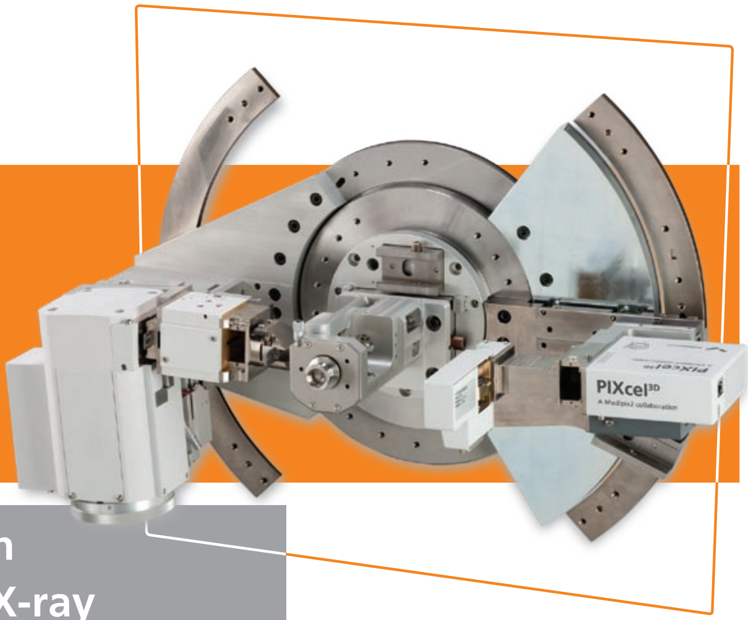
XRD APPLICATION NOTE

Small-angle X-ray scattering (SAXS)



Nanoparticle size distribution analysis on a multi-purpose X-ray diffractometer platform

Summary
A multi-purpose X-ray diffractometer platform was configured for small-angle X-ray scattering (SAXS) measurements. This technique was applied to nanoparticle and pore size distribution determination in nanopowders, colloidal dispersions, nanocomposites and porous materials in a range of 1-100 nm. SAXS is extremely versatile and yields truly ensemble-averaged results from a large sample volume, does not require knowledge about the refractive index or any other physical properties, and it is applicable to crystalline and amorphous materials alike. Furthermore sample preparation is minimal. Advanced data analysis software allows to reveal complex multimodal size distributions with unrivaled resolution. Data acquisition and analysis can be automated for routine production control. The instrument platform used can be reconfigured within minutes for a multitude of complementary X-ray analytical techniques, such as powder diffraction, thin film analysis, and computed tomography.

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, specific surface area, and degree of dispersion. 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 essential to control and quantify these aforementioned properties.

With most available experimental methods this task becomes increasingly challenging with decreasing sizes below 100 nm. 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. Powder diffraction allows for qualitative and quantitative analysis of crystalline phases, as well as for the determination of crystallite size. When extending such wide-angle X-ray diffraction (XRD, WAXS) 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 [1-2] 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. It is important to note that crystallite size and particle size are usually not the same. XRD and SAXS thus yield complementary structural information.

In this paper we present how SAXS measurements can be performed on a multi-purpose X-ray diffractometer platform. Application examples for nanopowders, colloids, nanocomposites and porous materials will be given. The advantages of SAXS as compared to other available measurement techniques will also be discussed.

Experimental details

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° and below. The smallest accessible scattering angle determines the upper limit of the structural feature size (e.g. particle diameter) that can be studied.

A multi-purpose X-ray diffractometer platform (Empyrean, PANalytical), which 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 residual stress and preferred orientation of crystallites in bulk materials as well as in thin films. It may also be configured for computed X-ray tomography. The system makes use of pre-aligned fast interchangeable X-ray (PreFIX) modules. Thus there is no need for realignment when changing between different setups.

Using this platform, SAXS measurements were done in a transmission geometry (see Fig. 1) using Cu Kα radiation (wavelength $\lambda = 0.154$ nm) from a long fine focus X-ray tube powered by a high voltage X-ray generator at 45 kV and 40 mA. A well-collimated, intense, monochromatic X-ray beam was obtained by using an X-ray mirror. The size of the incident beam at the sample position was set to approx. 20 mm x 50 µm by using a combination of low-angle slits and a beam mask.

