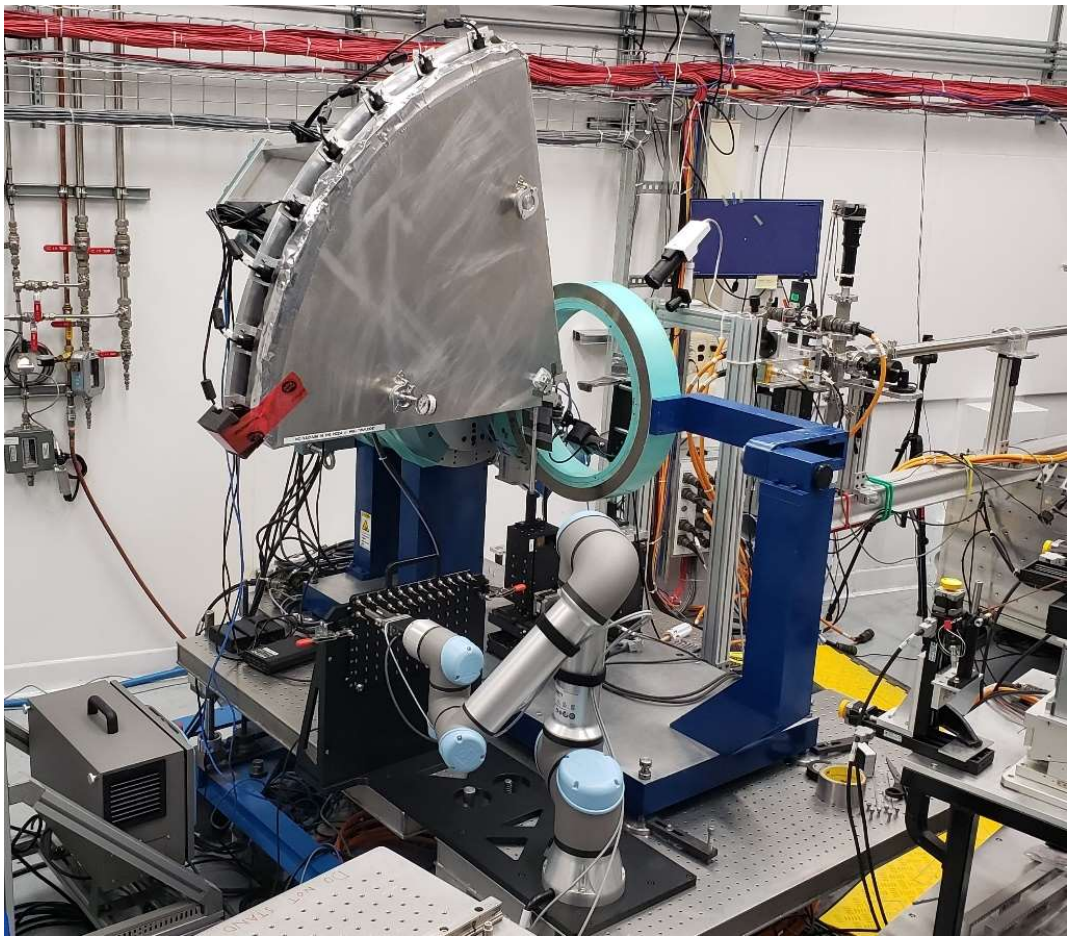
High-Resolution Powder Diffraction Endstation

Standard Operating Procedures



Adam Leontowich, Karim Louca
November 13, 2024
Revision 1

Brockhouse Sector (BXDS) Contact List

Note: First dial "9" to access an *external* line from a CLS phone. For CLS internal numbers, you only need to dial the 4-digit extension number.

Serious emergency (Fire/Ambulance):	**911**
U of S Security:	9-306-966-5555

Beamline and CLS staff:	**Extension**	**Personal cell**
Beatriz Moreno (beamline responsible)	3868	306-241-1999
Adam Leontowich	3555	306-850-0408
Graham King	3760	639-998-1886
Narayana Appathurai	3648	306-514-1384
Karim Louca	3583	226-504-1169
Al Rahemtulla	3530	519-993-9137
Joel Reid	3854	
Garth Steel (controls lead)	3730	
Deborah Nguyen (mech. eng. lead)	3656	
Brian Schneider (elec. eng. lead)	3841	

Call the beamlines:

Wiggler Low Energy beamline (WLE, SOE-1)	657-3821
Wiggler High Energy beamline (WHE, SOE-2)	657-3830
In-Vacuum Undulator beamline (IVU, SOE-3)	657-3832

Other important contacts:

Floor coordinator	657-3639
Control room	657-3570
User services office (USO)	657-3700
Health and safety (HSE)	657-3663
Front desk	657-3500

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Introduction

Some expectations and responsibilities for staff and users

Users are responsible for:

- Requesting the PXRD endstation in their proposals, understanding that the photon energy is fixed at 15.1 keV. We cannot change it.
- Sample preparation, including purchasing capillaries, grinding, diluting, loading and sealing the powders in capillaries.
- Documenting and communicating sample details, including calculating the absorption, labelling with a priority order, the compound name, and any special instructions (e.g., temperature ramp and hold times). *For the first visit, please discuss sample mounting with staff before sending samples.*
- Optional: Loading capillary samples on stubs, loading the stub and the sample plate, and operating the data collection software SPEC during measurements.
- Leaving a beamline unattended note if they leave the user area for more than 15 minutes.
- Cleaning up the area after the beamtime has ended.
- Reporting any perceived issues to beamline staff, before attempting to fix them.

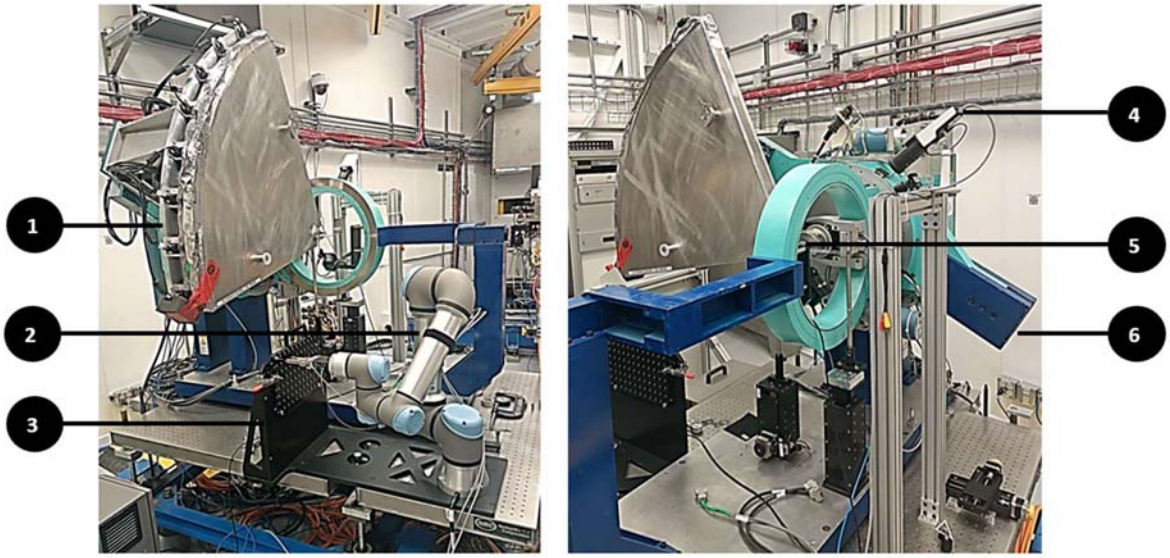
BXDS staff are responsible for:

