# x8 Powder XRD SOP

Powder XRD patterns can now be collected using the x8 instrument. Now you can compare an experimental powder XRD pattern (collected at the same T as your single crystal structure) with that calculated from your SC structure to determine the phase purity of your sample. You can take advantage of the low-temperature capabilities of the cryostream. With care and attention, you can even collect data of high enough quality for quantitative powder XRD analyses such as unit cell determination, crystallite size analysis, Rietveld analysis, etc. The suggestions and procedures below assume you will be working with a capillary sample.

Loading the Sample

(1) Cut ~1cm of 0.025" ID polyimide capillary[*] (see below for smaller capillaries)
   a. If the capillary length is too long (probably >2cm), it may collide with the cryostream.
   b. You will want to use the same capillary size for both your sample and the standard
   c. Glass capillaries can also be used, but polyimide is easier to handle/cut and may have a slightly lower background

(2) Put a small plug (~1mm) of modeling clay in one end

(3) Mount the capillary on the goniometer head pin, pushing the plug up at least ~4mm
   a. Having the plug in this position will allow you to store the sample and reuse it after removal from the pin.
   b. Putting the capillary on the pin at this point provides something to grip while filling the capillary.
   c. *Avoid creasing or bending the polyimide. If the capillary becomes bent/creased where the x-ray beam will be, you may need to make a new capillary.

(4) Fill the capillary (ideally with ~3-4mm of sample) and pack the powder as densely as possible
   a. Scoop or tap powder into the open end of the capillary.
   b. The cap of the sample vial provides a nice enclosed surface for doing this & allows for minimal sample loss.
   c. Tap the base of the pin on a hard surface to pack the powder down next to the plug.
   d. Repeat until the capillary is filled with well-packed powder & has ~1mm of space remaining at the top. You will want to view the capillary under a microscope to check for voids in the sample.

(5) Pack a small plug (~1mm) of modeling clay into the remaining space at the capillary's top

(6) Gently wipe excess powder & clay off the outside of the capillary

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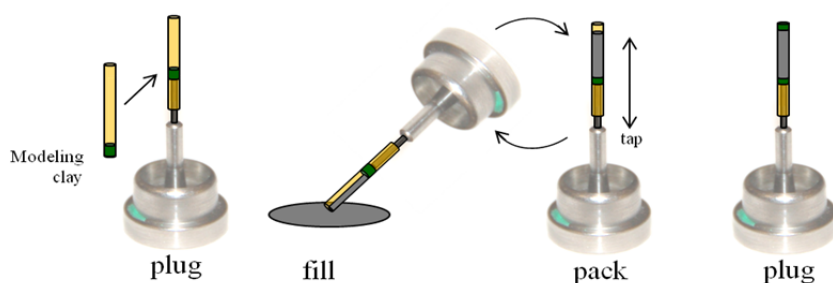
[*] You will need to determine the appropriate capillary size for your sample & standard based on their propensity for x-ray absorption. You can do this either by trial and error or by trying to predict the best capillary size based on the path length & x-ray penetration depth that can be calculated using Highscore Plus. In Highscore, click on Tools/MAC Calculator. Enter the correct anode material, the chemical formula of your sample or standard, and hit 'calculate penetration depth' twice. In the window that opens, enter the sample's density, set the incident angle to 90° (true-ish when chi=0) and set the packing to ~0.5 ("most pressed powder samples have a packing between 0.5 and 1.0," so ~0.5 may be a reasonable estimate for a tapping-packed capillary sample). The path length automatically calculated is the "length the X-rays travel through a material with the given characteristics, until 99% of the intensity is absorbed and only 1% of the initial intensity is transmitted." The penetration depth automatically calculated is "the thickness of the sample contributing 99% of the diffracted intensity for a given incident angle θ." Because we are dealing with capillaries and not flat samples, these estimates are not rigorously accurate, but they give you a fair sense of your sample's/standard's absorbing ability. For example, for a Si standard (density 2.329 g/cm3, packing 0.5, incident angle 90°) the calculated penetration depth is ~318 μm, which matches rather well the length of the medium capillary size that was determined by trial and error to be an adequate capillary size for Si.
   a. 0.0250" ID = 635μm
   b. 0.0122" ID = 310μm (*probably adequate for the Si standard)
   c. 0.0078" ID = 198μm

Variations

Air sensitive samples:
Follow the same procedure, but fill the capillary with powder and insert the second plug inside your glove box. Use a different material for the plugs (e.g. glue) if you need a better seal from the atmosphere. Obviously if using glue, check compatibilities of all materials involved and avoid permanently gluing the pin to your sample (unless you bought your own pin…).