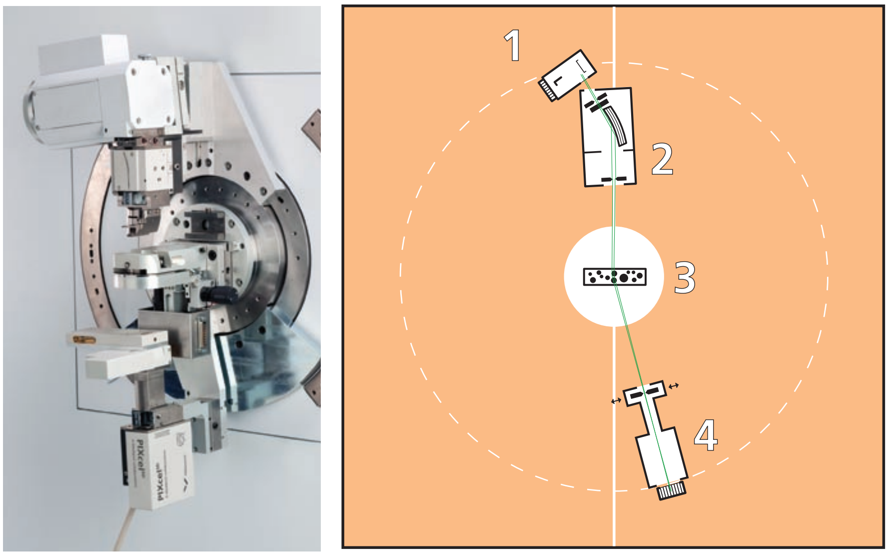


*Figure 1: Schematics and photograph of experimental SAXS setup:
1: X-ray tube, 2: beam defining slits and X-ray mirror, 3: sample stage, 4: anti-scatter slit and detector.*

The samples were placed in the center of the diffractometer; a reflection-transmission stage was used for solids, and a capillary holder for liquid samples. On the diffracted beam side a narrow anti-scatter slit was used to reduce parasitic scattering effects and a solid-state pixel detector (PIXcel^{3D}, PANalytical) to sequentially measure the scattered intensities as a function of the scattering angle 2θ. The latter is defined as the angle between the incident and the scattered beam.

Solid samples were placed in circular transmission holders between thin X-ray transparent polymer foils (see Fig. 2). Liquid samples were confined in quartz capillaries with a diameter of 1 mm. As SAXS is a non-destructive and non-intrusive method, the samples can be recovered from the sample holders after a measurement.

SAXS data were acquired by measuring the scattered intensities as a function of 2θ - typically up to 5 deg, with a step size of 0.01 deg. The background signal was measured using an empty sample holder or the dispersion medium (in case of nanoparticle dispersions). The profile of the direct beam (transmitted through the sample) was included in each measurement for the determination of the absorption factor of a given sample. The smallest accessible scattering angle was around 0.07 deg. Typical measurement times were 2-20 minutes for solid samples, and 30 minutes up to several hours for dilute liquid samples.

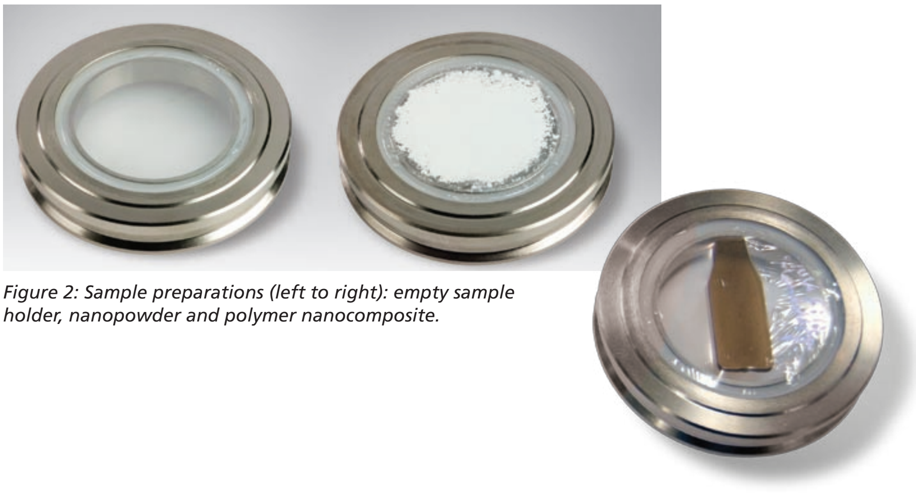


Figure 2: Sample preparations (left to right): empty sample holder, nanopowder and polymer nanocomposite.

Data analysis

SAXS data analysis was done using a commercial software package (EasySAXS, PANalytical) that was developed in cooperation with the European Molecular Biology Laboratory (EMBL, Germany). It is partly based on the ATSAS software suite [3].

