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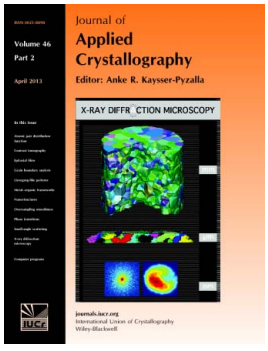


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# Development of powder diffraction apparatus for small-angle X-ray scattering measurements

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A novel type of X-ray collimation system attached to commercial powder diffractometers makes the structural characterization of nanomaterials possible in a wide size range from <0.1 to 100 nm by combination of the small- and wide-angle X-ray scattering techniques. There is no dead interval in the detection between the small- and wide-angle regimes. This device can be attached to any existing '$\theta/\theta$' powder diffractometer, providing a multi-functional small- and wide-angle X-ray scattering/diffraction (SWAXS) apparatus. After proper alignment and adjustment, the device can be removed and re-attached at any time to switch between normal and SWAXS functions.



## 1. Introduction

Large facilities such as synchrotrons and neutron sources make the structural characterization of nanomaterials possible worldwide by the use of small-angle scattering (SAS) techniques. The successful realization of measurements at these research centres, however, requires preliminary SAS experiments. Unfortunately, small-angle X-ray scattering (SAXS) laboratory apparatuses are not so widely used as X-ray powder diffraction (wide-angle diffraction X-ray scattering, XRD) equipment; therefore SAXS experiments are frequently hampered.

In laboratory practice, the so-called 'compact Kratky' camera is generally used (Kratky & Glatter, 1982; Kratky & Stabinger, 1984; Laggner & Mio, 1992). Despite its many advantages, the application of the unmodified version of this construction has some restrictions (extended reflection geometry is not possible; no wide-angle scattering range is available, or if it is, there is a dead interval between the small- and wide-angle regimes; measurements can be made under vacuum only). Recently, a modified Kratky camera has allowed a more extended scattering range, up to 40° (SAXSess mc$^2$; Anton Paar, 2012). Besides the Kratky camera, however, new point-focus SAXS cameras are presenting novel possibilities for nanoresearch (http://www.bruker-axs.com/nanostar.html; http://www.rigaku.com). In SAXS measurements the adjustment of the fine profile of the X-ray beam is the most crucial point; therefore the stable and robust collimation block of the Kratky camera has now been applied in a new type of SAXS camera (Mallett *et al.*, 2012).

Here we report a device with which an existing XRD apparatus can provide important nanostructural information by using a minor, but powerful, technical development. The upgrading of the XRD apparatus described below provides a multi-functional powder diffraction instrument (Bóta *et al.*, 2005). This construction allows a continuous scan in an extremely wide range from small to wide angles ($2\theta_{min} < 0.1°$, $2\theta_{max} \simeq 130°$) without any dead interval in the detection. This range corresponds to a real-space resolution from about 0.1 to 100 (200) nm, which is typical in materials sciences. For SAXS measurements this device was implemented on operating apparatuses without any change or reduction in their original functions.

## 2. Experimental setup

For SAXS measurements our device was implemented on two types of commercially available XRD apparatuses: an XRD 3003 TT ($\theta/\theta$) diffractometer from GE Germany (Ahrensburg; previously Seifert) and an X'Pert powder diffractometer from PANalytical (GE Measurement & Control, 2012; http://www.pananalytical.com). For the detection of SAXS, two main parts were constructed: a collimation system and a vacuum tube. The latter was mounted onto the detector directly. The collimation system contains three parts: two entrance slits (0.2 and 0.3 mm, for initial limitation of X-rays), a Soller collimation system (to achieve a parallel beam) and a special SAXS collimation block. The latter is fundamental in adjusting the incident beam in both the horizontal and the vertical directions, and is shown schematically in Fig. 1. The SAXS collimation block is made of alumina to achieve minimal weight and is placed inside a frame. It has four edges (made of iron–tungsten steel) for vertical collimation and three slits with fixed openings for horizontal limitation. The position of the frame can be adjusted in order to achieve the correct alignment with respect to the centre of gravity of the incoming X-ray beam. Additional fine adjustment of the block inside the frame makes the required cut of the beam possible. The idea of constructing the collimation block in this way was inspired by combining the operating principles of the Kratky collimation system with the slits used at synchrotron beamlines.