- Instructing the users on safe operation of the Sector (BSO training), endstation and software.
- Assisting with signing onto the experiment permit at the start of the run.
- Setting up, aligning and calibrating the beamline and endstation to enable the users' experiments.
- Loading capillary samples on stubs, loading the stub and the sample plate, and operating the data collection software SPEC during measurements.
- Prompt troubleshooting of any issues reported by users.
- Moving the users' data over to CLS long term data storage, after the run is complete.
- Updating and maintaining the online logbook in Confluence.
- Periodic maintenance and upgrades of the Huber endstation to support safe, trouble free operation.

Beamline staff are here to help – please ask us questions! Tell us your comments and suggestions!

The High-Resolution Power Diffraction Endstation

The core of the instrument is a four-circle diffractometer made by Huber. It was donated to BXDS by IBM and arrived at CLS in 2013. It had previously been in user operation at the X10A beamline of NSLS-I, Brookhaven, NY, USA. First user measurements at the BXDS-WLE beamline were performed in summer 2019, using a single Mythen detector and an in-house designed sample spinner with manual alignment. In March 2024, a major CFI funded upgrade to our PXRD instrument was completed. We added a robot arm, an automated sample spinning alignment system, and went from 1 to 8 Mythen detectors.



1. Series of Mythen Detectors
2. Robot Arm
3. Robot Sample Holder
4. Camera for PXRD Spinner
5. PXRD Sample Spinner
6. 2Theta Stage

Norman Huber inspecting our Phi stage in Summer 2018.

Control System

The PXRD endstation and the beamline are controlled using programs on the CLS desktop computer OPI1603-002, which runs a version of Scientific Linux. Upon starting or restarting the computer, log in with the following details:

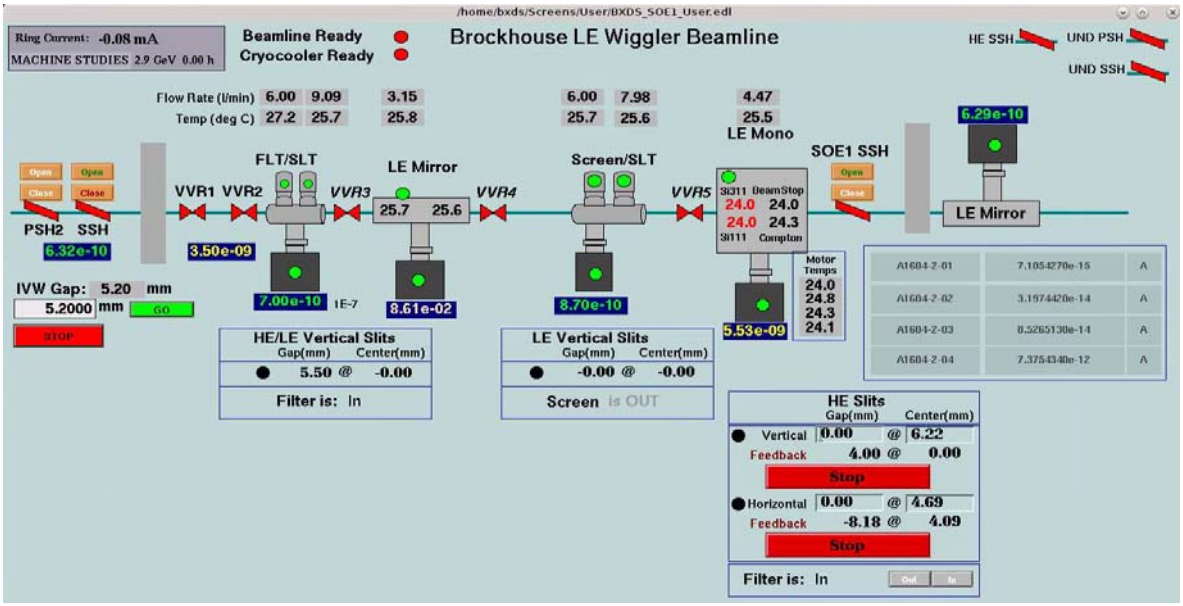
User name: Password:
This will bring you to the main screen:

From this screen one can access the four most important programs for running experiments:

- BXDS User
- BXDS Picoammeters
- SPEC
- PyMCA

There are also beamline cameras accessible on a separate computer, WKS-W004716 (monitors are located on top of the OPI1603-002 monitors and labelled). The beamline cameras are described in the WLE Beamline Manual.

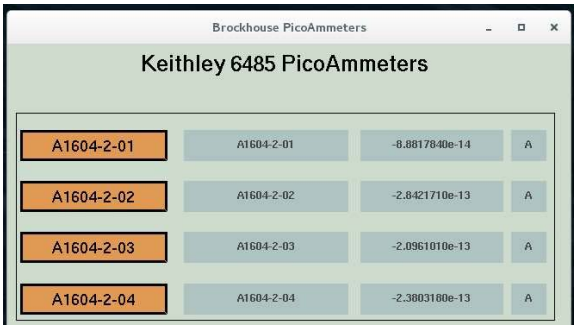
BXDS SOE1 User



This EPICS application provides an overview of the LE beamline, and presents the status and values of beamline components including vacuum, temperature, valves and shutters. **Users should be aware of how to open/close shutters using this screen.** This program can be opened and closed at will.

BXDS Picoammeters

This EPICS application displays the current readings of several Keithley 6485 picoammeters of the Sector. The top four readings are the picoammeters inside SOE-1. Typically, these picoammeters are connected to the four ion chambers. Sometimes they are temporarily set up to read diodes or active beamstops.

