A = 6.02\cdot10^{23}$ 1/mol) are constants. The skeletal density ρ_{sk} of the non-porous backbone or particle, respectively, as well as proton number Z and molar mass M_v of the solid phase are material properties, which have to be provided.

2 Experimental

2.1 Materials

The surface area of non-porous, macro- or mesoporous model materials with pore sizes larger than 4 nm can be accurately determined using the BET method if the right choice of adsorptive is considered. In this work, four different hydrophilic silica model materials were chosen, which fulfilled these requirements: Silica nanopowder was obtained from Sigma Aldrich (called *Silica 12* in our study). Silica nanoparticles with a mean particle size of about 80 nm (*Silica 80*) and Silica Particles with a mean particle size of 200 nm (*Silica 200*) were both obtained from General Engineering and Research. In addition, a controlled pore glass (CPG) *ERM-FD-121* obtained from the German Federal Institute of Materials Research and Testing (BAM) was used.

2.2 Scanning Electron Microscopy

Scanning Electron Microscopy images (SEM, type ZEISS ULTRA plus) were made to get a visual impression of the model materials investigated. To improve electrical conductivity of the silicas for imaging, the samples were sputter coated with gold-palladium.

2.3 Gas Adsorption

Prior to textural analysis based on gas adsorption, the materials were degassed at 150 °C for 12 h under vacuum. Textural properties of the model materials were analyzed using argon (87 K) and nitrogen (77 K) adsorption with an Autosorb IQ (Anton Paar QuantaTec, formerly Quantachrome Instruments).

Argon (87 K) isotherms were measured over the whole pressure range (from relative pressure p/p_0 approximately 10^{-5} up to 1) for each material. Pore size distributions were determined by applying a dedicated nonlocal density functional theory (NLDFT) kernel that confirmed the absence of micropores and narrow mesopores, demonstrating the applicability of the BET method for the chosen model materials.

The BET method (Eqs. (1) and (2)) was applied for surface area assessment in the relative pressure range of 0.05 – 0.3 using argon adsorption at 87 K (with a cross-sectional area of 0.142 nm^2). Multiple aliquots of each material were analyzed to investigate the reproducibility of the surface area assessment with argon adsorption. This also serves as an indicator for the homogeneity of the material. Additionally, the repeatability of the measurements was investigated by repeating the measurement multiple times on the same aliquot (see the supplementary material). In addition, the specific surface area was calculated using nitrogen adsorption at 77 K for all model materials. The standard cross-sectional area of 0.162 nm^2 was used in this case. Repeatability and reproducibility were also investigated using nitrogen. For comparison between argon/nitrogen adsorption and SAXS, the mean surface area was calculated for each material using all aliquots, including all repeated measurements (see the supplementary material).

2.4 SAXS

The SAXS measurements were performed with a SAXSpoint system (Anton Paar) using Cu-Kα radiation and a 2D areal detector (Dectris EIGER R 1M). A PIN-diode was used for X-ray transmission measurements and subsequent absolute calibration of the scattering signal. For the measurement, the samples were placed in a powder cell with two polyimide windows holding the powder in place, but open to the environment. The powders were packed so densely, that no setting during characterization could occur. The samples were measured under vacuum at ca. 1 mbar.

For surface area assessment with SAXS, 4 to 5 aliquots of each material were investigated to probe the reproducibility. With respect to repeatability, also several measurements with the same aliquot were performed. Prior to analysis, one aliquot of each material was additionally measured without explicit degassing. All other measurements were performed after degassing according to the gas adsorption experiments, i.e. 12 h at 150 °C under vacuum (ca. 1 mbar). For the calculation of the mean surface area, all aliquots and all measurements on the degassed samples were used (see the supplementary material).

For the calculation of the specific surface area according to Eqs. (3) and (4), the chemical composition of the model materials was assumed to be pure SiO_2. A skeletal density ρ_{sk} between 2.14 g cm^{-3} and 2.18 g cm^{-3} was determined for the silica model materials using He-pycnometry (MicroUltraPyc, Anton Paar QuantaTec) (see the supplementary material).

3 Results

3.1 Textural Characterization

The SEM images of the model materials in Figure 1 give a visual impression of the model materials investigated revealing an amorphous particulate structure for the *Silica 12* nanopowder, clearly almost monomodal spherical nanoparticles for the *Silica 80* and *Silica 200* samples and an amorphous pore structure for the controlled pore glass.

