

# Size Distribution Determination of Nanoparticles and Nanosized Pores by Small-Angle X-Ray Scattering (SAXS) on a Multi-Purpose X-Ray Diffractometer

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## Abstract

This paper presents the small-angle X-ray scattering (SAXS) technique for the investigation of crystalline and amorphous materials on a length scale ranging from ca. 1 - 100 nm. We will focus on the characterization of nanopowder materials, nanocomposites and porous materials. Dry powders or dispersions of inorganic and organic nanoparticles can be characterized with respect to their particle size distribution, specific surface area and inner structure. In case of porous materials the specific inner surface area and pore size distribution may be determined. Compared to BET, TEM and light scattering techniques, the method is fast and no specific sample preparation is required. It has a very good precision, particularly so for very small particles and pores with a size below 10 nm. It will be demonstrated that such type of measurements are possible on a multi-purpose X-ray diffractometer platform with an option for automation in routine production control. Application examples for the characterization of photocatalytic nanoparticles, nanocomposites and porous nanopowders will be discussed.

## Introduction

Nanoscaled materials are becoming increasingly important in various applications such as coatings, paints, cosmetics, ceramics, polymers, catalysis and drug delivery. Even at relatively low concentrations such additives may be highly effective in delivering significant improvements in the desired field of application. The properties and performance characteristics of nanoparticles are to a large extent determined by their size distribution and specific surface area. Similarly, with porous materials containing nanosized pores, as used e.g. in delivery systems, separation processes or catalysis, the pore size distribution and specific surface area are key quality parameters. It is thus well recognized in the industries and research labs that produce, develop or apply such materials, that it is essential to control and quantify these aforementioned properties.

With most available experimental methods this task becomes increasingly challenging with decreasing sizes below 100 nm. As an example, laser diffraction is a well established and powerful sizing method for particles in the range of micrometers down to 100 nm. However, with particles smaller than 100 nm and the wavelength of laser light being significantly larger, this technique is becoming less suitable. For nanomaterials characterization it is thus logical to make use of methods that are based on electromagnetic radiation of a shorter wavelength. X-rays having a wavelength of the order of 1 Å are widely used in diffraction experiments for the analysis of crystalline materials with atomic resolution. Qualitative and quantitative analysis of crystalline phases can be done from the diffraction peak positions and intensities measured with XRD from powder materials. The width of the peaks can be correlated with the crystallite size of the materials.

When extending such wide-angle X-ray diffraction (XRD) measurements down to very small angles, one is probing the electron density distribution on increasingly larger length scales in the range of nanometers. The small-angle X-ray scattering (SAXS) technique (ref. [1-3]) is thus ideally suited for the structural characterization of nanoscaled materials, and among others, allows for nanoparticle and pore size analysis and specific surface area determination. This was already recognized in the 1930's and since then the method has continuously been further developed and applied. However, unlike XRD, SAXS has been used mainly by academic researchers and is still not well known in industry. With the ongoing advances in nanotechnology, it may be expected though, that this extremely versatile and powerful technique will find more applications in industrial developments and quality control.

In this paper we will present how SAXS measurements can be performed on a multi-purpose X-ray diffractometer platform that allows the complementary techniques of XRD and SAXS to be performed on a single instrument. Examples for the determination of nanoparticle and pore size distributions as well as of the specific surface area from nanopowder and nanocomposite materials will be given. The advantages of SAXS as compared to other available measurement techniques will also be discussed.

## Theory

In the following sections about the SAXS theory, only the most essential formulae that are needed for the determination of the size distribution from nanoparticles and from nano-sized pores are summarized. It is also briefly explained how the specific surface area of these materials can be obtained. More details can be found in ref. [1-3].

### Scattering from single particles

The scattering intensity  $I_p(q, R)$  from a single, radially symmetric particle of radius  $R$  is given by

$$I_p(q, R) = \left[ 4\pi \int_{r=0}^{r=R} \Delta\rho_e(r) \cdot \frac{\sin qr}{qr} r^2 dr \right]^2 \quad (1) ; \quad q = |\vec{q}| = 4\pi / \lambda \cdot \sin(\theta) \quad (2)$$

where  $\Delta\rho_e(r)$  denotes the radial electron density difference of the particle and its surrounding medium, and  $q$  the magnitude of the scattering vector  $\vec{q}$ . The latter is a function of the wavelength of radiation  $\lambda$  and of the scattering angle  $2\theta$ . For a spherical particle with a homogeneous inner electron density distribution (on a nanometer length scale), this integral results in

$$I_p(q, R) = \Delta\rho_e^2 V_p^2 \left( 3 \cdot \frac{\sin qR - qR \cos qR}{(qR)^3} \right)^2 = \Delta\rho_e^2 V_p^2 I_0(q, R) \quad (3)$$

where  $V_p$  is the particle volume and  $I_0(q, R)$  the scattering intensity of the sphere, with its forward scattering normalized to unity.  $I_0$  is also often referred to as particle form factor  $P(q)$ . It is an oscillating function that decays quickly as a function of the scattering vector. SAXS data are thus commonly displayed on a logarithmic intensity scale. The oscillation frequency correlates with the size of the particle as demonstrated in the model calculations shown in fig. 1. A well-known analogous case from optics are the interference fringes that are observed on a screen when laser light passes a pinhole.

