

XRD User Guide

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Introduction

The X-Ray Laboratory onboard the *R/V JOIDES Resolution* performs diffraction analyses of minerals and rock powders.

The laboratory uses a Bruker AXS D4 Endeavor XRD. Associated software, DIFFRACplus and TOPAS, allow for powder diffraction analysis of minerals, including peak-matching and mineral and chemical compound identification. The XRD lab provides the scientist with a quick and reliable tool for mineral identification; particularly useful for identifying fine-grained minerals or mixtures of alteration minerals. In addition, XRD can be used to determine mineral proportion.

Theory of Operation

A mineral is a three-dimensional structure that forms a crystal lattice. When a focused X-ray beam is directed onto the crystal structure of a mineral, part of the beam is diffracted. X-rays are diffracted differently depending on the atomic composition and arrangement within the crystal lattice. Each mineral has a unique fingerprint that is determined based on a characteristic set of d-spacings (space between adjacent planes of atoms in the crystal lattice). This is a fundamental characteristic of minerals that allow mineral identification through X-ray diffraction. X-rays are generated in a vacuum tube and directed to a powdered sample, when the X-rays hit the powdered sample, they are diffracted onto a detector. The X-ray detector then converts the signal to a count rate. The angle between the X-ray tube, sample, and detector are varied during measurement to produce an X-ray scan. Using the angle between the X-ray tube, sample, and detector (2θ , which can be measured) and the wavelength of a generated X-ray beam (λ , which is known based on the material generating the X-rays), the scientist can determine the d-spacings by using Bragg's law:

$$n = 2d\sin\theta$$

n = order of the diffracted beam

λ = wavelength of the incident X-ray beam

d = distance between adjacent planes of atoms (d-spacings)

θ = angle of incidence of the X-ray beam

The d-spacings generated by an X-ray scan provide the unique fingerprint of the mineral or minerals present in the sample.

References

Cullity, B.D., 1978. *Elements of X-Ray Diffraction*, Second Edition. Addison-Wesley Publishing Company, Inc., Massachusetts.

Bish, D.L., and Post, J.E. (Editors), 1989. *Reviews in Mineralogy Volume 20, Modern Powder Diffraction*. The Mineralogical Society of America, Washington, D.C.

Apparatus, Reagents, and Materials

Laboratory Apparatus

- Haskris water chiller for X-ray tube
- Cahn Model 29 or 31 microbalance
- Mettler-Toledo XS204 dual-balance system
- Powdering equipment:
- Agate mortar and pestle
- Mixer mill
- Shatterbox
- X-Press
- Glass bottles
- Sonic dismembrator
- Glass rod
- Glass beakers
- Pasteur pipette/eye dropper
- Centrifuge and centrifuge tubes
- Desiccator
- Labconco Freeze Dryer

Reagents

- Ethylene glycol (clay glycolation)
- 2 M HCl: 16.4% v/v (carbonate dissolution)
- Glacial acetic acid, 10% v/v solution (carbonate dissolution)
- Distilled (reagent) water (DI)
- 1% w/v Borax solution

Instrument Hardware

- Bruker AXS D4 Endeavor X-ray diffractometer (XRD)
- Goniometer
- X-ray source (sealed vacuum tube with line focus)
- Tube housing (ceramic body that protects the tube and shields from X-rays)
- Mount
- Sample holder
- Vantec-1 detector
- Optics
- Slit systems

X-Ray Diffractometer

The Bruker AXS D4 Endeavor XRD can analyze powder, liquid, and solid samples in a variety of sample holders. The sequence of the beam path is X-ray source > primary X-ray optics > sample > secondary X-ray optics > detector.

Goniometer

The goniometer has 2 circles: the theta (θ) circle, which sets the sample position, and the 2θ circle, which moves the detector. The position of the X-ray tube remains fixed. The goniometer center is defined by the concentric circle axes.

Component	Specification
Measuring circle diameter	401 mm
Operating mode	Vertical, $\theta/2$
Max angular range	$-8^\circ < 2\theta < 170^\circ$
Smallest step width	0.0087°
Reproducibility of $\theta/2$ angle	$\pm 0.0002^\circ$
Absolute accuracy ($\theta/2$)	$< \pm 0.005^\circ$

Sample Holders

Sample holders for powdered XRD samples are steel or steel with a silicon or quartz spacer. The selection of a sample holder depends on the volume of sample to be analyzed.

Amount of Powdered Sample	Sample Holder
Large: 2.0 mm depth	Steel
Medium: 1.8 mm depth	Steel
Small: 1.0 mm depth	Steel with quartz or zero-background Si spacer
Smallest (vein/vesicles, scrapings)	Slurry (see Sample Slurry/Smear Slide Mounting for Small Sample Amounts)

Detector

The VANTEC-1 detector features the fastest simultaneous recording of XRD patterns within a wide 2 θ angular range. For powders, measurement time is reduced by a factor of up to 100 in comparison to other detectors.

Component	Specification
Active area	50 mm x 16 mm; 1600 pixels
Max 2 θ range covered	12° at 435 mm diameter; 11° at 500 mm
Usable wavelength	Cr–K to Mo–K
Max local count rate	400,000 cps
Spatial resolution	<50 μ m; >1600 channels
Gas fill	3.04 bar Xe-CO ₂ ; no external supply needed
Power rating	120 W
Ambient temperature	41°–104°F (5°–40°C)
Operating temperature	57°–93°F (14°–34°C)
Relative humidity	Maximum 80 %, noncondensing

Detector Optics

- Detector window slits
- Debye slits
- K filter: suppresses characteristic K radiation
- Antiscatter slits: reduce primary air scatter, which influences diffraction background patterns
- Soller slits: reduce primary and secondary air scatter
- Window opening scales

Instrument Software

- DIFFRAC.SUITE.EVA, version 3.0 software for evaluation
- DIFFRAC.TOPAS version 4.2.0.1 software for diffractogram analysis

Apparatus Preparation

The instruments in the lab need to be turned on in this order: (1) HASKRIS and (2) D4. The HASKRIS cools the water supplied to the D4 to prevent the X-ray tube from overheating. Turning the D4 on prematurely will damage the X-ray tube.

Procedure

1. Flip the "On" switch (*Figure 1C*) to the HASKRIS and the water in the tank will begin to cool. The water temperature needs to reach 69°F (*Figure 1A*).

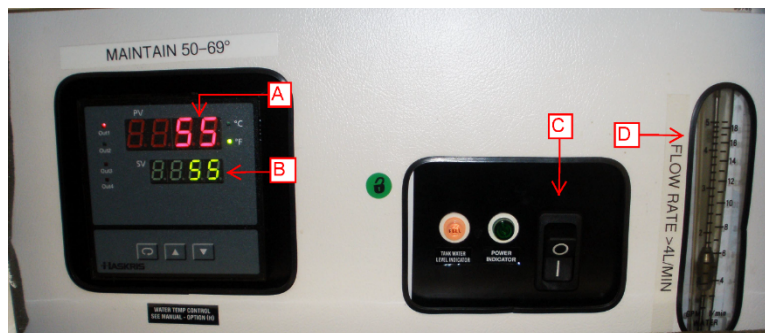


Figure 1. HASKRIS Control Panel. (A) Actual temperature. (B) Set temperature. (C) On/Off switch. (D) Flow meter

2. Flip the ON switch (*Figure 2A*) on the side of the machine.
 - a. The solid green "Low Voltage Ready" light (*Figure 2F*) turns on.
 - b. You will hear several beeps and the "System Activity" light (*Figure 2D*) will start flashing green.
3. Press the "High Voltage Enable" button (*Figure 2B*).
 - a. The "System Activity" light turns green.
 - b. An orange "High Voltage Ready" (*Figure 2E*) light will turn on.

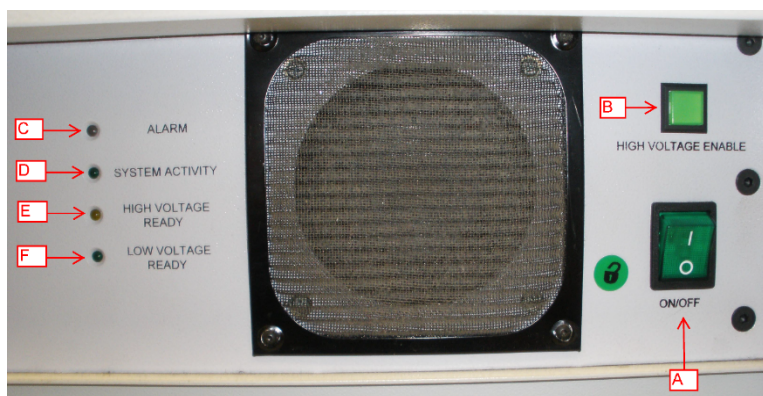


Figure 2. Side control panel on D4. (A) Power On/Off. (B) High voltage enable button. (C) Alarm light. (D) System activity flashing light. (E) High voltage ready light. (F) Low voltage ready light.

4. Go to the front of the machine and press the green circular button. This enables the mains power and activates the sample handler (see *Figure 3*).

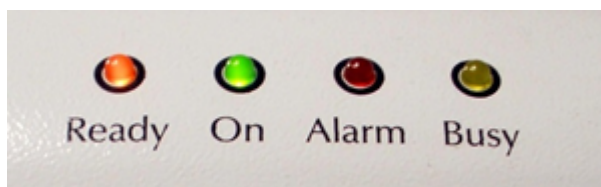


Figure 3. D4 top control lights.

5. Turn the “Generator Power” key to the right for a few seconds and look at the lights on top of the D4 (Figure 4)



Figure 4. D4 Front control panel.

6. When the “Alarm” light turns off and the “Ready” light turns on, release the key back into its middle position. The top of the machine should have a solid orange “Ready” light and a solid green “On” light.
7. If this is the first time in 24 or more hours that the D4 has been turned on, the X-ray tube now needs to be conditioned. Go to the Maintenance section under Tube Conditioning for instructions.

Sample Preparation

Sample preparations are split into two main categories:

- A. Bulk powder samples
- B. Clay separations

Before running samples, go over the methods with scientists and check for any special sample requests.

Bulk powder samples

Solid samples are prepared for X-ray diffraction by grinding, which depending on the sample matrix, the size of the sample, and/or quantity of prepared material needed can be accomplished by several different methods.

Sample Matrix	Use...
Soft clay	Agate mortar and pestle
Hard solids	Mixer mill
Hard solids in bulk quantities	Shatterbox
Hard sample too large to fit in the shatterbox	X-Press

Drying Samples

Freeze-dry sample(s) for at least 12 hours before grinding. If the samples still feel cold when removed from the dryer, the samples still have moisture in them and need to dry longer.

The freeze dryer is comprised of a sample "bell" chamber and a Labconco freeze-dryer. On the bell are two valves, as shown in *Figure 5*. Each valve has an "Open" and "Closed" position. The top valve controls the vacuum inside of the bell, and the bottom valve controls the air flow between the cooling coil and bell. A valve parallel with the tube is open and allows air flow; a valve perpendicular with the tube is closed. In *Figure 5*, configuration A (closed) will hold a vacuum, but configuration B (open) will not.

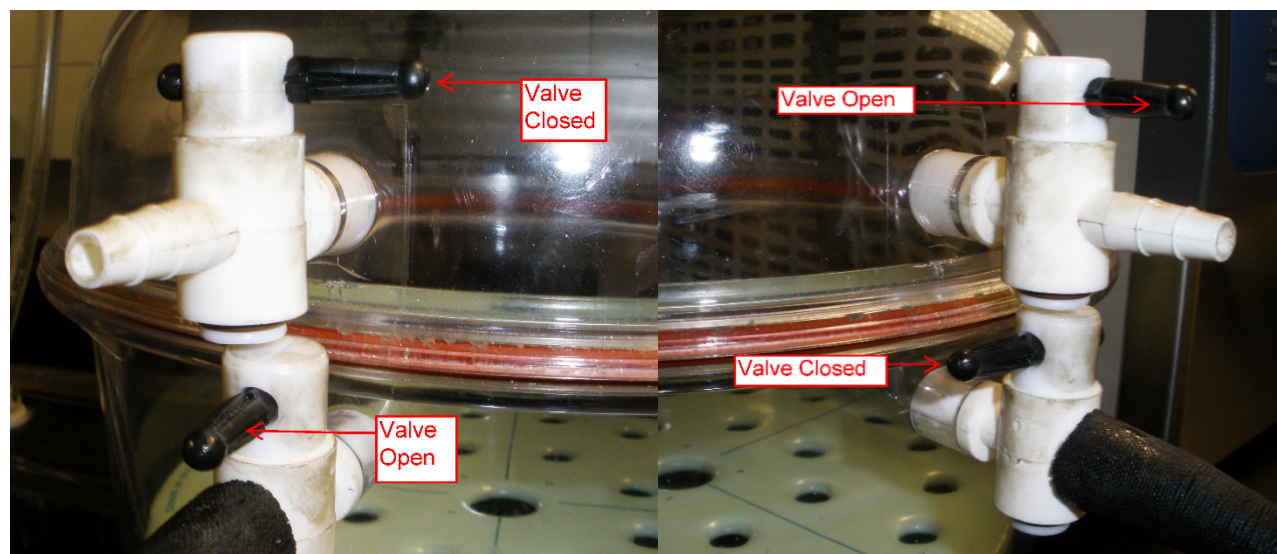


Figure 5. (A) Freeze dryer bell valves in closed position. (B) Freeze dryer bell valves in open position.

