FLEXIBILITY AND HIGH THROUGHPUT:
SUPPORTING SAXS USERS
AT A JOINT INDUSTRIAL ACADEMIC BEAMLINES

Steven Weigand¹
Ben Stillwell¹
William E. Guise²
John P.G. Quintana¹,³
Denis T. Keane¹

¹) Northwestern University – DND-CAT at APS/ANL, Argonne, IL 60439
²) E.I. DuPont de Nemours & Co., Wilmington, DE
³) currently employed at Argonne National Laboratory, Argonne, IL

ABSTRACT
From its inception, the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) at the Advanced Photon Source has had to adapt to the changing needs of industry as well as a diverse academic user base. This has resulted in a sector with support for a broad range of techniques and sample environments. Among the techniques supported at DND-CAT are small and wide angle scattering, reflectivity, spectroscopy, tomography, and powder diffraction. The D station on the insertion device line at DND-CAT (5ID-D) is a general purpose hutch that is primarily used for small angle X-ray scattering (SAXS). Approximately 10¹² photons/sec can be delivered to a .04mm² spot using multiple sets of slits with pinhole camera geometry. Scattering can be measured down to θ = 0.014° on a 10m long camera with 1.5Å to 0.7Å radiation. Many 5ID-D users are polymer scientists, thus standard techniques supported include SAXS and WAXS image collection simultaneous with thermal, extension/compression, shear, or calorimetric data. Often, an individual user will come with arrays of several sample types requiring different environments and/or camera configurations to fully analyze. This paper describes how the joint goals of flexibility and high throughput are balanced at 5ID-D for small and wide angle X-ray scattering. A unique simultaneous SAXS/WAXS detector system for collecting anisotropic X-ray scattering is described. Also a method for calibrating sample to detector distance for long tanks using a silicon diffraction grating is presented.
This document was presented at the Denver X-ray Conference (DXC) on Applications of X-ray Analysis.

Sponsored by the International Centre for Diffraction Data (ICDD).

This document is provided by ICDD in cooperation with the authors and presenters of the DXC for the express purpose of educating the scientific community.

*All copyrights for the document are retained by ICDD.*

Usage is restricted for the purposes of education and scientific research.

**DXC Website**  
– [www.dxcicdd.com](http://www.dxcicdd.com)

**ICDD Website**  
- [www.icdd.com](http://www.icdd.com)
INTRODUCTION
The DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) is a collaboration which began in 1991 to develop X-ray optics and instrumentation at sector 5 of the Advanced Photon Source (APS) of Argonne National Laboratory. This facility now supports a broad range of materials science X-ray analysis techniques for all three institutions. Additionally 25% of available time is given to general users through the peer review process which APS administrates. Three independent beamlines are maintained by DND-CAT. Two utilize different portions of the radiation spread from the sector 5 bending magnet. Techniques supported on the beamlines include high resolution powder diffraction, micro tomography, X-ray absorption spectroscopy, polymer diffraction, and related techniques. The final beamline uses a pair of silicon crystals in the (111) orientation, indirectly cooled with liquid nitrogen, to select a monochromatic portion of the spectrum delivered by an APS Undulator A (Dejus et al., 1994; Lai et al., 1993) insertion device. Harmonic rejection and 1:1 horizontal focusing are provided with a pair of ultra low expansion glass (ULE™) mirrors having bare glass, rhodium, and platinum stripes. The insertion device beamline has three successive experimental enclosures. High resolution powder diffraction, fiber and single crystal diffraction are supported in 5ID-B, the first experimental enclosure. The second enclosure, 5ID-C, has an ultra-high vacuum chamber on a diffractometer and a separate kappa diffractometer for reflectivity, standing-wave, and other surface science techniques. Approximately half of the available time on the insertion device beamline is given to small and wide angle scattering (SAXS and WAXS) in the final experimental enclosure, 5ID-D. Flexible configuration, sample environment, and calibration in conjunction with a novel detector system provide 5ID-D users with high throughput image collection that is ideally suited for polymer structural studies and useful for many other solution and solid phase nanometer scale science.

5ID-D BEAMLNE DESCRIPTION
Experiments in 5ID-D use multiple sets of consecutive slits to define beam size and collimation for a standard pinhole geometry camera. While the monochromometer has the angular range to provide a first harmonic energy range of 5 to 19keV, most experiments in 5ID-D are restricted to 8 to 17keV for convenience. An estimated $10^{12}$ photons/sec are delivered to a $200\mu m \times 200\mu m$ spot at the sample position. With a maximum sample to detector distance of 9m (for most
configurations) or 10m (for the large vacuum chamber configuration) possible, a minimum momentum transfer vector \( q = 4\pi \sin \theta / \lambda \) of 0.001 \( \text{Å}^{-1} \) can be collected.