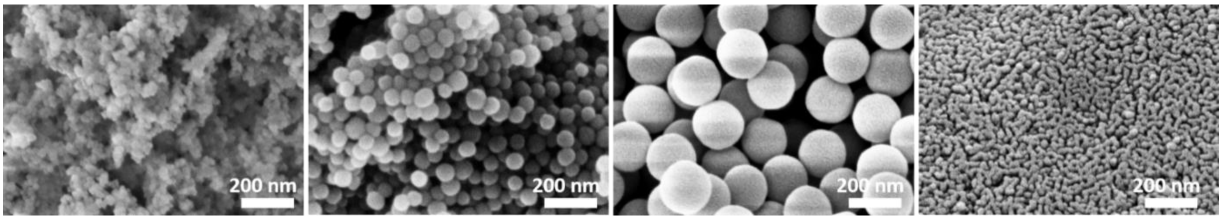

Figure 1: SEM images of the model silica materials: left to right: (a) *Silica 12*, (b) *Silica 80*, (c) *Silica 200*, (d) CPG *ERM-FD-121*.

The gas adsorption experiments show that all model materials exhibit a well-defined type II (*Silica 12* and *Silica 200*) or type IV(a) (*Silica 80* and CPG *ERM-FD-121*) isotherm, which indicates the applicability of the BET method (see Figure 2).

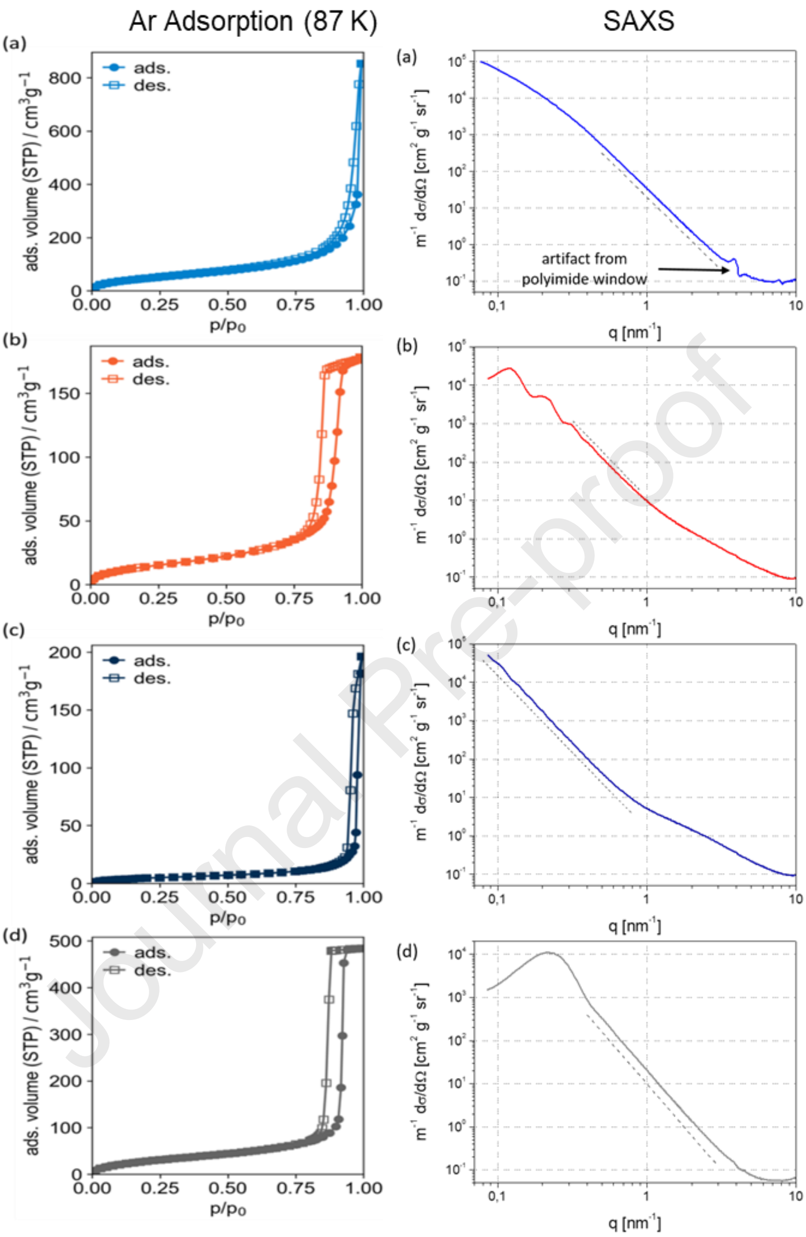

Figure 2: Argon adsorption isotherms at 87 K and SAXS data of the different model materials. (a) *Silica 12*, (b) *Silica 80*, (c) *Silica 200*, (d) CPG *ERM-FD-121*. The dashed lines in the SAXS curves represent the Porod power law ~ q^{-4}.