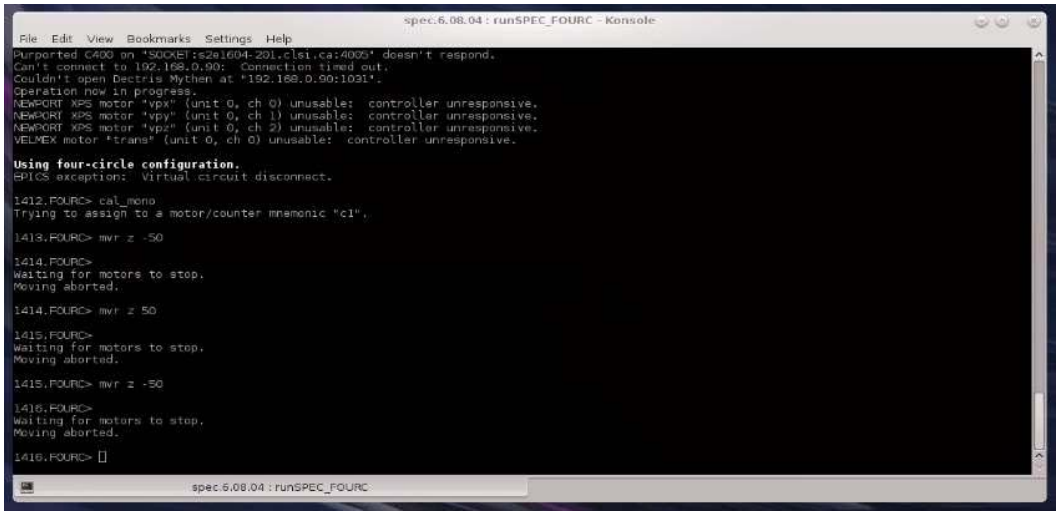


01 – Downstream of the Slit 1 and the filter wheel but upstream of the M2 mirror. Useful for setting Slit 1 and the filter wheel.
02 – Optional. Just downstream of the M2 mirror. Useful for setting the M2 mirror angle.
03 – At the end of the LE translation table, and downstream of Slit 2. Useful for setting slit 2 and determining the flux on the sample.
04 – Optional. On or downstream of the endstation.

Values of 10^{-13} A or less are the baseline noise level. This program can be opened and closed at will.

SPEC

SPEC is the main piece of software used to run experiments. SPEC features a command line interface, and controls all of the motors, takes data from all of the detectors, runs scans, shutters, saves the data, etc.



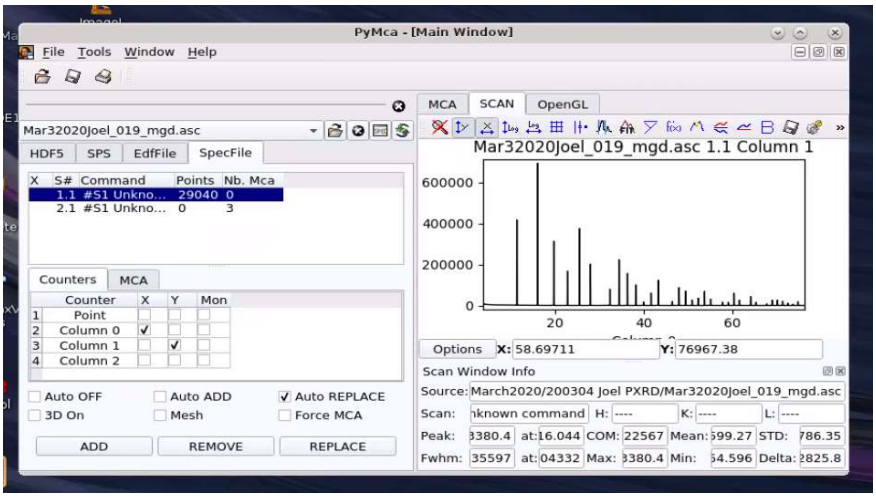
Use the command "ctrl-C" to stop a motor move or any operation in progress!!
Users will need to learn a handful of commands to run their experiments independently. The SPEC manual and tutorials can be found on the company's website, https://www.certif.com/spec_manual/idx.html , and a printed copy is available at the beamline.

To run SPEC:

Click on the SPEC folder on the desktop, and then click the ***FOURC.desktop*** version. SPEC can be closed by typing "quit" in the command line. When SPEC is closed, most information such as the motor positions and soft limits will be retained. However, some information such as the Mythen calibration setup details will be lost. Therefore, **users should avoid closing and re-opening SPEC.**

PyMCA

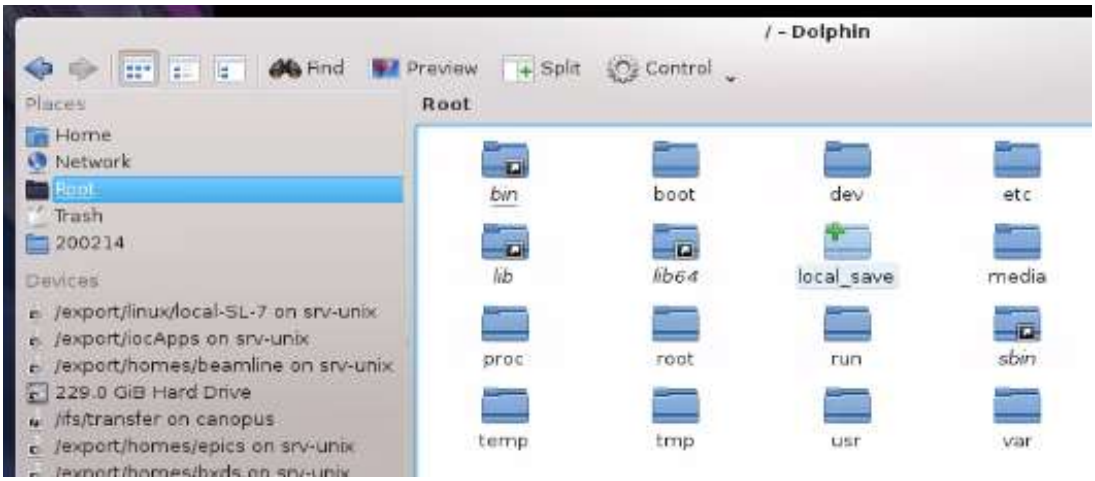
PyMCA is a free program (http://pymca.sourceforge.net/) that is very useful for data analysis on the fly, particularly for looking at Mythen or SPEC data files. This program can be opened and closed at will.



Data Handling

Data is saved automatically to a folder on a local hard drive during the measurement. Navigation and creation of folders can be done from a terminal or the File Manager application,

At the start of a user run, beamline staff will create a folder inside the directory root/local_save. This is the local hard drive on OPI1603-002. Don't use special characters or blank spaces in the directory name.