The software performs primary data handling steps, such as absorption correction, background-subtraction, and conversion of the scattering angle 2θ to the scattering vector q. Determination of nanoparticle or pore size distribution was done by an indirect integral transform technique that relates experimental SAXS data to the volume distribution function Dv(R) using a regularization procedure [2-3].

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, rather complex, multi-modal size distributions can also be revealed. This is a significant advantage of the indirect transformation technique over direct model fitting procedures.

Experimental results

Nanopowder

A commercial sample of a titania nanopowder with photocatalytic properties was investigated. A quick XRD scan revealed the presence of 95% of anatase and 5% of rutile.

Due to the effective collimation used in the experimental SAXS setup, the background quickly decreases at lowest angles and then remains on a very low level. The characteristic hump that is observed in the steeply decaying, background-corrected scattering curve indicates the presence of nanoparticles with a rather well-defined particle size (Fig. 3). 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. For the determination of the size distribution of the primary particles, this region was thus excluded from further data analysis.

The result from size distribution analysis (Fig. 3) indicates that the sample contains particles having a radius predominantly in the range of 15-75 Å, with a volume average of 48 Å and a relative standard deviation (size polydispersity) of 24%. The specific surface area of the particles was determined to 189 m^2/g. These results are in good agreement with those obtained from the same samples using TEM (Transmission Electron Microscopy) and the gas adsorption (BET) method.

Note that these SAXS results were obtained within 5 minutes only. Due to the non-avoidable agglomeration effects in nanopowders, the dynamic light scattering method does not allow to determine the size of the primary particles from such a sample. Instead only a signal from the large agglomerates is observable.

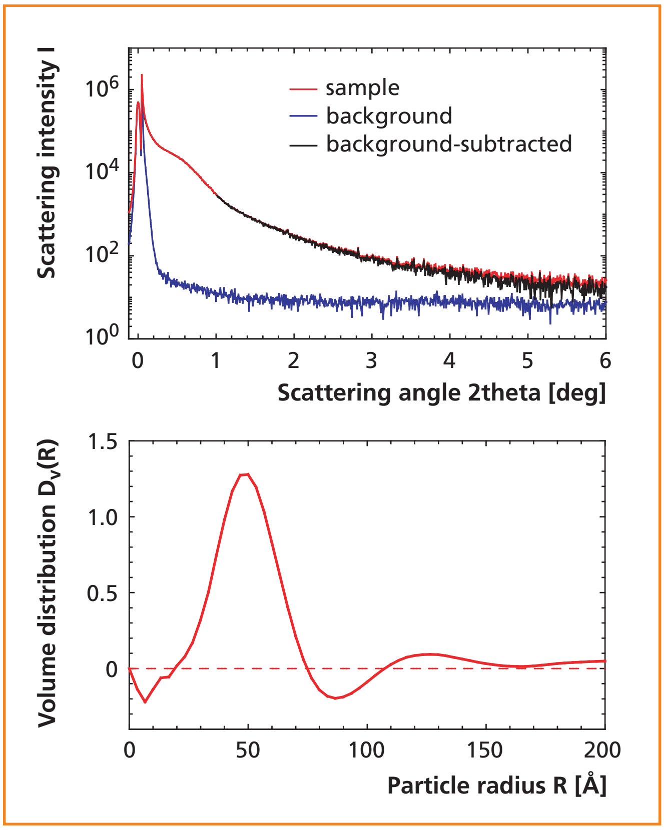


Figure 3: SAXS data from a titania nanopowder (top) and the determined volume distribution (bottom)

Experimental results

Colloidal dispersion

An aqueous dispersion of silica at a concentration of 0.8 Vol.% was measured and analyzed with SAXS. This was a control experiment in which three samples of colloidal silica were mixed in an equal ratio. The goal was to demonstrate the superior capability of SAXS to analyze complex, multimodal size distributions.

In spite of the very low concentration, a pronounced excess signal from the nanoparticles over the background could be observed down to as low as 0.07 deg 2θ (Fig. 4). Data analysis was performed without any presumption with respect to the shape of the size distribution curve. The result from SAXS indeed clearly revealed a trimodal distribution in which the three fractions only have a small difference in size (namely 5, 8 and 14 nm). Furthermore, the 1:1:1 mixing ratio that was used for sample preparation is correctly found back in a deconvolution of the size distribution curve. The SAXS data also show clear evidence for monodispersed, non-aggregated particles.