A detailed example of the argon (87 K) physisorption isotherm of CPG *ERM-FD-121* is shown in Figure 3. The material shows a perfect type IV(a) isotherm, which is typical for solely mesoporous materials. This is also reflected in the pore size distribution (Figure 3(d)). No pores smaller than 4 nm are present in the sample, which ensures a reliable surface area assessment with the BET method. Figure 3(c) shows the BET plot, which illustrates the perfectly linear shape for these model materials. Hence, the BET method in combination with argon (87 K) adsorption can be used to generate benchmark surface area data for these model materials.

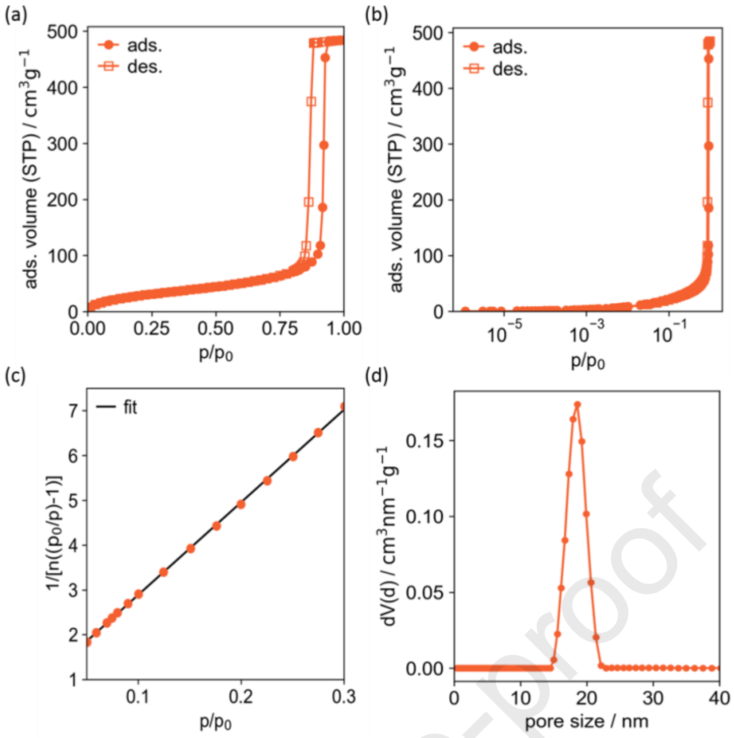

Figure 3: Physisorption characterization of CPG *ERM-FD-121*. (a) Linear and (b) logarithmic plot of the argon (87 K) physisorption isotherm, (c) linear BET plot in the relative pressure range p/p_0 = 0.05-0.3, (d) pore size distribution determined by applying NLDFT on the argon (87 K) adsorption isotherm.

The surface areas determined with argon (87 K) and nitrogen (77 K) adsorption determined by the BET-equation (Eq. (1) and Eq. (2)) for the different silica model materials are summarized in Table 1.

Table 1: Comparison of specific surface area of silica model materials determined with SAXS, argon (87 K) adsorption and nitrogen (77 K) adsorption. Good agreement of SAXS and Ar (87 K) surface areas. Due to the uncertainty in the cross-sectional area depending on the surface chemistry, which is caused by the quadrupole moment, nitrogen leads to an overestimation of the specific surface area.

