2D Synchrotron Diffraction

Eric Dooryhee **Phone: 631-344-2409**

Email: dooryhee@bnl.gov

Checklist

1. Sample conditioning and mounting
2. Energy
3. Resolution
4. Beam size
5. Angle range
6. Background
7. Acquisition time
8. Run NIST standards or known samples
9. Test data correction and processing: convert to 1D
10. QA: pattern fitting to validate above parameters

1 - Sample Mounting

1. **Reflection**
   a. Stationary sample; shadow on the detector (obstructed signal)
   b. $\theta/2\theta$ condition not fulfilled (diffracted beam size varies with 2θ)
2. **Transmission** (beam stop needed!)
   a. No alignment error, more forgiving if sample position shifts (particularly $\perp$ beam)
   b. No beam over spilling the sample
   c. Not sensitive to sample surface
3. **Spinning – minimize preferred orientation** (spotty rings)
   Not needed in case of nano-grains/crystallites
4. **Packing and containment** (affects scattering power)
   a. > 50% of bulk density
   b. powder grains walking away from the beam

2 - Energy

1. **Effect on Q coverage** (Qmax increases with energy)
2. **Minimize absorption correction – optimize $\mu R \sim 1.2$**
   a. 11bm.xray.aps.anl.gov/absorb/absorb.php
   b. purple.ipmt-hpm.ac.ru/xcalc/xcalc_mysql/transmission.php
   c. henke.lbl.gov/optical_constants/filter2.html
3. **Avoid absorption edges** (minimize fluorescence)
4. **Detector efficiency dramatically changes with energy**
5. **Effect on resolution: $\Delta 2\theta = \frac{1}{2}\, \Delta\lambda/\lambda \tan\theta$**

3 – Resolution (ΔQ)

1. **Peak width** – driven by beam size and sample size (gauge volume), whichever is smaller, and divergence
2. **Number of steps per peak** – driven by pixel size 
3. **Peak overlap** – driven by peak width and distance to detector (PDF is fairly forgiving)
4. **Parallax error** – occurs for too close a detector

Note: for PDF the low angular resolution of the data limits the real-space correlation range that can be studied to a few tens of Å.

4 - Beam Size

1. **Affects resolution**

2. **Scattering volume** (gauge volume) **should contain enough crystallites for good powder averaging**

3. **Asymmetric beam size (aspect ratio ≠ 1)** – results in anisotropic width of the diffraction rings and affects the peak profile after azimuthal integration

5 - Q (or 2θ) coverage: Q_{max} (or $2\theta_{max}$)

1. **Sample-to-Detector Distance**

   a. trade-off between Qmax (R-space resolution) and ΔQ (Q-space resolution)

   b. www.bio.aps.anl.gov/xraytools.html

   c. Qmax and intensity dramatically decrease with distance

2. **(off)-centering of the detector**

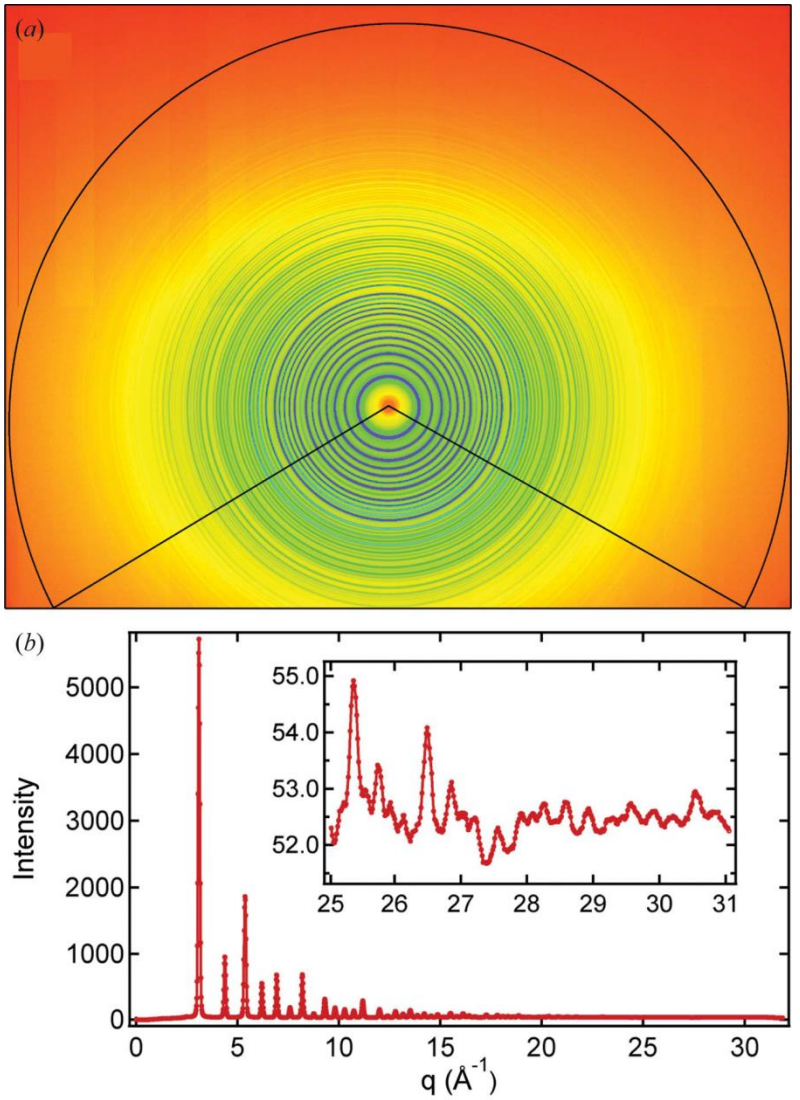
   a. beware some software cannot find the beam center (≅ center of the diffraction rings) if it falls out of the image