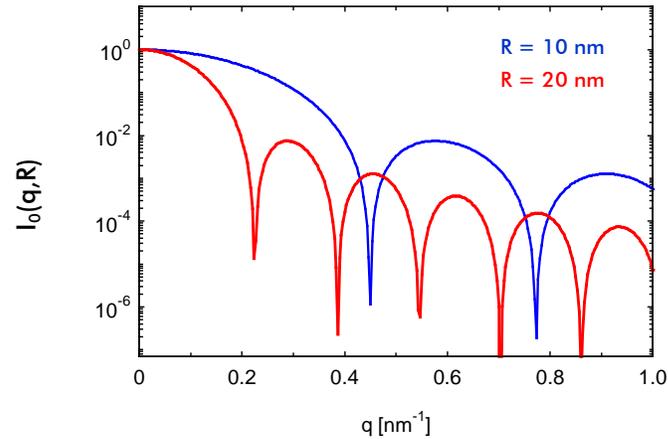


Fig. 1: Simulated SAXS data for different size spherical particles.

### Scattering from a polydisperse ensemble of particles

The scattered intensity  $I(q, R)$  for a polydisperse system of non-interacting particles with the same shape and electron density, but different size parameter  $R$  can be expressed by the following equation:

$$I(q, R) \propto \int_{R=0}^{R=R_{\max}} D_n(R) \cdot R^6 \cdot I_0(q, R) dR \propto \int_{R=0}^{R=R_{\max}} D_v(R) \cdot R^3 \cdot I_0(q, R) dR \quad (4) \quad \text{where } D_v(R) \propto D_n(R) R^3 \quad (5)$$

Here  $D_n(R)$  is the number distribution of the particle size, whereas  $D_v(R)$  denotes the distribution of the particle size by volume (also referred to as volume-weighted size distribution or volume distribution). In this approximation, the scattering intensities of all fractions of particles simply add up. It may thus be readily understood that with increasing width of the size distribution the pronounced oscillations that are observed in the scattering curve of a single particle (see fig. 1) become more and more smeared out. This is a result of the summation of different oscillation frequencies that are related to different size fractions that are present in the sample. This effect can be seen in the results of a model calculation displayed in fig. 2.

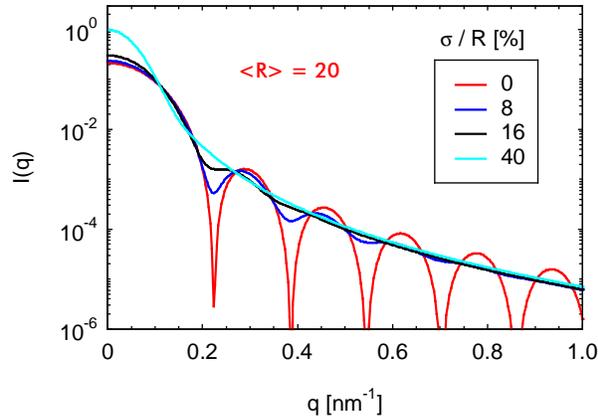


Fig. 2: Simulated SAXS data from polydisperse ensembles of spherical particles. The size distributions were assumed to be Gaussian with a standard deviation  $\sigma$ , and the average particle radius  $\langle R \rangle$  was set to 20 nm. Calculations were done for different size polydispersities, given by the ratio of  $\sigma$  and  $\langle R \rangle$ .

### Introduction of simplified structural models

In a first approximation, the SAXS intensities from homogeneous nanoparticles (present in air as a nanopowder, dispersed in a liquid, or incorporated in a solid matrix material) and from nanosized pores can all be described by eqns. 3 and 4. Here it is assumed that the particles and pores all have the same (spherical) shape and homogenous structure, and that they are randomly distributed (see fig. 3). The shape of the scattering curve contains the information about the size distribution, whereas the electron density contrast  $\Delta\rho_e$  between the particles (or pores) and the surrounding medium solely acts as a scaling factor for the intensity. Within this model, sizing of nanoparticles and pores with SAXS does not require knowledge about the density or any other specific physical property of the material under consideration.

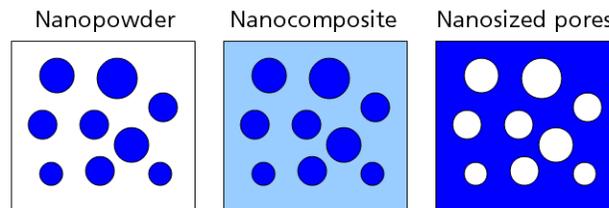


Fig. 3: Simplified structural models of nanopowders, nanocomposites and porous materials.

### Specific surface area of nanoparticles

The specific surface area  $S/m$  [ $\text{m}^2/\text{g}$ ] of spherical nanoparticle samples was determined either

i.) from the volume distribution  $D_V(R)$  and mass density  $\rho$  through

$$\frac{S}{m} = \frac{1}{\rho} \int_{R=0}^{R^{\max}} \frac{3}{R} D_V(R) dR \quad (6) \quad \text{where} \quad \int_{R=0}^{R^{\max}} D_V(R) dR = 1 \quad (7)$$

or ii.) by  $\frac{S}{m} = \frac{4}{\rho} \frac{\tilde{k}}{\tilde{Q}}$  (8) where  $\tilde{k} = \lim_{q \rightarrow \infty} (\tilde{I} \cdot q^3)$  (9) is the slit-smear Porod constant that is

determined from the asymptotic behavior of the scattering curve at higher angles and where  $\tilde{Q} = \int_0^{\infty} \tilde{I}(q) \cdot q dq$  (10) is the slit-smear scattering invariant which in a plot of  $(\tilde{I}(q) \cdot q)$  vs.  $q$  is given by the area under the curve.