The experimental setup of the small- and wide-angle measurements for the XRD 3003 TT diffractometer in the transmission arrangement is also presented in Fig. 1. The installation was completed with a vacuum tube to ensure a significant reduction of the small-angle X-ray scattering in air. The collimation system was mounted in the X-ray tube by taking the geometry and mechanical specifications of the goniometer into account.

## 3. Experimental details and data processing

The Seifert and PANalytical apparatuses contain a 1.6 kW (operated at 40 kV and 30 mA) and a 2.2 kW (operated at 40 kV and 30 mA) X-ray tube, respectively. Both are equipped with proportional gas

detectors with exchangeable entrance slits, a fine one for detecting the beam profile (0.001°) and a broader one for measuring the scattering curves (0.01°). Ni-filtered Cu $K\alpha$ radiation ($\lambda$ = 1.542 Å) was used in both instruments. As the measurements were performed by using a slit collimation, the SAXS intensity curves were corrected for line focus smearing considering the geometry of the beam profile, using the direct method described by Singh *et al.* (1993).

Point-focus small- and wide-angle X-ray scattering measurements were made for reference on silver behenate at the synchrotron beamline B1 of the storage ring DORIS III at HASYLAB/DESY, Hamburg, Germany (Haubold *et al.*, 1989). The beam used was point collimated (1 × 0.7 mm) and monochromated to 9626.7 eV with an Si(311) double-crystal monochromator. The scattering pattern was obtained by using two experimental setups with 883 and 3583 mm sample-to-detector distances. In the small- and wide-angle X-ray scattering regimes a two-dimensional (PILATUS 300k, Dectris Ltd, Switzerland) and a one-dimensional (MYTHEN, Dectris Ltd, Switzerland) detector were used, respectively (Broennimann *et al.*, 2006; http://www.dectris.com; Schmitt *et al.*, 2003). Radial scattering curves were calculated from the images and normalized to absolute units.

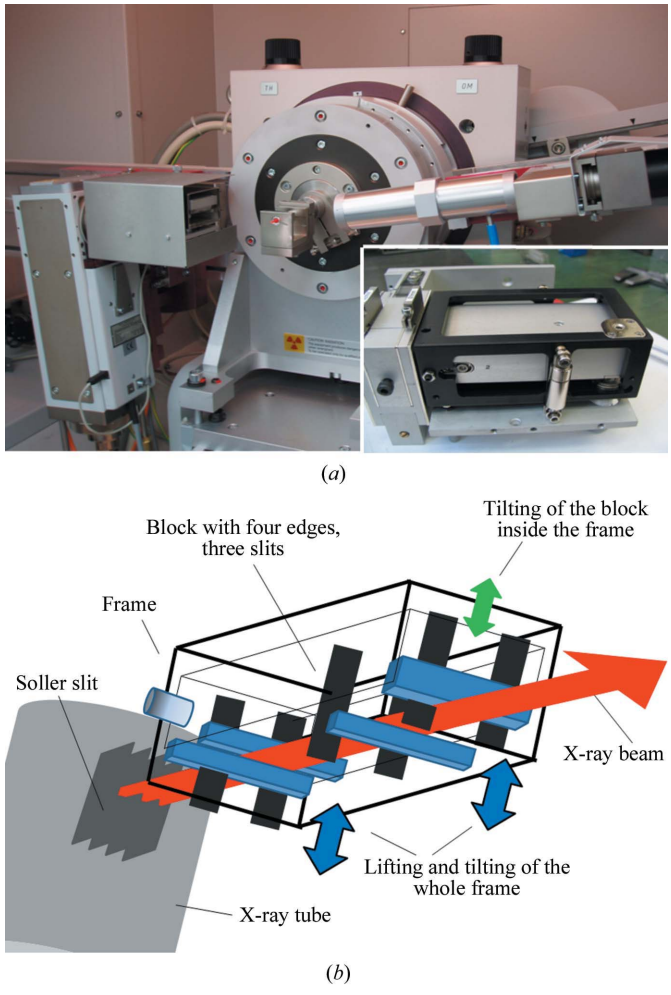


**Figure 1**
Modified XRD 3003 T/T powder diffractometer (inset collimation block in frame) (*a*) and a schematic view of the novel SAXS collimation system (*b*). The position of the frame containing the block can be adjusted (blue arrows) with respect to the incoming beam. Further fine adjustment can be made by a gentle tilting of the block inside the frame (green arrow). All four edges (blue columns) can be positioned.