For analyzing multimodal size distributions of particles of such small size as in this example, SAXS is the most accurate experimental method. With dynamic light scattering only a monomodal, broad distribution would be observed (Fig. 4). Whereas with SAXS and electron microscopy the actual, hard sphere particle radius is determined, hydrodynamic methods yield effective radii that include also the hydration shell.

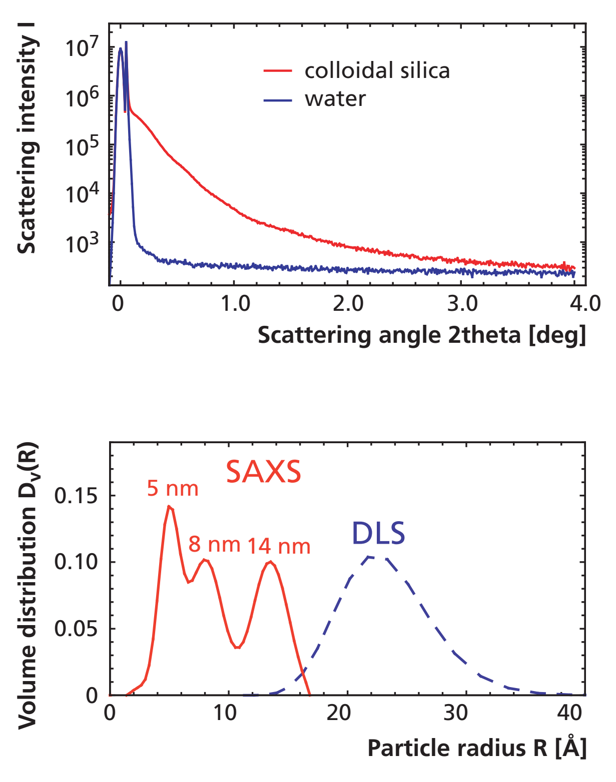
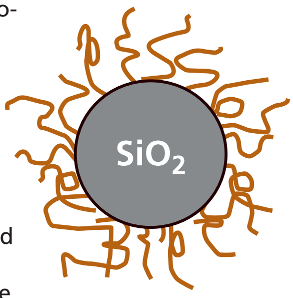


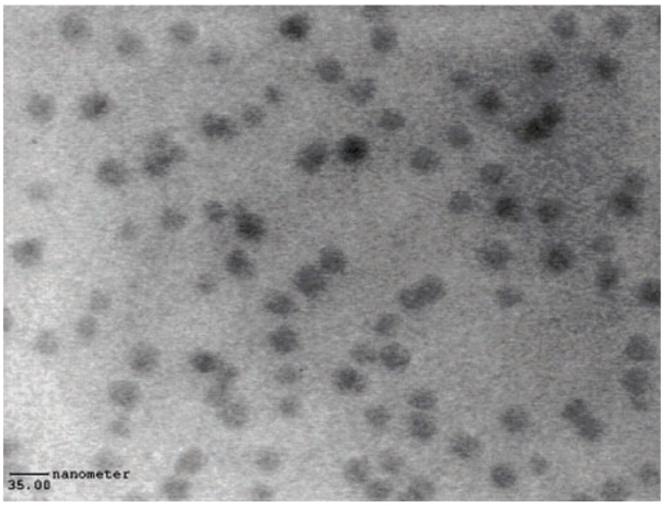
Figure 4: SAXS data from 0.8% colloidal silica (top) and the determined trimodal volume distribution (bottom), together with a typical result from dynamic light scattering.

Experimental results

Polymer nanocomposite

PMMA (Polymethylmetacrylate) was modified with 3 wt.% of silica nanoparticles in a melt compounding process to yield a nanocomposite with improved thermal and mechanical properties [4] (sample and TEM courtesy Claude Becker, Public Research Centre Henri Tudor, Luxembourg). SAXS data from this sample allowed to determine the nanoparticle size distribution and to confirm that the surface-functionalized particles are well dispersed in the polymer matrix, which is crucial for the application properties (Fig. 5). These findings are in good agreement with observations from TEM. However SAXS has the important advantage of quickly delivering such information over a relatively large volume of the sample, and with minimal sample preparation.