3. **Arcs (portions of rings) vs. entire rings (2π)**

Q (or 2θ) coverage: Q_{max} (or $2\theta_{max}$)

Example of a powder diffraction pattern collected from Fe during a 0.4 s exposure (a). The radially integrated pattern from the indicated region (b) shows good peak statistics to q-values in excess of 30Å^{-1}.

Daniels and Drakopoulos et al. JSR 16 (2009)



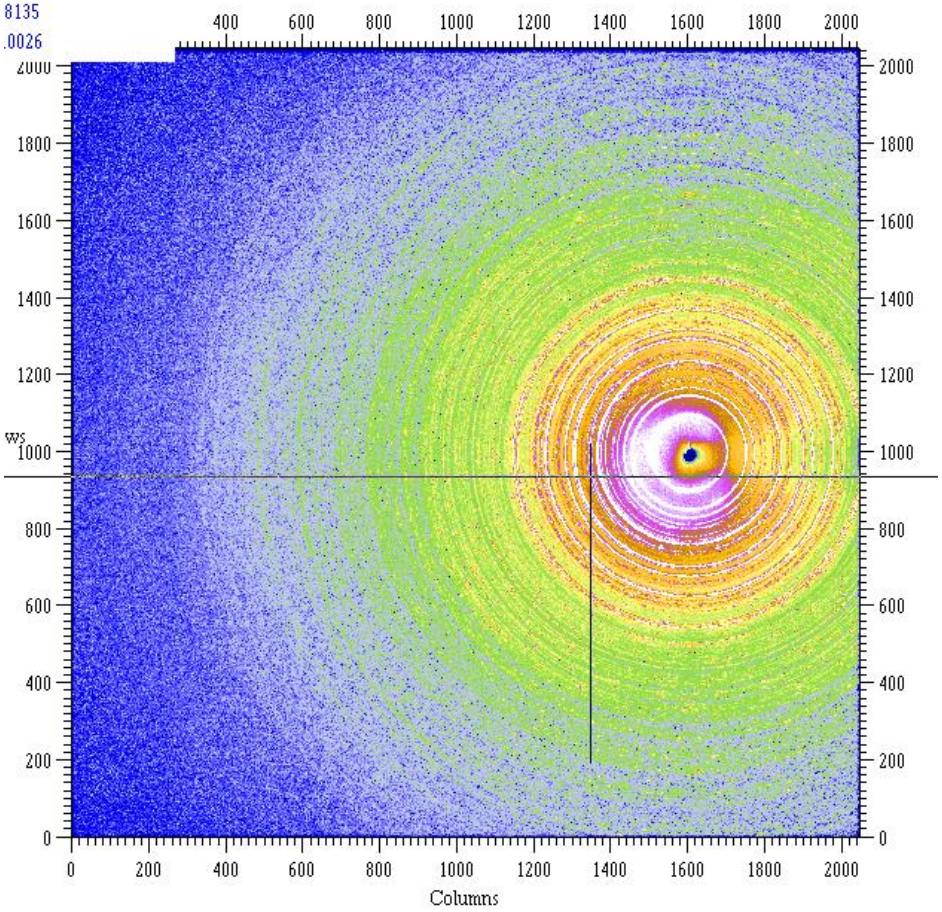
6 - Background

1. **Air scatter** (depends on direct beam path in air)
2. **Beam stop** (alignment, size and distance) **– mind Qmin**
3. **Inelastic and Compton scattering from sample**
4. **Scatter from substrate, windows, surrounding,** *etc…*
5. **Electronic readout**
6. **Collect an "empty" image** (nothing in the beam path)
7. **Collect a background image**, *e.g*. empty holder, bare substrate or empty cell