### Specific surface area of porous materials

In case of porous materials with known porosity  $\phi_p$  the specific surface area is determined from

$$\frac{S}{m} = \frac{4}{\rho} \cdot \frac{\tilde{k}}{\tilde{Q}} \cdot \phi_p (1 - \phi_p) \quad (11)$$

The approaches that make use of  $\tilde{k}$  and  $\tilde{Q}$  have the advantage that no assumptions are made about the shape of the particles or pores. For both methods it is sufficient to have scattering intensities available on a relative intensity scale. Absolute scattering intensities, that are difficult to obtain, in particular from powder samples, are not required.

## Experimental Details

### Experimental setup

Setups for SAXS measurements require a narrow, highly collimated and intense X-ray beam, the effective suppression of any parasitic scattering, and a detector with a high linearity range. The objective is to measure the scattered intensities in the immediate vicinity of the direct beam, typically down to 0.1 deg and below. The smallest accessible scattering angle determines the upper limit of the dimension (e.g. particle diameter) that can be studied. A description of the experimental configuration that was used for the experiments follows.

A multi-purpose X-ray diffractometer platform (X'Pert PRO, PANalytical) that can be configured for a variety of applications by choosing the optimal combination of optical modules, sample stages and detectors was used. Typical applications on this platform range from the identification of unknown crystalline phases and quantification of mixtures, to the determination of microstructural properties such as residual stress and preferred orientation of crystallites in bulk materials as well as thin films. The instrument also allows for a quick change between a reflection and a transmission geometry. As the system makes use of pre-aligned fast interchangeable X-ray (PreFIX) modules there is no need for realignment when changing between different setups.

SAXS measurements on this diffractometer platform were done in a transmission geometry (see fig. 4) using Cu K $\alpha$  radiation (wavelength  $\lambda = 0.154$  nm) from a sealed long fine focus X-ray tube powered by a high voltage X-ray generator (PW3830/00, PANalytical) at 45 kV and 40 mA. Working with a line focus rather than with a point focus has the advantage of yielding significantly higher intensities. On the other hand experimental data acquired with a line focus are distorted ("smeared") due to the finite beam dimensions, which must be taken into account in the data analysis. A well-collimated, intense, monochromatic X-ray beam was created by using multilayer X-ray optics (such as an elliptical or a parabolic mirror) The incident beam size at the sample position was set to ca. 20 mm x 50  $\mu$ m by using a combination of low-angle slits and a mask. The samples were placed on a reflection-transmission sample stage in the center of the diffractometer. On the diffracted beam side a narrow anti-scatter slit was used to reduce parasitic scattering effects and a solid-state linear pixel detector (PIXcel, PANalytical) to sequentially measure the scattered intensities as a function of the scattering angle  $2\theta$ . The latter is defined as the angle between the incident and the scattered beam.

By adding an automatic sample changer in combination with an automatic beam attenuator to this configuration, a whole batch of samples could be measured automatically without any intervention. These automation features are particularly interesting for unattended routine measurements in production control, for trend analysis, and whenever a larger number of similar samples are to be characterized with a high throughput.

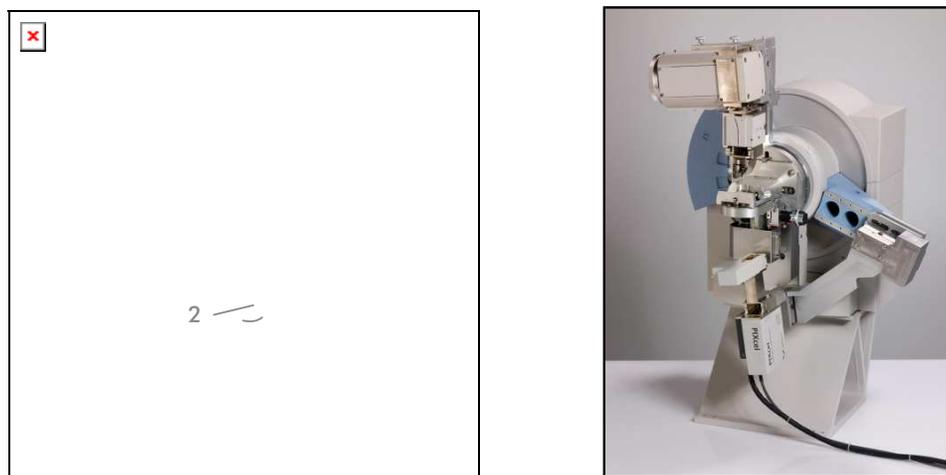


Fig. 4: Schematics and actual experimental SAXS setup: 1: X-ray tube, 2: beam defining slits and focusing mirror, 3: sample stage, 4: anti-scatter slit and detector.