Users and staff can direct the data to save in these locations using the following SPEC commands:

- newfile, the general SPEC log file
- mname, for Mythen data

Check that data files are saving as the data is coming in. Press F5 to refresh the file folder. Users can transfer their data to a removable USB drive during the experiment or when the experiment is complete.

At the end of the user run, BXDS staff will manually transfer the data to a folder on Loki corresponding to the project number for that specific user group. Any folders or files in the directory root/local_save should be deleted after the transfer is complete.

We will endeavor to store user data as long as possible, at least one year. We also use globus.org to transfer large data sets to remote users.

Sample Preparation Guidelines

We highly recommended discussing any questions about sample prep and mounting before arriving for beamtime. The data acquisition is very rapid, and the beamline is oversubscribed. Therefore, users are strongly encouraged to prep all samples as detailed below before your scheduled time. *Help keep our workspace safe by preparing all samples in the Life Science Lab, not in the user area*.

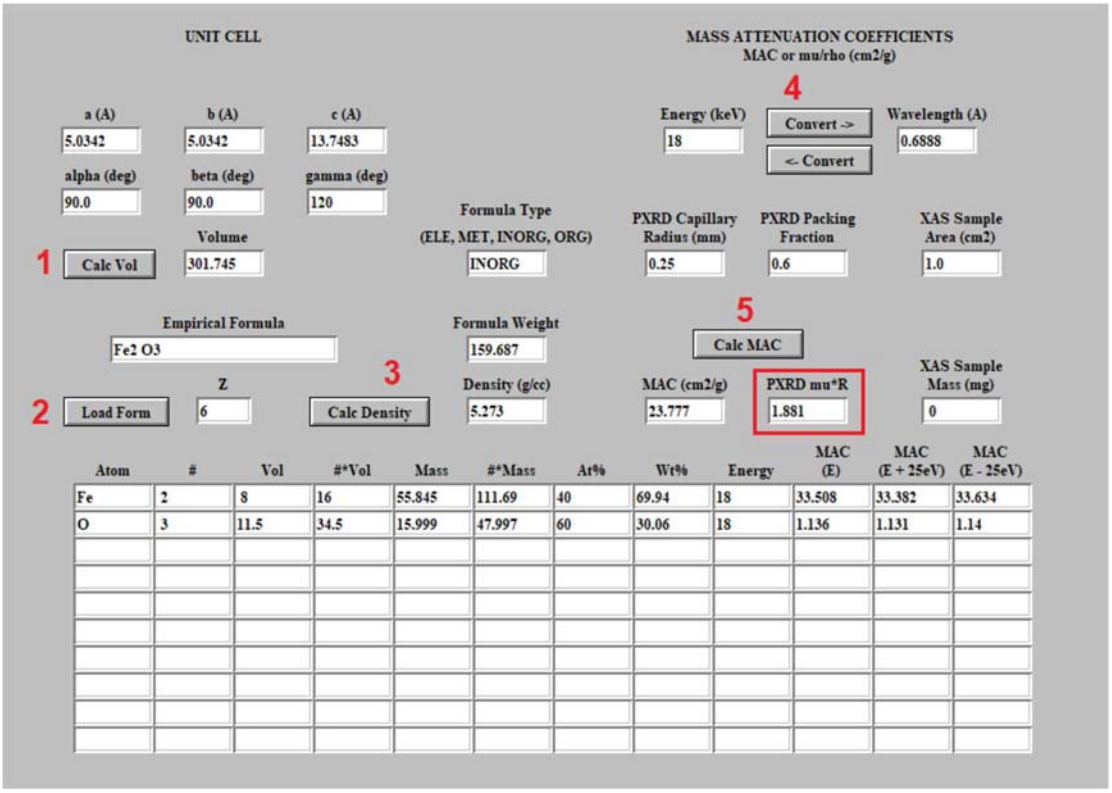
Purchase your capillaries:

Users will purchase their own capillaries, and pack their powdered samples into capillary tubes. Standard capillaries for this endstation are polyimide/Kapton, 0.5 mm inner diameter. These capillaries are sourced from VWR, part MFLX95820-04. Samples which are very air-sensitive, or those which are simply not compatible with Kapton can be loaded in quartz capillaries and flame sealed. These can be purchased as a custom order from Friedrich and Dimmock: 0.5 mm ID, 0.7 mm OD, 75 mm total length.

Consider sample absorption:

For each sample, users must calculate the sample absorption (also called µR) at our wavelength of 0.81931 Å. We use the free program MAC 3.0 for the calculation.

1. Type in the unit cell and press the **Calc Vol** button.
2. Type in the elemental formula, and press the **Load Form** button. The estimated number of formula units (Z) should be close to the correct value, but change it to the exact value.
3. Press the **Calc Density** button.
4. Type in either the energy or wavelength for the experiment and press the appropriate **Convert** button to calculate the wavelength or energy.
5. Type in the radius of the capillary for the experiment (not the diameter) and press the **Calc MAC** button. The **PXRD mu*R** will be calculated.



Absorption (µR) value	Interpretation
0 to 0.5	Low absorption, no correction needed during Rietveld refinement.
0.5 – 1.0	Normal absorption, correction may be needed for precise displacement (thermal) parameters during Rietveld refinement.
1 – 2.5	High absorption, correction recommended for Rietveld refinement.
>2.5	Absorption is too large, consider an alternative sample preparation (dilute the sample, possibly smaller capillary diameter, or higher energy).

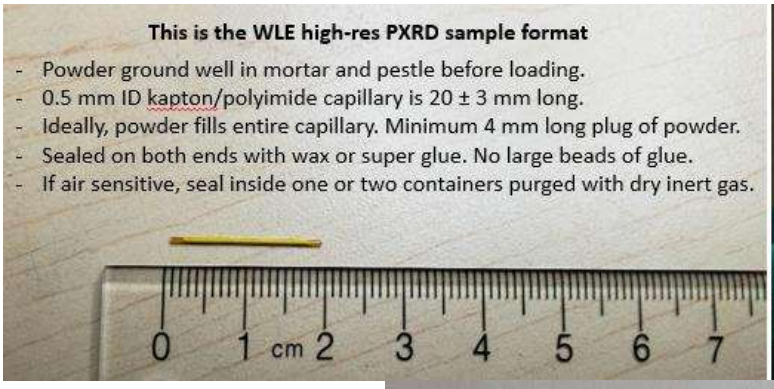
If calculated absorption is >3 in a 0.5 mm capillary, the sample can be diluted. Crushed up fused silica glassware works well for diluting samples. Dilute highly absorbing samples so that the µR is less than 3… µR around 2 seems to be best. Dilution up to a factor of 16 has been successful. A factor of 20 was found to be too dilute.