Background

Low scatterer with inappropriate beam stop size and parasitic air scatter (anisotropic)

Data collected at XPD on a coronene-metal complex.
Courtesy: Dalice Pinero Cruz (University of Puerto Rico)



7 - Acquisition time per image

1. **Avoid saturation** (depends on the dynamic range of the detector: 12 to 17 bits)

2. **Optimize signal/background and signal/noise for weak peaks** – often advantageous to acquire multiple, shorter exposure images as opposed to one long exposure image (*i.e*. 120 × 1sec might be better than 1 × 120sec because detector might saturate if exposed for a long time)

3. **No remanence of strong signal** (current image can be polluted by previous image residual signal)

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9 – Masking (conversion to 1D)

1. **Remove outlier pixels** (zero or saturated; *e.g*. dead pixels, beam stop shadow or Bragg spots)
2. **Remove detector edge pixels**
3. Apply mask consistently across whole stack of images
4. Integrate all rings over the same azimuthal interval (≡ pie)

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Standard Errors

1. **Calculated estimated standard deviations of the fitted parameters can only be calculated correctly when the true uncertainties of the measured intensities are known**

2. **Standard weighting schemes result in meaningless Goodness-Of-Fit values**, *e.g.* $\chi^2 < 1$ in least-squares refinement

3. **Error estimates for intensities derived from area detector data should be calculated** (*e.g.* see High Pressure Research 17 (2000) 315-323)

Detector Market

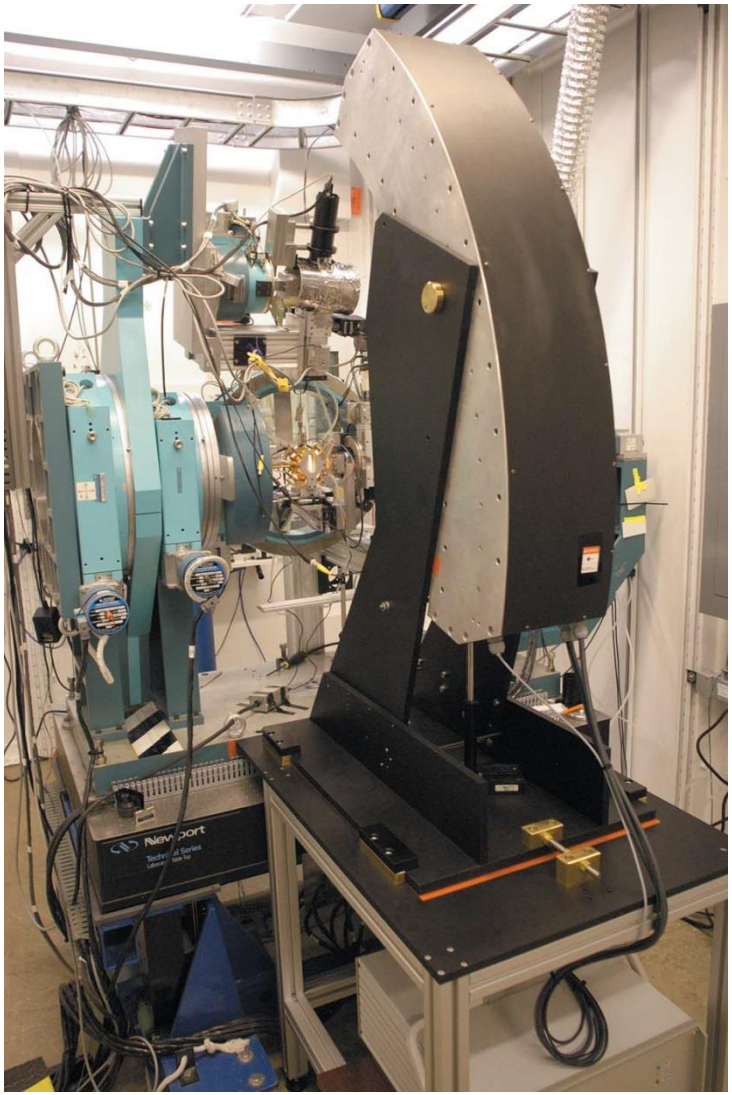
	Specs	Vendors	Comments
Image plates	In/off-line readout (90sec)	MAR345 Fuji	Photosensitive rigid or soft phosphor (*e.g.*, BaFBr :Eu^{3+})
CCD	50μm $(170mm)^2$	MarResearch Princeton RayoniX Rigaku	Fiber-coupled phosphor (with demagnification) to Charge Coupled Device
Amorphous Silicon – CsI:Tl	43cm FOV Up to 100fps 100-200μm pixel	Varex Imaging General Electrics Trixell (Pixium) Anrad (AXS)	Sensor can remain active during readout (no shuttering) rapidly replacing CCDs in many imaging applications, due to reduced cost, higher speed (video rates), and larger size.
CMOS	28.2 x 29.5 cm 75-300μm pixel Up to 90 fps Dynamic range ~ 14,000 Shutterless	Dexela	
Pixel array	55μm pixel 250mm x 25mm CdTe (preferred) or SI	Dectris (Pilatus, Eiger) Pixirad Quantum detectors (Medipix) ADSC	Photon counting absence of readout noise and dark current direct detection of X-rays for a minimum point-spread function

