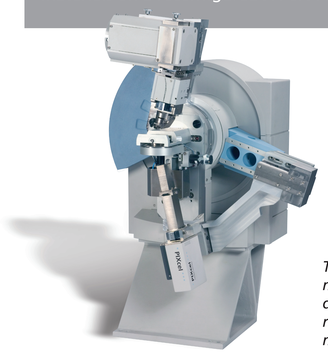
# DETERMINATION OF SPECIFIC SURFACE AREA AND SIZE DISTRIBUTION BY SMALL-ANGLE X-RAY SCATTERING

J. Bolze, D. Beckers, PANalytical B.V., Almelo, The Netherlands
V. Kogan, DANNALAB, Enschede, The Netherlands

## Abstract
The Small-Angle X-ray Scattering (SAXS) technique allows structural analysis of amorphous and crystalline materials on a mesoscopic length scale ranging from ca. 1 - 150 nm. Powders or dispersions of organic and inorganic nanoparticles can be characterized with respect to their particle size distribution and inner structure. In case of porous materials the specific inner surface area and pore size may be determined. A precise control of these properties is important for the application in e.g. drug carrier systems with controlled release porperties. We present SAXS measurements of such materials on a reconfigured X'Pert Pro X-ray diffractometer using a line focus in combination with collimating optics.



*The X'Pert Pro multipurpose powder diffractometer reconfigured for SAXS measurements.*

## Instrumental
A multi-purpose diffractometer (X'Pert Pro MPD) was configured for SAXS measurements.

Various multilayer optics were combined with a collimator system to achieve good low-angle resolution and high intensity.

The samples were placed in circular holders between thin Mylar sheets and mounted horizontally on a reflection-transmission sample stage. Some of the measurements were done in an automatic mode using an automatic sample changer.

Scattering intensities were measured with a point detector (proportional counter) in transmission geometry by 2 Theta scans . Direct beam profile measurements (using an attenuator) were included in all scans to determine the attenuation factors of the samples. Scans were performed in a 2 Theta range from -0.1° up to ca. 6°. The FWHM of the direct beam was in the range of 0.02-0.04° in 2 Theta.

The background scattering measured with an empty sample holder was recorded separately and subtracted from the sample measurements, properly taking into account the attenuation factor.

Depending on the optics chosen, the measurement time per scan was 15-40 minutes.

## Data treatment and evaluation
The measured data were background-corrected and the scattering angle $2\theta$ was converted to the scattering vector $q = 4\pi/\lambda \cdot \sin(\theta)$ [nm$^{-1}$].

An indirect Fourier transformation method was used for the determination of the (volume-weighted) size distribution $D_V(R)$ of the nanoparticles or pores. Within this procedure, smearing effects due to the finite beam size are taken into account. The particles or pores are assumed to have a spherical shape and a homogeneous structure. We did not make any pre-assumptions concerning the shape of the distribution curves.

The determination of the specific surface areas S/m [m²/g] was done either from the size distribution function and mass density $\rho$ through

$$\frac{S}{m} = \frac{1}{\rho}\frac{S}{V} \quad \text{where} \quad \frac{S}{V} = \int_{R\,\min}^{R\,\max} \frac{3}{R} D_V(R)\, dR \quad \text{and} \quad \int_{R\,\min}^{R\,\max} D_V(R)\, dR = 1$$

or from the (slit-semared) invariant $\tilde{Q}$ and Porod-constant $\tilde{k}$ by

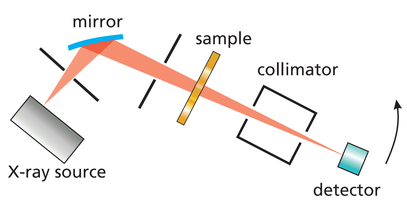
$$\frac{S}{V} = 4\frac{\tilde{k}}{\tilde{Q}} \cdot 10^3 \quad \text{for nanoparticles and} \quad \frac{S}{V} = \frac{\tilde{k}}{\tilde{Q}} \cdot 4 \cdot \phi_p (1-\phi_p) \cdot 10^3$$