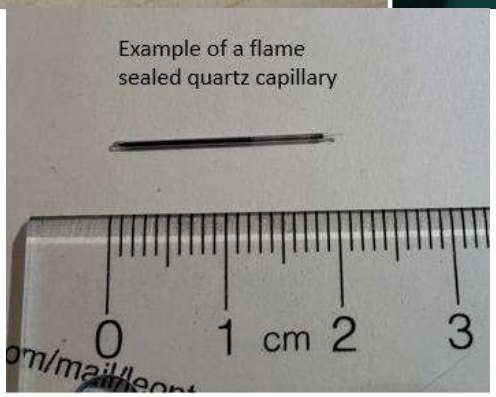
Prepare a nice powder:

Large grains will reduce the quality of the data. If the sample is a mixture, and the mixture is not homogeneous within the beam area (150 µm V × 450 µm H FWHM), the phase fractions measured will not be reproducible. The solution is to grind samples well with a mortar and pestle (or mechanically micronized, if possible) to a crystallite size on the order of 1 µm, provided this can be completed without inherently damaging the sample. Mineralogical and inorganic materials samples can generally (but not always) be grinded or micronized to reduce crystallite size without significantly changing other properties of the sample (like the crystallographic phase observed or the phase composition of multiphase mixtures). Conversely, pharmaceutical and organic samples are often more sensitive to grinding, which may induce phase changes to new crystalline polymorphs, undesirably produce nano-crystalline size or transformation to an amorphous phase.

Fill and seal the capillary:

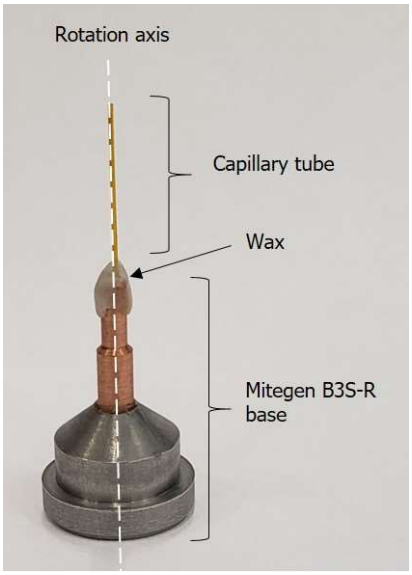
Proper size and sealing is important: The capillary should ideally be 20 mm long (not more than 25 mm, and not less than 10 mm). Pack the powder in to create a plug of material at least 4 mm long (preferably as full as possible). You can use a small diameter wire, or small diameter Kapton capillary to pack powder into the capillary. Kapton capillaries must be sealed on both ends with wax or superglue, even if the compound is not air sensitive. Take care not to form a bead of glue at the end which is wider than the capillary, or it may not be possible to fit it in the magnetic stub holder. If the sample is air-sensitive, ship it within one or two air-tight containers purged with dry inert gas (for example, a capillary in a small glass vial inside a small plastic bag). These packages can be opened at the beamline immediately before the data collection.

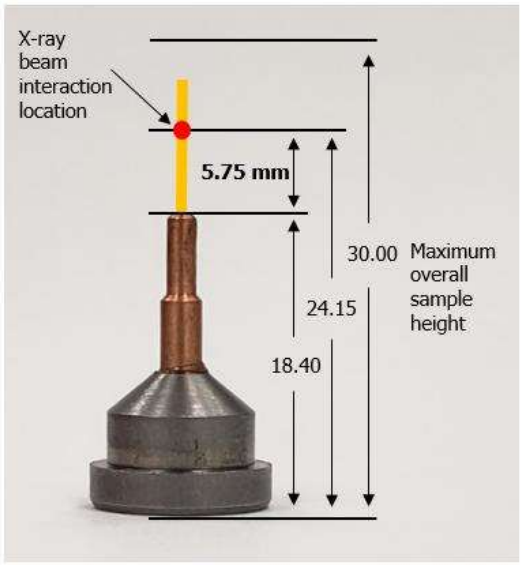




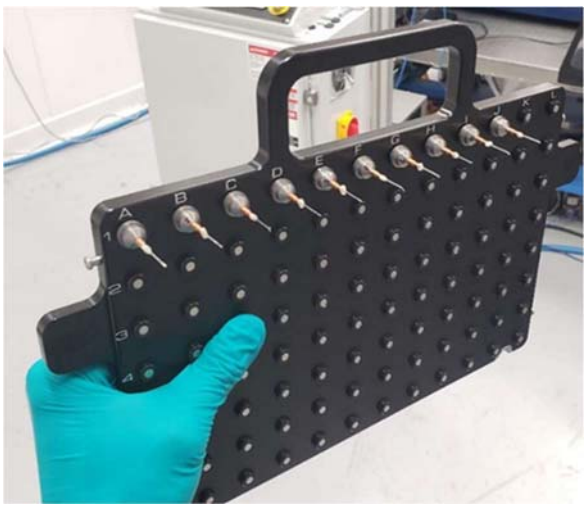
The sealed capillary is then mounted on a reusable magnetic stub with a small amount of wax. The magnetic stubs are from Mitigen, Goniometer Base Type B3S-R, GB-B3S-R-40. We will provide the stubs for users. We generally do not mail stubs or capillaries to users. You send or bring the pre-prepared capillaries, which are mounted to stubs on-site. Some users buy their own set of stubs so all sample prep steps are complete in advance.

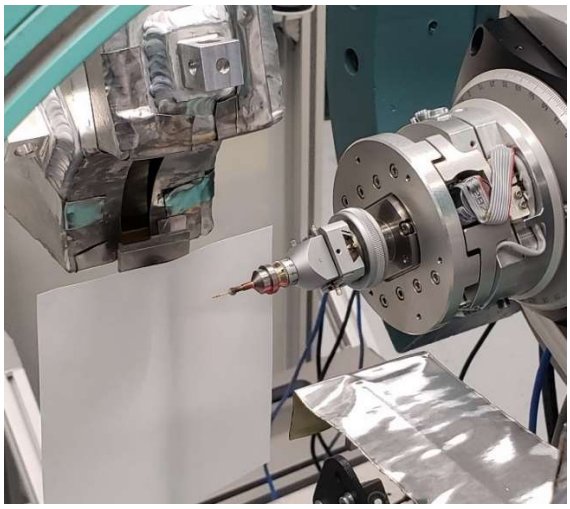
The capillary needs to be aligned colinear with the rotation axis of the stub. Rotate, check and set it by hand when installing the capillary in the stub. The spinning sample must be aligned so that the wobble is less than 0.5x the capillary diameter (Bergamaschi et al., JSR, 17, 653 2010), or else the peak shape will change significantly. The capillaries are measured oriented horizontally at a slight downward angle of 2° (this keeps loose powder particles from moving out of the beam during measurement), and spinning at a rate of 2 Hz.