To freeze-dry samples

1. Cut open the sealed sample bags and fold the top edge over to keep the bag open.
2. Take the top of the bell off of the dryer and arrange samples in the bell, making sure no sample bags are pinched closed.
3. Close the vacuum valves slowly so that you do not cause a large rush of air to blow the samples around. *Figure 5A* shows the configuration to dry samples and *Figure 5B* shows the configuration for loading and unloading samples.
4. Set the freeze dryer to resemble the settings shown in *Figure 6* and flip the "On" switch located on the right side of the machine.
5. Press the "Auto Refrigeration" button (*Figure 6A*) and then the vacuum button (*Figure 6B*). The temperature will start to drop and the vacuum pump will turn on.
 - a. When the temperature drops to -40°C , the vacuum is created in the bell and the pressure drops.
 - b. Expect the temperature to be between -42°C and -52°C and the pressure to be ~ 0.350 mBar.
 - c. The indicator lights (*Figure 6D*) show how the cooling and pressure reduction are progressing. When all indicator lights are on the freeze dryer is at its peak performance.
 - d. If there is an error the red "Alarm" light will turn on. Press the "Menu" button (*Figure 6C*) to view it and clear it
6. After samples are dry, slowly open the valves to let out the vacuum in the bell. Remove the samples from the bell and store them inside the desiccator until they are ready to be ground to prevent reabsorption of moisture.

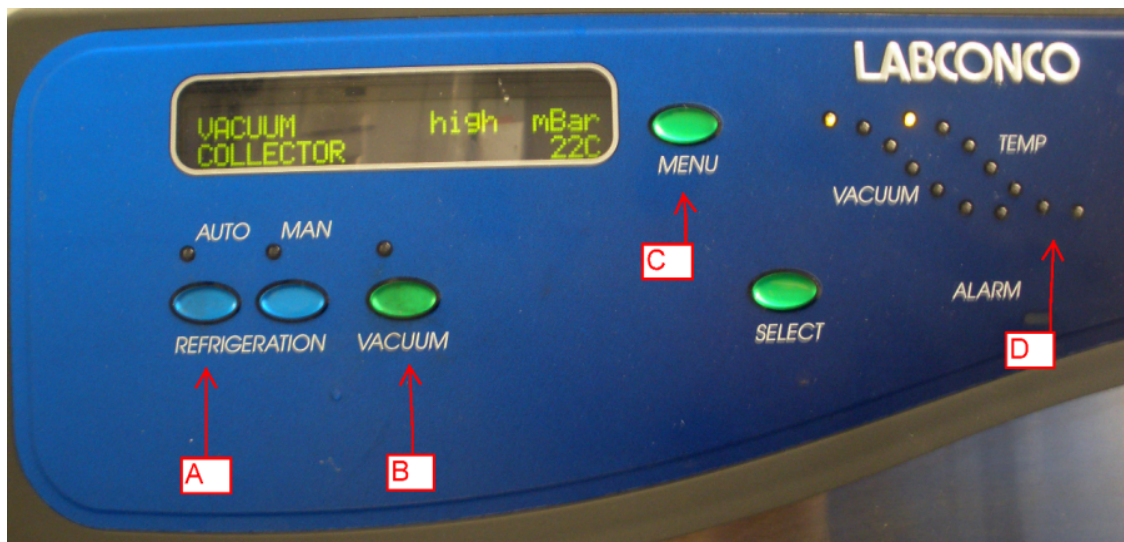


Figure 6. Freeze dryer control panel.

Grinding Solid Samples

There are three primary ways to grind samples:

- With an agate mortar and pestle
- With a Spex shatterbox
- With a Spex mixer mill (tungsten carbide, hardened steel, agate, or alumina ceramic)

Mortar and pestle is the most common method. Below, each method is outlined.

Mortar and Pestle

Choose the appropriate mortar and pestle size (large or small) and place it on the counter (Figure 8). Obtain a glass slide, a sample holder, and a scoopula (Figure 8). Clean all items after each use with isopropyl alcohol and a KimWipe.

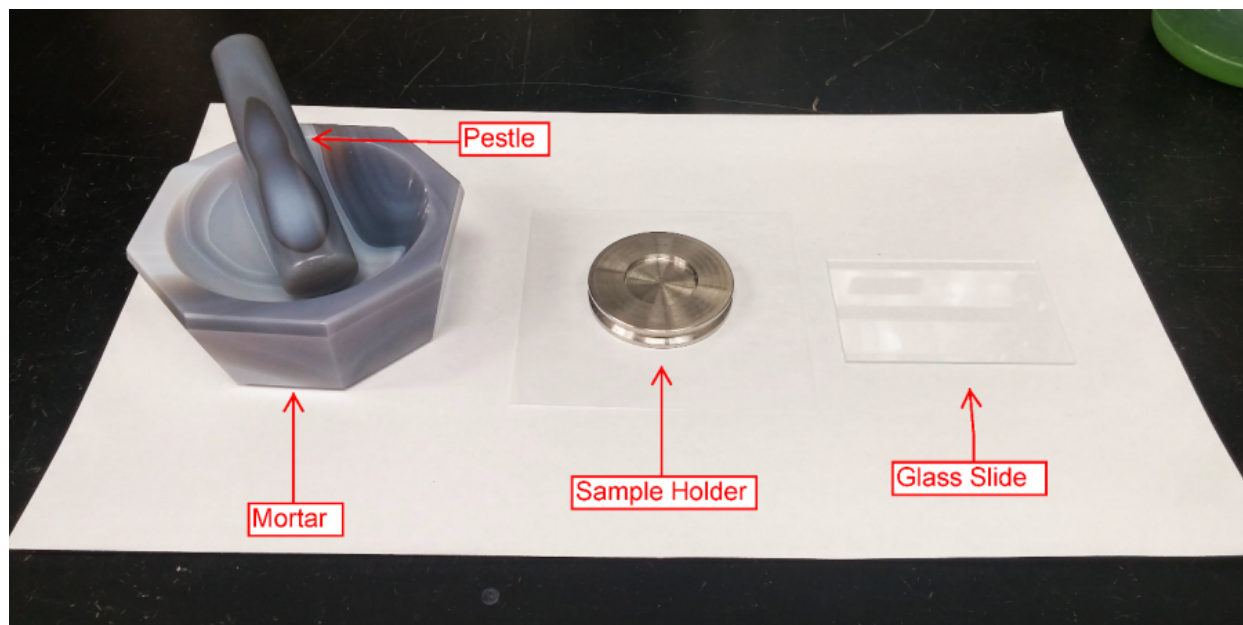


Figure 8: Mortar and pestle sample preparation set up.

Pour sample into the mortar and grind the sample with the pestle. When finished, the sample should be the consistency of talc powder. Test the sample by taking a pinch and rubbing it on your skin. If the sample feels gritty, it needs to be ground more. If the texture is good and the sample looks homogenous, you can pack the sample into a sample holder to be placed in the D4.

Mixer mill

There are two mixer mills located in X-Ray Prep. Both mills operate very similarly but do have slight differences (*Figure 9, Figure 10*). The 8000 is featured on the top and the 8000M on the bottom.

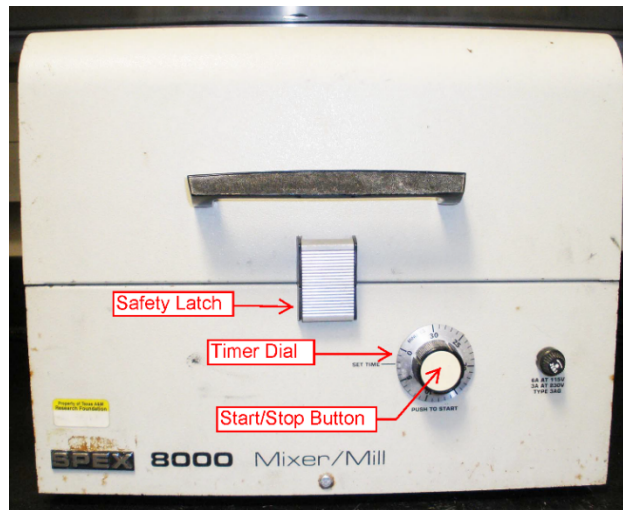


Figure 9: 8000M mixer mill. (A) Safety latch (B) Minute timer (C) Seconds timer (D) Start button (E) Pause/Stop button (F) Timer countdown LCD display.



Figure 10: 8000 mixer mill. An older simplified version of the 8000M. Featured are the safety latch, timer dial, and start/stop button in the middle of the dial.

The main difference between the two mixer mills is the timer. The 8000M timer uses 2 buttons to adjust the minutes (*Figure 9B*) and seconds (*Figure 9C*), 2 separate buttons to start (*Figure 9D*) and manually stop (*Figure 9E*), and counts down time on the LCD display (*Figure 9F*). To operate the 8000 mixer mill, turn the knob to the desired time and press the "Start" button in the middle. That button will also stop the mixer mill. The dial does not move automatically, so if it is turned to 5 minutes it will stay there. The dial does not need to be set back to 0 to work.

Grinding Vessels

There are three types of grinding vessels available: alumina ceramic, tungsten carbide, and hardened steel (*Figure 11*). Tungsten carbide and steel vessels are better for more robust grinding, and alumina ceramic is better for minimizing contamination. Check with the Science Party to see which vessel type is preferred.

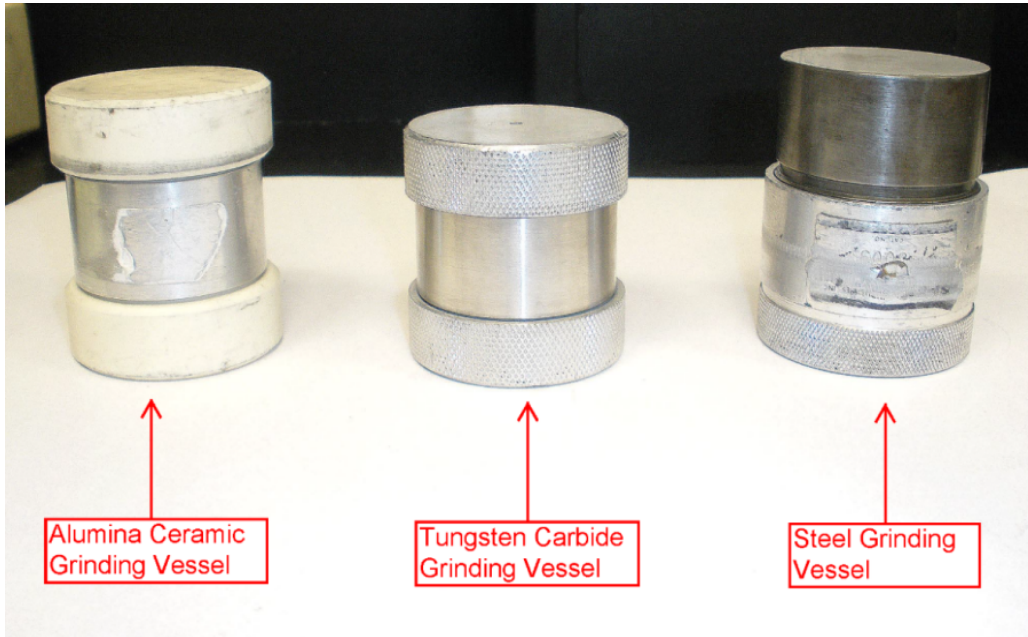


Figure 11: Three types of mixer mill grinding vessels.

Each grinding vessel has its own components. Parts should not be shared among the different types of vessels. Combining pieces made of different materials can cause severe damage to the pieces involved.

Below are the components for each type of vessel. The steel (Figure 12) and tungsten carbide (Figure 13) both have a vessel body with attached lid and one separate lid that is screwed on. Cross-threading is very easy with these containers, so be very careful when screwing on the lid. Also note that the steel container has an O-ring, whereas the tungsten carbide does not. The alumina ceramic vessel (Figure 14) is assembled differently than the other two vessels: two cork rings are placed inside each lid, and the lids slip onto either side of the vessel body.