Note: see www1.aps.anl.gov/Detectors/Area-Detectors

Curved Image Plate

The curved image plate (CIP) detector at the 33BM-C beamline at APS, records the X-ray diffraction pattern over a 38.7 2θ range using a 15 mm-wide slit.
Angle pitch 0.00095°
Readout and cleanup time is ~30sec

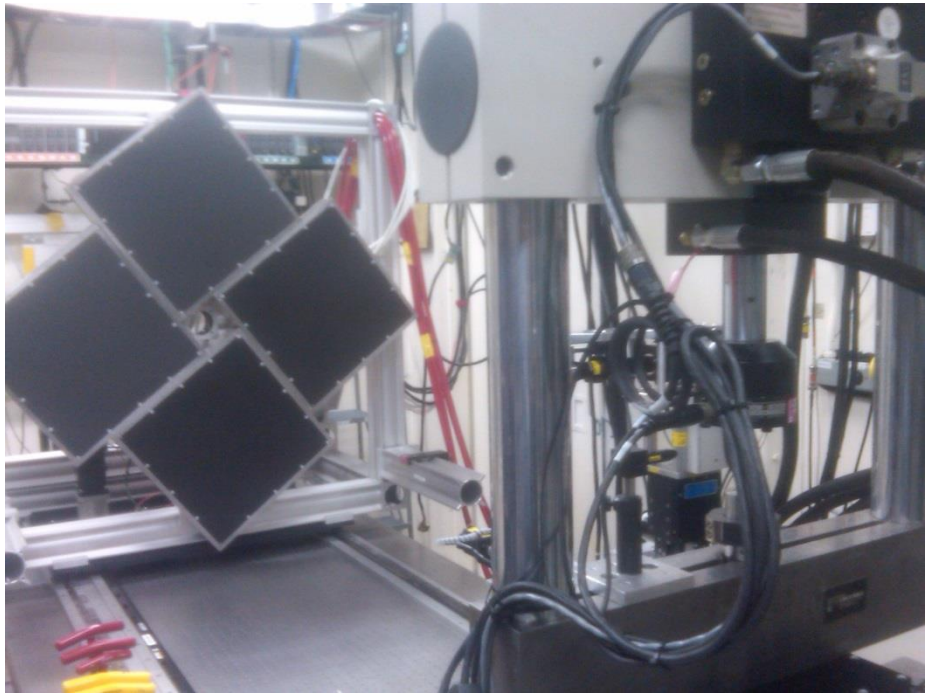
P. Sarin et al. JSR 16 (2009)