5ID-D can accommodate a wide variety of user supplied sample environments. Additionally, a large number of standard environments are available on-site for regular use. The first sample environment along the path of the beam is a large 12 inch, 6-way cross vacuum chamber (Landes et al., 2003; Quintana, 2003). The chamber is equipped with a perforated wheel mounted normal to the beam, which can be loaded with static samples for small or wide angle data collection. The upstream beam pipe and downstream scatter pipe both connect directly to the chamber, allowing for a window-free configuration, where only the detector is external to the \( \sim 10^{-6} \text{torr} \) vacuum chamber. A supply of 86-hole wheels is available for pre-mounting such that data collection interruption need only be the approximate 15 minutes it takes for the vacuum pumps to evacuate the beam path and chamber. It is also possible to mount vacuum compatible user environments within the chamber (Brinker et al., 2005).

One meter downstream of the vacuum chamber and offset from the beam path, a small tower containing heavy duty motorized linear slides provides X-Z translation for sample environments mounted on the end of rigid arms (in a style similar to a fork lift). Using these arms, sample environments can be assembled above, below and on either side of the sample position. The slides have a 160mm range of motion and thus provide enough space for changing between multiple samples.

This sample tower is the primary location for most sample environments in 5ID-D. A collection of holders is available for mounting samples (Figure 1). Each holder is mounted on the top-plate of a magnetic kinematic mount such that it places the sample in the same position along the X-ray beam propagation direction. This allows for easy changing between holders without the need to re-calibrate sample to detector distance.
Figure 1. Sample environments available at 5ID-D.

*Back row, left to right:* Linkam THMS600 modified to include a quartz capillary flow cell. Linkam DSC; Linkam THMS600. Each have 0.001 inch thick Kapton® windows. *Second row:* comb sample holder for holding thin polymer samples edge-on to the beam, short capillary holder for heat-sealed sealed capillaries. *Front row:* long capillary holder for full length thin-walled X-ray capillaries (Wolfgang Muller Glas Technik via Charles Supper Company), flat sample holder. All the holders shown would be mounted such that the X-ray beam would be passing through the back toward the viewer in this figure.

Many user-supplied sample environments have also been accommodated at 5ID-D. These include extruders, spinners, injection molders, rheometers, flame reactors, flow-cells and others. DND-CAT also has an Instron Corp. model 8500 Materials Testing System (MTS) for in situ stress-strain experiments in 5ID-D. Dual actuators with a total of 16 inches of travel allow the center of the sample to remain in the beam during the experiment. Load, position, and strain variables can be independently controlled. Several load cells are available: 0 - 10 lb, 0 - 50 lb, 0 - 200 lb, and 0 - 1000 lb. The MTS can be inserted at the sample tower position (either by removing the sample tower arms, or by spreading them to either side of the MTS.

Flexibility in sample position as well as camera length are facilitated by a collection of differing length 8 inch vacuum pipes and mobile 1m tables with linear actuator controlled optical breadboards. These tables can be moved anywhere in the hutch and are used primarily for supporting the two ends of the scattering camera.
SAXS/WAXS DETECTOR SYSTEM
There are two main detector systems used at 5ID-D. The first is a MarUSA (now Rayonix) 162mm MarCCD. It is a phosphor fiber-optic coupled CCD detector with a 2048×2048 pixel CCD and a corrected pixel size of 79µm/pixel with the lowest binning option. Multiple binning options are available yielding lag times of 4.1s to 7s. The second detector system was designed by Roper Scientific (now Princeton Instruments) to allow for simultaneous collection of half of the wide-angle scattering cone and the full small angle scattering cone, with a small blind zone between. The system consists of three detector modules. Each module has a phosphor fiber-optic coupled EEV Ltd. CCD with 1350×1300 pixels, a 1MHz ADC and a final corrected pixel size of 79µm/pixel with 1×1 binning. Lag times for this system are smaller than the MarCCD and vary from 0.26s to 2.4s dependent on binning option.

Two of these modules are mounted side-by-side in a nearly seamless mosaic inside the WAXS detector. This detector has a vacuum compatible beam path through the center of one edge to which one of two available nose-cones with mica windows at their tips is attached (Figure 2 and Figure 3). The first (sample to detector distance = 136mm) provides a WAXS 2θ range of 46° to 6.0° while allowing SAXS data under 2.08° to pass through. The second (236mm) provides a 31° to 3.5° range on the WAXS detector and under 1.43° on the SAXS detector. These configurations allow for visualization of non-isotropic scattering based on the orientation of nano-scale domains on the SAXS detector and atomic scale features on the WAXS detector. Aluminum masks are available for selective attenuation to match dynamic range of the detectors to each other, or selectively mask portions of the detectors to extend dynamic range (Cookson et al., 2006).