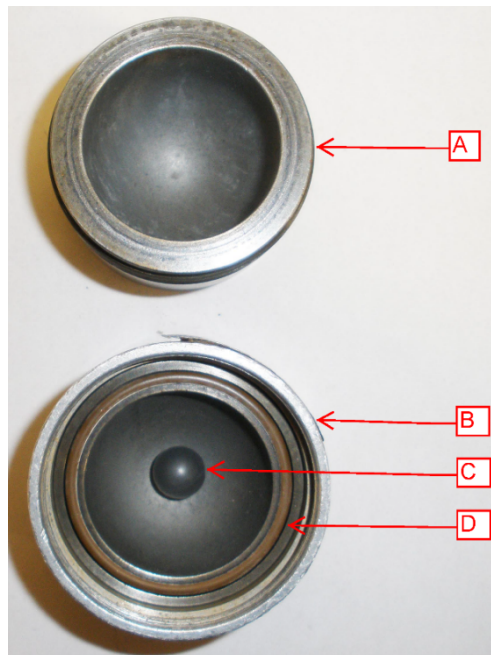


Figure 12: Steel vessel components. (A) Lid (B) Container (C) Steel Grinding Ball (D) O-Ring

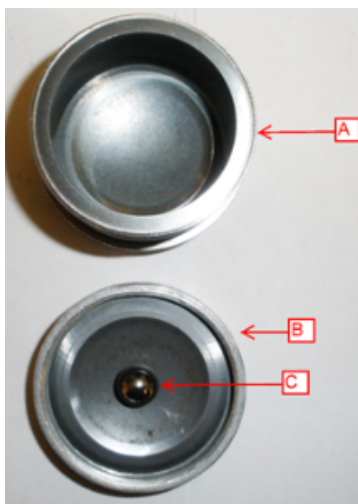


Figure 13: Tungsten carbide vessel. (A) Vessel container (B) Lid (C) Tungsten carbide grinding ball

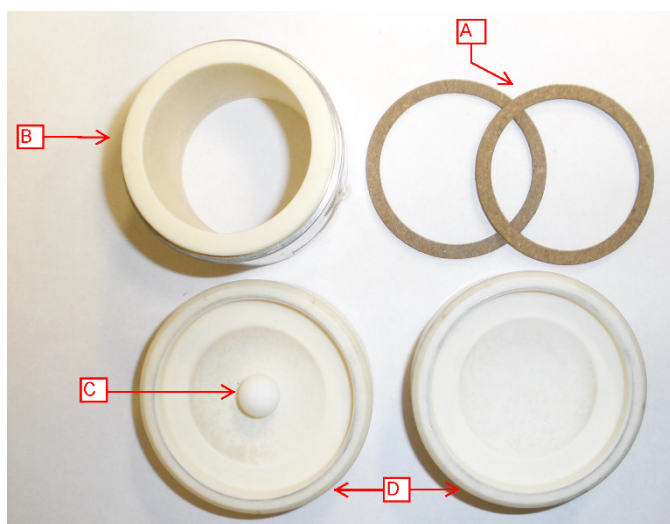


Figure 14: Alumina ceramic vessel components. (A) 2 cork rings (B) Vessel body (C) Alumina ceramic grinding ball (D) 2 lids

Label the vessel with a small printed label of the sample it holds. After the sample is ground, transfer that label to an 8 or 16 mL snap cap bottle that will hold the powder.

Loading the Grinding Vessel into the Mill

Put your sample inside the vessel. The material should be approximately the size of a pea to prevent any jamming and to ensure all pieces are ground up. Place 1 to 2 grinding balls inside the container. Tungsten carbide and steel vessels can take up to 2 balls. The alumina ceramic vessel is more brittle and 1 ball is recommended. Finish assembling the grinding vessel and open the lid to the mixer mill.

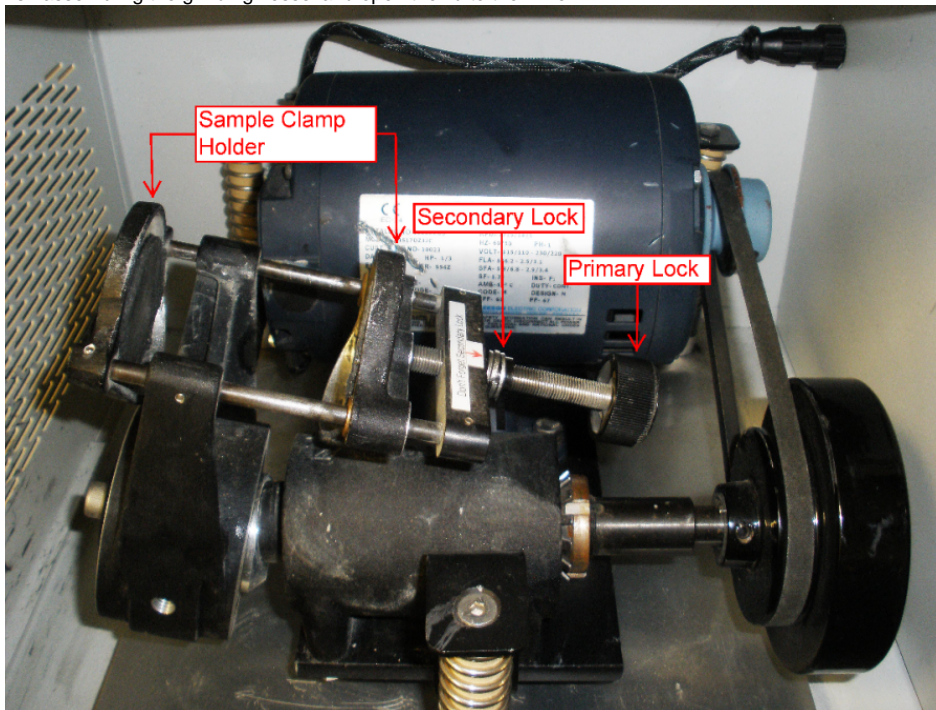


Figure 15: Inside the 8000M mixer mill. Highlighted is the sample holder clamp that holds the grinding vessels, the primary lock, and the secondary lock.

Hold the grinding vessel between the sample holder clamps (Figure 15), flush against one side. Still holding the vessel, start turning the primary lock. The holder will begin to clamp down on the sample. When the vessel is secured, you can remove your hand and continue tightening the primary lock until the sample is firmly gripped. Then tighten the secondary lock until it feels firm. Check the vessel to make sure the lids are resting flat on the clamps. If the vessel is ajar inside the clamp, when the motor starts the vessel can start grinding away at itself or fly loose into the machine.

Starting the Mill

Set the timer to the desired grinding time. The time will vary depending on sample material. Start with a conservative time, 2 to 3 minutes, check the material, and add more time if the sample still feels gritty. Harder rocks can go up to 10 minutes or beyond to grind down to the right sample consistency. When the mill finishes grinding, remove the vessel the same way as it was put into the clamp: hold the vessel firmly against one clamp while unscrewing the primary lock. Keep the vessel straight and hold it firmly. If one of the lids starts to crack open, sample material will spill into the machine. If this happens, clean up the powder with a damp towel. Any leftover powder can get into the motor and damage it.

Transferring Powder

Collect a metal tray, weigh paper (large or small), 8 or 16 mL clear snap cap bottles, a scoopula, Kim Wipes, and isopropyl alcohol. Clean all materials with isopropyl alcohol. Place a piece of weigh paper on the metal tray. Pour the sample material from the grinding vessel onto the weigh paper. Use the scoopula to scrape the sides and lids of the vessel to remove extra material. Transfer the sample from the weigh paper into the glass vial. Label the vial with a small printed label and label the cap with a permanent marker.

Cleaning the Vessels

Clean the grinding vessels with a toothbrush and DI water. In some cases the vials are still dirty or have sample stains on them. If so, take a small amount, approximately 5 mL, of silica sand and grind it in the mixer mill for ~3 minutes. Then pour out the sand and clean the vessel with DI water and a toothbrush or Greenie Meanie. Lay out cleaned vessel parts on a Kim Towel and dry with a Kim Wipe. The cork rings take a longer to dry, so collect fresh, dry rings before grinding the next sample. Then can now pack the samples.

Shatterbox

Shatterbox vessels are not commonly used for powder XRD samples. Please refer to the ICP Prep User Guide for instructions for using the shatterbox.

Preparing Sample Holders for the D4

There are three ways to load a sample holder: front load, side load, and backload. Front and side loading methods uses the same sample holders and back-loading uses unique holders. Front Loading is the most common method. Back and side-loading are ideal for reducing preferred orientation and should be used over frontloading if preparing samples for semi quantitative analysis.

Collect Enough Material to Fill a Sample Holder

1. Unless the sample material is very small, select the appropriate sample holder (see [Sample Slurry/Smear Slide Mounting for Small Sample Amounts](#)).
2. Label the sample holder with a unique identifier to keep the samples organized (e.g., text ID or 14H2 77-78)

- Place enough powder from the labeled sample bottle to fill an empty sample holder. Gently press the powder flush with the sample holder using a glass slide. Roll the glass slide over the powder to fill any gaps in material and smooth the surface of the powder. The surface of the powder must be smooth. Remove excess powder from the sample holder edges and carefully place the holder in the D4 sample magazine.

The material needs to be flush with the sample holder. The beam is set to focus on the height of the sample holder. If the sample is above or below that focal point, the geometry of the beams do not converge properly, the peak resolution decreases, and the peaks are shifted.

Side-Load Samples

Side-loading samples is a preparation method to reduce mineral orientation. This method may be desirable for quantitative XRD

- Take a 2mm or 1.8mm sample holder and hold it on its side.
- Tape a piece of cover glass across the well leaving a very small gap at the top
- Keep the holder on its side and pour powder into the open gap.
- Tap the holder while filling in powder to evenly distribute it

This method will leave a small gap in the well of no powder. For this packing method it is ok and the material should be tightly packed in.

Back-Load samples

Back-loading samples is a preparation method to reduce mineral orientation. This method may be desirable for quantitative XRD

There are 10 back-loading holders. The holder has an empty ring and backing piece that snaps in from behind (*Figure 16*). There are also two loading pieces. One piece helps funnel the powder in and the other taps down the powder into a flat surface.

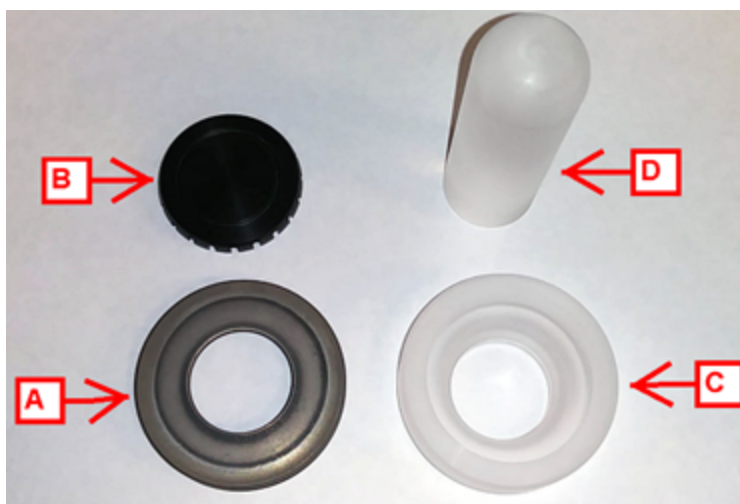


Figure 16. Back-loading sample holder pieces. A. Sample Ring B. Back piece C. Funneling piece D. Tapper

- Take a front-loading holder and put a clean glass slide over it.
- Take the ring, flip it upside down and put it on the slide (*Figure 17*). Now the powder will fall on a smooth flat surface that will be easy to flip over.

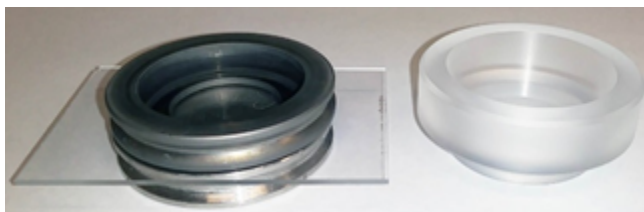


Figure 17. Ring upside down on glass. Funnel piece next to unit.

- Take the funneling piece and put it inside the ring (*Figure 18*).

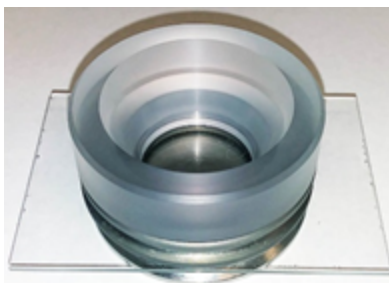


Figure 18. Funnel inside ring.

4. Load powder into the ring. Try to load the powder evenly across the well.
5. Take the tapping piece and lightly tap down the powder. The idea behind this method is not applying pressure to the measuring face will reduce mineral orientation. Do not tap the powder too firmly or you may unnecessarily orient the minerals.
6. Remove the funneling piece when the powder surface is flat and smooth.
7. Take the back piece and snap it into the ring. Be wary of air displacement.
8. Hold the sample holder and the glass slide. Flip the whole unit over and set it down.
9. Remove the glass. The powder needs to be flush with the holder. It may take a few tries to get the right amount of powder in.

Very Small Amount of Material

Sample Slurry/Smear Slide Mounting for Small Sample Amounts

The following technique is modified from the *U.S. Geological Survey Open-File Report 01-041, A Laboratory Manual for X-Ray Powder Diffraction*. For a very small amount of sample material (i.e., end of a tooth pick), samples may be ground to a fine talc-like powder and smeared onto one of the quartz disk inserts. Although not useful for semiquantitative analysis, this method is useful for rapidly determining bulk mineralogy.

Preparing Smear Slurry/Smear Slide

1. Place a small amount of sample powder in the center of a quartz or single crystal quartz disk.
2. Add 2–3 drops of 70 % isopropyl alcohol or distilled water to the sample. **Note:** Isopropyl dries faster than water.
3. Spread the sample to a thin layer using a glass rod. The slurry should be spread evenly across the disk. If there is not enough material to cover the entire disk, concentrate the sample in the middle of the disk where the X-rays will contact the sample.
4. Place the sample in the desiccator to dry before running in the XRD.

Clay Separations

Clay Separations focus on separating the clay size fraction, <2 μm , from the rest of the material. In order to get only that size fraction we prepare the sample in a different way. Do not freeze dry samples waiting for clay separations. If the samples have already been dried the treatments will still work but using fresh, wet samples is easier. Below are outlined various treatments and methods we do on board.

Removing Carbonates before Clay Separation

It may be necessary to dissolve the carbonates in the sediment to better identify the clay minerals. The goal is to remove as much carbonate as possible to isolate the material contained within the carbonate for analysis. There are two standard methods for removing carbonate aboard the *JOIDES Resolution*: hydrochloric acid (HCl) and acetic acid. Ask the Science party which method they prefer. If there is no preference, use acetic acid.