Beam size: 150 µm vertical × 450 µm horizontal





Sample Measurement

For best results, we encourage users to,

1. Prepare all samples in capillaries ahead of the scheduled beamtime.
2. Create a priority list. Ensure that your most important measurements get done first in case there are unexpected problems.
3. Use a very simple naming convention for your samples (A1, A2, A3, B1, B2, C1, etc.). This makes it much easier for staff who receive hundreds of samples a week.
4. *For a PXRD proposal, estimate 2 hours for initial instrument setup and calibration, and 10 minutes per sample at room temperature. If temperature control is required, mention you require the Oxford Cryostream for temperature control, and any proposed ramps.*

Reminders for staff:

- Log onto the permit
- Make a daily entry in the Confluence logbook.
- Disable unnecessary detectors to simplify the user screen information ("disable c1 c2 c3 c4 ccdtot roinet").
- Lighting is important: All hutch lights need to be on for the auto-alignment routine to work well.
-

"Division by zero" error : Mythen mcal needs to be re-entered.

Measurement range
λ = 0.81931 Å (15132.8 eV) ← This value can be determined exactly by refining LaB6
2θ = 1.6° - 84°
q = 0.22 Å-1 - 10.26 Å-1
d spacing = 28.5 Å - 0.61 Å
Effective 2θ step size: 0.0025°

Ctrl + C command will stop whatever SPEC is doing. Use this command if you notice something wrong.

Fully automated batch mode measurement

- Enter in the sample locations and file names in the script "powder", the file name must be in quotations, "test".
- Save it in local_save
- Type "do powder"

Batch will run, repeat when finished

Automatic loading and aligning, but manually running samples

- robot_unload
- robot_load(1) (Where 1 is the sample position in the sample tray)
- mname _____
- ascan tth -7 3 40 2
- robot_unload

Repeat when sample is unloaded

Manual loading, aligning and running samples

- spin off
- Remove old sample, hand align new sample → (Watch the sample on the camera screen while rotating the spinner by hand. Center the sample by shifting the stub on the magnetic base. If necessary, remove the sample stub, reposition the capillary in the stub, and add it back on the magnetic base.
- Move the capillary into or out of the magnetic stub to position the sample inboard-outboard.)
- Lock up hutch
- open the shutter
- spin on
- mname _____
- ascan tth -7 3 40 2

Repeat when scan is finished

SPEC macros for robot operation

- robot_load(num) – loads sample from palette to diffractor and runs the sample alignment. num is an integer corresponding to sample number in the palette. Note the palette is alphanumeric but sample number increases left to right (A1 = 1, A2 = 13, A3 = 25…).
- robot_unload – unloads a sample currently mounted on the diffractometer and returns it to its designated spot on the palette. Note, this only works for samples loaded onto the diffractometer using the robot.
- single_sample(sample_name, num) – loads sample, aligns sample, runs two-theta scan, unloads sample. Requires mythens to be set up and shutters open.

Reviewing and Processing the Data

Three types of files are produced in the data collection process,

Files with the extension .xye are the important PXRD data after merging. The format is essentially that of TOPAS data with no header. The first column is 2θ, the second column is intensity in total counts, and the third column is error.

The files with no extension are the individual frames from the scan, and can be viewed with PyMCA. These frames get merged together to form the .xye files. Typically users will not need these, but they can sometimes be useful.

Lastly, there are files that end in _spec. These contain additional information collected during the scans, such as ion chamber readings and the ring current for each point in the scan.

PyMCA

We use PyMCA at the beamline for initial overviews of the diffraction patterns. When the scan is complete, ensure that the data appears as a merged file, and review in PyMCA. To see the file. Open → file: 001_mgd.xye

- Auto replace, choose the first file.
- Column 0 → X
- Column 1 → Y

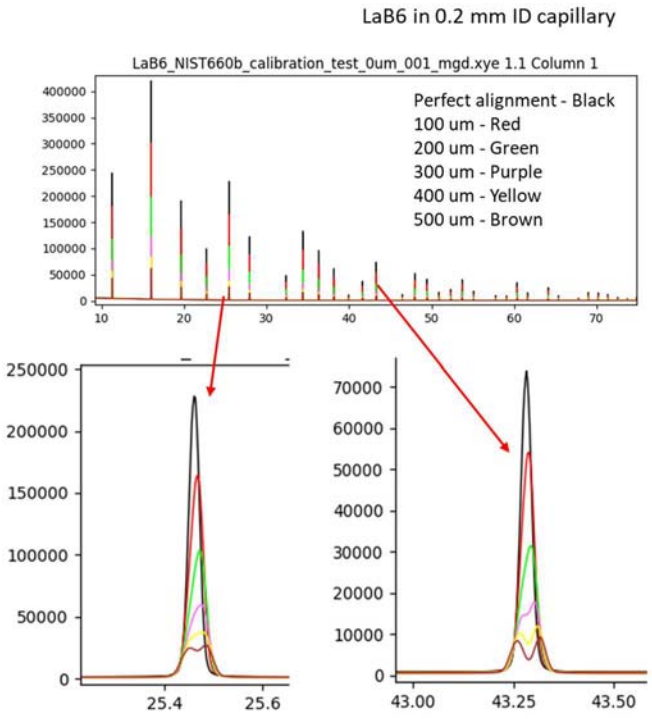
GSAS-II

The .xye files open in GSAS-II (import, powder data, guess format from file).
When it asks for an instrument parameter file, use one provided by the beamline staff to start. Now the data file should open. By refining the data for the calibration standard LaB_6, using the .cif file for LaB_6 available for download from our webpage, you can create, save, and apply your own instrument parameter file to the data.

What Should I Check for While Reviewing the Data?

Capillary rotating off axis

Keep an eye on the spinning sample. A wobble greater than half the capillary diameter can begin to affect the data quality. See A. Bergamaschi et al., Journal of Synchrotron Radiation, 2010, 17, 653-668 (pg. 662).



Displacement (um)	wR (%)
0	3.41
100	5.70
200	7.24
300	7.68

Maximum signal level

The Mythen detector limit of is linearity in the configuration we are using is 700,000 Hz. Look at the counts on the most intense peaks in the pattern. If the count time for the scan is for example, 2 seconds, and the most intense peak has ≥1,400,000 counts, this will not be accurate. Attenuate the beam by adjusting the filter wheel (filter1 X). Then restart the scan.