High absorption samples:
Use a smaller capillary (see below) or coat the outside of the capillary with powder. To do this, put a *very* thin film of Vaseline on the outside of the capillary and coat it with a very thin film of the powder; try to get the coating of powder as even as possible. Not ideal for storage, multiple uses, or recovering your sample, but potentially effective for collecting data.

Small sample sizes:
Use a smaller capillary (see below) or coat the outside of the capillary with powder (see above).

Small capillaries:
Sometimes capillaries smaller than 0.025" ID must be used. These will not fit on the pins; instead, you can use a small portion of the 0.025" capillary as a sheath for the smaller capillaries (see images below). Otherwise, the sample-loading process is very similar:

(1) Cut ~0.7-1.0 cm of the appropriate-sized* polyimide capillary
   a. Note: the smaller capillaries can be difficult to handle & keep track of – resting them on the sticky part of a post-it note to keep them in place and using tweezers to (gently!) handle them can be helpful. (Again, avoid bending or creasing the capillary.)
(2) Put a plug of modeling clay in one end (~1-5mm)
   a. Leave ~4-5mm of the capillary open for the sample and second plug
(3) Fill the capillary (ideally with ~3-4mm of sample) and pack the powder as densely as possible
   a. Scoop or tap powder into the open end of the capillary.
      i. The cap of the sample vial provides a nice enclosed surface for doing this & allows for minimal sample loss.
   b. Tap the base of the capillary on a hard surface to pack the powder down next to the plug.
   c. Repeat until the capillary is filled with well-packed powder & has ~1mm of space remaining at the top. You will want to view the capillary under a microscope to check for voids in the sample.
(4) Pack a small plug (~1mm) of modeling clay into the remaining space at the capillary's top
(5) Gently wipe excess powder & clay off the outside of the capillary, & set it aside for the moment
(6) Make the sheath:
   a. Cut ~5-6 mm of the 0.025" polyimide capillary
   b. Put a large plug (~2-3 mm) of modeling clay in one end
   c. Mount the capillary on the goniometer head pin, pushing the plug up ~2-3mm
(7) Insert the smaller capillary into the sheath, sticking it down into the large plug of clay so that it is as vertically aligned and centered within the sheath as possible
   a. This may make centering it on the instrument a bit nicer.
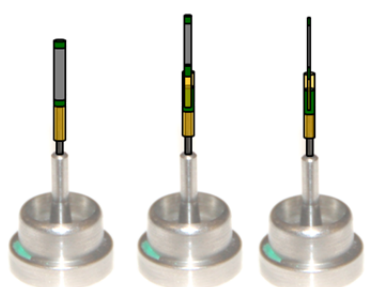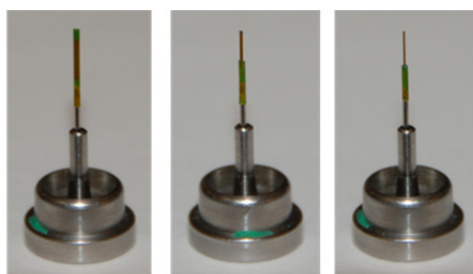
| 0.025" | 0.0122" | 0.0078" | | 0.025" | 0.0122" | 0.0078" |

Centering the sample

As with a single crystal, use the APEX2server program (on computer input #1) to center the capillary in the x-ray beam. In the Simple Scans tab, move the goniometer to a good mounting/centering position. Suggestions:

Cu source settings: Mo source settings:

Detector Distance = 150 mm   Detector Distance = 150 mm
2Theta = -30°   2Theta = -60°
Omega = 180°   Omega = 150°
Phi = -52°   Phi = -52°
Chi = 55°   Chi = 55°

(Using chi = 55° instead of chi = 90° decreases the speed at which ice crystals begin to form on the capillary.)