Acetic Acid Treatment

This is the recommended treatment for carbonate removal. The process is slightly more involved than the HCl procedure, but far less damage is done to the mineral structure. The following steps are from Kitty Milliken (UT-Austin).

1. Place sample in centrifuge tube with 25 mL of 10 % Acetic Acid for at least 1 hour to decarbonate (it helps to place the centrifuge tubes on the agitator in the cold room)
 - a. Please note, that sample with a large amount of carbonate (more than 50%) may require more than 1 treatment of Acetic to reach complete decarbonation.
2. Centrifuge for 15 mins at 1500 rpm, decant and wash with 25 mL of nanopure water (3X to remove all Acetic Acid)

Hydrochloric Acid Treatment

HCl is the simplest method for removing carbonate from sediment but does have severe drawbacks. Strong acids damage the mineral structure, especially within trioctahedral minerals. Before proceeding, be aware that this treatment may affect clay crystallinity.

1. Place undried sample on a glass slide or quartz disk.
2. Using a Pasteur pipette, slowly drop 2M HCl on the sample until bubbling/fizzing stops.
3. Desiccate and transfer sample to sample holder for analysis.

Separating Clay

There are various methods for separating clay from coarser material involving a series of centrifuging or gravity settling. Those listed below are methods used on-board.

If you removed carbonates first, start here after your water washes are finished and the water has been decanted. If you did not remove carbonates, take approximately 5 mL of sample material and put into a centrifuge tube.

Suspending Material

Get the sonic dismembrator case and probe power source. Using the dismembrator is a very effective way to fully and randomly suspend the material. Suspended material can then separate out according to size, with the largest grain size on the bottom and the very small clay size fraction on top.

The dismembrator setup is shown on the left in *Figure 19*. The power source is connected to the probe. The probe fits into the case through a hole in the top. Put the probe into the top clamp and the sample tube into the bottom clamp. Adjust the positions so the probe goes into the tube. The probe should be about half-way into the sample material without touching the sides of the tube. The probe releases a lot of energy, and if it touches the sides it will heat up the tube and the sample.

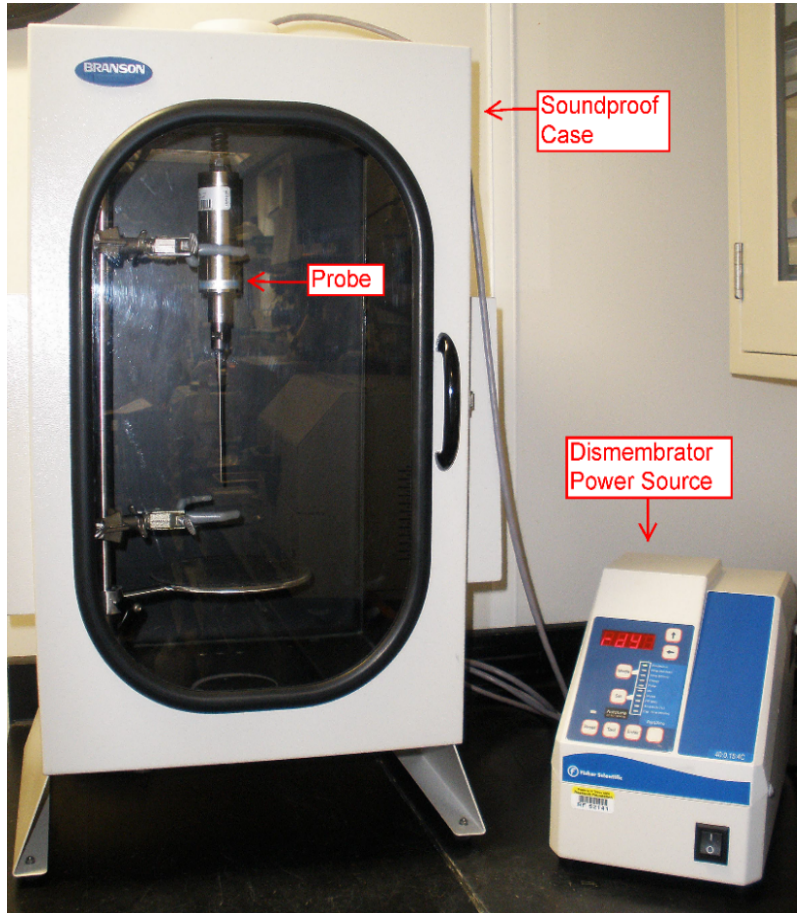


Figure 19 (above): The dismembrator set up. Included is the soundproof box and the Probe with power source.



Figure 20: Dismembrator power source control Panel. (A) On/Off switch (B) Start button (C) Set button (D) Mode button

The probe power source is shown on the left in *Figure 20*. Flip the "ON" Switch (*Figure 20A*). The settings are already set to our needs. To run as is, press the "Start" button (*Figure 20B*). If you need to change a setting, see the "Set" button (*Figure 20D*) and the "Mode" button (*Figure 20C*). From these two panels, you have access to the power, time, and displayed units. For more information, reference the Manufacturer Manual located in the side pocket of the dismembrator case.

1. Add ~25 mL of a 1 % borax solution into the centrifuge tube. Borax prevents the sample from flocculating. Too much Borax however will increase flocculation.
2. Put the tube into the bottom clamp inside the dismembrator case. When satisfied with the positioning, press the "Start" button on the probe power supply (*Figure 17B*). If the material does not appear to be circulating throughout the whole tube or the tube is heating up, adjust the probe position and start the dismembration over.

Standard IODP Clay Separation Method: Not for Semi-quantitative Analysis

1. In centrifuge tube, mix a small amount of bulk sample (~5 mL; fresh, not dried) with 1% borax solution. Use agitator or dismembrator, if necessary to suspend particles.
2. Centrifuge the borax solution/sample mix at 750 rpm for 4 minutes to remove the >2 μm size fraction
3. Decant the supernatant liquid (containing suspended clay) into a new centrifuge tube
4. Centrifuge the <2 μm fraction for 15 mins at 1500 rpm to remove the Borax solution
5. Decant the borax solution and add 25 mL of nanopure water to wash the clay
6. Repeat Steps 4 and 5 as necessary to remove the borax (USGS recommends repeating up to 4-5 times)

Alternative method from Exp. 379

1. Add 25 mL of 1% Borax solution to the clay plug
2. Dismembrate the sample (machine is auto set on time), to remove the >2 μm clay fraction
3. Centrifuge for 4 mins at 750 rpm, decant the supernatant liquid into a separate centrifuge tube (you should end up with a ~full centrifuge tube of suspended clay)
4. Repeat steps 1–3 on the remaining >2 μm fraction
5. Centrifuge the <2 μm fraction for 15 mins at 1500 rpm to remove the Borax solution
6. Decant and add 25 mL of nanopure water
7. Centrifuged for 60 mins at 3000 rpm, the liquid decanted before loading onto a zero background silica disk.

Preparing the Mount

Clay mounts are put onto a zero-background silicon disk that fits into a 2 mm steel sample holder (*Figure 21*). Only put the disks into sample holders that have a hole drilled in the bottom. The hole allows the disks to be taken out, otherwise they are stuck inside the holder. The disk should sit flush with the sample holder. Some of the disks are at different depths, so a quartz insert disk can also be put in the bottom of a sample holder with the silicon disk on top.

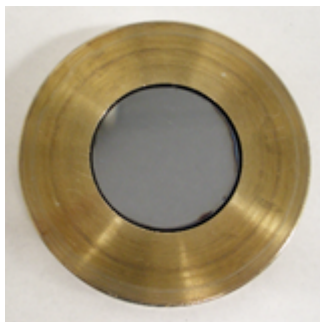


Figure 21: Steel sample holder with silicon disk

1. Remove the $<2\ \mu\text{m}$ size fraction by collecting the uppermost 1 cm of solution with an eye dropper (it helps to add a little isopropanol). If necessary resuspend flocculated clay particles using the dismembrator and add more borax solution.
 2. If material is still very suspended, try centrifuging the samples for 4 minutes at 750 rpm. In this instance, the $>2\ \mu\text{m}$ size fraction will be the only fraction suspended in the liquid and all the larger grains will be packed in the bottom. Take the suspended material with an eyedropper and put it on the quartz disk.
 3. Make an oriented clay mount by placing 2–3 drops (enough to cover the disk) of clay suspension directly onto the silicon disk. If the material is not spreading evenly, add a drop or two of 70% isopropanol and spread the material around with a small glass rod. Once spread, let the sample dry in the desiccator. The clay particles orient themselves as the solution dries on the disc.
- Once the sample is dry, you are ready to run it through the D4. If there are additional treatments requested, continue to the sections below.

Additional Clay Treatments before Scanning

Treating with Ethylene Glycol

The following techniques are modified from the *U.S. Geological Survey Open-File Report 01-041, A Laboratory Manual for X-Ray Powder Diffraction*. Ethylene glycol can be used to expand swelling clays (e.g., smectites, montmorillonite, nontronite, and beidellite), some mixed-layer clays, and vermiculite as an aid to mineral identification. There are two ethylene glycol treatment methods:

1. Vapor
2. Quick

Vapor Treatment

The advantage of the vapor treatment is less disturbance of the sample and less amorphous scattering of X-rays by excess liquid than in the Quick method.



Figure 22: Glycolator

1. Find the "glycolator" container (*Figure 22*) stored in the ICP preparation sink cupboard.
2. Pour ethylene glycol to a depth of ~1 cm in the bottom of the container.
3. Take off the lid and place the samples on the rack inside the glycolator.
4. Place glycolator in an oven (60°–70°C) overnight (~12 hours).
5. **Figure 19: Glycolator.** Keep samples in the glycolator until ready to run through the D4. **Glycolation only lasts for 4 hours after the samples are removed from the glycol atmosphere.**

Before placing samples in the D4, wipe all sides of the sample holder with a Kim Wipe to remove any ethylene glycol. Ethylene glycol is sticky and can damage the grabber arm and sample spinner.

Quick Treatment

1. Using a glass rod or eye dropper, apply a drop of ethylene glycol directly to the surface of the sample mount.
2. Samples are ready to be analyzed as soon as the glycol is uniformly absorbed on the sample mount. Excess ethylene glycol may be gently mopped up with a Kim Wipe.

Heating Samples

Several clays have intensity peaks at very similar angles making it difficult to distinguish one clay from another. Heating clays is a way to work around this. We can run a sample through the D4, heat the sample in the muffle furnace, run again, and then compare the scans. For example, kaolinite and chlorite have overlapping peaks, making it hard to differentiate one from another. Heat morphs kaolinite, and it develops an amorphous signal, essentially removing its presence in the scan and leaving only the chlorite signal. The amount of kaolinite and chlorite can be determined by comparing these scans.

1. Prepare an oriented clay mount by adding several drops onto a zero-background Si disk in a sample holder and spreading it out evenly with a glass rod.
2. Put the clay mount in the desiccator until it dries.
3. Put the sample in the muffle furnace in the Chemistry Laboratory.

Different temperatures and heating times are used when trying to identify different minerals. Confer with your scientist to determine the parameters.

1. When the muffle furnace has finished its program and is cooling down, wait until the temperature reaches between 100° and 200°C before removing the sample. The sample can be placed in the desiccator until it reaches room temperature. Once it has completely cooled down it can be run in the D4.

Clay Separation Method for removal of Chlorite

For the double peaks of Kaolinite and Chlorite, heating the sample only suggest that one of the minerals is present, it will not give final and complete results for a sample that contains both Kaolinite and Chlorite. In order to determine which mineral is present, an additional treatment is necessary.

1. Take the <2 μm clay fraction, this should be rinsed and free of any treatments, in centrifuge tube add ~20 mL of 1N HCl
2. Vortex the sample to completely dislodge all material before pouring sample into a 100 mL beaker, add stir bar once sample is in place
3. Set hotplate to 300°C (boiling point of HCl is ~101, but in order to maintain a continuous boil the hotplate needs to be much hotter)
4. Set the stir RPM below 100, this is only to keep the material suspended within the HCl
5. Start time once the samples have come to a complete boil, leave for 2 hours — add more HCl as necessary (DO NOT, let the sample go dry and burn)
6. Once the sample has boiled for 2 hours, turn off hot plate and allow sample to return to room temperature before pouring beaker contents back into a clean centrifuge tube, rinse beaker with DI water to collect all material
7. Centrifuge down for 15 mins at 1500 rpm, decant acid and rinse with 25 mL nanopure (3X)
8. After samples has been washed 3X and is free of HCl, centrifuge for 60 mins at 3000 rpm

References

Jackson, M.L., 1956. *Soil Chemical- Analysis Advanced Course* by Hsueh-Wen Yeh, Hawaii Institute of Geophysics, 1980.
Moore, D.M., and Reynolds, R.C., Jr., 1989. *X-ray Diffraction and the Identification and Analysis of Clay Minerals*. New York (Oxford University Press).

Running Samples in the D4

Running a regular XRD sample requires the following steps:

1. Scan the samples on the XRD.
2. Convert the raw sample results to an UXD file.
3. Export the raw scan to a PDF or PNG file.
4. Upload the raw UXD and PDF/PNG files to the LIMS database.

Scanning Samples

Before beginning this procedure, discuss the desired scan parameters with the Science Party. If you need to make a parameter file, please reference Making a Parameter File under Maintenance and Troubleshooting.