### Sample preparation

As shown in fig. 5, the samples were placed in circular transmission holders between thin X-ray transparent polymer foils (mylar, 6  $\mu\text{m}$ ). Special care was taken to choose an appropriate sample thickness; increasing the amount of sample results in a larger scattering volume, but also leads to higher absorption. The best compromise between these opposing effects is achieved when the absorption factor of the samples is between 2.5 and 3 (ref. [2]). Note that too thick samples of strongly scattering materials show multiple scattering effects that may lead to errors in the analysis results if these effects are not properly taken into account. As SAXS and XRD are non-destructive and non-intrusive methods the samples can be recovered from the sample holders after a measurement.



Fig. 5: Typical sample preparations between thin mylar foils: left – empty sample holder for a background measurement, middle – nanopowder sample, right – polymer nanocomposite.

### Measurement procedures

SAXS measurements were run using the X'Pert Data Collector software (PANalytical). The detector was moved in  $2\theta$ -scans in an angular range of typically  $-0.12$  to  $5$  deg with a step width of  $0.01$  deg. The scattering curve of the background was acquired by measuring the scattering intensity with an empty sample holder inserted. The profile of the direct beam (transmitted through the sample) was included in each measurement so as to be able to determine the absorption factor of the sample from the ratio of the transmitted intensities in the absence and presence of the sample. A beam attenuator was inserted in the  $2\theta$  range up to  $0.05$  deg to ensure a linear response of the detector when scanning through the direct beam. Typical measurement times were 2-20 minutes per sample. XRD measurements in the range of  $5$ - $90$  deg  $2\theta$  were done in the same transmission geometry and with the same sample preparations, but using wider slit settings.

### Data analysis

SAXS data analysis was done using a commercial software package (EasySAXS, PANalytical) as well as some FORTRAN codes. EasySAXS was developed in cooperation with the European Molecular Biology Laboratory (EMBL, Germany) and is partly based on the ATSAS software suite (ref. [4]). It performs primary data handling steps, such as absorption correction, background-subtraction, and conversion of the scattering angle  $2\theta$  to the scattering vector  $q$ . For the determination of nanoparticle or pore size distribution EasySAXS uses an indirect integral transform technique that relates experimentally measured SAXS intensity data to the volume distribution function  $Dv(R)$  in real space using a regularization procedure. Details on this technique can be found in the original literature of Svergun et al. (ref. [3]). In this approach the optimum regularization parameter leading to the highest stability of the solution is chosen automatically which greatly improves user-friendliness. Another advantage of this indirect Fourier transform (FT) technique is that it is not prone to problems with termination effects of experimental data, as encountered when applying inverse FT transformation procedures. Furthermore, "smearing" effects (ref. [1-3]) in the experimental data, due to the finite dimensions and spread of the incident X-ray beam, are taken into account in this analysis.

Whereas the nanoparticles or pores are assumed to be (quasi-)spherical, no further assumptions about the shape and modality of the size distribution curve are made. By using this general approach, multi-modal size distributions can also be revealed. This is a significant advantage of the indirect transformation technique over direct fitting procedures. In the latter approach the size distribution  $D_n(R)$  is assumed to be of a certain type that can be described by a few parameters (e.g. a Gaussian characterized by an average radius  $R$  and a standard deviation  $\sigma$ ) which are then determined in a least-squares fitting method that fits this model to the experimental data using eqns. 3 and 4.

## Application Examples

### 1. Combined SAXS and XRD for the characterization of nanopowders

A commercial sample of a titania nanopowder with photocatalytic properties was measured with SAXS and XRD. The results are displayed in fig. 6. From XRD the major crystalline phase was found to be anatase, which is also known to be the preferred phase when photocatalytic properties are targeted. Some small peaks (marked by arrows) indicate the presence of rutile phase impurities. The very broad diffraction lines confirm that the size of the crystallites is of the order of a few nanometers only. However, the size of nanoparticles may not necessarily equal the crystallite size; a nanoparticle may be made up of several small crystallites. The strong increase of the scattering intensity at smallest angles in the SAXS region is due to the scattering from the nanoparticles, rather than to a high background, which has already been subtracted in the displayed data.

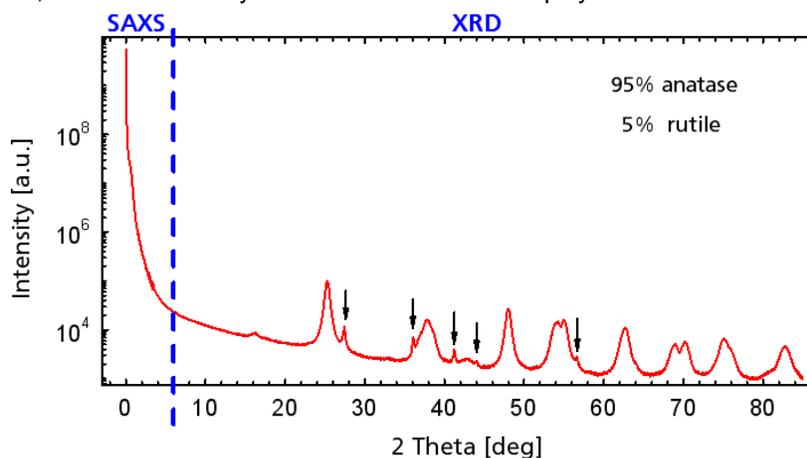


Fig. 6: Combined SAXS and XRD measurements on a nano-titania powder sample.

Fig. 7 shows a magnification of the SAXS data measured from this nanopowder (before and after background-correction) as well as the background scattering curve. Due to the effective collimation used in the experimental setup, the background quickly decreases at lowest angles and then remains on a very low level. The comparison of the measurement data of the sample before and after background correction shows that in this example the background is only significant at scattering angles  $2\theta$  above 3.5 deg.