Material	***S / m^2 g^{-1} (SAXS)***	***S / m^2 g^{-1} (Ar, 87 K)***	***S / m^2 g^{-1} (N_2, 77 K)***	***N_2 Overestimation compared to Ar***
Silica 12	*165.7 +/- 3.4*	*162.6 +/- 3.0*	202.5 +/- 3.8	24.6 %
Silica 80	*39.2 +/- 1.1*	*47.1 +/- 0.2*	57.5 +/- 0.3	22.1 %
Silica 200	*13.3 +/- 0.4*	*15.6 +/- 0.1*	18.9 +/- 0.1	21.2 %
CPG ERM-FD-121	*100.0 +/- 1.0*	*98.6 +/- 0.6*	118.6 +/- 1.1	20.3 %

The argon and nitrogen measurements show quite good repeatability, i.e. deviations < 2.3 % for the specific surface area assessment can be observed by repeating measurements. The deviations between different aliquots of the same material from the mean surface area are also minimal (< 3 %) (see the supplementary material), indicating that the chosen model adsorbent materials exhibit good homogeneity; which provides a good basis for the comparison between different characterization methods.

3.2 Surface Area Assessment with SAXS

Figure 2 gives an overview over the differential scattering cross sections for the model materials investigated. As expected, the samples show quite different scattering characteristics. The modulation of the scattering of *Silica 80* towards small q-values indicates a high monodispersity of the particle diameter, whereas for *Silica 200* the main part of the oscillation lies outside the measurement range and only the tail is yet visible. Contrary, *Silica 12* does not show this characteristic oscillations but rather a broad hump as indication for a disordered porous structure with a broad distribution of characteristic lengths (particle, pore sizes). These findings are in accordance with the SEM-images of Figure 1. Nevertheless, for all model silicas a Porod power law ~ q^{-4} can be identified.

Figure 4 shows exemplarily the mass specific differential scattering cross section of CPG *ERM-FD-121* before and after degassing in a double-log representation. Both scattering curves are almost identical with only minimal differences that are within the range of repeated measurements on the same aliquot. The calculated specific surface areas of the scattering curves in Figure 4 deviate < 1 %. The Porod range ($\sim q^{-4}$) evaluated for calculating the specific surface area is indicated by the dashed line.

The mean specific surface areas for all silica model materials investigated by SAXS are compiled in Table 1 along with the respective values from Ar and N_2 adsorption. A comparison to the particle size determined from SEM is included in the supplementary material.

The SAXS measurements show a good repeatability, i.e. deviations < 3.6 % can be observed by repeating measurements. The deviations between different aliquots of the same material from the mean surface area are also minimal (< 4.3 %) (see the supplementary material).

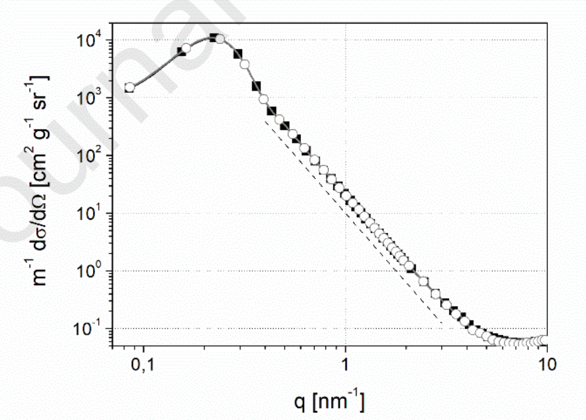

Figure 4: Differential scattering cross sections of CPG *ERM-FD-121* before (open circles) and after degassing (black squares). The dashed line represents the Porod's power law dependence ~ q^{-4}.

4 Discussion

As already mentioned, the orientation of the nitrogen molecule on the adsorbent's surface depends on its surface chemistry leading to an uncertainty in the resulting cross-sectional area and consequently errors in the surface area assessment. Our results confirm this, i.e., the surface areas determined with N_2 (77 K) on our silica adsorbent materials are up to ca. 25 % higher as compared to the BET surface areas obtained from Ar (87 K) adsorption. On the other hand, we can assume that the specific surface areas obtained from Ar (87 K) adsorption are reliable, which allows us to compare the surface areas obtained from SAXS and physical adsorption in a straightforward way. Indeed, the respective results compared in Table 1 and Figure 5 show excellent agreement between the two methods for all four silica model materials. Within this context, one has also to consider that the respective overall uncertainty for both techniques is between 3 and 5 %, which may also include small contributions from respective material inhomogeneities (as also reflected in the results obtained from different aliquots of the same material).