Open the XRD Commander program using the icon on the toolbar. *Figure 23* is the initial window.

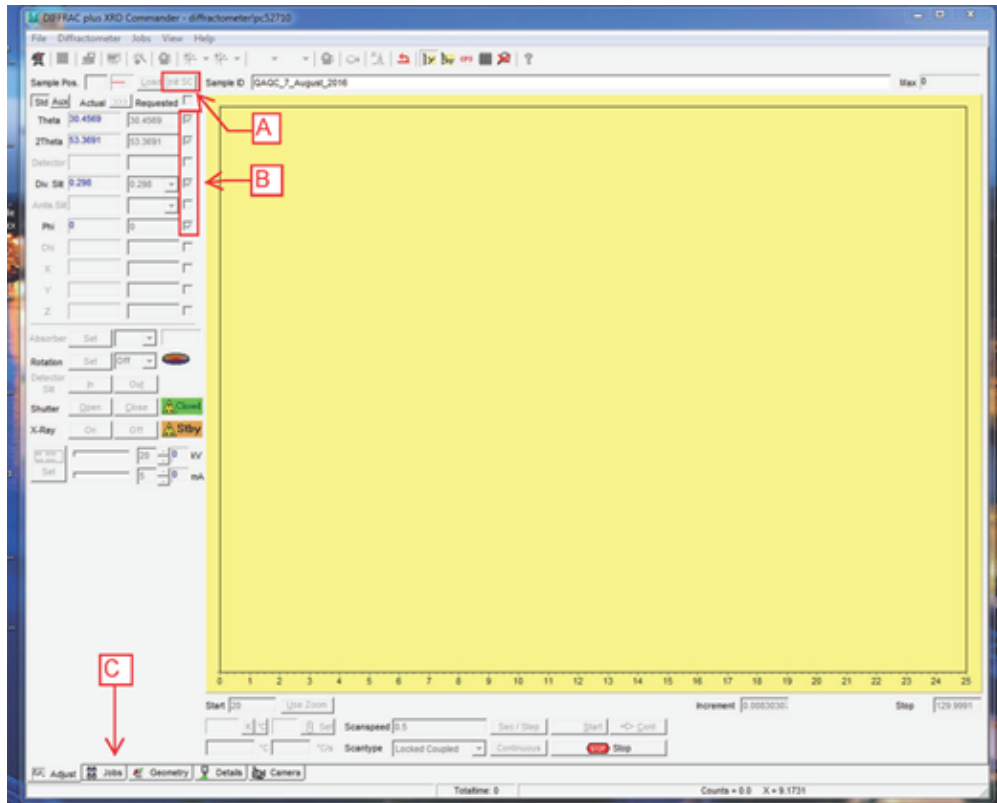


Figure 23: XRD Commander main window. (A) Initialize Sample Changer button (B) Initialize Driver Request checkmarks (C) Jobs tab

First initialize the Sample Changer by clicking on **Init SC** (*Figure 23A*). The checkmarks (*Figure 23B*) indicate the drives that will be initialized. Check the "Div. Slit" box before initializing; the program typically remembers the Theta, 2Theta, and Phi drives. Successfully initialized drives will turn blue. If one or more stay red, you can try restarting the program and reinitializing. If that does not work, close XRD Commander and open D4 Tools and XRD Commander cannot be open at the same time. Go to the drives that will not initialize and click the "Adjust" button. Then close D4 Tools and reopen XRD Commander. The "Adjust" command can also initialize the drives. The diffractometer's sample-changer drives will adjust inside the instrument. If you hear a crash or the program gives an error, see the procedure for readjusting the sample handler in the Bruker manual. This is a lengthy process.

Click on the Jobs tab (*Figure 23C*). On the Jobs screen, click on "Create Jobs".

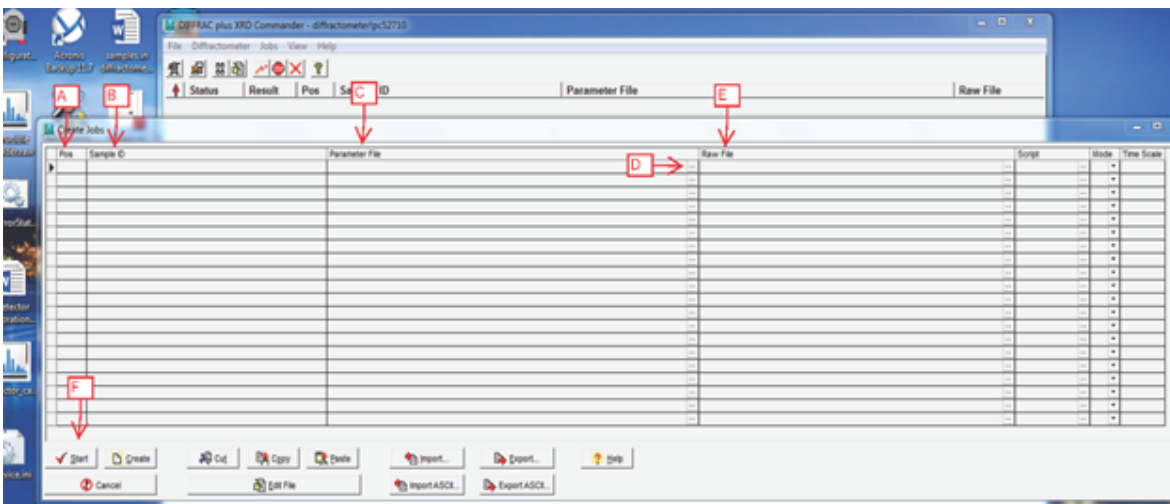


Figure 24: Create Jobs window. (A) Sample position In D4 sample magazine (B) Sample ID (C) Parameter file (D) Open Directory button (E) Raw file (F) Start button

The window shown in *Figure 24* will pop up. Fill in the Position, Sample ID, Parameter File, and Raw File columns.

- **Position:** This is the position of the sample in the loading magazine in the D4, from A1–A6 to K1–K6.

- **Sample ID:** Scan in the label for your sample here. The only format that MegaUploadaTron (MUT) will recognize is Site_Core_Top offset_Bottom offset_TextID (e.g., U1481A_32R4_91_92_QRND8021751). The barcode scanner in the XRD Laboratory is programmed to scan in this exact format including underscores.
- **Parameter File:** This is a premade DQL file that sets the conditions under which samples will be scanned. Access the file by clicking on the "Open Directory" button (*Figure 24D*) This directs you to the Control Panel. Follow the path "Local Disk C: > DIFFDAT1 > DIFFDAT1_old computer pre March 2013". This has a list of all the parameter files. Select one.
- **Raw File:** Sets the location where the results will be saved. Set the location by clicking on the three dots at the end of the cell. Then follow the path "Local Disk C: > DATA > IN". Copy the sample ID into the "Open" line in the window. The sample ID and the name entered into the "IN" Folder must be identical or else the information will not be stored correctly.

The other fields will automatically populate. These should not need to be adjusted. Only change the other settings if you know what to do and refer to the D4 Commander User Manual.

Starting a Scan

When all fields have been filled in for all samples, click on the "Start" button on the bottom left corner of the screen (*Figure 24F*). The program will hesitate for a moment and then load the first sample into the measurement position and a second sample into the sample changer.

Processing Sample Results

When the scans have finished, the results will show up in the "DATA > IN" folder. Two additional file types will be made before uploading the data to the LIMS database. The D4 outputs a RAW file and we create a UXD and PNG file. In addition to the LIMS upload, it is also helpful to create an XRD Data folder for the scientists in DATA ([\NOVARUPTA\S:> Uservol > 1Lab_C_Sedimentology_Petrology](#)) that has a copy of the RAW files. After all three file types have been made, they can be uploaded to the LIMS database through MUT.

Converting a RAW File to an UXD File

The RAW file is only readable by the Eva software, whereas the UXD file is a text file that can be read by other programs. Click the *File Exchange* software icon on the desktop (*Figure 25*).

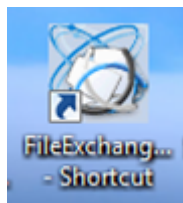


Figure 25. File Exchange Desktop Icon

The initial window (*Figure 26*) will open. The left half of the screen is the file input where you select the files you want to convert. The right half of the screen is where you select the new converted file type and where the files should go.

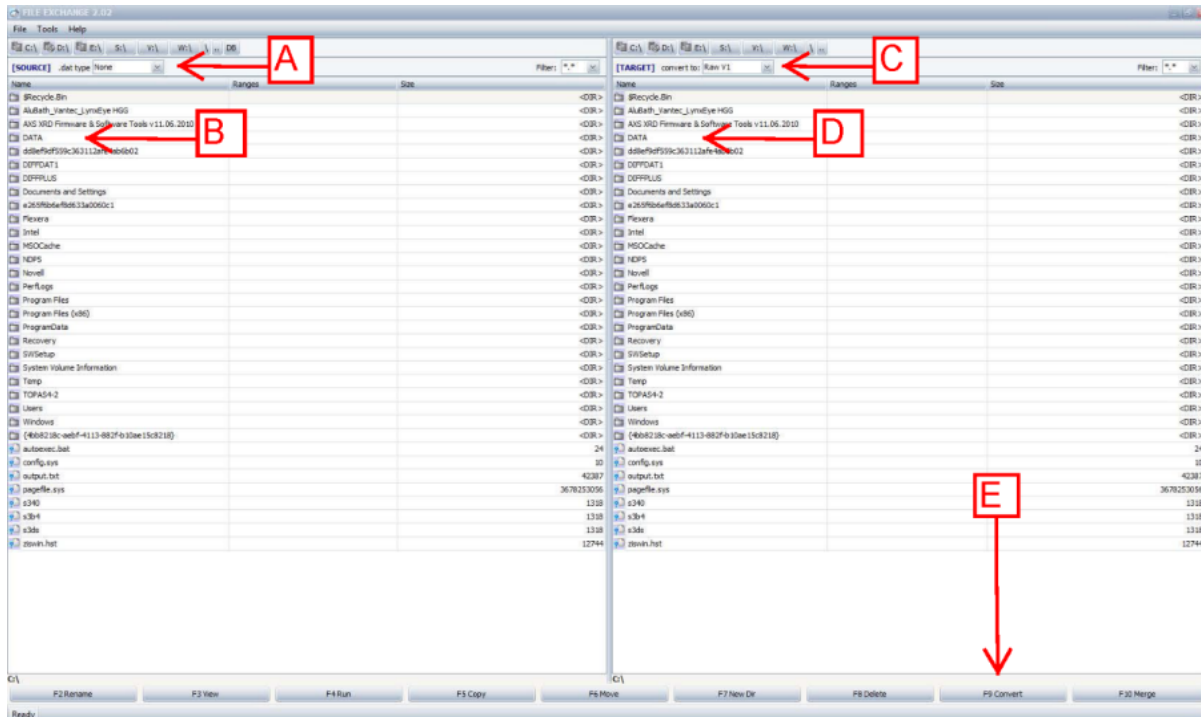


Figure 26: First window in File Exchange. (A) Input File Type dropdown menu (B) Input DATA folder (C) Output File Type dropdown menu (D) Output DATA folder (E) Convert button

First, direct where new files should be saved and select the converted file type. On the right side, click on the file type dropdown menu (Figure 26C) and select "UXD". Then double click on the DATA folder (Figure 26D) and direct files to the "IN" Folder. Move to the left side of the screen and select your input files. The file type (Figure 26A) should already be set to "Raw". Click on the DATA folder (Figure 26B) and go to the "IN" folder. Here you will see all your samples. Select all the samples and then click the "Convert" button (Figure 26E) on the bottom right of the screen. The new UXD files will show up on both sides and you can close down the program.

Printing Scan to PDF or PNG

Go to the DATA > IN folder where all the sample files are currently stored. Double click on the RAW file and it will open in the Eva software.

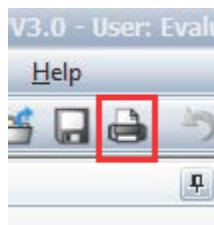


Figure 27. Print Icon

1. Click on the Printer icon at the top of the software outlined in red in Figure 27. A Print Preview window will open up. On the top bar, click the icon for "Export as a PNG" outlined in red in Figure 28. This opens the File Save window. Save with the same name as the RAW file. If the names do not match exactly, the files will not upload. Then close the windows and repeat the process for the next sample.



Figure 28: Export Image as PNG Icon

Uploading Files to LIMS

The XRD files are uploaded using the MegaUploadTron 5000 program. Three files are needed for each scan (RAW, UXD., and PNG):

1. Open the uploader. Make sure the correct Expedition is selected or else your data will not upload properly. Samples that have all the necessary files will have green check marks next to them. A purple question mark indicates that one or more file types is missing for a sample or something else is not quite right. Investigate further. "Check all the files you wish to upload and then click "Upload." Green and orange arrows will pop up next to the samples while MUT is uploading them. When finished uploading, the samples move out of the uploader and from the "IN" folder to the "Archive" folder. Any problematic samples will either remain in the uploader with a question mark or move to the "Error" folder.
2. Check that the files moved into the archive directory and uploaded into the LIMS database.

Cleaning Sample Holders

After the scan results are uploaded, clean the scanned sample holders.

Tap out the powder from the holder and, transfer it back into the sample bag or vial. Clean out the holders with isopropyl alcohol and a Kim Wipe.