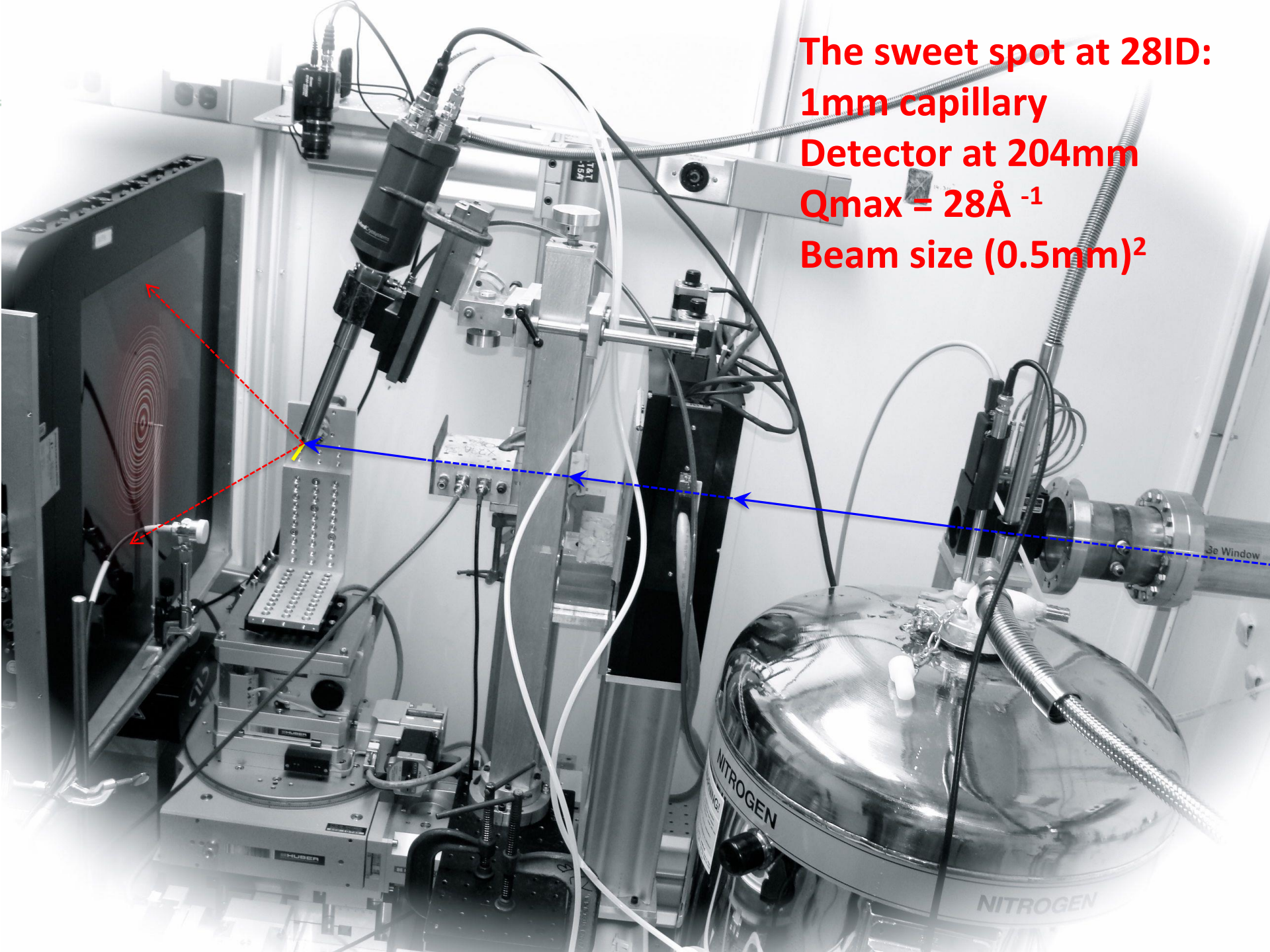
APS - Sector 1

- either coverage of a fairly significant diffraction range at lower angular resolution, with the detector positioned very near the sample

- or the detector well away from the sample to match the pixel size to instrumental resolution, but at the expense of angular range and possible need to combat air absorption.



B. Toby et al. JAC 46 (2013)


The sweet spot at 28ID:
1mm capillary
Detector at 204mm
Qmax = 28Å -1
Beam size (0.5mm)2
Be Window
NITROGEN
NITROGEN

International Tables for Crystallography

Home page = http://it.iucr.org/

H. Powder Diffraction (new: 50 chapters, 800 pages)

1. Introduction to the principles of powder diffraction.
2. Instrumentation for laboratory X-ray studies, synchrotron, neutron and electron diffraction, 2D diffraction, and special environments (temperature, pressure, magnetic fields, reaction cells).
3. Different methodologies used in powder diffraction.
4. Structure determination and validation.
5. Defects, texture and microstructure: stress and strain, grain size and thin films.
6. Review of available software.
7. Applications to: macromolecules, zeolites, mining, ceramics, cement, forensic science, archaeology and pharmaceuticals.

Conclusion

a. **Know your sample prior to 2D work**
   a. Lab data, phase ID, crystallite size, grainy or single crystals, *etc*

b. **Thorough start-up**
   a. How do I distinguish a bad image from a good image?

c. **No complacency**
   a. Can you trust the results? Perform sanity checks.
   b. Refrain from "blindly" collecting 100s of datasets - verify and check before

d. **Execute the checklist !**

Notes:
Your model can only be as good as your diffraction pattern
Exponentially harder to model bad data than good data

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