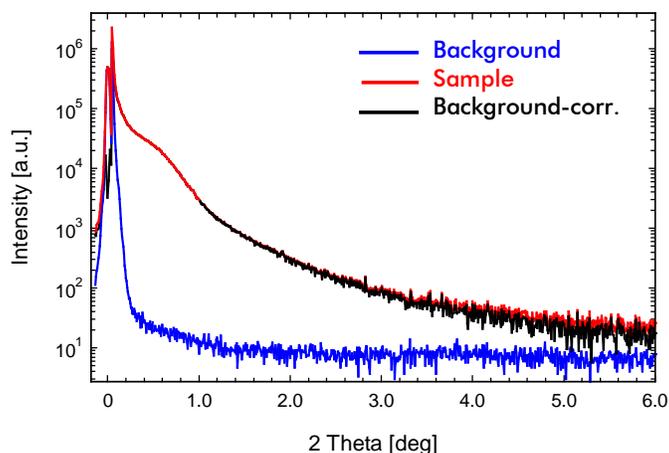


Fig. 7: Experimental SAXS data from a titania nanopowder, before and after background correction, together with the background measurement. In this comparison, the data are already corrected for absorption by the sample.

The scattering curve of the sample as measured around the direct beam is displayed in fig. 8. For the measurement of the direct beam profile an attenuator was inserted. At 0.05 deg  $2\theta$ , where the intensity of the direct beam has reached a relatively low level, the attenuator was removed and the actual scattering curve from the powder sample could be measured. The attenuation factor of the sample is determined by the factor that is needed to scale the direct beam profile measured in the presence of the sample to the one measured in a background scan with the empty sample holder inserted.

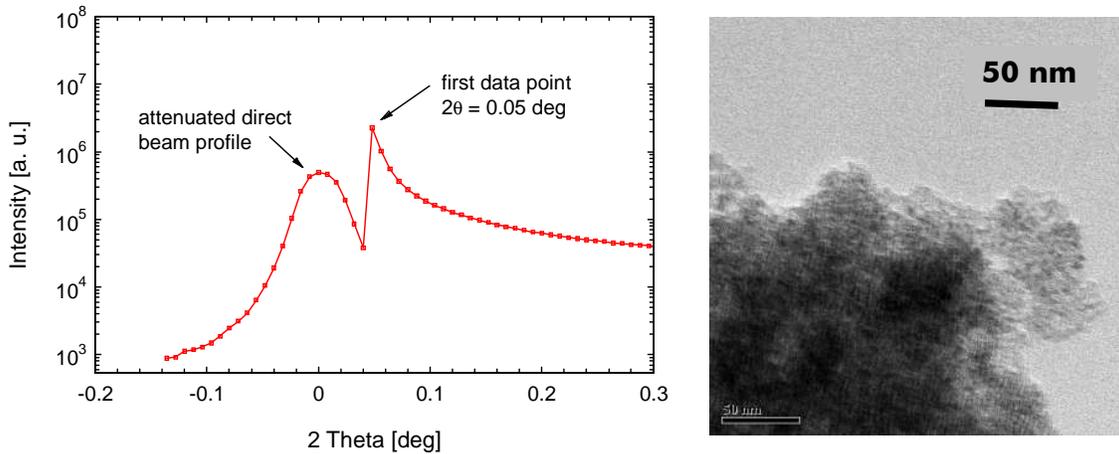


Fig. 8: Left: SAXS data measured from the titania nanopowder (before background correction) displayed around the direct beam. Right: Electron micrograph of the nanopowder.

The evaluation results of the SAXS data are shown in fig. 9. The upper graph displays the background-corrected data. The characteristic hump that is observed in the steeply decaying scattering curve indicates the presence of nanoparticles with a rather well-defined particle size. A strong upturn of the scattering intensity occurs towards lowest angles, where the largest dimensions are being probed. This may be attributed to the presence of micron-sized, loose agglomerates of primary particles, which were also evidenced with TEM (fig. 8). For the determination of the size distribution of the primary particles, this region was thus excluded from further data analysis. The vertical dashed lines indicate the boundaries of the  $q$ -range within which data evaluation was done, whereas the red line represents the fit curve that approximates the experimental data very well.