Quality Assurance/Quality Control

At the beginning of each expedition, use the NIST 1976 corundum standard to check instrument alignment and detector intensities. Use the Excel instrument verification spreadsheet saved in C:\Documents and Settings\daq\Desktop\XRDdocs\Standard QAQC file name QAQC Corundum std Equipment Verification 3.3.xls. This Excel spreadsheet also has imbedded instructions explaining how to analyze the scan in EVA.

Removing the Anti-Air Scatter Screen

Before running the NIST standard, carefully remove the anti-air scatter screen. Failure to do this may result in a collision of the drives. The screen is only removed when running the corundum standard to check and adjust system alignment. The anti-air scatter screen should always be on when running samples.

1. With two people, carefully remove the cover over the sample staging area, making sure not to hit any wires. The cover is not fastened to the base and will lift off directly.
2. Open D4 Tools and click "Online Status".
3. Click the computer icon to connect with the configuration files in the instrument.
4. Click "Positioning Drives" and "Sample Changer Y" direction.
5. Click "Go", enter "360", and hit "Enter". The sample changer will move in the Y-direction to position 360. This allows you to open the front door and remove the anti-air scatter screen.
6. Open the front door with a socket wrench. Loosen the two bolts on the door and slide the bolts to their opposite side. Carefully let down the door.
7. Remove the anti-air scatter screen. Using an Allen wrench, unscrew the four screws holding up the anti-air scatter screen. These screws are very tiny and easy to drop inside the D4. Be very careful while unscrewing them. The screws are the main support for the screen, so hold onto the screen while removing the screws or else it can fall.
8. When the screws are removed, take off the screen without hitting the theta drives. If the theta drive is knocked, the instrument may signal a hard limit switch error.
9. Close the front door and use the socket wrench to slide the bolts back to their original position and tighten. Go back to the software and move the Y-drive back to Position 1. (Enter "1", "Go", and press "Enter".)

Scanning the NIST 1976 Standard and Verifying QA/QC

Running the Scan

Run the scan as you would for a sample. With D4 Tools closed, open XRD Commander. Initialize the drives and click on the "Create Jobs" tab. Enter the sample position. The corundum standard does not have a text ID, so name it with an informative convention (e.g., Corundum NIST 1976 X342). Make the sure the name matches the name entered in the "Raw File" column. The parameter file, Corundum QAQC continuous 20 to 130.dql, is found at Local Disk C: >DIFFDAT1>DIFFDAT1_old computer pre March 2013. Under the "Raw File" tab, set the path to the DATA>IN folder; this scan will not be uploaded to the LIMS database.

Click **Start** and wait for the scan to finish.

Processing the Scan

1. Open scan (remember the QAQC parameter file Corundum QAQC continuous 20 to 130.dql ran without the anti-air scatter screen).
2. Subtract the background (do not append, just simply close background menu) (*Figure 29*).

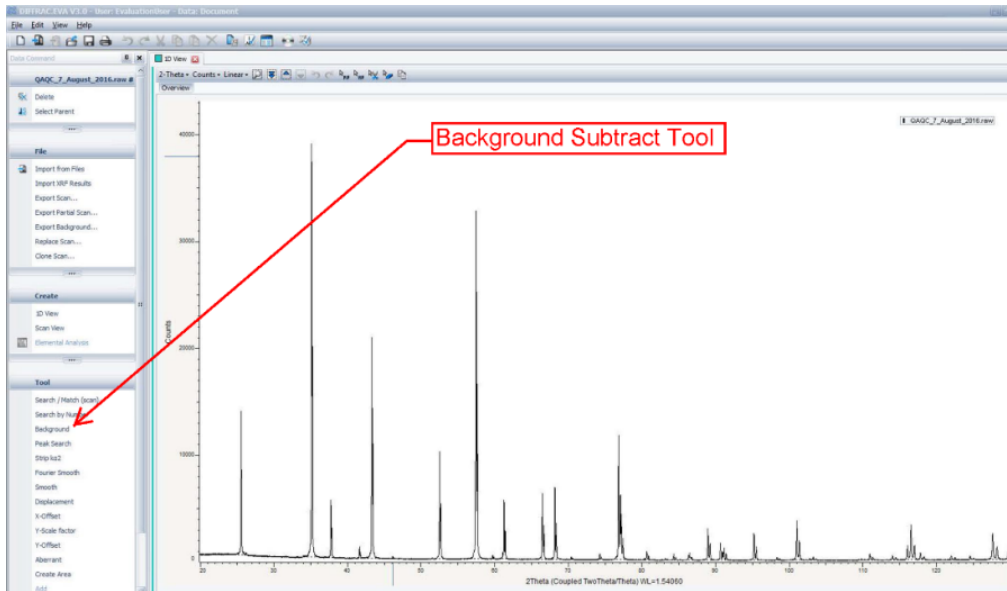


Figure 29: EVA diffractogram.
The arrow points to the Background Subtract tool.

3. Strip K_2 and Append (Figure 30).

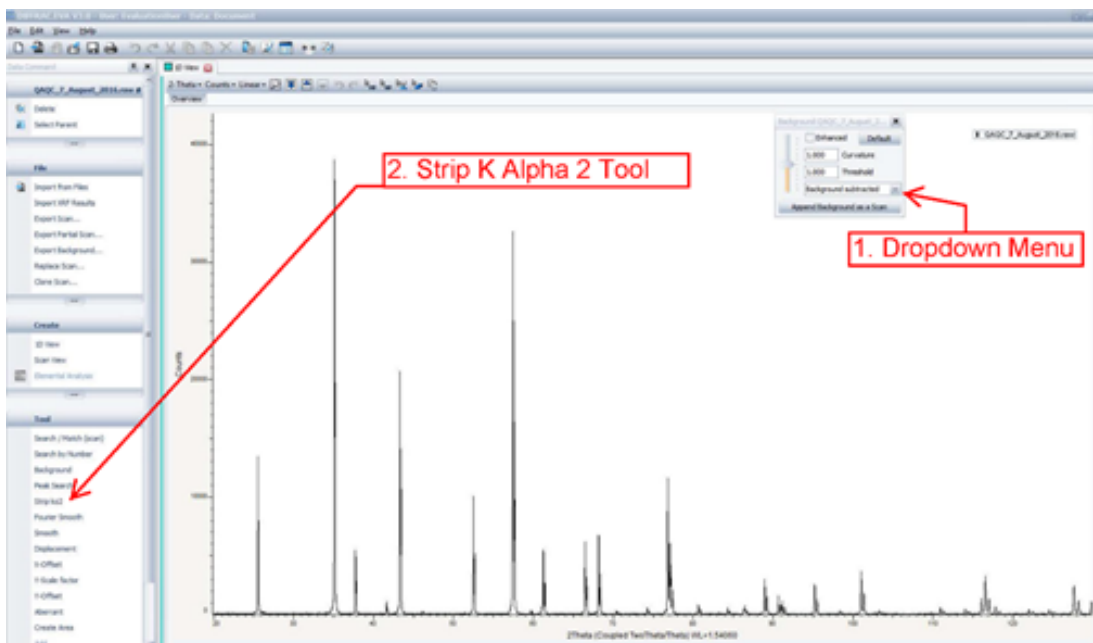


Figure 30: EVA diffractogram with the background subtracted. (1) Dropdown Menu to Append Scan
(2) Strip K_2 Tool

4. In the "Data Tree" panel there are two scans: Background Subtracted Scan and K_2 Subtracted Scan (Figure 31). For both of these scans, you will "Create Area" and "Append Area" for four angle ranges. This will insert area information as a subtree entry under that scan.

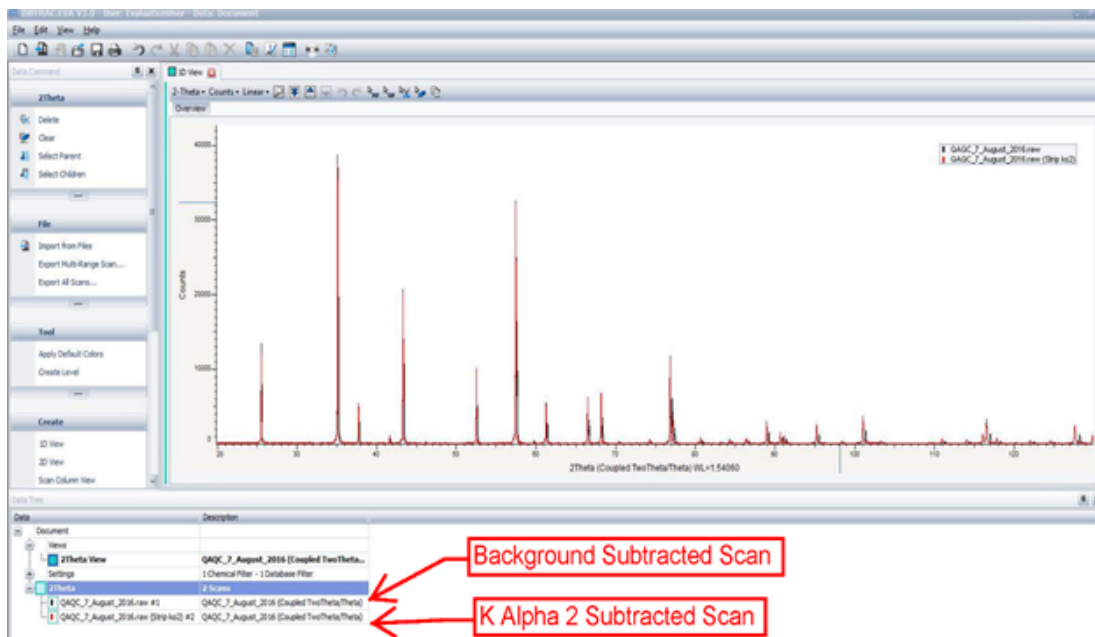


Figure 31: Diffractogram with two scans in Data Tree panel. Top arrow points to the Background Subtracted scan. The bottom arrow points to the K2 scan

5. Select the area around each peak as shown below in Figure 32. Click on either scan so that it is highlighted (Figure 32). Then click "Create Area" (Figure 32-2). A New window will pop up where you can enter the left angle and right angle (Figure 32-3, 32-4).

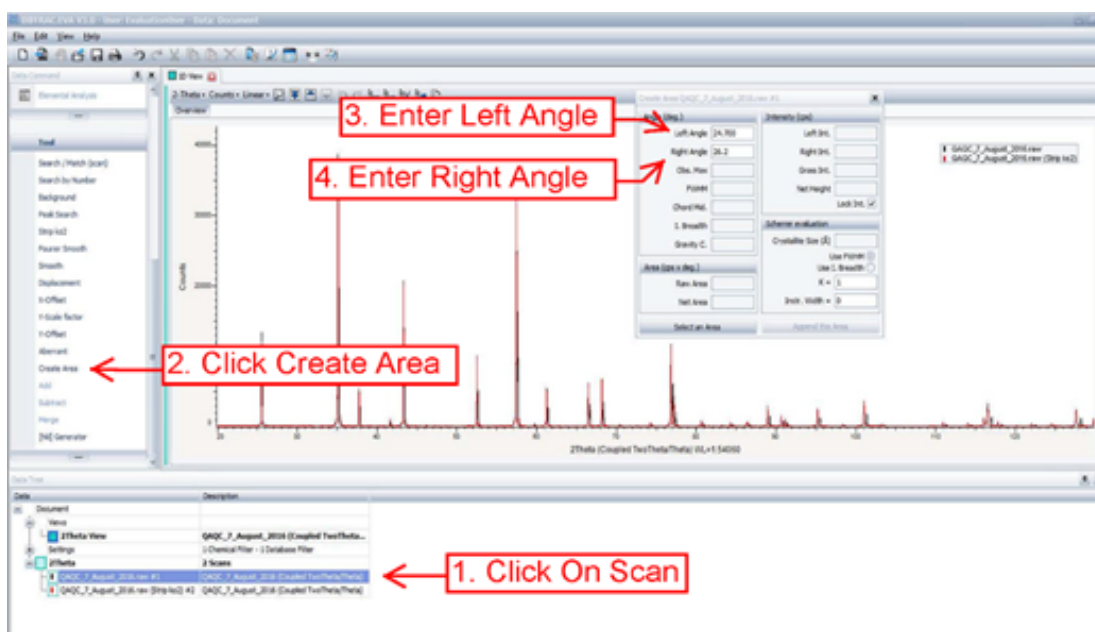


Figure 32: Create Area for Scan Angles. (1) Arrow points to scan name (2) Create Area tool (3) Left Angle entry field (4) Right Angle entry field

6. After you enter in both angles click again on the left angle. This populates the rest of the fields. When all fields are populated, you can click on "Append Area" (Figure 33). Do this for each of the following angle ranges for both scans:

- 25.576°2 (24.7°–26.2°2)
- 35.149°2 (34.0°–36.2°2)
- 88.993°2 (88.1°–89.7°2)
- 126.8–129.0 (angle range is not necessary but recommended)



Figure 33: Create Area Window A. Append this Area button.

7. Right-click on the "Area List #" subheader for background-subtracted scan and select "Create and Area Column View" (Figure 34). Do the same for the K₂ appended scan. This creates another tab on top with the Area data in column format.