The SAXS and WAXS detectors were calibrated for distortion and variation of pixel response via published methods (Barna et al., 1999; Hammersley et al., 1995) using FIT2D (Hammersley, 1997; Hammersley, 1998). Flat field calibration data was obtained by placing the detectors perpendicular to the beam path and 1m away from a Multicomponent Glass (NIST SRM 1412), and collecting the fluorescence which results from excitation at 16150eV. Distortion spline calculation was done in FIT2D using data collected (in the same manner as the flat field) through a brass mask with 5.08mm spaced holes.
Dark frames are collected regularly during a user's normal data collection for the same exposure time (though without X-rays) as the sample. A collection of Perl scripts which issue background calls to FIT2D in “nographics” mode, are used to apply dark frame, flat-field and distortion corrections for the SAXS and WAXS images; and merge the final WAXS frames (Goodell et al., 2008).

Figure 2. Diagram of SAXS/WAXS detector system.
Green arrows are used to show the X-ray beam and the scattering cones. The sample position is shown by the cyan dot, and the beam stop (which is inside the vacuum chamber just before the SAXS detector) is shown by the blue dot. This diagram shows the beam stop centered on the SAXS detector.

Figure 3. SAXS/WAXS detector system.
System is shown from a similar angle as the diagram in Figure 2. The WAXS detector can be seen on the far right, but the view of the SAXS detector is blocked by the vacuum pipe.
RADIAL INTEGRATION AND TRANSMISSION CORRECTION

Perl scripts are used to automate azimuthal integration via FIT2D (Hammersley et al., 1996) and transmission correction using the counts from a PIN diode in the beam stop. Since we have had difficulty with PIN diodes becoming unresponsive after long exposures to high energy X-rays (17keV), the diode we use for transmission correction is mounted in its 4mm diameter beamstop behind a cadmium tungstate scintillating crystal and a 1mm aperture (Figure 4). This has proven to give a linear response and is less susceptible to X-ray damage.

![Figure 4. Diagram of Beam-stop diode.](image)

The magnet in the back of the beam-stop is used to mount it with a small partner magnet on either a Kapton® film or a shaft inside the scattering vacuum pipe just in front of the Kapton® exit window. The cadmium tungstate is coated with a titanium oxide paint to reflect visible light toward the diode.

The collected data can also be put on an absolute scale using the measured transmission, the sample thickness, and a scale factor derived from user collected data of a sample of glassy carbon (Alpha Aesar) available at 5ID-D. A scale factor can thus be determined by comparing the user collected data with that collected on the same glassy carbon sample at the APS Ultra-Small-Angle X-ray Scattering Facility (Ilavsky, 2004).
DISTANCE CALIBRATION

Calibration of the sample to detector distances and direct beam positions are done using the Calibrant option under the Powder Diffraction menu of FIT2D (Hammersley, 1998). Typically lanthanum hexaboride powder (NIST SRM 660a) is used for calibrating the WAXS detector distance and beam position, and silver behenate is used for SAXS detector distance (Huang et al., 1993). However with its lowest angle diffraction ring appearing at a d-spacing of 58.38Å, it cannot be used for the longest camera lengths. Inspired from the critical dimension SAXS work done at 5ID-D (Hu et al., 2004) we now use a 3600lines/mm constant pitch optical diffraction grating from LightSmyth Technologies to calibrate long sample to detector distances. By collecting the data in transmission and rotating (1Hz) the grating around the beam we produce a powder-like pattern suitable for FIT2D with the first ring at 2778Å.

![Figure 5. Diffraction from a Rotating Silicon grating.](image)

The image on the right shows the diffraction grating mounted on the rotation stage. The X-ray beam propagates from right to left in this image, exiting the beamline vacuum path through a silicon nitride membrane window, diffracting from the grating on the rotation stage, and into SAXS camera beam path through a mica window tipped nose cone. The image on the left shows a portion of the SAXS image which results.
ACKNOWLEDGEMENTS

DND-CAT is supported by the E.I. DuPont de Nemours & Co., The Dow Chemical Company, the U.S. National Science Foundation through Grant DMR-9304725 and the State of Illinois through the Department of Commerce and the Board of Higher Education Grant IBHE HECA NWU 96.


The diode beam stops were constructed at DuPont by Robert F. Knox and Mark G. Bradigan under J. David Londono’s direction.
REFERENCES