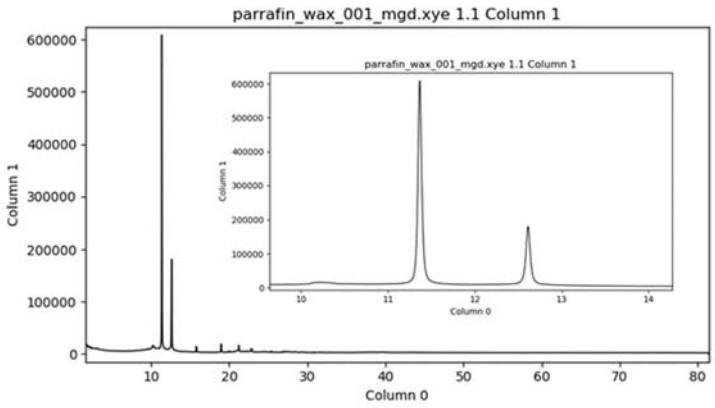
The maximum count rate on the most intense peak should be between 10,000 and 50,000 counts, to keep values of Chi squared to reasonable values. In other words, even if the count rate on the detector is within the linear range, counting too long can be problematic.

Radiation damage

There is a fast shutter in the beamline that is gated to the acquisition time of the Mythen detectors. This means the sample X-ray exposure is minimized to just the data acquisition portion of the scan, not during the sample alignment or motor moves. Still, radiation damage can happen. Overplotting repeat scans of the same sample will reveal any radiation induced changes. If there area changes and more scans are required, the capillary can be manually shifted inboard-outboard on the stub to expose a fresh region.

Extra peaks in the diffraction pattern

Parrafin wax, for mounting samples, has two big peaks at 11.366° and 12.614° 2θ (λ = 0.82023 Å).



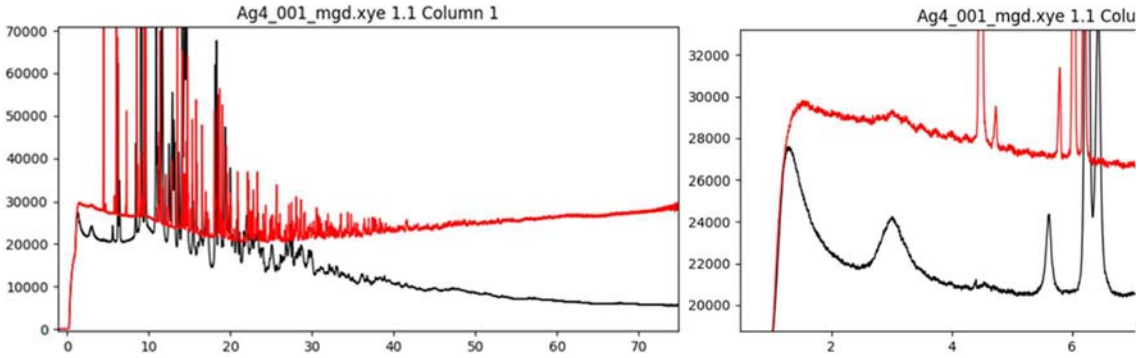
An empty Kapton tube also has broad peaks around 3° and 10° 2θ (λ = 0.82023 Å).

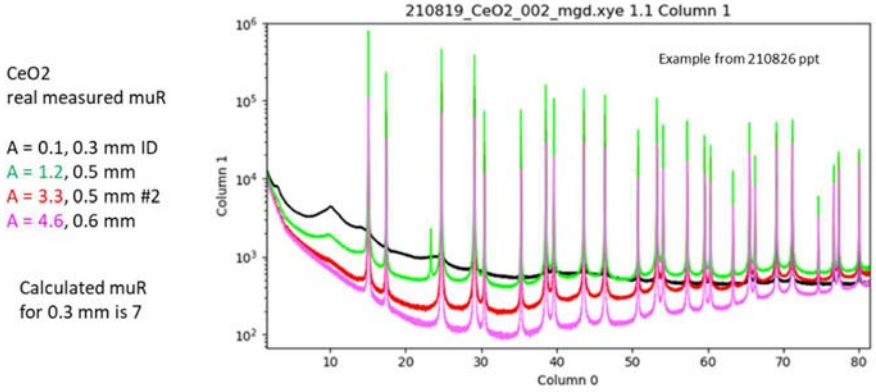
Add in empty Kapton tube data

Sample absorption

How to spot it

1. Background has a smile shape. It is decreasing but then starts increasing around 20 - 40°.
2. Background has sawtooth-like repeating pattern in the region below 10°.
3. If the capillary is Kapton, the 3.0° peak from Kapton is weak or not visible.



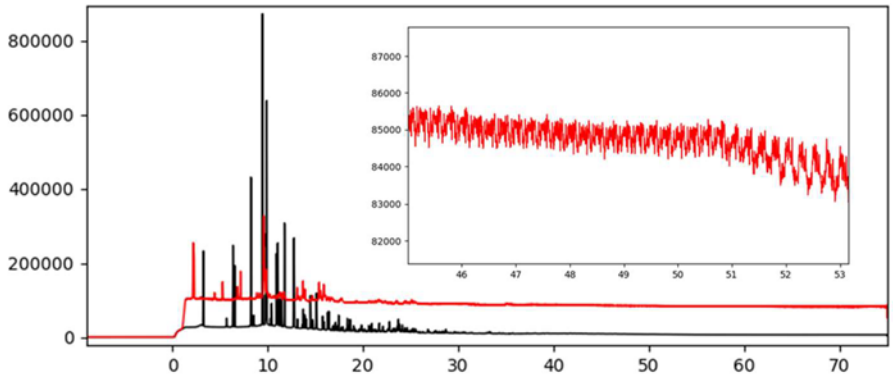


The solution is calculating what the absorption is before the measurement, and if it is >2-3, the sample should be diluted. Dilution up to a factor of 16 has been successful. A factor of 20 was found to be too dilute.

X-ray fluorescence

How to spot it

1. Background is significantly higher for specific samples than others in a series.
2. Background has characteristic repeating noise pattern throughout entire range, not just at low angle.