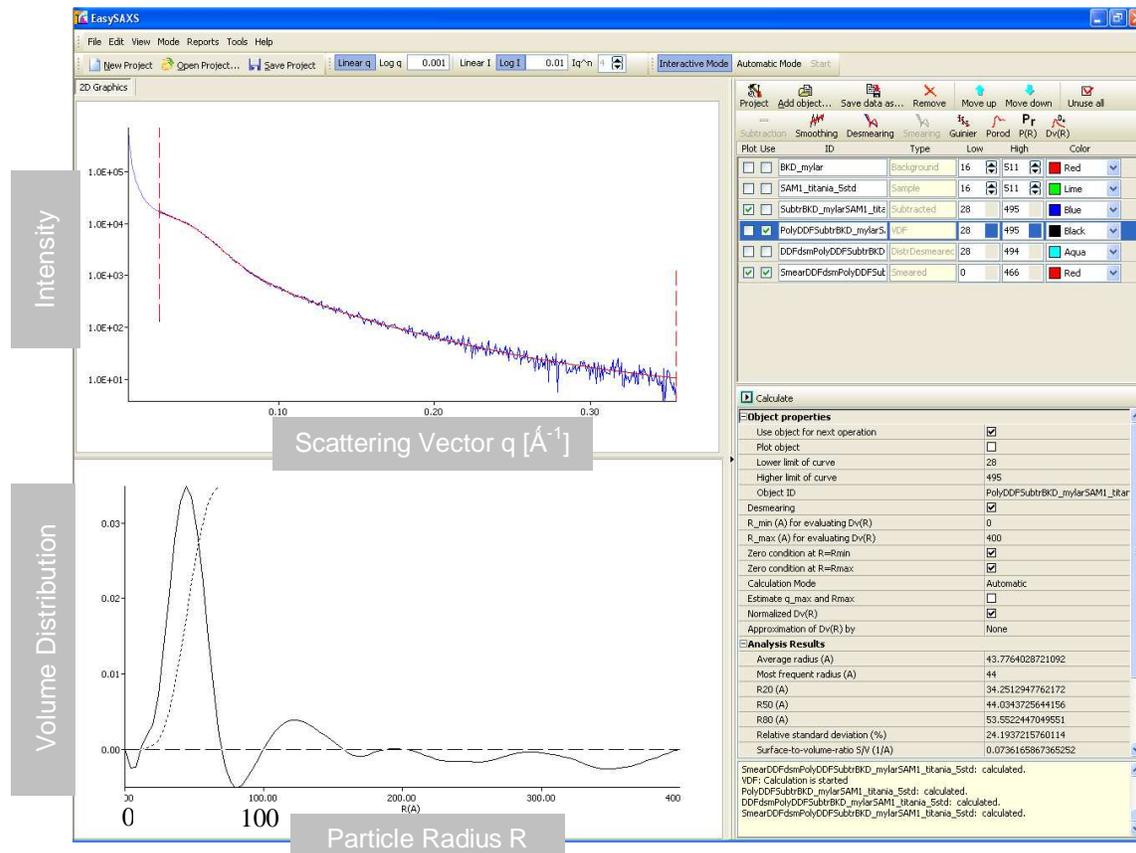


Fig. 9: Particle size distribution analysis of the titania nanopowder. Top: background-corrected SAXS data (blue line) together with the fit curve (red line). The vertical dashed lines indicate the angular region in which data analysis was performed. Bottom: volume-weighted size distribution  $D_V(R)$  of the primary particles (solid line) and cumulative undersize distribution (dotted line).

The volume-weighted size distribution corresponding to the fit curve is displayed in the lower graph of fig. 9. It indicates that the sample contains particles having a radius predominantly in the range of 15-75 Å, with a volume-average of 44 Å and a relative standard deviation (size polydispersity) of 24%. The surface-to-volume ratio  $S/V$  was determined from  $D_V(R)$  to be  $0.0736 \text{ Å}^{-1}$ . By taking into account the mass density of anatase ( $3.9 \text{ g/cm}^3$ ), the specific surface area of the particles is then calculated from this value to  $189 \text{ m}^2/\text{g}$  according to eqn. 6. These results are in good agreement with those obtained from the same samples using TEM and the gas adsorption (BET) method. Note that the minor oscillations that are observed in the solution for  $D_V(R)$  are some non-avoidable artifacts originating from the indirect Fourier Transformation (FT) method. This is a known, minor trade-off with this method. On the other hand, its full benefits are becoming evident when more complex size distributions are present, as it is the case in the example described in the next paragraph.

### Analysis of a bimodal size distribution

To demonstrate the excellent performance of the SAXS method in revealing also multimodal size distributions, a mixture of two titania nanopowder samples of different particle size was prepared using equal amounts of each sample. The background-corrected SAXS data that were measured from this sample (see fig. 10) show weak modulations of two frequencies in the decaying curve, reflecting the superposition of the scattering signals from the two size fractions in the sample. In the data analysis the bimodal distribution could be clearly revealed (see fig. 10) and the average particle sizes of the two fractions could thus be determined to 23 Å and 65 Å, respectively. Furthermore, the ratio of the integrated areas of the two fractions as determined from the deconvoluted distribution curve is in quantitative agreement with the mixing ratio used for sample preparation.

This example shows the strength and benefit of the indirect FT method that does not make any assumptions about the modality and/or about the shape of the distribution curve. To our best knowledge, no other experimental method is available that could analyze multimodal size distributions of such small particles (diameter of 15 nm and below) with the same accuracy as SAXS.

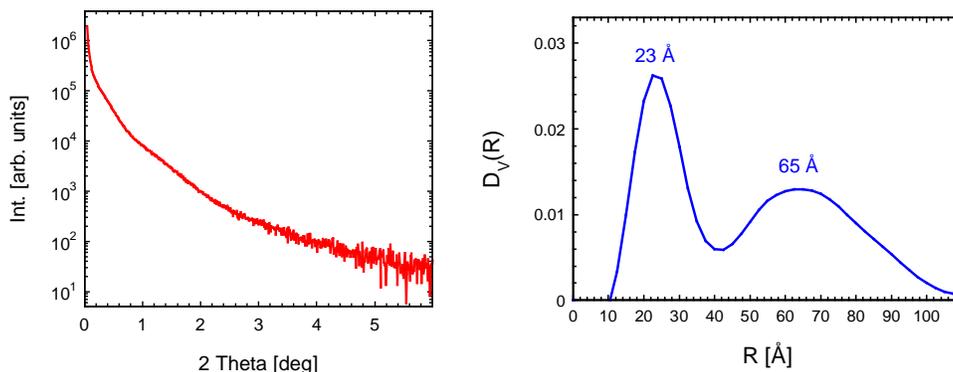


Fig. 10: Left - SAXS data from a 1:1 mixture of two titania nanopowder samples containing particles of different sizes. Right - Bimodal size distribution by volume as determined from the SAXS data.