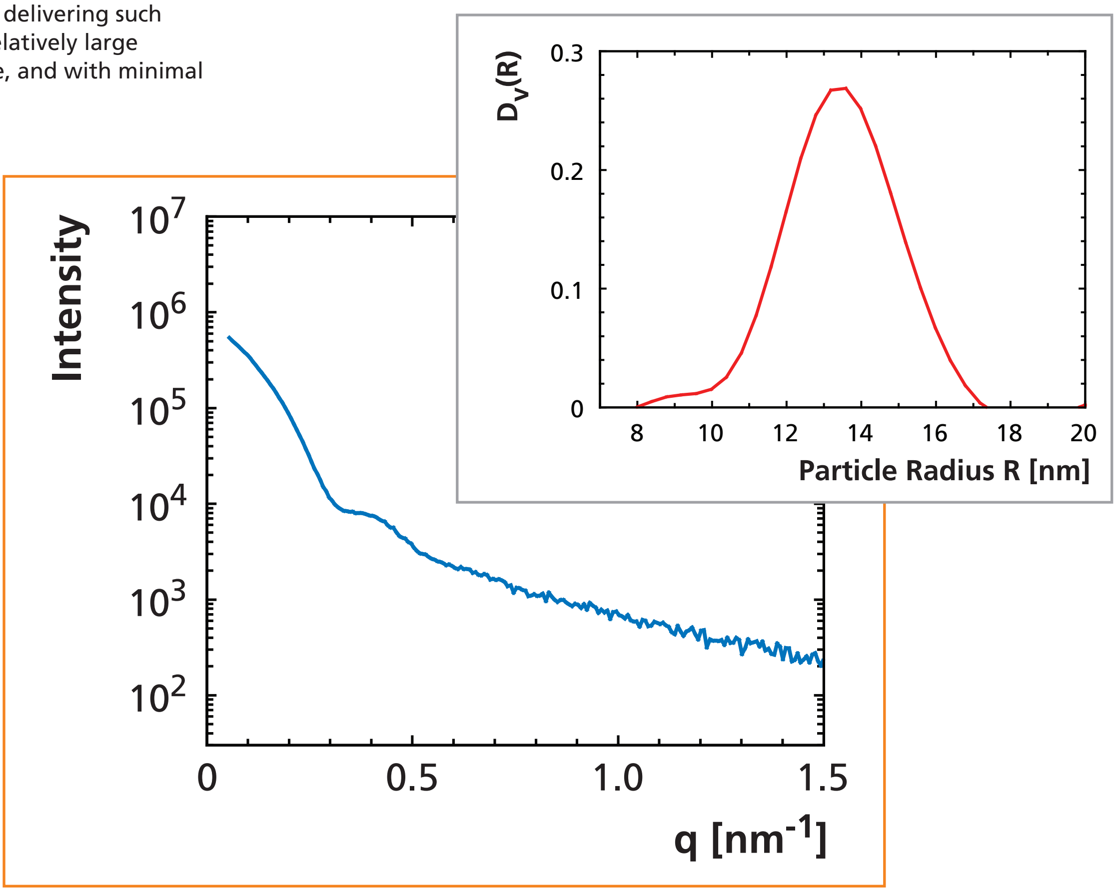


Figure 5: SAXS results from a PMMA-silica nanocomposite and a comparison with TEM.

Experimental results

Porous materials

Pore size distribution analysis results obtained with SAXS from two silica samples with a random porous structure are shown in Fig. 6. The measurement time per sample was only 5 minutes. The data were analyzed assuming spherical pores and the distributions correlate well with results from the mercury intrusion method.

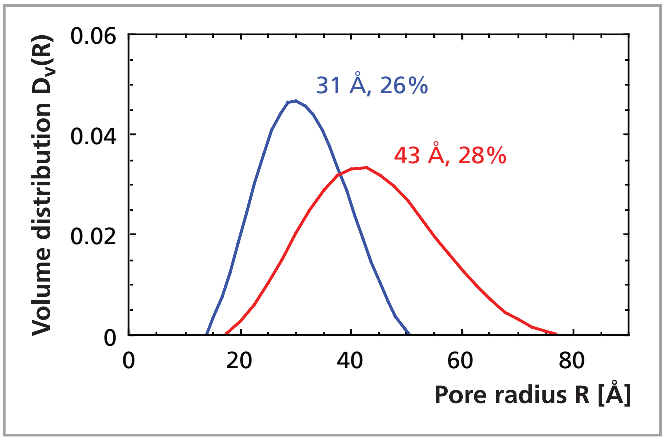


Figure 6: Pore size distributions determined with SAXS

Conclusions
SAXS is a versatile technique that is complementary to XRD. It allows to analyze monoparticle size distributions and nano-structures in powders, liquids and solid materials. High quality SAXS data can be obtained on a multi-purpose X-ray diffractometer platform, with limited additional investment.

References

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