## 4. Experimental setup and performance

### 4.1. Beam profile and background curve

This new type of collimation system provides a very narrow X-ray beam, which makes the measurement of small-angle scattering possible. The collimation is demonstrated in Fig. 2(*a*), presenting the X-ray beam profile in the vertical direction. The measurement of the attenuated beam was carried out using copper filters. The fine adjustment allows a sharp cut on the positive side of the profile, whereby the 'first measurement point' can be adjusted so that it falls below $2\theta = 0.1°$, which extends the measurement in real space up to $2\pi/q_{\min} = 100$ nm [$q$ is the absolute value of the scattering vector, defined as $q = (4\pi/\lambda)\sin\theta$, where $\lambda = 0.1542$ nm is the wavelength of the Cu $K\alpha$ fluorescence line]. For a better understanding, the profile of the primary beam is also plotted in logarithmic scale (Fig. 2*a*, upper curve). Without using any filter, we can observe the background scattering in the extended $2\theta$ regime, shown in Fig. 2(*b*). For practical reasons, the first measurement point is at the lowest $q$ value where the background intensity is 10–20 times higher than the nearly constant value observed at higher angles. The intensity is approximately 0.3 counts per second (c.p.s.) between 2 and 14°, and, as a consequence, the first measurement point is $2\theta = 0.1°$ (1.75 mrad) (shown as insets in Fig. 2).

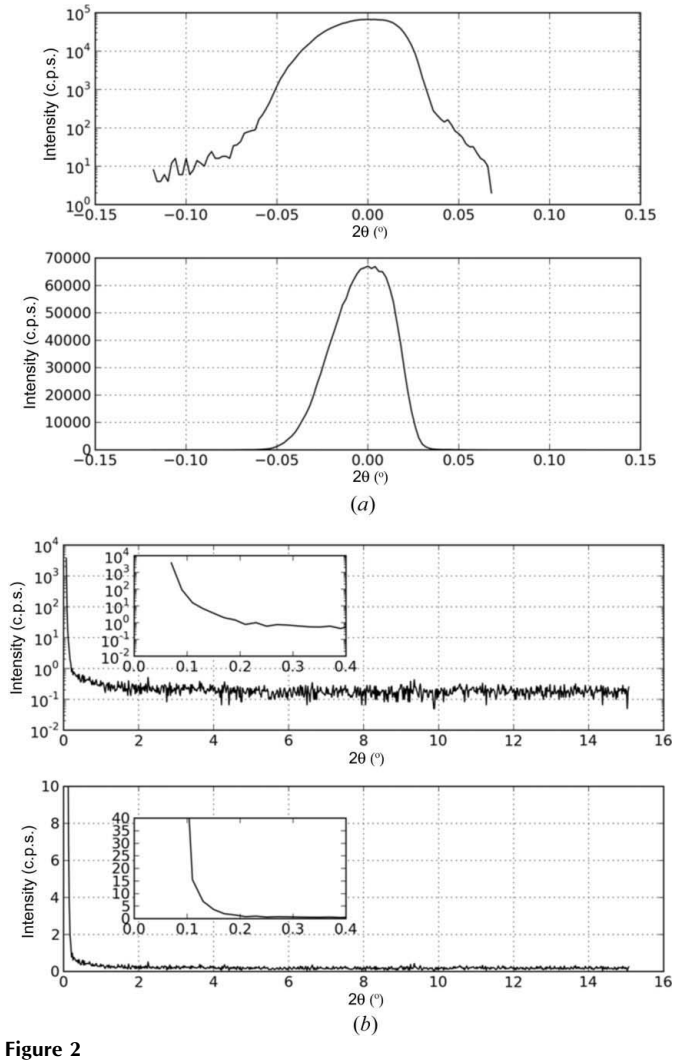


**Figure 2**
Vertical profile of the collimated X-ray beam measured by using copper filters (*a*). Background scattering measured in small- and wide-scattering regimes (*b*).