## 2. Investigations on polymer nanocomposite materials

Polymers modified with nanomaterials are commonly referred to as polymer nanocomposites. This class of materials shows unique advantages over non-modified polymers as well as over polymer composites that contain conventional filler materials. Examples are an increased tensile strength, superior thermal resistance, and improved barrier properties. Due to the dramatically increased surface area of nanofillers, these effects may be achieved at a lower filler loading which in some cases also results in better cost-effectiveness. In this application it is essential to control the particle size of the filler material and to ensure that the particles are homogeneously distributed in the polymer matrix. The following example shows the application of SAXS for the structural analysis of a polymethylmethacrylate (PMMA) based nanocomposite is given.

PMMA was modified with 3 wt.% of silica nanoparticles in a melt compounding process (ref. [5]). To achieve the desired improved thermal and mechanical properties at a minimal filler level, it is essential to ensure a good dispersion of the nanoparticles in the polymer matrix. The silica particles were thus surface-functionalized with PMMA chains aiming improving their compatibility (fig. 11, left). The TEM of the nanocomposite shows that the nanoparticles are indeed well dispersed and possess a narrow size distribution (ref. [5]). SAXS data were collected from the same polymer composite material with a sample thickness of 2 mm. Due to the high penetration depth of X-rays in organic materials, the

measurements could be done in transmission with only moderate attenuation. The data obtained from the composite were corrected for the scattering contribution of the non-modified polymer matrix that was measured separately.

Even at this relatively low particle concentration, a distinct scattering signal from the particles could thus be obtained. The background-corrected data show distinct oscillations as well as a characteristic, steady curvature towards smallest angles (Guinier's Law) which clearly confirms the presence of well-defined, monodispersed particles. Furthermore, the quantitative analysis of the particle size distribution from SAXS (average particle radius 13 nm, size polydispersity 11%) yielded results that are in good agreement with those from TEM. Note that the PMMA shell around the silica nanoparticles is invisible to X-rays, due to the vanishing contrast of its electron density with respect to the polymer matrix.

In a control experiment (fig. 11, right), using the same nanoparticles but without surface-functionalization, TEM indicated that the particles have a high tendency to form aggregates (ref. [5]). This was also readily evidenced from the measured SAXS pattern that shows distinct differences as compared to the case discussed above: a pronounced correlation peak and a strong upturn of the intensity towards smallest angles. The correlation peak may be attributed to interferences of intensities scattered from spatially correlated particles, whereas the behavior towards smallest angles originates from the scattering of the envelopes of larger aggregate structures made up of primary particles. In this way, already a qualitative inspection of these two features in the SAXS data allows the extent of aggregation to be quickly judged.

Compared to TEM, the SAXS method has the advantages of easy and quick sample preparation and relatively short measurement times. It is specially noteworthy that SAXS is probing a macroscopic volume of the sample, with an illuminated sample area of approx. 20mm x 50  $\mu\text{m}$  and a sample thickness of 2 mm, thus gaining structural information that is representative for the whole sample. In contrast, with TEM only a very small area of the sample is probed, which may not be representative at all. It is noteworthy that SAXS (low-angle diffraction) is also a highly useful tool for the structural analysis in polymer-clay nanocomposites. In particular it allows to determine the degree of intercalation of polymer chains between the clay layers or give evidence to an exfoliated structure.

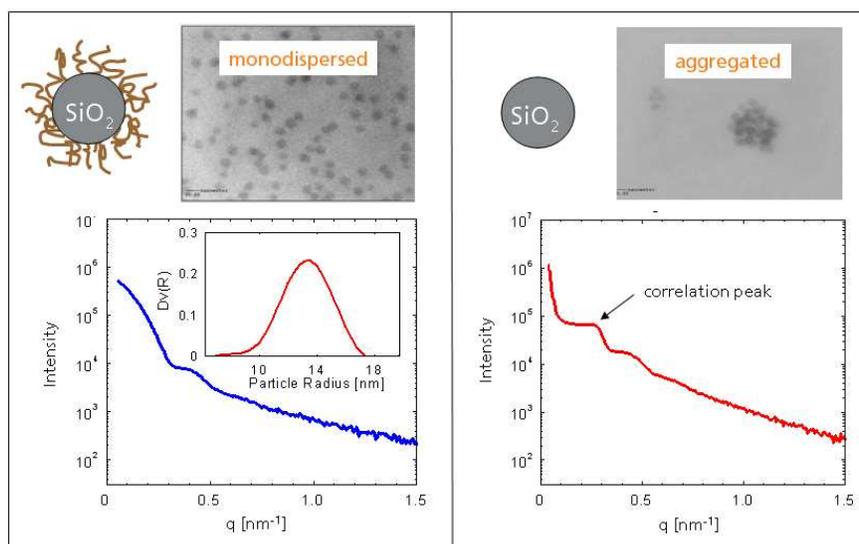


Fig. 11: Left – TEM of PMMA-silica nanocomposite and schematic structure of the surface-modified nanoparticle filler used. Shown below are the background-corrected SAXS data and the deduced size distribution of the nanoparticles. Right – Comparison with results that were obtained when the pristine nanoparticles without surface-modification were used. Samples and electron micrographs courtesy C. Beckers, Inst. Henri Tudor / Luxembourg (ref. [5]).