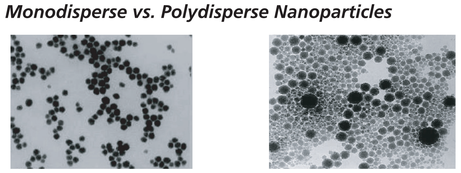
for porous materials with porosity $\phi_p$

$$\tilde{k} = \lim_{q\to\infty}(\tilde{I} \cdot q^3) \quad \text{and} \quad \tilde{Q} = \int_0^\infty \tilde{I}(q) \cdot q\, dq$$

## 1. SAXS Measurements on Nanoparticles
The properties of nanoparticles are strongly related with their size and size distribution, but also with their specific surface area.
In the pharmaceutical industry surface-functionalized nanoparticles are used as drug carriers.

Below we present examples of SAXS measurements on powders of inorganic and organic spherical nanoparticles. Those nanoparticles differed considerably in the width of their size distribution (monodisperse or polydisperse) as well as in their average sizes and degree of atomic order (crystalline vs. fully amorphous).

### Experimental setup


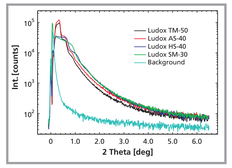

### *Monodisperse vs. Polydisperse Nanoparticles*


*Monodisperse (narrow size distribution)*

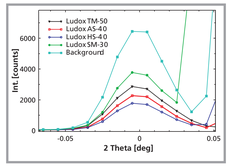
*Polydisperse (broad size distribution)*

Ludox® silica particles (Grace)
Source: www.grace.com

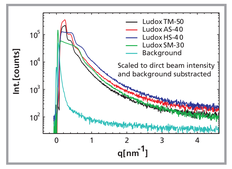
### *1.1 Silica Nanopowder*
Water-based colloidal silica dispersions (Ludox®, Grace) were dried at room temperature to yield powder samples. These discrete silica particles are characterized by a spherical shape, a uniform size, a non-porous structure and no detectable crystallinity.
A set of samples with different particle sizes was measured.



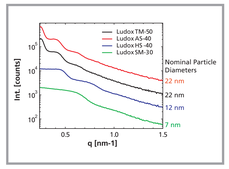

*Experimental data as measured*




*Direct Beam Profiles*



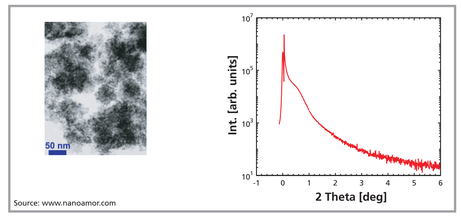

*Background-corrected experimental data*



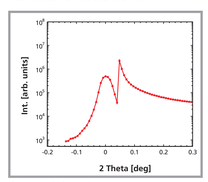

*Magnification at small angles*

The uniform particle size is evidenced by the distinct oscillations that were observed in the SAXS patterns. The different oscillation frequencies are related to differences in the particle size.

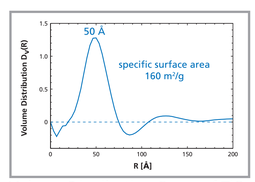
### *1.2 $TiO_2$ Nanopowder*
This type of material has anti-microbial and UV-blocking properties.




*Background-corrected SAXS data. The steep upturn of the scattering curve at smallest angles indicates some aggregation effects. This angular range was taken into account in the further evaluation.*



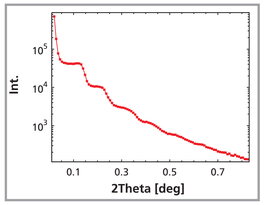

*Magnification at smallest angles*




*Volume Distribution Curve of $TiO_2$*

The particles exhibit a well-defined size distribution with an average radius of ca. 50 Å.

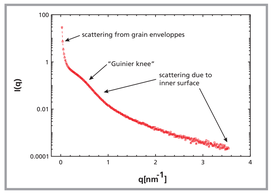
### *1.3 Polystyrene Nanospheres*
These polymer particles have an average radius of 45 nm and a very narrow size distribution. The distinct oscillations could be resolved with a very good resolution down to very small scattering angles.




## 2. SAXS measurements on porous materials
Materials with nano-sized pores are widely used in separation processes, sorbents, catalysis, dielectrics etc.

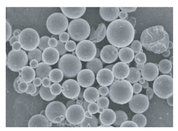
The pore size, porosity and specific surface area are decisive parameters for the performance in these applications.

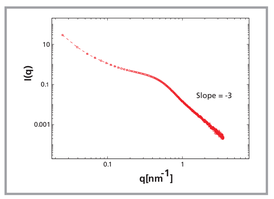
### *2.1 Granular, porous alumina*
This certified standard material (BAM PM-104) was used to verify the precision of our SAXS measurements and data evaluation procedures.




Granular alumina standard material:

Porosity ca. 50%
Grain size ca. 50 µm



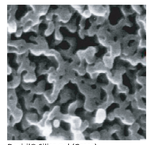



Specific surface area calculated from Porod-constant $\tilde{k}$ and Invariant $\tilde{Q}$
$S/m \sim \tilde{k}/\tilde{Q}$

$S/m$ = 91 m²/g
(cf. BET: 80 m²/g)

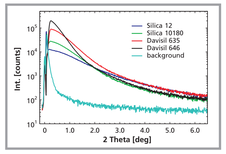
The specific surface area determined by SAXS is slightly larger than that determined by the BET method. This may be explained by the existence of some (closed) pores that are inaccessible by the gas molecules.

### *2.2 Silica Gels*
Silica gels are amorphous substances with a distinct pore structure and a large specific surface area. The investigated samples had a porosity in the range of 50-70% and differed in their pore size.

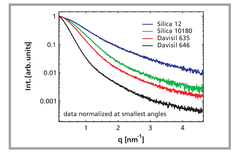


Davisil® Silica gel (Grace)
source: http://www.grace.com

**Application in pharmaceuticals:**
- active agent carrier
- controlled release properties
- allows the formation of powders from liquids
- adsorption of wound secretions
- tabletting aid

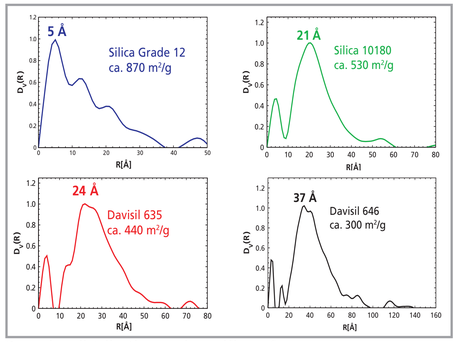



*Experimental raw data*

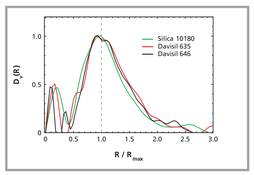



*Background-subtracted data*

Differences in the pore size and specific surface area are clearly evidenced by the the different curvatures at smallest angles and by the different slopes at higher angles.




*Pore size distribution and specific surface areas*




*Universal Pore Size Distribution Function*

It was found that the various samples exhibit a universal pore size distribution function.

## Conclusions
**SAXS measurements on strongly scattering samples, such as nanpowders and porous materials, may be readily performed on a reconfigured powder diffractometer. By using multilayer optics in combination with a secondary collimator, measurements can be extended down to very low angles, parasitic scattering effects may be minimized, and an intense primary beam may be obtained.**

**Careful data evaluation procedures allow to determine important parameters such as particle and pore size distributions, as well as the specific surface area of nanomaterials.**