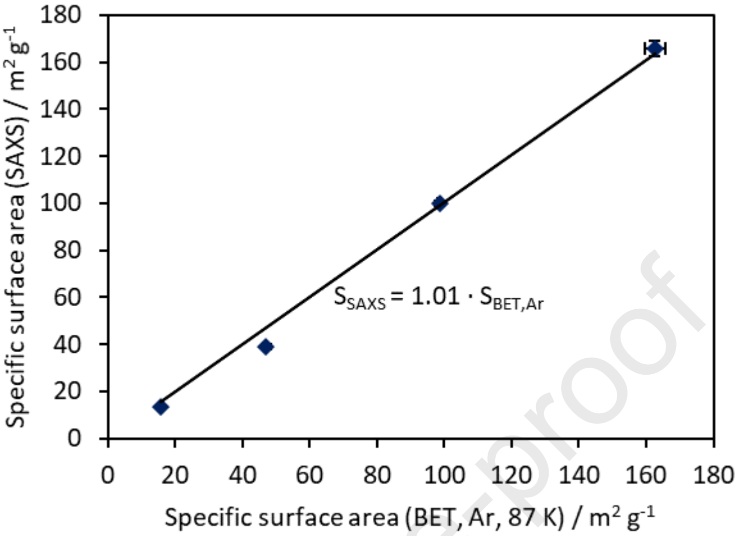

Figure 5: Correlation (linear fit) between specific surface areas determined from SAXS and argon (87 K) adsorption for the four silica model materials investigated

The excellent agreement between the obtained SAXS and BET (Ar, 87 K) surface areas demonstrates clearly the suitability of SAXS for reliable surface area assessment. Furthermore, our experiments show that (at least for the materials chosen in this work) a significant reduction of the outgassing time, or even omitting the degassing step altogether has no appreciable effect on the surface area determination by SAXS. Hence, compared to gas adsorption, with SAXS one can significantly reduce the overall experimental time for reliable surface area assessment because of far less strict requirements on sample preparation/degassing along with analysis times of a few minutes per sample only.

Furthermore, the large difference between the surface areas determined with SAXS compared with nitrogen (77 K) adsorption (Table 1) also confirms that nitrogen adsorption does not allow for a reliable surface area assessment of materials with polar surface sites (such as silicas), while argon 87 K adsorption is here the proper tool for physisorption characterization.

5 Conclusions

To our knowledge, our investigation can be considered the first systematic study where the surface areas obtained from SAXS were compared with true benchmark surface area data. In fact, the obtained results reveal excellent agreement of specific surface areas obtained from SAXS and Ar, 87 K adsorption for four selected silica model materials, while surface areas obtained from N_2 (77 k) adsorption overestimate the specific surface area up to ca. 25 %. In fact, we demonstrate that the determination of specific surface area can be brought with SAXS to a new level, where parameters such as size of the probing adsorptive and its orientation/ effective cross-sectional area (when adsorbed on the surface) are no longer affecting the value of the specific surface area determined. Furthermore, SAXS was shown to be significantly faster than gas adsorption analysis. This is because we could show that (i) degassing of materials prior to the SAXS analysis is not necessary (at least for non-microporous silica materials), and (ii) the analysis time per sample is a few minutes only. Hence, coupled with state-of-the-art multi-sample holders, which would allow for an automated processing of multiple samples, SAXS provides an accurate and extremely fast, high-throughput approach. This is very valuable for both, applications in quality control and nanoporous materials development.

In addition, particularly for materials where gas adsorption and the BET methodology cannot be applied in a straightforward way, e.g., where sorption causes a change in the state of the adsorbent (e.g., swelling/deformation), as present in various pharmaceutical materials and polymers, the application of SAXS should be advantageous; more work is here in progress. Further *in-depth* studies combining adsorption and SAXS analysis are necessary to extent the applicability of SAXS for surface area assessment of materials exhibiting significant amounts of microporosity. This would also provide support for advancing necessary novel adsorption based methodologies (beyond BET) for a reliable surface area assessment of microporous materials such as MOFs, zeolites or microporous carbons.

This fundamental study can be considered a major step in enabling SAXS for reliable surface area assessment, thus boosting SAXS for surface area determination in general , but in particular also for materials where the usage of gas adsorption is restricted or not possible at all.

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Highlights

- Benchmark BET surface areas based on Ar 87 K adsorption on model silicas
- Excellent agreement of SAXS and Ar 87 K BET surface areas
- SAXS surface area analysis significantly faster than gas adsorption
- SAXS as alternative approach to gas physisorption for reliable surface area assessment

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: