Bruker D4 XRD User Guide

Training and maintenance videos can be found on the XRD technician computer, Desktop/XRD_ICP Prep Documents/Bruker TRAINING VIDEOS

Table of Contents

Introduction

The X-Ray Laboratory onboard the R/V *JOIDES Resolution* (Foc's'le deck) performs diffraction analyses of minerals and rock powders. The laboratory uses a Bruker AXS D4 Endeavor XRD (a.k.a. Bruker or D4) and a PANalytical Aeris XRD (a.k.a. Aeris) diffractometers (*Figure 1*).

Bruker-associated softwares, DIFFRACplus XRD CommanderEVA, and TOPAS, allow for powder diffraction analysis of minerals, including peak-matching and mineral and chemical compound identification. XRD scans from the Bruker can also be analyzed using HighScore Plus software (used for the Aeris measurements). The X-Ray lab provides scientists with a quick and reliable tool for mineral identification; particularly useful for identifying bulk mineralogy, clays, fine-grained minerals or mixtures of secondary minerals. In addition, XRD can be used to determine mineral proportion.

Figure 1. A. Bruker D4 Endeavor XRD. B. PANalytical Aeris XRD in the X-Ray lab

Principle of X-Ray Diffraction

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 (2, which can be measured) and the wavelength of a generated X-ray beam (, which is known based on the material generating the X-rays), the scientist can determine the d-spacings by using **Bragg's law** (*Figure 2*):

n = 2d*sin*

n = order of the diffracted beam
 = wavelength of the incident X-ray beam
d = distance between adjacent planes of atoms (d-spacings)
 = angle of incidence of the X-ray beam

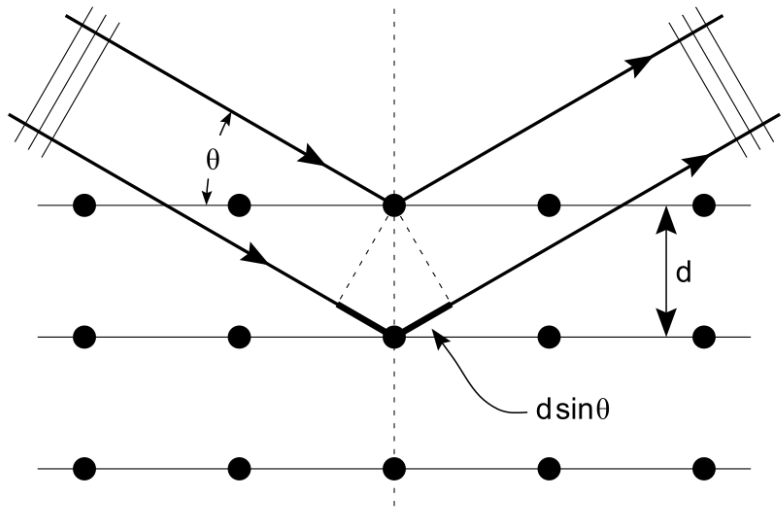


Figure 2. Bragg's law

References - Further reading

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.

Books are available in the X-Ray lab upon request.

Instrument Apparatus and Hardware

This section presents instrumental characteristics of the Bruker AXS D4 Endeavor X-ray diffractometer (XRD) in the X-Ray lab. For the Aeris, see the Aeris Advanced User Guide.

The Bruker is composed of:

- Goniometer
- X-ray source (sealed vacuum tube with line focus): on the JR, a Siemens ceramic X-ray tube KFL Cu-2K, 2.2 kW, 60 kV, 0.4mm x 12mm is used
- Tube housing (ceramic body that protects the tube and shields from X-rays)
- Mount
- Sample holders
- Vantec-1 detector
- Optics
- Slit systems
- Haskris water chiller for the X-ray tube

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 (*Figure 3*).

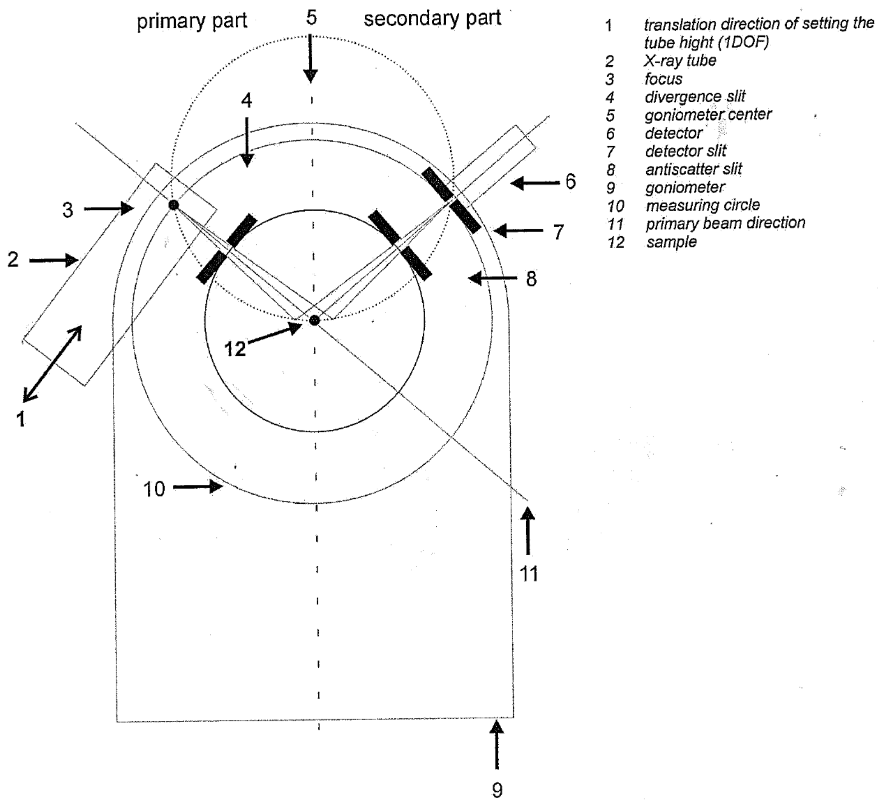


Figure 3. Schematic drawing of the beam path of the Bragg Brentano geometry in the Bruker (from the D4 Endeavor User Manual).

The X-Ray radiation generated by the electron beam in the anode material (i.e., Cu for our instrument) of the X-ray tube hits the sample in the goniometer center and is diffracted by the crystalline properties of the sample (*Figure 3*). The diffracted radiation is detected by an X-ray sensitive detector and gives qualitative and quantitative results according to the properties of the sample (i.e., chemical composition and physical properties like crystallinity).

During the measurement of the characteristic diffraction pattern of a polycrystalline sample, the sample rotates with a constant angular velocity around the goniometer center (circle). Simultaneously to this rotation the detector rotates at double angular velocity around the goniometer center (2 circle) and sample, respectively. The 2 rotation is perpendicular to the measurement plane as well and concentric to the circle. In other words, the diffraction angle 2 where the detector is positioned is the angle between the primary beam direction and the diffracted beam direction.

Goniometer

The goniometer has 2 circles: the theta () circle, which sets the sample position, and the 2 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, /2
Max angular range	–8° < 2 < 170°
Smallest step width	0.0087°
Reproducibility of /2 angle	±0.0002°
Absolute accuracy (/2)	<±0.005°

Detector

The VANTEC-1 detector features the fastest simultaneous recording of XRD patterns within a wide 2 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 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 µm; >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 %, non condensing

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

Sample Holders

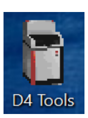
Sample holders for powdered XRD samples are steel or steel with a silicon or quartz spacer. The selection of a sample holder depends on the volume of sample to be analyzed.

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)

Instrument Software

DIFFRAC Plus XRD Commander 

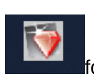
is the running software of the Bruker D4 XRD.

D4 Tools 

is a "troubleshooting' software for the D4.

Two other software applications are needed to analyze the diffractograms obtained with the D4:

- **DIFFRAC.SUITE.EVA**, version 5.1 is available 

- **DIFFRAC.TOPAS** version 4.2.0.1 software  for diffractogram analysis

Instrument Preparation

The instruments in the lab need to be turned on **<u>in this order</u>**: (1) HASKRIS water chiller and (2) D4 XRD. The HASKRIS cools the water supplied to the D4 to prevent the X-ray tube from overheating. **Turning the D4 on prematurely (i.e., before the water chiller) could damage the X-ray tube.**

Procedure for Turning on Instruments

Turning on Haskris and Bruker D4

1. Flip the "ON" switch *(Figure 4C*) to the HASKRIS and the water in the tank will begin to cool. The water temperature needs to reach 69°F (*Figure 4A*). The Haskris temperature can range between 65°F to 69°F (18-21ºC). Ensure all water valves to/from Haskris are open. The flow rate should be greater than 4L/min.

Figure 4. HASKRIS Control Panel. (A) Actual temperature. (B) Set temperature. (C) On/Off switch. (D) Flow meter

2. Flip the "ON" switch (*Figure 5A*) on the side of the Bruker D4 XRD.
   a. The solid green "Low Voltage Ready" light (*Figure 5F*) turns on.
   b. You will hear several beeps and the "System Ready" light (*Figure 5D*) will start flashing green.
3. Press the "High Voltage Enable" button (*Figure 5B*).
   a. The orange "High Voltage Ready" (*Figure 5E*) light will turn on.

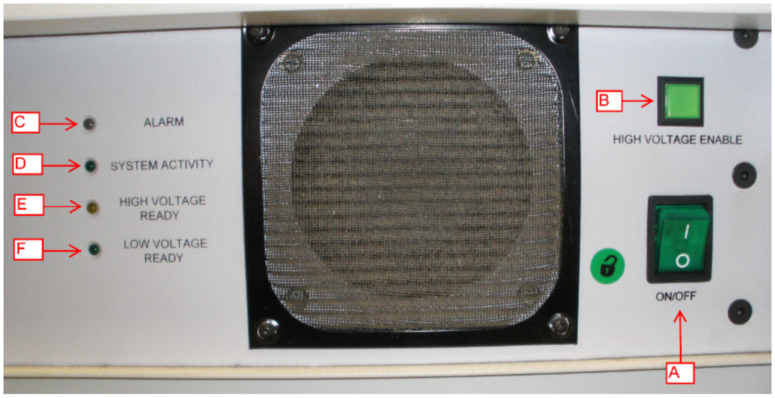


Figure 5. Side control panel on D4 XRD. (A) Power On/Off. (B) High voltage enable button. (C) Alarm light. (D) System Ready flashing light. (E) High voltage ready light. (F) Low voltage ready light.

4. Go to the front of the machine and press the green circular button (*Figure 6*). This enables the mains power and activates the sample handler.

Figure 6. D4 Front control panel.

5. Turn the “Generator Power” key to the right and hold it for a few seconds and look at the lights on top of the D4 (*Figure 7*). When the "Alarm" light turns off and the “Ready” light turns on, as well as the lights at the sides of the top of the D4, release the key back into its middle position.

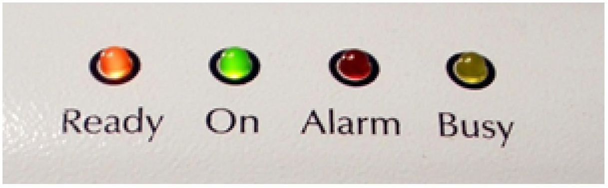


Figure 7. D4 top control lights.

6. 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 more than 4 days that the D4 has been turned on, the X-ray tube needs to be conditioned. Go to the **Maintenance** section under **Tube Conditioning** for instructions and log the date of tube conditioning in the XRD maintenance log in XRD's Lab Notebook on Confluence.

Shutting Down the Bruker D4

The Bruker D4 can be kept on when not in use. However during extended periods such as Tie-ups or if there is not someone to check on the instrument it can be shut down. The Haskris can also remain on, or it can be turned off if no one is able to monitor it. **If the Bruker D4 is on, the Haskris must be on as well.**

1. Turn the X-Ray generator off by turning the key counterclockwise (*Figure 6*).
2. Push the Red mains button (*Figure 6*).
3. Turn off the High Voltage button B as shown in *Figure 5*.
4. Turn off the detector button A as shown in *Figure 5*.

Sample Preparation

NOTE: Sample Preparation for XRD Analyses is in the main Laboratory Manuals, Guides and Resources>XRD confluence page.

Sample preparation is split into 3 main categories:

1. Bulk Sediment
2. Hard Rock
3. Clay Separation

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

Preparing Sample Holders for the D4

There are three ways to load a sample holder: front load, side load, and back load. 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 front loading if preparing samples for semi-quantitative analysis.

Make sure the sample from the sampling table (in the Core lab) is enough material to fill a sample holder - sample size for bulk powder is generally a 1-2 cm QRND (Quarter Round) from the section half.

Front-Load Samples

This technique is commonly used to prepare samples to be measured with the D4.

1. Unless the sample material is very small (see Sample Slurry/Smear Slide Mounting for Small Sample Amounts), select the appropriate sample holder (*Figure 8A*).
2. Label the sample holder with a unique identifier to keep the samples organized (e.g., text ID or 14H2 77-78)
3. Place enough powder from the labeled sample bottle to fill an empty sample holder (*Figure 8B*). Gently press the powder flush with the sample holder using a glass slide (*Figure 8C*). Roll the glass slide over the powder to fill any gaps in material and smooth the surface of the powder (*Figure 8D*). **The surface of the powder must be smooth.** Remove excess powder from the sample holder edges with a brush or a Kimwipe (*Figure 8E*) and carefully place the holder in the D4 sample magazine .

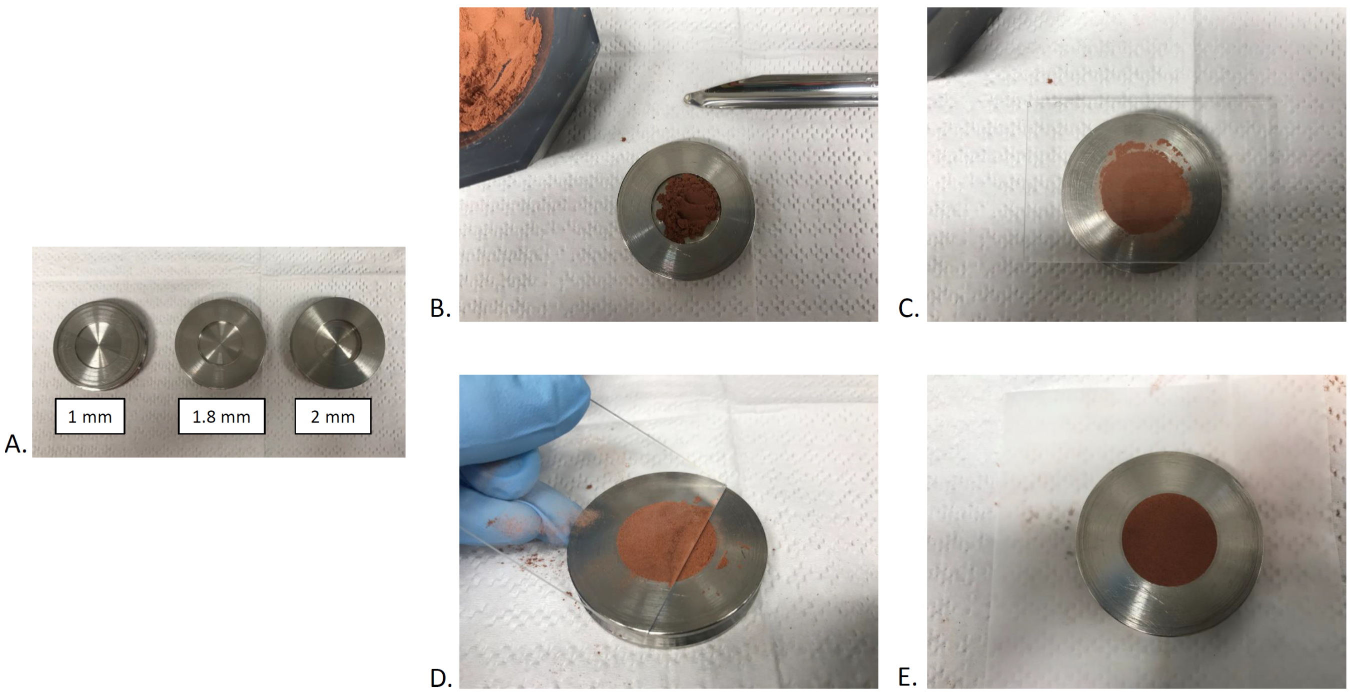


Figure 8. A. Front-loading sample holders available for the D4. B. Front-loading sample preparation for XRD analysis with the D4

The sample 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.

1. Take a 2mm or 1.8mm sample holder and hold it on its side.
2. Tape a piece of cover glass across the well leaving a very small gap at the top
3. Keep the holder on its side and pour powder into the open gap.
4. Tap the holder while filling in power 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 (*Figure 9A*) and backing piece (*Figure 9B*) that snaps in from behind. There are also two loading pieces. One piece helps funnel the powder (*Figure 9C*) in and the other taps down the powder into a flat surface (*Figure 9D*). *Note: If the layer of sample is not think enough or the sample is composed mostly of very light elements (such as freeze-dried calcareous ooze), the sample holder material (PMMA plastic) will show as a low broad peak at ~7.3º 2 in the diffractogram.*

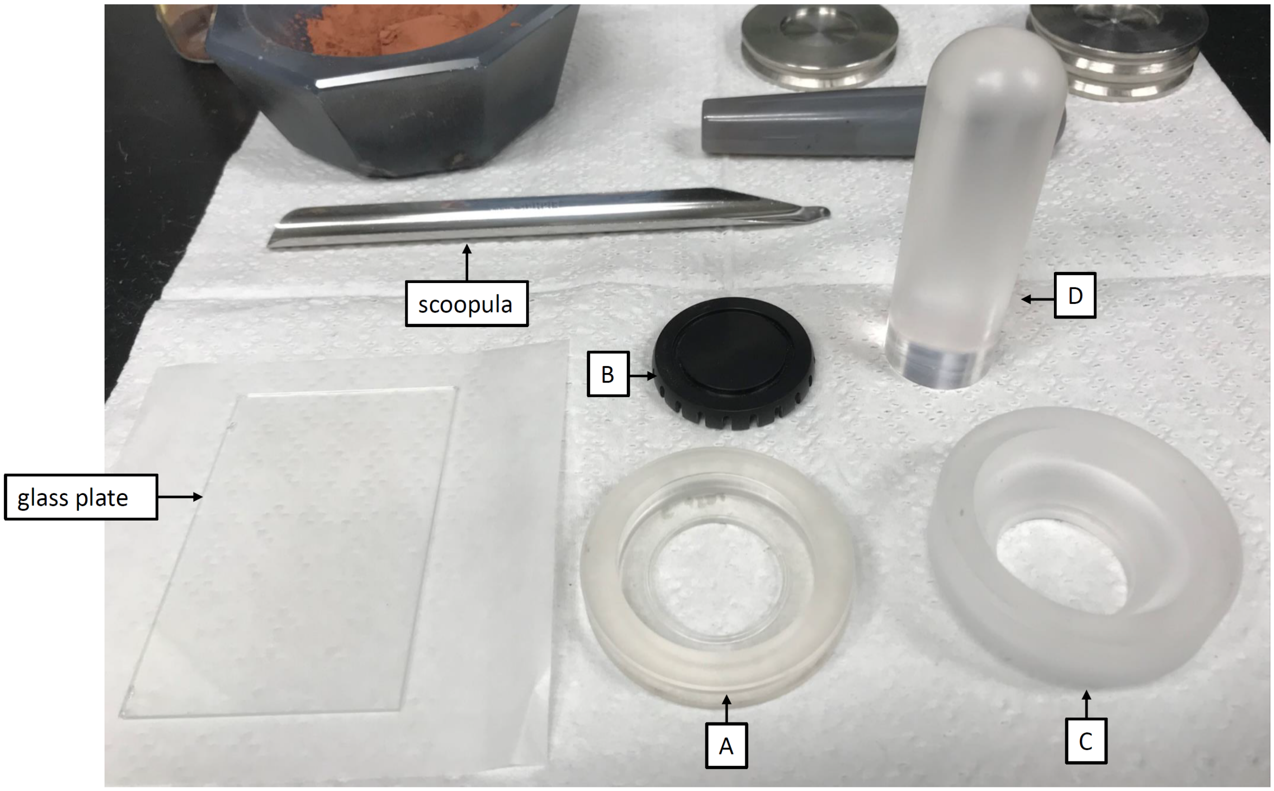


Figure 9. Back-loading sample holder pieces. A. Sample Ring B. Back piece C. Funneling piece D. Tapper

Figure 10 shows the different steps to prepare back-loading samples.

1. Take a front-loading holder and put a clean glass slide over it.
2. Place the sample ring of the sample holder upside down on a glass/plastic plate. Now the powder will fall on a smooth flat surface that will be easy to flip over.
3. Place the funneling piece on the top of the sample holder.
4. Load the powder into the ring. Try to load the powder evenly across the well.
5. Take the tapping piece and lightly tap down the powder. Use the tool as softly as possible in order to flatten the surface. 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. Keep the glass on the sample holder. Flip the whole unit over and set it down.
9. Set it down and remove carefully the glass.
10. The powder needs to be flush with the holder. It may take a few tries to get the right amount of powder in.

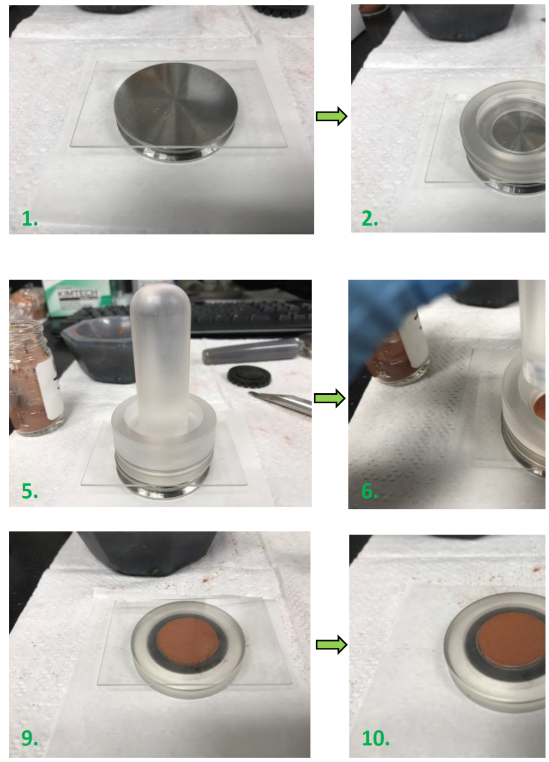


Figure 10. Back-loading sample preparation for the D4 sample holders.

Very Small Amount of Material (tooth pick, small crystals, secondary minerals or void filling material)

See XRD Sample Preparation for a small amount of material

Scanning Samples with the D4

Before beginning measurements, confirm the scan parameters (singles, step and time) with the Science Party. Scientists can use previous Expeditions for examples of ideal scan parameters. **Generally the D4 is used to scan from 5 to 70 º2.**

If you need to make a parameter file, please see **Making a Parameter File** under **Maintenance and Troubleshooting**. There are several parameter files from previous expeditions saved in the C:\DIFFDAT1 folder. Generally a previous expedition file is satisfactory for most expeditions. There are scan variations for Bulk samples versus Clay separations. Those parameter files are labeled accordingly in the C:\DIFFDAT1 folder. Generally clays are scanned to include much lower angles (<5 º2).

Open the **XRD Commander** program using the icon 

on the desktop or toolbar. *Figure 11* is the initial window. Be sure you are in the 'Adjust' tab (bottom left, *Figure 11*).

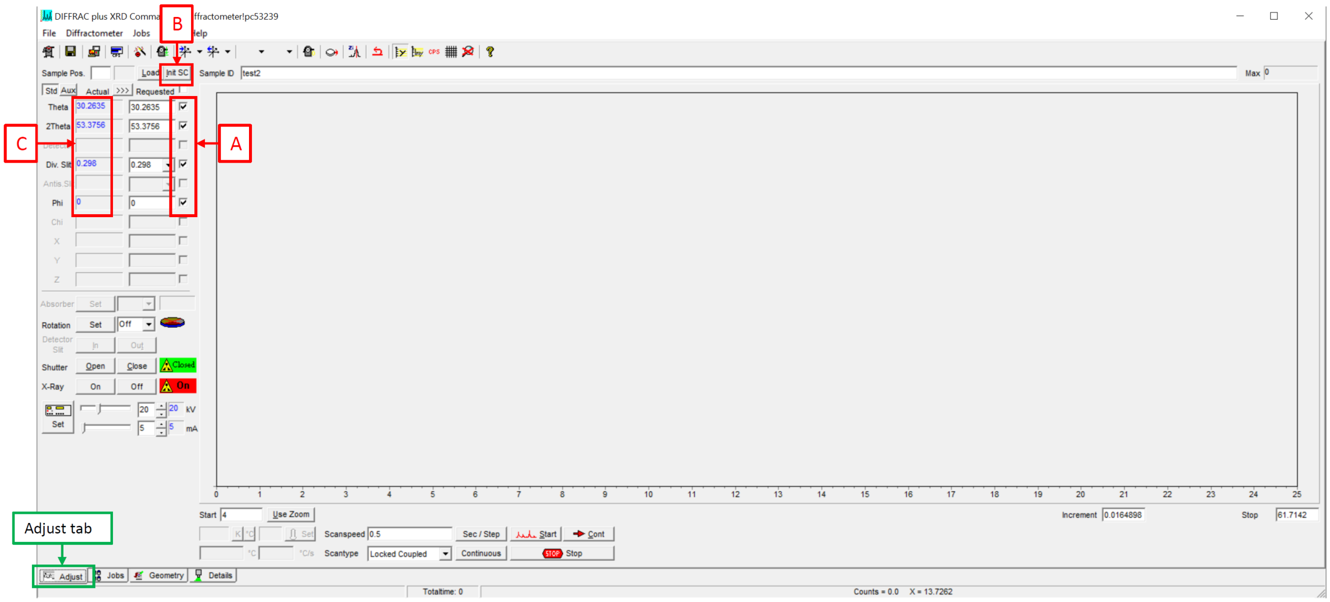
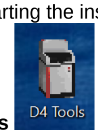
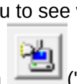


Figure 11. XRD Commander main window. (A) Initialize Driver Request checkmarks, (B) Initialize Sample Changer button, (C) Successful driver initialization

The checkmarks (*Figure 11A*) indicate the drives that will be initialized. Check all boxes with values before initializing: Theta, 2Theta, Div. Slit, Phi. Click on **Init SC** to initialize the Sample Changer (*Figure 11B*). The program then 'locates' all the mechanical drives in the D4. It typically remembers the Theta, 2Theta, and Phi drives but the Divergence Slit sometimes does not initialize. That should not be an issue for scanning samples as our Div. Slit is not mechanical, however if the software won't scan a sample because one or more of the drives did not initialize (successfully initialized drives will turn blue, *Figure 11C*) you can try restarting the program and reinitializing, and/or turning off the D4 and the XRD Commander software and restarting the instrument then the XRD Commander software and repeating the steps above. If that does not work, close XRD Commander and open **D4 Tools** 

from the desktop. **Note D4 Tools and XRD Commander cannot be open at the same time.**

D4 Tools allows you to see what is causing an error in the D4 instrument and remediate it. When D4 Tools open, click "Online Status" (*Figure 12*). In D4 Tools, click the icon  ('online refresh ON/OFF') on the left (*Figure 13A*), this connects the D4 Tools software with the D4 instrument and completes a diagnostic (identifies any errors). The diagnostic screen (*Figure 13*) shows the instrument status. Any red square indicates an error. You can investigate the error by clicking on the square. **Only trained techs should be troubleshooting errors (errors other than drive initialization) on the D4**.

To initialize the drive(s) that did not initialize with the XRD Commander software click the '+' of 'Positioning Drives' to expand the menu, then click the drive that did not initialize (*Figure 14A*). Click the 'Adjust' button  (*Figure 14B*). Please note that when you initialize the drives you can hear the drives moving inside the D4. If you hear a clank or bang and the instrument stops working, you will have to get a trained D4 tech. There is a in-depth sample changer procedure to correct for misalignment in the Bruker Manual (in the cupboard in the X-Ray lab) but it should only be preformed by trained techs. Alternatively, you can contact Bruker company and they can advise or remote into the D4 to fix any errors. Note that some errors can be fixed by clicking the 'First Aid' icon  (*Figure 14C*). The program can identify and fix some errors. **Try that icon before contacting Bruker company.**

Figure 12. Opening D4 Tools.

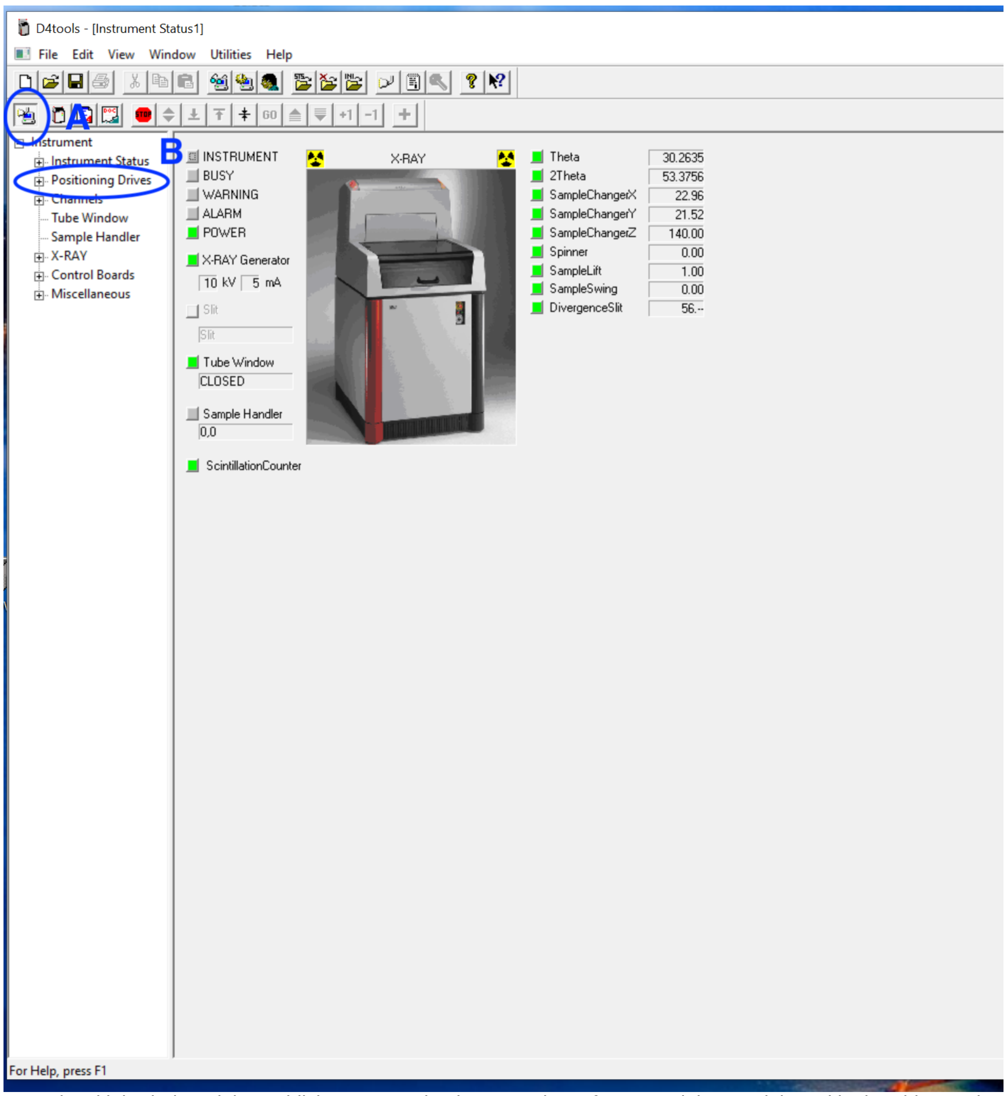


Figure 13. D4 Tools Initial Window. (A) Establishes connection between the software and the D4. (B) Positioning drives select drop down.

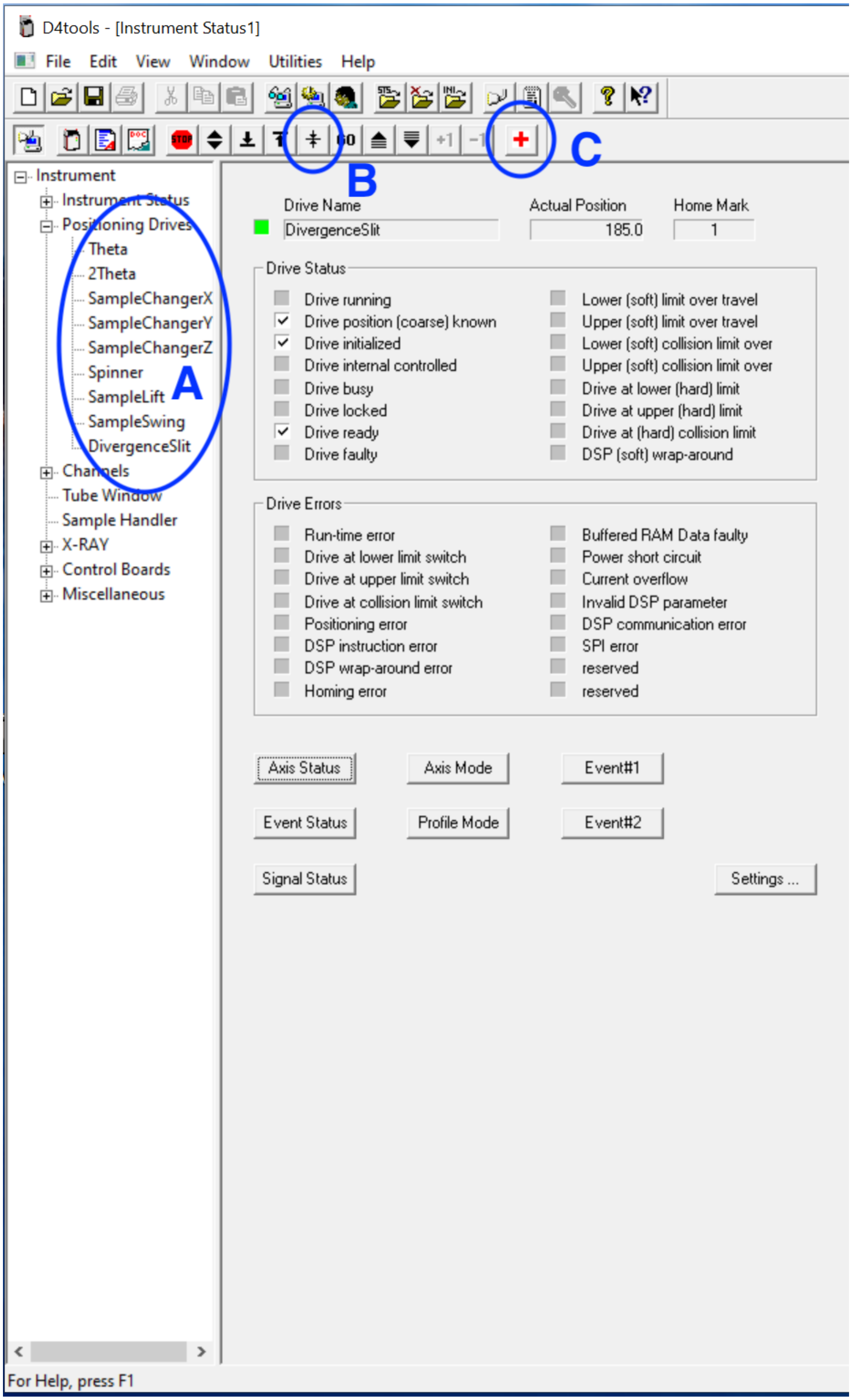
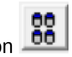


Figure 14. Adjusting a motorized drive via D4 Tools. (A) Select the drive to initialize. (B) Initialize button. (C) First Aid button may help with positioning errors or other errors with the window.

Entering Sample information into the XRD Commander

In the XRD Commander, click on the 'Jobs' tab next to the 'Adjust' tab (see *Figure 11*) . On the 'Jobs' screen, click on the "Create Jobs" icon  in the toolbar (*Figure 15A*).

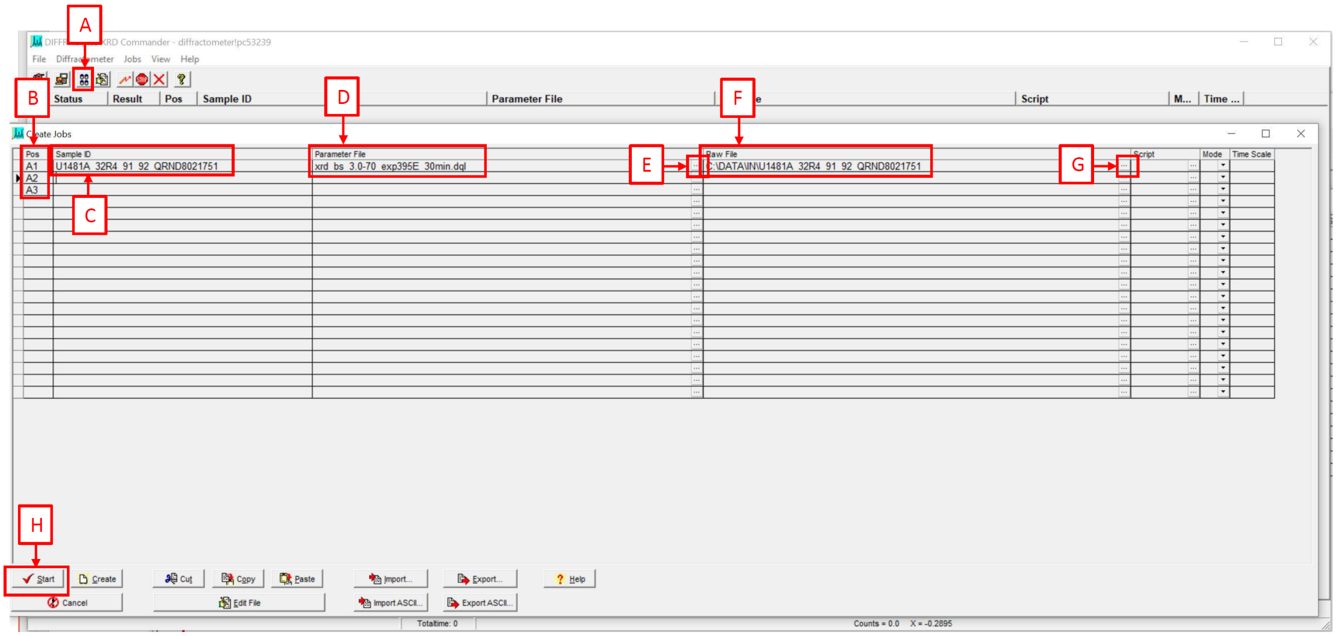


Figure 15. Create Jobs. (A) 'Create Jobs' icon, (B) Sample position in the D4 sample magazine, (C) Sample ID, (D) Parameter file, (E) Open Directory button, (F) Raw file, (G) Start button

The window shown in *Figure 15* will pop up. Fill in the '**Position**', '**Sample ID**', '**Parameter File**', and '**Raw File**' columns.

- **Position** (*Figure 15B*): This is the position of the sample in the loading magazine in the D4, from A1–A6 to K1–K6. Enter the position manually in the column.
- **Sample ID** (*Figure 15C*): 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 X-Ray Laboratory is programmed to scan in this exact format including underscores. For special treatments such as clay, glycol or heat treated, you must include the treatment in the file name. Add the treatment in the following way U1565A_1R1_3_4_clay_WDGE11053881.
- **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 15E*) This directs you to the Control Panel. Follow the path "Local Disk C: > DIFFDAT1 > D4 Bruker ". This folder has a list of all the parameter files from previous expeditions. Select the one that is best suited for your scan parameters.
- **Raw File** (*Figure 15F*): Sets the location where the results will be saved. Set the location by clicking on the three dots at the end of the cell (*Figure 15G*). 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. Click "Open".

The other fields will automatically populate, you do not need to fill these in and they should not need to be adjusted. Refer to the D4 Commander User Manual for more info on these fields.

Starting a Scan

When all fields have been filled in, click on the "Start" button on the bottom left corner of the screen (*Figure 15H*). 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. The program will automatically run the samples sequentially. The measurement is finished when it is displayed 'Finished' in the "Status" column of the 'Jobs' tab. If there is an error while scanning the program will stop and notify the user of the error. You can try restarting the software and/or the D4. A sample handler crash may require an experienced D4 XRD tech or you may need to contact Bruker. With the D4 off you can manually move the Z-drive and the sample swing loader, just be aware that the moveable drives are set up to avoid each other during the sample loading sequence, if you move a drive it may cause a crash on start up.

Processing Sample Results

When the scans have finished, the results will show up in the "C: > DATA > IN" folder. Two additional file types need to be made by the X-Ray lab technician before uploading the data to the LIMS database. The D4 outputs a **.RAW** file. The X-ray lab technician additionally has to create a **.UXD** and **.PNG** files. In addition to the LIMS upload, it is also helpful to create an "XRD Data" folder for the scientists in DATA (\\NOVARUPTA)(S:> Uservol > File Name) to save copy of the **.RAW** and **.UXD** files (or any file the scientist would like to have access to). After all three file types (.RAW, .UXD, and .PNG) 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 not readable for most other software, whereas the **.UXD** file is a text file that can be read by other programs. Therefore, we upload both of files types to LIMS. **DIFFRAC.Eva** can open/import .raw and .xy files, whereas **HighScore Plus** (available to the scientists via a virtual computer, see High Score Plus Quick Start Guide) can open .raw, uxd, .xrdml, and .xy XRD file types. See the Aeris Advanced user Guide for instructions on converting .xrdml (Aeris) files to .xy.
To convert a **.RAW** file to an **.UXD** file, click the **Diffrac.File Exchange** software icon on the desktop (*Figure 16*).

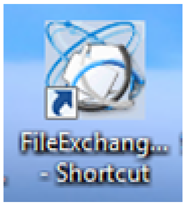


Figure 16. File Exchange Desktop Icon

The initial window (*Figure 17*) 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.

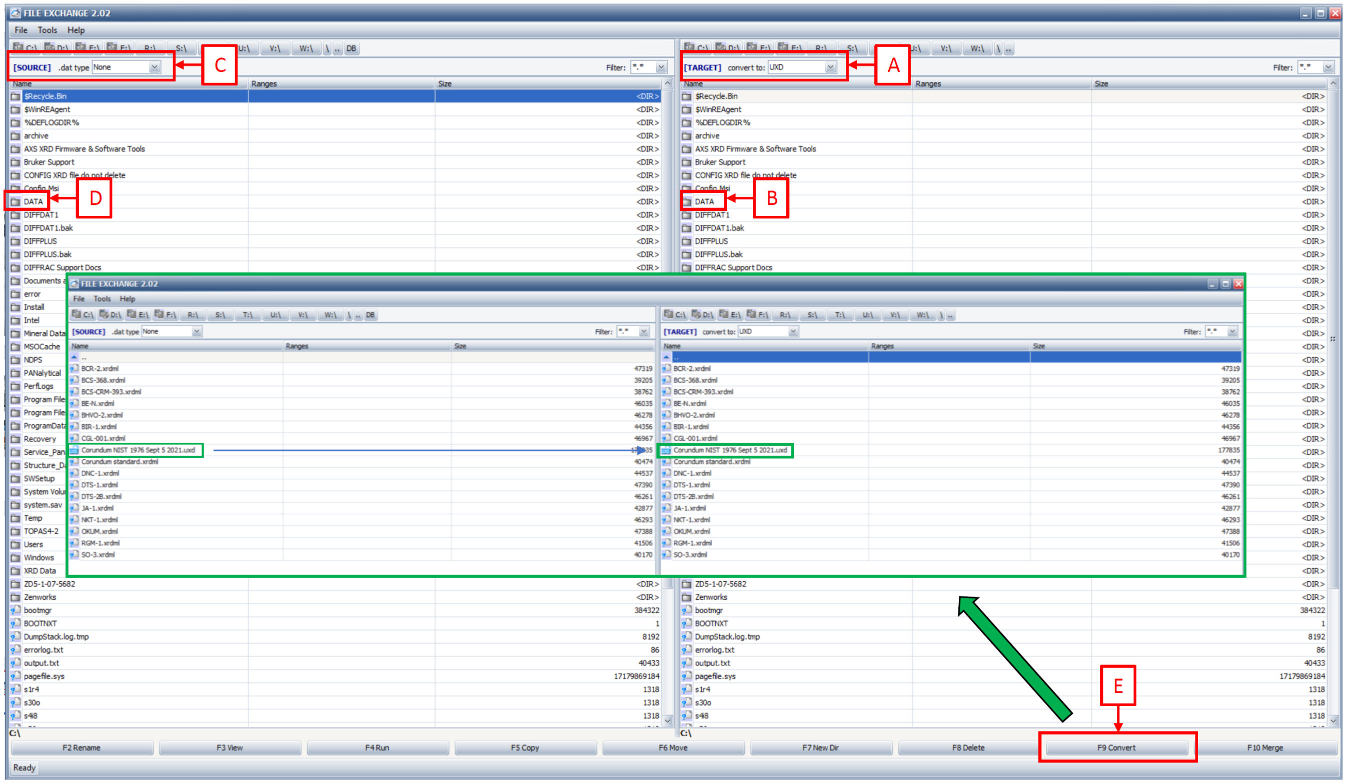


Figure 17. First window in File Exchange. (A) Output File Type dropdown menu, (B) Output DATA folder, (C) Input File Type dropdown menu, (D) Input DATA folder, (E) Convert button

First, direct where the new files should be saved and select the converted file type. For that, on the right side, click on the file type dropdown menu (*Figure 17A*) and select ".UXD". Then double click on the "DATA" folder (*Figure 17B*) and direct files to the "IN" Folder.
Next, move to the left side of the screen and select your input files. Select the file type "None" (*Figure 17C*). Click on the "DATA" folder (*Figure 17D*) and go to the "IN" folder. Here you will see all your samples. Select all the samples and then click the "Convert" button (*Figure 17E*) on the bottom right of the screen.

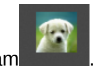
The new **.UXD** files will show up on both sides (window circled in green in *Figure 17*) and you can close down the program (click on File > Exit).

Printing Scan to PDF or PNG

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

Click on the 'Print Preview' icon  in the toolbar at the top of the software window. A Print Preview window will open up. On the top toolbar, click the icon for "Export Image" . This opens the File Save As window. Save as **.PNG** with the same name as the **.RAW** file. If the names do not match exactly, the files will not upload to LIMS. Then close the windows and repeat the process for the next sample.

Uploading Files to LIMS

The XRD files are uploaded using the MegaUploadaTron 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 three of the necessary files (.RAW, .UXD and .PNG) 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. Make sure the name of the file is the same for each. If you have issues uploaded contact one of the software application developers onboard. 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 on C:\DATA. Any problematic samples will either remain in the uploader with a question mark or move to the "Error" folder, again you may need to notify a programmer to help remediate uploading issues.
2. Check that the files moved into the archive directory and uploaded into the LIMS database.

If you are running clay samples you will end up with multiple runs that have the same sample info. To make sure we can differentiate this in the database you must add extra text before the TextID so that it looks like these examples. Do this step when entering the sample name in the Bruker software so that it gets included in the metadata of the file. MUT will recognize the files written this way as long as there is matching file names. However, only one .png file is allowed per TextID, so a .png of the combined pre- and post- heated scans was uploaded.

U1565A_1R1_3_4_clay_WDGE11053881.raw
U1565A_1R1_3_4_heated_WDGE11053881.raw
U1565A_1R1_3_4_glycolated_WDGE11053881.raw

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

The following QA/QC is for the Bruker D4 Endeavor XRD.

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. Be careful not to hit any of the limit switches within the D4 as this will cause error and possible collision of the motorized drives. The screen is only removed when running the corundum standard to allow a larger range of angles without any interference. The anti-air scatter screen should always be on when running samples. (Review the video on *Desktop/XRD_ICP Prep Documents/Bruker TRAINING VIDEOS to see this done before proceeding).*

1. Make sure the X-ray generator is off (Key on front is in off position and Red 'X-ray is On' lights are off).
2. 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.
3. Open **D4 Tools** and click "Online Status".
4. Click the computer icon to connect with the configuration files in the instrument.
5. Click "Positioning Drives" and "Sample Changer Y" direction.
6. 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 to the XRD and gain access to the anti-air scatter screen.
7. Open the front door with a socket wrench (tools specific for the XRD are on the XRD Sample Area). Loosen the two bolts on the door and slide the bolts to their opposite side. Carefully let down the door.

8. Remove the anti-air scatter screen (*Figure 18*). 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.
9. 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.
10. 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".)

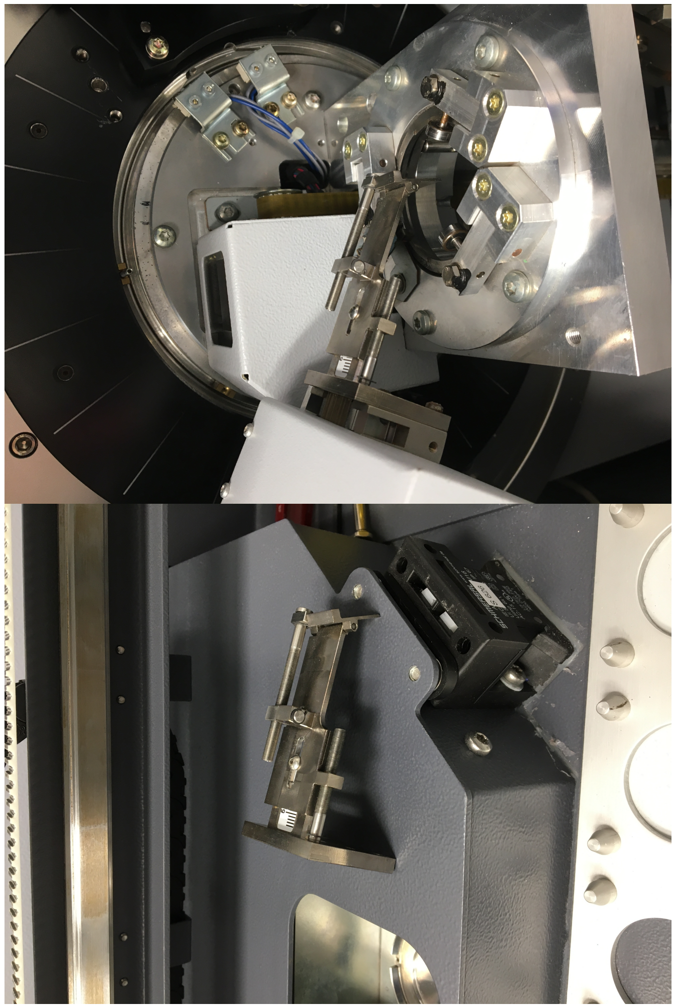


Figure 18. Anti-air scatter screen in place inside the instrument (top image) and after being removed (btm image).

Scanning the NIST 1976 Standard and Verifying QA/QC, homing the axis inside the XRD.

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 X396). 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. 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 in EVA (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 19*).
3. Strip K_2 and Append (*Figure 20*).

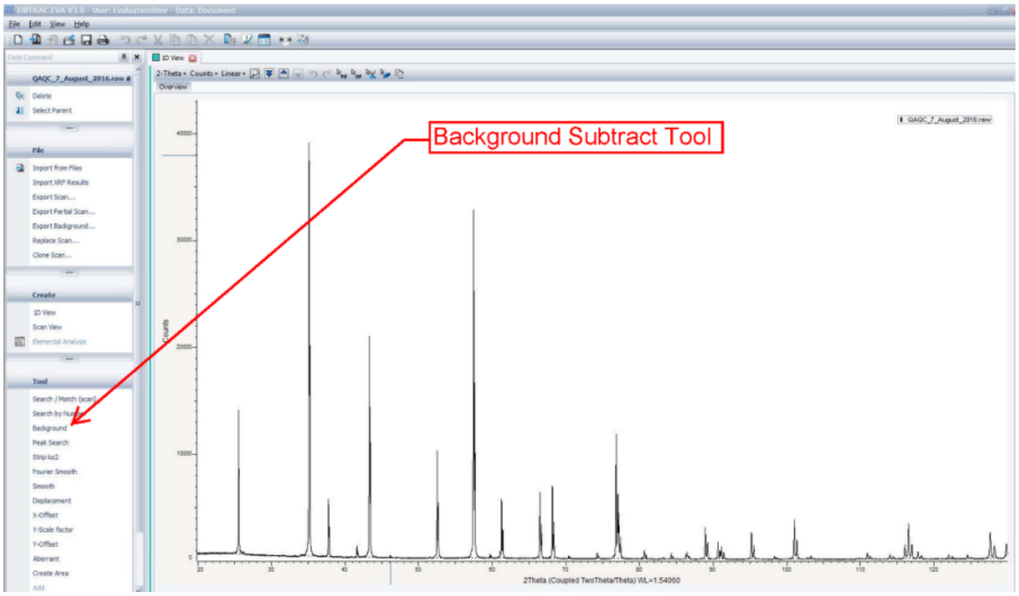


Figure 19. EVA diffractogram.
The arrow points to the Background Subtract tool.

Figure 20. EVA diffractogram with the background subtracted. (1) Dropdown Menu to Append Scan
(2) Strip K2 Tool

4. In the "Data Tree" panel there are two scans: Background Subtracted Scan and K2 Subtracted Scan (*Figure 21*). 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 21. 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 in *Figure 22*. Click on either scan so that it is highlighted (*Figure 22-1*). Then click "Create Area" (*Figure 22–2*). A New window will pop up where you can enter the left angle and right angle (*Figure 22–3*, 22-*4*).

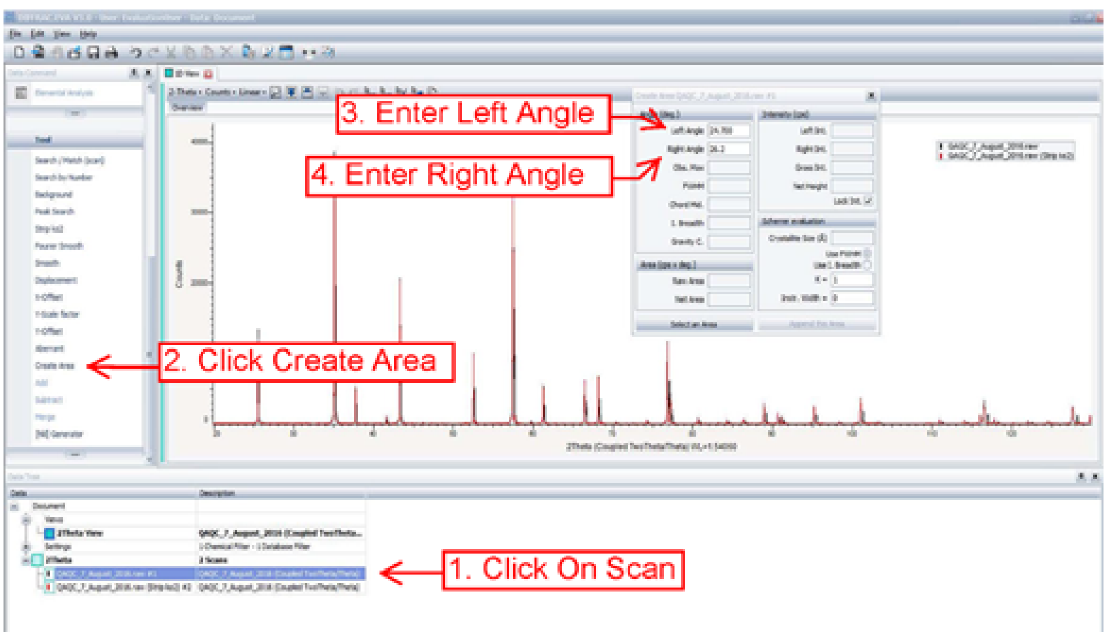


Figure 22. Create Area for Scan Angles. (1) Arrow points to scan name (2) Create Area tool (3) Left Angle entry field (4) Right Angle entry field

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 23*). 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).

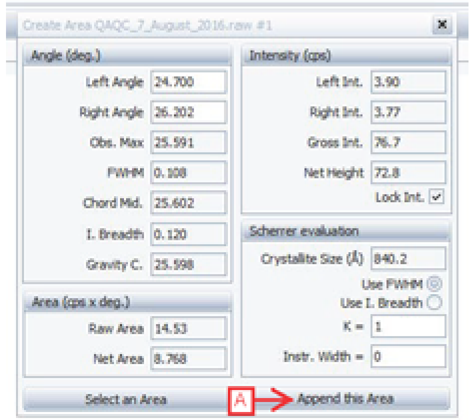


Figure 23. Create Area Window A. Append this Area button.

7. Right-click on the "Area List #" subheader for background-subtracted scan and select "Create and Area Column View" (*Figure 24*). Do the same for the K, appended scan. This creates another tab on top with the Area data in column format.

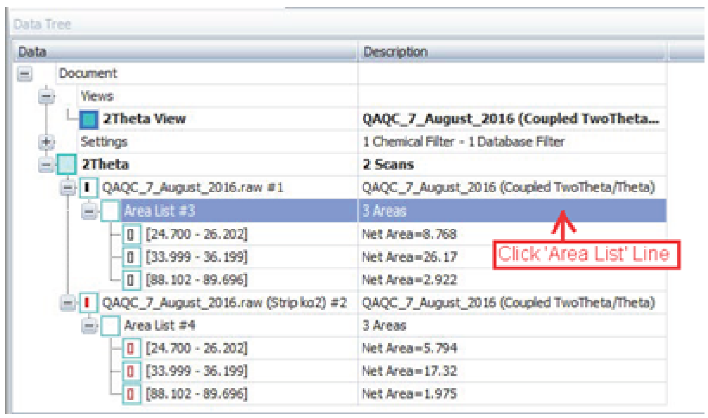


Figure 24. Data Tree panel Scan Area list.