Use the goniomter head tool to adjust the knobs on the goniometer head until the image of the capillary from the camera remains centered while performing 90° and 180° phi scans in the 'Center Crystal' tab.
You can double check your centering by setting chi = 0 and performing 90° and 180° phi scans. This is the easiest location from which to spot misalignment but the cryostream makes it not ideal for adjusting the centering.

Preliminary scans

You may wish to do some preliminary 360° Phi scans (in the Simple Scans tab) of your sample to check the signal/absorption, determine the necessary exposure time, choose the most appropriate λ, etc. Suggested settings for these quick scans:

Detector Distance = 150 mm
2Theta = ±15, ±30, ±60, +90, +120° (or whatever angles you anticipate peaks/rings)
Omega = 6° (omega can remain at 6° at all 2theta if chi=0° but omega must be ½ 2theta if chi≠0° to imitate Bragg-Brentano geometry)
Phi = 0°
Chi = 0°

Setting the exposure time: Move the detector to a 2Theta region containing weak (but still visible) peaks/rings and optimize the exposure time based on this region to ensure that all necessary peaks are visible. (Make sure you are not saturating the detector with the strong peaks/rings, though.)

Selecting the x-ray λ: Things to consider:

- Angular range
    - o Mo radiation will allow you to probe a larger range of Q-space because of its smaller λ
    - o Mo also has a larger range of data uninhibited by the beamstop due to the instrument geometry
        - Positive scan direction: The Mo source can attain an angular range between 0-111°2θ. Here, the low angle range of the Cu source is limited by the double beamstop shadow, making its usable angular range 33-150°2θ.
        - Negative scan direction: Here, the low angle range of the Mo source is the one that is limited by the double beamstop shadow, but the high angle range for *both* sources is truncated by the cryostream anchor making the usable angular range 0 to -102°2θ for Cu and -33 to -126°2θ for Mo.

- NOTE: Currently, there is no convenient or automated way of combining the low and high angle data from the negative and positive scan directions, though it can be done manually†.
- Peak Resolution
  o Mo may probe a larger range of Q space, but Cu radiation will spread the rings further apart, allowing for more well-resolved peaks in the 2D XRD pattern. You will need to decide which is more important, range or resolution.
- Absorption and/or fluorescence
  o Some samples have severe absorption or fluorescence issues with certain x-ray sources (which issues should be avoided). For example, samples containing Fe, Co, or Ni fluoresce under Cu radiation, giving highly inconvenient backgrounds and low signal/noise ratios. Also, LaB_6 had severe absorption issues under Cu radiation in all three mentioned capillary sizes.

Setting up the run

In Apex II (on computer input #2), create a new project in your group login under the name P_yy### where 'yy' is the year (13 for 2013) and '###' is the next consecutive sample number for powder samples run that year (for example, the first powder sample run in 2014 will have the name P_14001, the second sample will be P_14002, etc.).

In the Experiment tab of your new project:

(1) Change the default time to the desired optimized setting (30s, 60s, 90s, 120s, etc.)
(2) Check the box next to "unwarp images" (very important!)
    a. The frames will be collected as individual, stationary phi 360 scans every 12° along the 2θ axis. The frames are thus like tangents along a semicircle, so the information at the edges is 'warped' compared to the center. They must be 'unwarped' to be combined.
(3) Click on 'Load Table' at the bottom of the screen to load one of the following preset run strategies from z:/frames based on the radiation you are using (Cu or Mo) and the aims of your experiment:
    a. Powder_chi0_Cu.exp or Powder_chi0_Mo.exp → will give more accurate quantitative analyses
        i. Chi = 0 is the preferred chi angle because it should maintain the most constant irradiated volume of sample (if the sample is well-centered) which is necessary for doing quantitative analyses such as crystallite size estimates, Rietveld refinements, etc. with the powder pattern.
        ii. This setting may lead to more significant temperature gradients throughout the sample.
    b. Powder_chi54_Cu.exp or Powder_chi54_Mo.exp → use to get (potentially) more accurate temperature control when the low temperature capability of the cryostream is your aim
        i. A chi angle of 54.8 *might* allow the N_2 stream to pinpoint the region of sample in the beam and control its temperature more accurately (this has not been verified). The irradiated volume may not be completely constant, however, inhibiting quantitative analysis (though the differences might be small enough to be negligible).
        ii. Note that in the chi = 54.8 strategy, ω = θ (or ω = ½ 2θ). If you edit the file or create your own run strategy, it is important to maintain this ratio when chi ≠ 0 to mimic the normal powder Bragg-Brentano geometry and keep the irradiated sample volume as constant as possible.