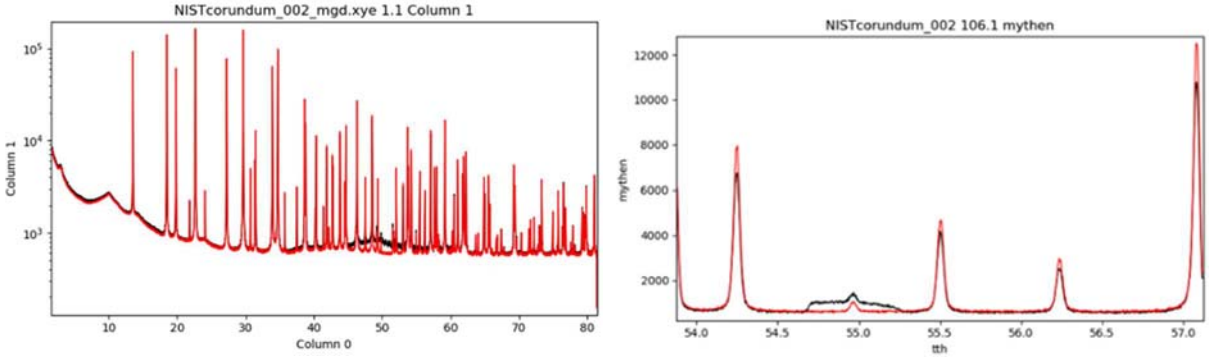


In this example, out of a series of 16 pharmaceutical samples in 0.5 mm Kapton capillaries, two had much higher background. These two samples had Br in the structure, while the rest were CHNO. Similar samples in this list had F or Cl and present no similar issue.

Samples which we have seen noticeable fluorescence are Br, Ge, As, and possibly Fe and Ni. It is something to be aware of, not necessarily a showstopper.

Strange signals at certain angles

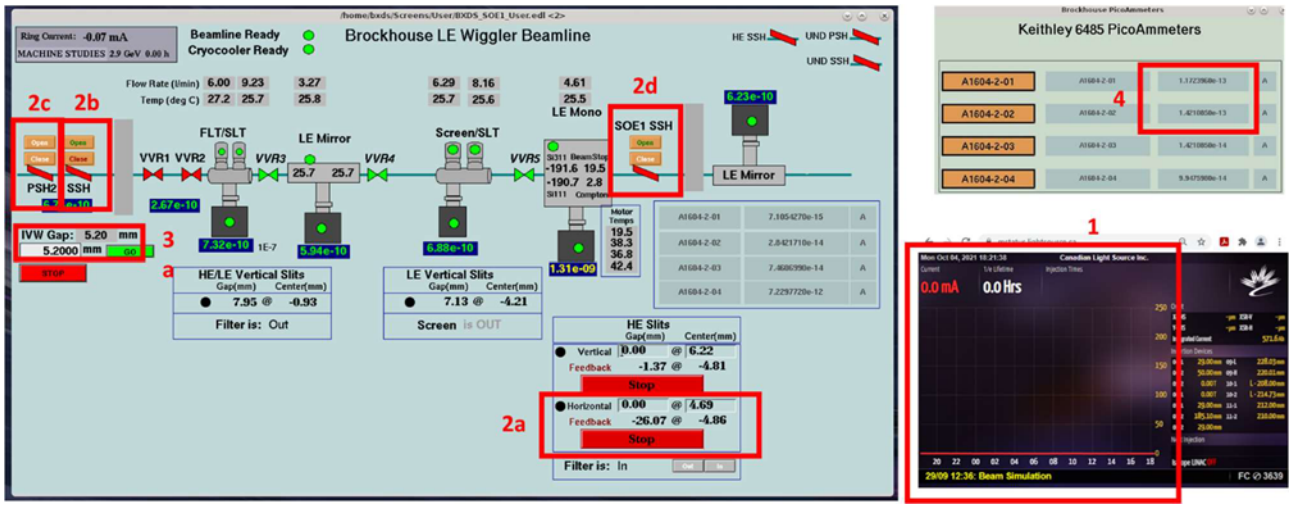
Some extra signals can occur between 35 and 60^{o} 2Theta when there is no lead tape around the Mythen detector.



Coarse grained samples

Recovering From a Beam Dump

Hey, where'd my beam go?



1. Is beam available at CLS?
Check the beamline status screen (machine.lightsource.ca)

- If the screen is RED, there is no beam available, sorry!
- If the screen is YELLOW, and the ring current is 220 mA, then beam should be available for users. The status message at the bottom of the screen should say "Beam available"

There is often a delay of several minutes from the moment where the ring current recovers to 220 mA, to the point where the operator allows users to open shutters and play with insertion device gaps.

2. Are all the shutters open?
When the beam trips, the operators will typically close our front end shutters for the recovery process. They usually re-open them when beam is back. If they don't do it, this must be done by users or staff.

2a – Check the SSH button (box 2b). If you see a message above the SSH button that says "Close HE horizontal slits", then you must first close the horizontal slits behind the HE mono (these normally close automatically if the beam trips). Only do this step if the message "close HE horizontal slits" appears above the SSH button: Click on the box shown above (2a), type -20 in the gap box (even if it already says -20, you need to retype it), and hit enter. The gap feedback value should start changing… it takes a while for these slits to fully close.

2b – Open the SSH shutter by clicking the OPEN button. If it is GREEN it is open.

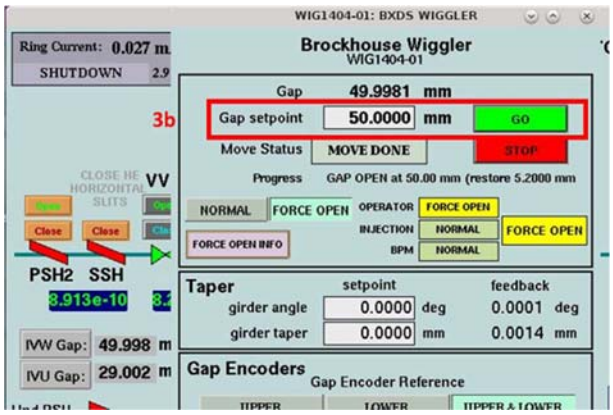
2c – Then open the PSH2 shutter by clicking the OPEN button. If it is GREEN it is open.
If you click OPEN but these two shutters do not open, then check to see if POE1 has been searched and locked up. The floor coordinator can help with this.

2d – Open the SOE-1 hutch shutter by clicking the OPEN button. If it is GREEN it is open. The shutter will only open if the hutch has been searched and locked up.

3. Is the wiggler gap closed to 5.2 mm?
When the beam trips, the operators will open our wiggler gap to 50 mm for the recovery process. They usually close the gap back to our normal operating value of 5.2 mm after recovery, but not always.

3a – Check if the gap is 5.2 mm. If it is, go to step 4.

3b – If the gap is not 5.2 mm, click on the "IVW Gap" box. The "Brockhouse Wiggler" window will pop up, as shown below. Click on the gap setpoint box, enter the value 5.2, then click the GO button.



If you are able to open the SSH and PSH2, but the gap will not close to 5.2 mm after a few attempts, wait a few minutes, try again, then call the operator. Sometimes they forget to hand over control of the gap.

4. Is there now beam in the hutch?
Check the ion chamber readings for A1604-2-01 and A1604-2-02. Both of these ion chambers typically read in the 10^{-6} A range when beam is on.