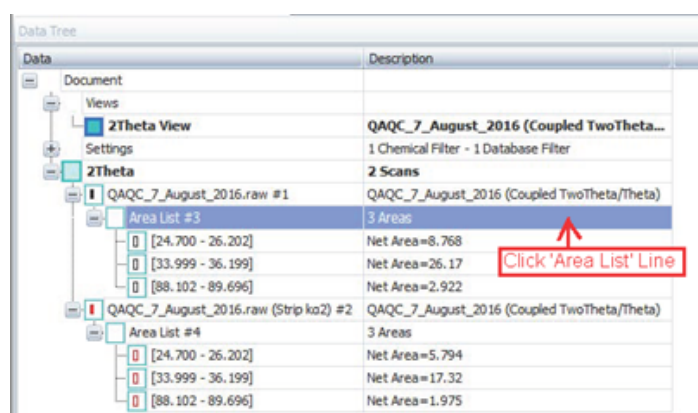


Figure 34: Data Tree panel Scan Area list.

8. Open the QAQC corundum standard Equipment Verification 3.3.xls Excel spreadsheet.

9. Enter your name and date and select "Vantec-1" for the detector.8. Enter the following values into the spreadsheet (Figure 35, Figure 36):

- For 2 Obs, use the Chord. Mid values from the K₂ appended scan areas (Figure 31–1)
- For I Obs, use Net Area from the background subtracted scan areas (Figure 32–1)
- For FWHM, use the FWHM from the K₂ appended scan areas (Figure 31–1)

Index	Name	Parent	Scan	Left Angle	Right Angle	Left Int.	Right Int.	Obs. Max	d (Obs. Max)	Gross Int.	Net Height	FWHM	Chord Mid.	d (Chord Mid.)	I. Breadth	Gravity C.	Net Area
1	[24.700 - 26.202]	Area List #1	QAQC_7_August_2016.raw (Strip ko2) #2	24.700	26.202	2.62	2.54	25.504	3.47059	68.0	65.4	0.072	25.583	3.47921	0.089	25.51	
2	[33.999 - 36.199]	Area List #4	QAQC_7_August_2016.raw (Strip ko2) #2	33.999	36.199	1.98	1.65	35.156	2.55063	206	204	0.067	35.135	2.53070	0.085	35.15	
3	[88.102 - 89.696]	Area List #4	QAQC_7_August_2016.raw (Strip ko2) #2	88.102	89.696	0.583	0.669	88.994	1.09906	16.5	15.9	0.093	88.996	1.09904	0.124	88.96	

Figure 31: K₂ subtracted Scan Area column view. (1) Chord Mid value (2) FWHM value

Scan	Left Angle	Right Angle	Left Int.	Right Int.	Obs. Max	d (Obs. Max)	Gross Int.	Net Height	FWHM	Chord Mid.	d (Chord Mid.)	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area	Cryst. Size	K	Instr. Width
QAQC_7_August_2016.raw #1	24.700	26.202	3.90	3.77	25.591	3.47016	76.7	72.8	0.108	25.602	3.47659	0.120	25.598	3.47710	14.53	8.768	840.2	1.000	0.000
QAQC_7_August_2016.raw #1	33.999	36.199	2.83	2.47	35.157	2.55054	234	211	0.106	35.175	2.54931	0.124	35.184	2.54867	32.01	26.17	872.9	1.000	0.000
QAQC_7_August_2016.raw #1	88.102	89.696	0.874	1.05	88.994	1.09906	16.9	15.9	0.248	89.073	1.09829	0.183	89.080	1.09822	4.453	2.922	499.2	1.000	0.000
QAQC_7_August_2016.raw #1	126.802	129.003	1.15	1.33	127.680	0.85821	14.4	13.2	0.363	127.681	0.85820	0.317	127.668	0.85752	6.902	4.175	1229.7	1.000	0.000

Figure 32: Background Subtracted scan area column view. (3) Net Area value

10. The spreadsheet has the calculations already embedded.

If the RED "*ZI correction must be applied*" shows up, you will need to open the Configuration and adjust the home position for the 2Theta drive. If there is no message just save the worksheet under a new name and no more action is needed.

Apply ZI Coorection

Open the Configuration Program on the desktop (*Figure 33*).



Figure 33. Configuration program icon

In the left side panel navigate to **Motorized Drives > 2Theta** (*Figure 34*). In this window go to **Zero Reference - Home of the Axis**. Enter the corrected ZI value from the excel spreadsheet into the 'Zero' space (*Figure 34*).

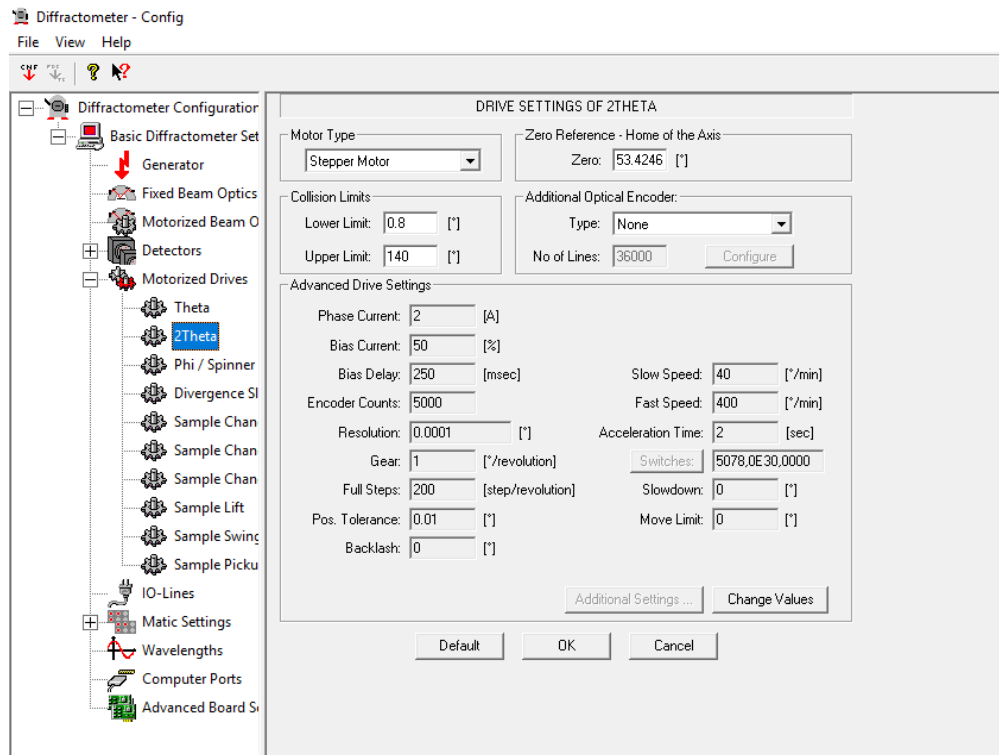


Figure 34. Configuration 2Theta page

Select 'File' > 'Save and Download' or click on the red CNF arrow.

DO NOT CHECK THE BOX FOR THE PSD CONTROLLER. Downloading the config file to the PSD Controller corrupts the Controller. For more information see the Troubleshooting section. Always backup the config.file on the server. With **ONLY** the 'Save Configuration' and 'Download Configuration to Diffractionmeter' boxes checked select 'OK' (*Figure 35*). The new configuration will take a moment to download to the Diffractionmeter.

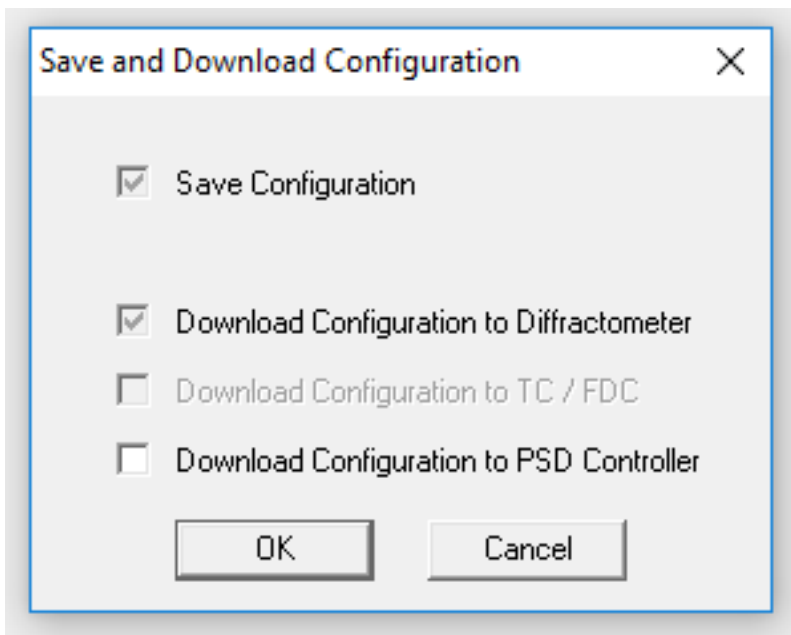


Figure 35. Save and Download Configuration page. Correct settings to save

Now that the scan is complete put the Anti Air Scatter Screen back on. Move the y drive to the 360 position and open the front door. Line up the Screen with the screw holes. There is a small divet and you will feel the Screen settle into place when positioned correctly. Then carefully put on the screws. When the Screen is back in place close the door and put the cover back on the base.

Health, Safety, and Environment

The D4 Endeavor has several safety issues that should be reviewed. Please see the *Bruker Manual D4 Endeavor XRay Diffractometer – Introductory User Manual* for the list of precautions.

Warnings

Danger: Radiation

The diffraction system has a strong X-ray source, and the direct source beam is very intense. Exposure to radiation for even a fraction of a second can cause severe burns. Longer exposure can cause severe or even lethal injury.

Emitted radiation is minimized by shielding and safety equipment to be $<2.5 \mu\text{Sv/h}$ during operation. The enclosure of the diffraction system serves as protection against the scattered radiation produced during the measurement. Ensure the enclosure is configured correctly as follows:

- The goniometer must be fixed in the interior of the radiation protection enclosure.
- The X-ray tube mount must be attached to the goniometer.
- The primary optics must be mounted.
- The radiation protection enclosure must be installed completely.

Danger: High-Voltage

Voltages up to 50 kV are generated, but they are not accessible from the outside of the system. High voltages exist in the high-voltage generator, the X-ray tube, and the high-voltage cable.

Caution: Electrical Shock

When equipment is connected to the mains supply, some terminals of the mains distribution unit may be live. Switch off the external mains supply before opening the side panel; it is not sufficient to simply turn the "Power Off" button.

To prevent electrical shock, turn off the D4 main power supply before:

- Touching components on the main distribution board
- Inserting/removing fuses
- Exchanging the fluorescent tube or USB hub
- Connecting/disconnecting electrical devices to the AC outlets
- Installing or removing an internal or external cooling unit
- Connecting or disconnecting an external water valve

Caution: Moving Mechanical Components

The cover of the sample magazine can be opened at any time during measurement. When the cover is open, sample handler drives stop and stay frozen until the cover is closed again; however, active measurements being made inside the X-ray enclosure will continue. If the S604 key switch is activated, sample handler drives will not stop when the magazine cover is open and the drives inside the radiation enclosure will continue to run even if the front or rear panel is removed. Do not touch any moving components when the key switch is activated.

Danger: Injury

Goniometer components move quickly during operation. If parts of the radiation enclosure are removed, the goniometer may be accessible during operation. When opening or closing the sample magazine, hold the cover with your hand until the final open or close position is reached. Do not release the magazine cover in an intermediate position.

Danger: Beryllium

Do not touch the front window of the X-ray detector or the X-ray tube, as they contain beryllium. Beryllium is potentially hazardous if ingested, inhaled, or absorbed through the skin.

Warning: Batteries

Disposal of batteries from electronic boards must comply with safety regulations.

Emergency Stop

The "Emergency Stop" button located on the front of the D4 Endeavor, when pressed, stops all control electronics, high-voltage generator, and all components connected to the three mains sockets on the mains distribution unit. The X-ray source is turned off and all moving drives will stop immediately. Use only in an emergency.

Chemical Hazards

Ethylene Glycol

Ethylene glycol is toxic and should not be ingested. It is also harmful if inhaled or absorbed through the skin and eyes. Proper personal protective equipment should be used when handling this compound.

Borax

This chemical largely consists of potassium sulfate and is not expected to be a health hazard.

Nitric Acid, Concentrated, or 10%–15% for the Water Bath

Concentrated nitric acid (50%–70% HNO_3 v/v) is highly dangerous. It can cause severe tissue damage on contact, is highly toxic, and the fumes present similar risks of poisoning and chemical burns. When mixed with water, nitric acid liberates large quantities of heat, so appropriate care should be used when diluting this compound. This compound is also a strong oxidizing agent, so nitric acid waste should not be mixed with any organic materials. Note that the nitric acid used in the water bath is still dangerous and should be treated with the appropriate care.

Hydrochloric Acid, Concentrated, or 2 M for Carbonate Dissolution

Concentrated hydrochloric acid (~12M) is highly dangerous. It can cause severe tissue damage on contact, is highly toxic, and the fumes present similar risks of poisoning and chemical burns. When mixed with water, hydrochloric acid liberates large quantities of heat, so appropriate care should be used when diluting this compound. Note that the 2 M hydrochloric acid used in the carbonate dissolution procedure is still dangerous and should be treated with the appropriate care.

Acetic Acid, Glacial, or 10% for Carbonate Dissolution

Glacial acetic acid (~100%) is highly dangerous. It can cause severe tissue damage on contact. When mixed with water, glacial acetic acid liberates a lot of heat, so appropriate care should be used when diluting this compound. When diluted to ~10% concentration, it is very similar to white vinegar, so while it is still acidic and could cause tissue damage, it is not as hazardous.