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† Collect the positive and negative scans at the same time (with the same centering) to minimize differences in intensity due to different sample mountings. Correct for any small offsets in the background intensity between the two scans, and merge the data at a point where the slopes of the background intensities are aligned.

Integrating the data

(1) In the Pilot tab in the left column of the Apex II software, click on the XRD^2 Eval icon

(2) Click on the open folder icon to the right of the empty (and tinted pink) drop-down box

(3) Navigate to your data folder and simultaneously select all of the frames for *either* the negative (scans 1-8 for Cu, 1-11 for Mo) *OR* positive (scans 9-20 for Cu, 12-21 for Mo) scan directions. Click open. The program will then read in and merge all frames.

    a. If you forgot to check the 'unwarp images' box, you will get an error here saying "The frames below are not unwarped and cannot be integrated." You will need to recollect the data, with the box checked this time.

(4) For data from the positive scan direction, right click on the merged image and select 'Flip Image' so that the 2θ values ascend from left to right as is typical in powder patterns.

(5) Click on the integration tool (the yellow square with a notch taken out of its left side)

(6) Draw a region in the merged ring pattern (Click on the left then the right ends of the ring pattern)

(7) Use the integration window at the bottom of the screen to adjust the values of the integration region

    a. Choose a start and an end angle, cutting out any low angle areas affected by the beamstop or any high angle areas where the intensity drops off

    b. Select a region height. The signal from each ring seems to be normalized by the number of pixels contributing to it, so the signal/noise ratio is best when the region height is large. Because of the merging process and other inconsistencies at the top & bottom edges of the frames, you may not want to extend the region height to its maximum, but a region height of 490 (out of 511) seemed to work well.

        i. Note: the apparent shape of the integration region as seen on the screen does not affect the integration.

(8) Right click in the integration region on the image and select 'Integrate'. Your 2D powder pattern will appear in the graph at the bottom of the screen.

(9) With the integration region still selected, right click again and select 'Create Raw File'. Give it a name, and you have your powder pattern.

The .raw file can be read by most powder diffraction analysis programs, including the PANalytical Highscore Plus program installed here. If necessary, you can convert your pattern to a different format using the freely available PowDLL Converter program (that is installed on the desktop of Mike's old computer).

Removing & Storing the sample

NOTE: If chi=0 angles were used, the pin will be *very* cold when the run finishes. Wait a few minutes for it to warm up before pulling it off of the goiniometer or you will freeze-burn your fingers. Trust me.

(1) Remove the capillary from the pin

    a. Use tweezers to grip the pin and hold it in place, and use your fingers to grip the base of the capillary

    b. Gently pull up on the capillary (be careful not to crease or bend it). If the lower modeling clay plug sticks to the pin, push the capillary back down and try again. Try twisting.

        i. NOTE: the top of the pin is slanted, so if you reuse the sample, it will have a 'preferred orientation.' =]

(2) Make a label for the capillary

    a. One way to do this is to cut a small strip of a post-it note (from the sticky part) and fold it over on itself with the capillary in the middle, making a sort of mini flag on which you can write the sample ID. The join can be reinforced with tape if necessary.

    b. For the small capillaries in sheaths, store the capillary and sheath together as-is (don't disassemble it). Setting the whole thing on the sticky part of a post-it note (with the sample ID on the other side) is an easy way to store it.

        i. The labels can be useful handles, too.

(3) Clean the pin and put it back in its place

Data analysis

See Scott Speakman's powder XRD and Highscore Plus tutorials that are freely available on the web:
http://prism.mit.edu/xray/tutorials.htm