### 4.2. SAXS of silver behenate

For a demonstration of SAXS measurements on the diffractometer, the scattering curves of silver behenate are presented in Fig. 3. This material serves as a standard for $q$ calibration at several synchrotron SAXS beamlines, because of its accurate periodicity of 5.84 nm (Binnemans *et al.*, 2004). The consequence of its one-dimensional arrangement is the appearance of small-angle X-ray diffraction (SAXD) peaks along the scattering profile. Therefore, we can detect the Bragg reflection in a number of orders on the scattering curves. Besides the SAXS curve detected in the XRD apparatus, a pattern obtained at a synchrotron station (DESY/HASYLAB/B1 beamline) is also plotted in Fig. 3. Comparing these curves, we can observe the smearing effect of the line focus of the collimation, resulting in the broadening and deformation of the Bragg reflections, especially in the case of the first and the second orders. The desmeared SAXS curve is also plotted to compare the pattern after the reconstruction of results of a line focus beam profile in relation to the point-focused SAXS (B1) beamline. It is important to note that the point-spread function of the PILATUS 300k detector is lower than one pixel; thus no cross-talk exists between the neighbouring pixels, in contrast to the case of multiwire proportional chamber gas detectors (Vaino *et al.*, 2009, 2012).

The advantage of this development is evident: an extended scan can be carried out covering both the small- and wide-angle regimes, referred to as small- and wide-angle X-ray scattering (SWAXS). It must be noted that SWAXS measurements are generally not feasible at synchrotron SAXS stations. At the B1 beamline, it was possible to insert the one-dimensional detector into the extremely large sample chamber, whereby the angular range of the measurement was extended up to $2\theta = 40^\circ$ (Vainio, 2012). One can see the higher orders of small-angle diffraction of silver behenate even at $2\theta = 18^\circ$, clearly demonstrating the extended SAXS regime of scattering of this colloidal system. This feature cannot be observed by using a conventional compact camera with fixed sample–detector distance (generally about 20 cm). In the wide-angle range ($2\theta > 20^\circ$), several Bragg reflections from the 'ångström' length scale can be observed, clearly demonstrating that the hierarchical colloidal ('nano') and atomic structures overlap, and the extent of the SAXS/SAXD toward higher scattering angles depends on the actual material studied. We mention that for the $q$ calibration in the wide-angle regime other materials, *e.g.* tripalmitin or silicium carbide, are also used but these are not discussed here.

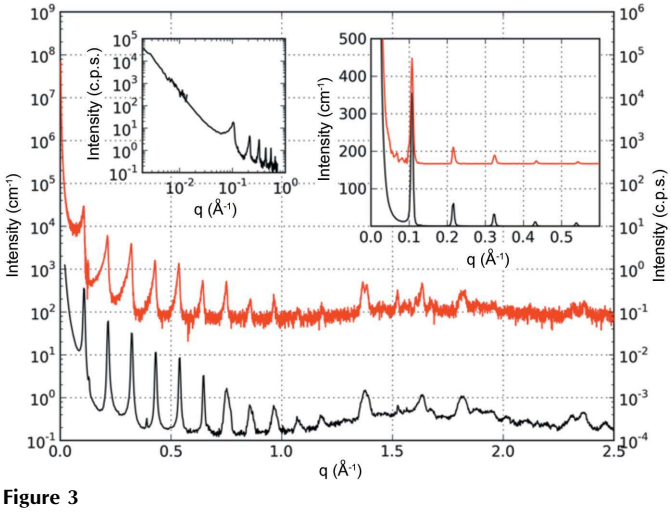


**Figure 3**
Small- and wide-angle scattering/diffraction of silver behenate [measured on an XRD diffractometer (red) and at a synchrotron station (black)]. Inset (left): ultra-small-angle scattering; inset (right): desmeared and direct experimental (point focus/synchrotron) data. The intensity is given in absolute units ($cm^{-1}$) for synchrotron data.

On closer inspection, one can observe that the reflection peaks lie on a continuously decreasing baseline, which arises from the small-angle scattering of the heterodisperse 'crystallites' of silver behenate. To obtain information from a larger size range (>100 nm), the extension of SAXS measurement is required to an extremely small $q$ regime, known as the 'ultra-small-angle' scattering regime (USAXS). A long collimation system (20 cm, which is twice as long as the one shown in Fig. 1) was constructed for the XRD 3003 TT apparatus to allow for the measurement in this 'ultra-small' $q$ regime. The SAXS measurement was executed in two different adjustments: with an extremely narrow profile and with a slightly broader one, resulting in two sections in the scattering curve. Their fit to each other is also depicted in an inset in Fig. 3. One drawback of the extremely fine beam profile is the reduced scattering intensity; therefore the measurements in the ultra-small regime require substantially longer exposure times.