Maintenance and Troubleshooting

Maintenance

Tube Conditioning

If X-rays have not been turned on in longer than 24 hours you must turn on tube conditioning to avoid damaging the X-ray tube. In D4 Tools select "X-RAY" under the Instrument tree, then Utilities -> X-Ray Utilities -> Tube Conditioning ON/OFF (*Figure 36*).

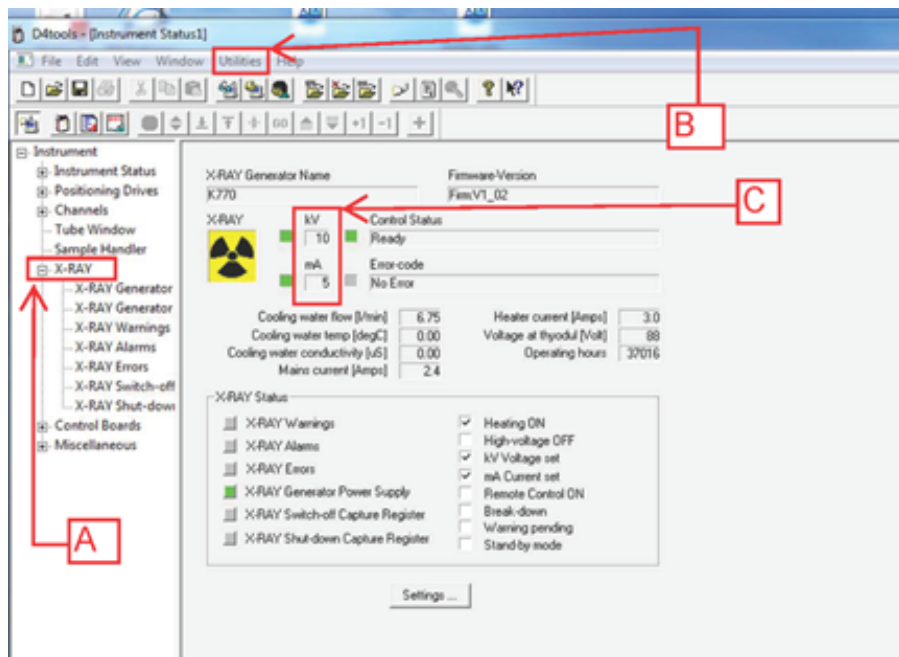


Figure 36: D4 Tools X-ray subtree window. (A) X-ray subtree button (B) Utilities command (C) Standing kV and mA

Only click on tube conditioning on/off once. In the bottom right corner of the screen you should see a message 'Tube Conditioning On' (*Figure 37*).

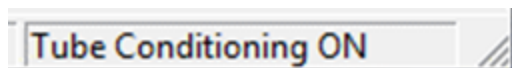


Figure 37: Tube Conditioning On Indicator

After about a minute the kV will start to increase in increments from 20kV to 55kV. The whole program takes about one hour and when kV returns to 20 the program is complete. Note the operational status on the maintenance spreadsheet posted in the lab. To do this click on Manual Control (small head icon) and type GS11. The resulting number is the status number.

Turning off the D4 and HASKRIS

First turn off the D4 in the opposite order that you turned it on: Turn the key to off, turn off the mains power, disengage high voltage, and turn off the power switch The Haskris chiller must remain running for at least one hour after turning off everything else to properly cool down the x-ray tube. The D4 can be off while leaving the chill water on, but if the HASKRIS is off the D4 must be off.

Cleaning the Diffraction System

To clean the interior of the enclosure and exterior of the detector components, use dry cleaning utensils only. Do not use water or aggressive cleaning agents.

Air flow is critical to maintaining proper operation of the detector electronics. Do not place anything on the controllers that may restrict air flow. Regular cleaning includes removal of air flow restrictions, including dust.

Changing HASKRIS Tank

Regularly check the filter in the HASKRIS tank. If there is a lot of debris it may be necessary to drain the tank and **refill with DI water only**. The filter can be sprayed off in a sink taking care not to puncture the screening. If the water flow rate to the system begins to drop close to 4 L/minute it may mean there is a clog in the quick disconnect points behind the back panel or the sprayer head in the X-ray tube housing needs to be cleaned.

Checking QAQC Files

Compare the QAQC corundum scan with past results. X-Ray Tubes deteriorate. When the intensity of the Corundum scan is approximately half of what it was at the date of installation it is time to replace the tube. Check the scans for Tungsten lines, if any appear it is time to replace the X-Ray tube even if the intensity is still acceptable.

Making a Parameter File

A parameter file tells the D4 the conditions that a sample will run under. This is a DQL file made with the XRD Wizard program. The parameter file includes scan settings, scan parameters, generator settings, and beam optics. Some of these settings are constant because they are hardware features of our D4. To start, double-click the XRD Wizard icon on the Desktop (*Figure 38*).



Figure 38. XRD Wizard Desktop Icon

An empty gray screen will open. There options on the top bar to either open a preexisting file or open a completely blank sheet. It is better to open and edit an old file and save it under a new name. Many settings are fixed, and editing a file reduces the chance of entering in a wrong value. After a file (new or old) is opened, this first screen will open (Figure 39). Change the "Operator" to your name and click "OK" at the bottom of the page. You can click "Update" to get the current date and time.

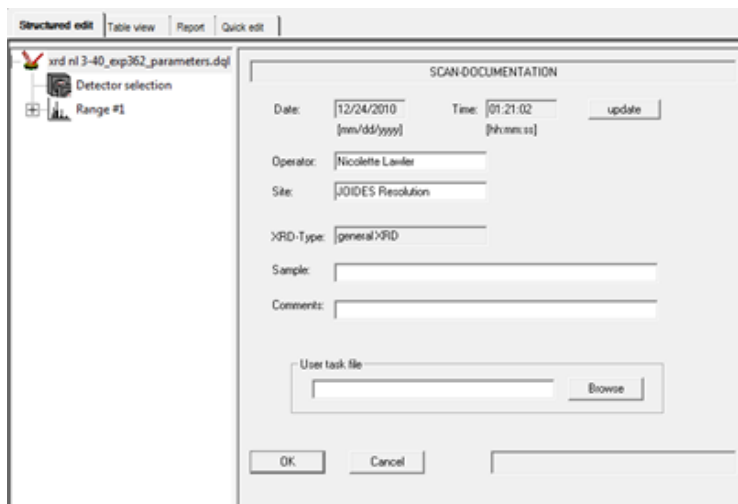


Figure 39: First page of parameter file setup.

The second page declares the detector and PSD electronic window (Figure 40). These settings are PSD: VANTEC-1 and 3. Do not deviate from these values. Click "OK" and continue to Scan Settings.

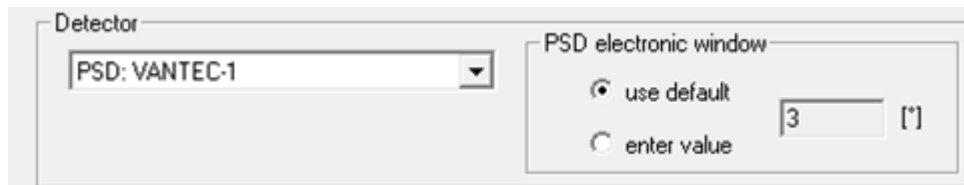


Figure 40: Detector declaration.

Scan Settings includes Scan Type and Sample Rotation (Figure 41). Scan Type should stay set to "Locked Coupled". This is a hardware setting indicating that the theta and 2theta positions move together. Under Sample Rotation, the Spinner can be set on or off. This spinner spins the sample while being scanned. This is typically on because it captures all potential angles of the sample giving a complete image of the material. Rotation Speed is set to 30 rpm and .5 rps (you only have to enter in one of these fields). Click "OK" and continue to scan parameters.

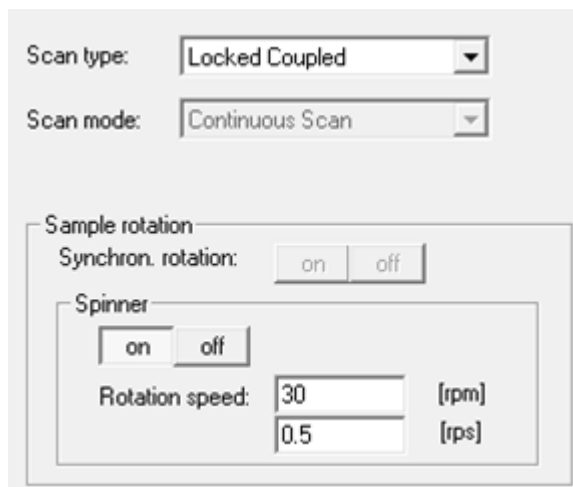


Figure 41: Scan Settings parameter window.

Scan Parameters includes the scanned angle range, angle step size, number of steps, time per step, and delay time (Figure 42). Adjust the angle range depending on the material and scientific objectives. For example, if looking for clays, set a low angle (3°–30°). The step size determines how much the goniometer will move before recording more data. The number of steps will adjust itself based the step size and angle range. Time/Step controls how long each step is measured. The Delay Time will add in an amount of time to wait before scanning the next sample. The machine does have limits on these settings and if something is entered outside of its range it will alert you. Click "OK" and move onto Generator Settings. At low angles (2–4°2theta) there is a very sharp peak. This is caused by beam overspill onto the sample holder.

Scan Parameters

Scan axis: 2Theta Theta

Start: 3.0000 [°] 1.5000 [°]

Stop: 39.9985 [°] 19.9992 [°]

Step size: 0.01660614 [°] 0.0083 [°]

No. of steps: 2228

Time/Step: 0.8 [s]

Use Encoder:

Delay Time: 0 [s]

Tot. scan time: 0:32:10 [hh:mm:ss]

Figure 42: Scan Parameters window.

Generator Settings contains the X-Ray Tube Configuration and Generator Configuration (Figure 43). The X-Ray Tube values are constant. You can adjust the kV and mA in the Generator Settings. The voltage is typically between 30 and 40 kV and the current is 40 mA. Lowering these values too far can reduce peak intensity. Click "OK" and continue to the Beam Optics window.

Tube:

Element: Cu k-Alpha1: 1.54060 [Å] Bond: [] [Å]

k-Alpha2: 1.54439 [Å] k-Beta: 1.39222 [Å]

Generator

Voltage: [] 40 [kV]

Current: [] 40 [mA]

Figure 43: Generator Settings window.

The Beam Optics settings lists the Divergence Slit and AntiScattering Slit (Figure 44). Both of these are constant values based on our hardware setup. The Divergence Slit should be set to .300°. Click "OK" and you will have finished all the settings and will loop back to the first window.

Motorized slits

Divergence Slit: 0.300 [°]

Antiscattering Slit: []

Figure 44: Beam Optics window.

Save the file under a new name to the path Local Disk C: > DIFFDAT1 > DIFFDAT1_old computer pre March 2013. You can print this file by clicking the "Report" tab at the top the subtree window and then clicking the print icon. Occasionally scientists will ask for a printout of the settings to put in their reports.

Checking Quality of a Scan

A peak should have a minimum of 5 data points above the halfway up a peak. During an active scan in XRD Commander go to the main 'Adjust' tab and right click in the measurement window. Select 'dots'. The scan changes from a continuous line to the individual data points. Zoom in on a few peaks and count how many dots are above the halfway point on a scan. It is fine to have more than 5 points but less than 5 means the peak shape is not well resolved. If less than five suggest to scientist a longer measuring time.

Troubleshooting

For specific errors or instructions on adjusting or realigning components on the D4 please refer to the D4 hardware maintenance binders in the XRD lab.

Display data on computer screen has flatlined or is nonexistent

Ensure the detector type *VANTEC-1 PSD* is selected in the "Details" tab of the *COMMANDER* program.
Ensure the detector setting matches the factory setting and the setting in the *Config* program. Set the detector to factory settings using the "Set Detector" button.

Angular accuracy peak position data is greater than +0.01° of expected value.

Run the NIST 1976 standard (see *Quality Assurance/Quality Control*) and import the values into the instrument verification spreadsheet. Perform a Zi correction if needed. Calibration of the VANTEC-1 detector may be required. See the detector manual.

Poor instrument resolution (FWHM > 0.065° of the 104 reflection of NIST 1976)

Repeat alignment of the 2 DOF mount for the VANTEC-1 detector.

Scan outside software limits

Using fixed scan mode, the start to stop range is determined by the configuration and cannot exceed the geometry angle set in Config (max = 12°).

Appendix A: Running Samples in Manual Mode

At some point it may be necessary to run samples in manual mode, for example the automatic sample grabber is not working. Manually loading samples does require the user to load in samples one by one, making a more labor intensive process.

To run the D4 on manual mode:

1. Place the sample, by hand, into the sample transport (Sample swing).
2. Set up the Job in XRD Commander
3. In the Job tabs, create a new job
4. For sample position, enter "man"
5. Set the rest of the job up as normal, i.e. dql file, raw file...
6. Select start
7. The sample will swing back into place, and lift it into measuring position
8. When the measurement is done, the sample will be brought back to the front of the sample transport.
9. Multiple dql files can be used only if the same sample is being measured.

There is no way to set up multiple runs with this method. Please note a sample can also be loaded in the 'Adjust' tab by entering 'Man' in the Sample Position box and then selecting the 'Load' button.

Credits

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