### 3. Investigations on porous materials

Two mesoporous alumina standard materials with a disordered pore structure were purchased from the Bundesanstalt fuer Materialforschung (BAM, Germany). The SAXS data measured from these samples (see fig. 12) show similar features as reported in fig. 9 for the titania nanopowder. Here the upturn of the intensity at lowest angles results from the scattering of the micron-sized alumina grains, whereas the observed hump in the decaying curve is attributed to the scattering from the nano-sized pores. The results from pore size distribution and specific surface area analysis based on these SAXS curves are in good agreement with those reported from the supplier of the samples based on the mercury intrusion and BET methods. Note that in contrast to the BET method SAXS also probes for closed pores, which may explain possible differences in the results obtained from these two

methods. SAXS (low-angle diffraction) is also an indispensable tool for the geometrical characterization of highly ordered pore structures as present e.g. in the mesoporous silica samples of the type MCM-41 or SBA-15.

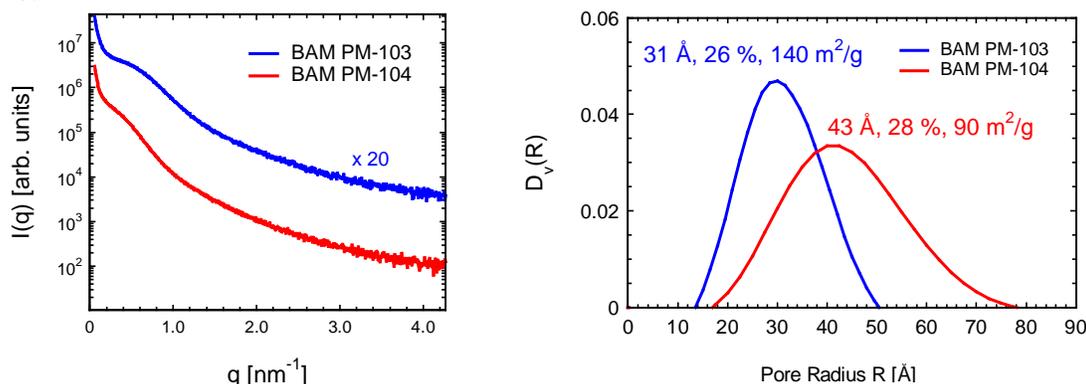


Fig. 12: SAXS data from porous alumina samples (left) and corresponding analysis results (right) for the pore size distribution and specific surface area.

## Summary and conclusions

SAXS is one of the most versatile and powerful methods in the characterization of a big variety of nanostructured materials in a size range of 1- 100 nm. Compared to other techniques commonly used for nanoscale analysis, SAXS has a number of unique benefits and advantages:

- Particle and pore size analysis with SAXS does not rely on the knowledge of any specific physical properties of the material under investigation, such as the refractive index (which however is required for static and dynamic light scattering) or the mass density (as required in sedimentation measurements, such as disc centrifugation). Furthermore, calibration of the instrument against a standard material is not needed.
- SAXS measurements do not require temperature control as e.g. dynamic light scattering or time-consuming outgassing procedures as in gas absorption measurements. Compared to imaging techniques (such as TEM or AFM), sample preparation is very easy and quick; samples can often be analyzed in dry powder form without the need of dispersion in a liquid. This is possible as long as the powders are available in free-flowing form and only forming some soft agglomerates, rather than hard aggregates. Different from e.g. mercury intrusion porosimetry, SAXS is a non-destructive and non-intrusive method and valuable samples may thus be recovered after the measurement.
- When working with the line focus of an X-ray tube, typical beam dimensions at the sample position are 20 mm x 50  $\mu$ m. Thus SAXS delivers representative, ensemble-averaged size distribution data from a very large number of particles. Electron or atomic force microscopies, on the other hand, yield highly localized information about individual particles and only a very small portion of the sample, which may not be representative at all, is probed.
- Due to the high penetration depth of X-rays, measurements can be done in a transmission geometry with a sample thickness ranging from a few microns up to 2-3 mm, depending on the absorption of the material under investigation. As an example, this allows to characterize nanoparticles that are embedded in a polymer matrix without the need of preparing ultra-thin sections.
- Multimodal distributions of nanoparticles where the various fractions differ only slightly in size, can be analyzed with better accuracy than with light scattering techniques.
- Very small particles, with a size of just a few nanometers, often require very long measurement times with sedimentation methods, whereas SAXS data on such powder samples are often acquired within a few minutes.
- Though not demonstrated within this paper, SAXS also allows to study the inner structure (e.g. core-shell) of nanoparticles. Furthermore it may deliver information about the particle shape.

With the increasing availability of easy-to-use SAXS analysis software and hardware configuration options, in particular also on multipurpose X-ray diffractometers, it is to be expected that SAXS, just like XRD, will become an attractive analytical tool not only in academic research but also for development and quality control in industry.

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