Finally, we mention an additional opportunity of our developed diffractometer, whereby the apparatus provides a unique extension in structural studies, namely, both transmission and reflection measurements can be carried out. This combination is rarely accessible even at synchrotron stations because the beam and the detector are positioned on one mutual axis. The precise collimation (first measurement point at $2\theta = 0.1^\circ$) makes the characterization of multilayered structures and interfaces possible by using reflection geometry.

## 5. Conclusion

By the use of horizontal slits, the X-ray beam can be reduced to a nearly point-focused one, providing further opportunities. For example, using a two-dimensional detector the measurement of grazing-incidence small-angle X-ray scattering is feasible. Once it is set up and aligned correctly, the device can be reversibly removed with a simple movement (tilting the collimation system by the fine micrometer), which resets the original operating conditions of the diffractometer.

The collimation block is a stable working tool; after its removal and replacement, it provided practically the same quality measurements (tested in the case of the X'Pert apparatus). The parallel measurements executed on the upgraded diffractometers and the dedicated synchrotron SAXS beamline have served as a means of validation for our developed method.

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## References


Anton Paar (2012). *Modular Tool for Nanostructure Analysis: SAXSess mc²*, http://www.anton-paar.com/Modular-Tool-for-Nanostructure-Analysis-SAXSess-mcsup2/SAXS/60_UK_en?product_id=320.

Binnemans, K., Van Deun, R., Thijs, B., Vanwelkenhuysen, I. & Geuens, I. (2004). *Chem. Mater.* **16**, 2021–2027.

Bóta, A., Stirnal, P. & Haase, A. (2005). 19th ECIS Conference, 18–23 September 2005, Geilo, Norway.

Broennimann, Ch., Eikenberry, E. F., Henrich, B., Horisberger, R., Huelsen, G., Pohl, E., Schmitt, B., Schulze-Briese, C., Suzuki, M., Tomizaki, T., Toyokawa, H. & Wagner, A. (2006). *J. Synchrotron Rad.* **13**, 120–130.

GE Measurement & Control (2012). *Diffractometer System XRD 3003 TT*, http://www.ge-mcs.com/download/x-ray/analytical-x-ray/GEIT-30154GB_diffractometer-system-xrd3003tt.pdf.

Haubold, H.-G., Gruenhagen, K., Wagener, M., Jungbluth, H., Heer, H., Pfeil, A., Rongen, H., Brandenburg, G., Moeller, R., Matzerath, J., Hiller, P. & Halling, H. (1989). *Rev. Sci. Instrum.* **60**, 1943–1946.

Kratky, O. & Glatter, O. (1982). Editors. *Small Angle X-ray Scattering*. London: Academic Press.

Kratky, O. & Stabinger, H. (1984). *Colloid Polymer Sci.* **262**, 345–360.

Laggner, P. & Mio, H. (1992). *Nucl. Instrum. Methods Phys. Res. Sect. A*, **323**, 86–90.

Mallett, C., Le Magueres, P., Criswell, A. R., Ferrara, J., Suzuki, N., Degen, M., Jiang, L. & Sasaki, K. (2012). BioSAXS-1000, Advanced Photon Source, Center for Nanoscale Materials, Electron Microscopy Center, Users Meeting, Chicago, USA. Poster A-02.

Schmitt, B., Brönnimann, Ch., Eikenberry, E. F., Gozzo, F., Hörmann, C., Horisberger, R. & Patterson, B. (2003). *Nucl. Instrum. Methods Phys. Res. Sect. A*, **501**, 267–272.

Singh, M. A., Ghosh, S. S. & Shannon, R. F. (1993). *J. Appl. Cryst.* **26**, 787–794.

Vaino, U. (2012). *Beamline: B1*, HASYLAB, Hamburg, Germany, http://hasylab.desy.de/user_info/available_instruments/x_ray_scattering/b1.

Vaino, U., Schubert, T., Botta, S., Blume, J., Wacha, A., Lohmann, M., Kracht, T. & Gehrke, R. (2009). *New in situ SAXS/WAXS Setup and Other Refurbishments at the ASAXS Beamline B1, HASYLAB*. Annual Reports, HASYLAB, Hamburg, Germany.