8. Open the QAQC corundum standard Equipment Verification 3.3.xls Excel spreadsheet. QAQC Corundum std Equipment Verification X384.xls on the XRDIH computer (*Figure 25*)

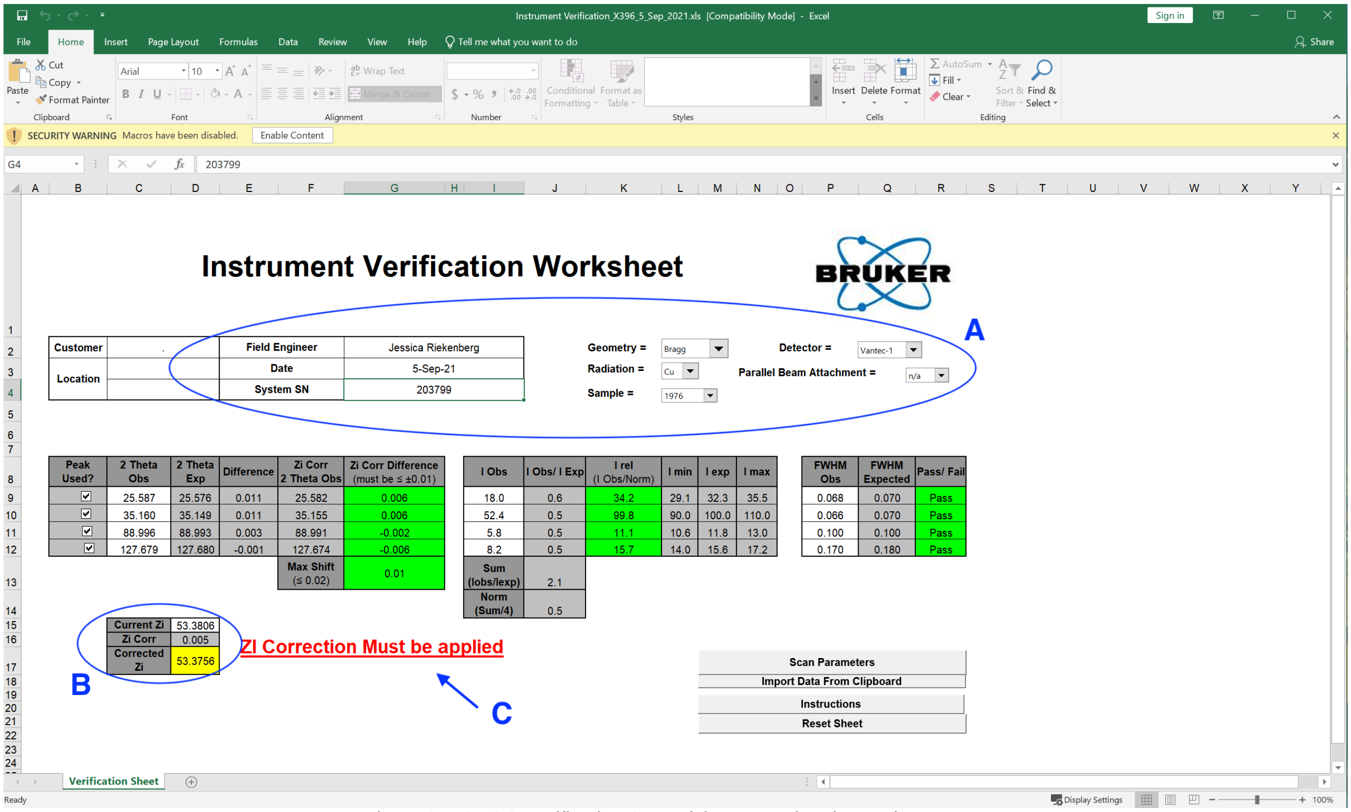


Figure 25. QAQC Verification Spreadsheet. Zeroing the goniometer.

9. Instructions provided by the vender can be found via the Instruction cell in the QAQC sheet. Enter your name and date and select "Vantec-1" for the detector (*Figure 25A*). Enter the following values into the appropriate columns:

- For 2Theta Obs, use the Chord. Mid values from the K_2 appended scan areas (*Figure 26–1*)
- For I Obs, use Net Area from the background subtracted scan areas (*Figure 27-3*)
- For FWHM, use the FWHM from the K_2 appended scan areas (*Figure 26–1*)

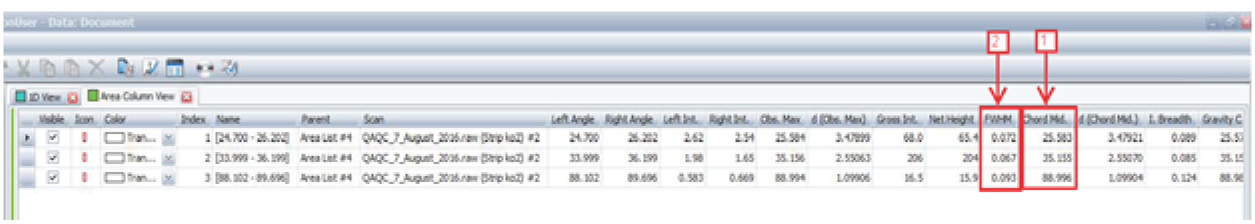


Figure 26. K_2 subtracted Scan Area column view. (1) Chord Mid value (2) FWHM value

Figure 27. Background Subtracted scan area column view. (3) Net Area value

10. The QAQC verification spreadsheet has the calculations already embedded.

11. Enter the XRD's Current Zi into the QAQC verification spreadsheet (*Figure 25B*). The current Vi value is found in the Configuration program on the desktop (icon *Figure 28*). Open Config program, Password is: **DIFFRAC**. Click **Motorized Drives > 2 Theta**. Use the value under **Zero Reference - Home of the Axis** (*Figure 29*).

If the RED "*ZI correction must be applied"* shows up (*Figure 25C*), you will need to enter the corrected Vi into the Config program. This will adjust the home position for the 2Theta drive. If there is no message just save the worksheet under a new name (Expedition) and no more action is needed.

Apply ZI Correction to the XRD

1. Open the Configuration Program on the desktop (*Figure 28*). Password: **DIFFRAC**.

Figure 28. Configuration program icon

2. In the left side panel navigate to **Motorized Drives > 2Theta** (*Figure 29*). 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 29*).

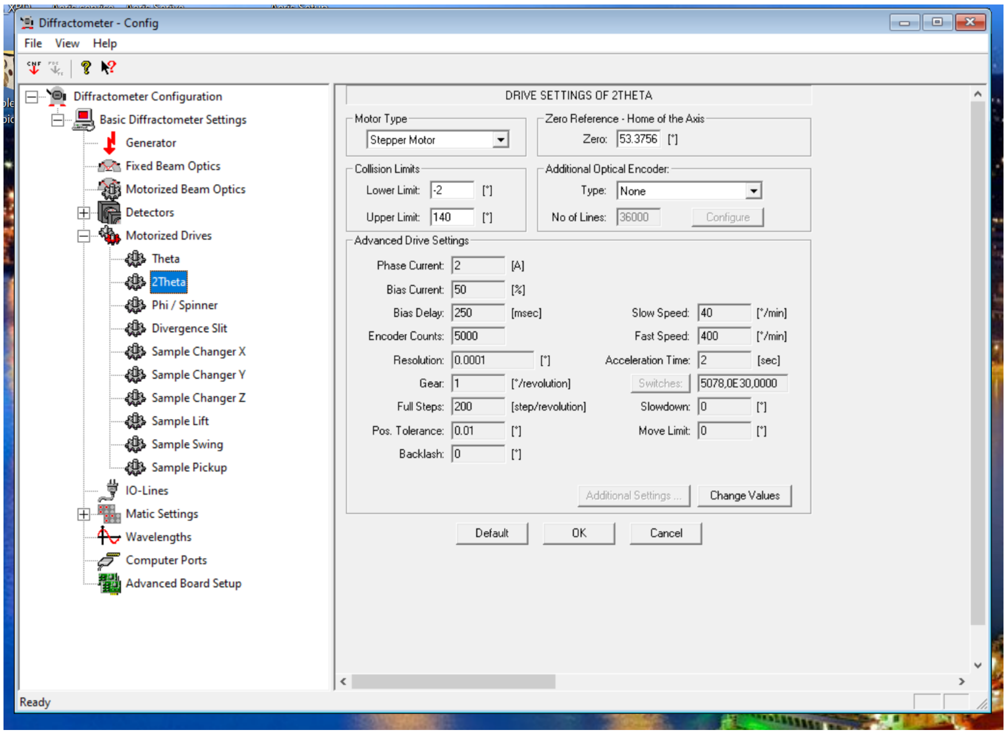


Figure 29. Configuration 2Theta page

3. 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 Diffractometer' boxes checked select 'OK' (*Figure 30*). The new configuration will take a moment to download to the Diffractometer.

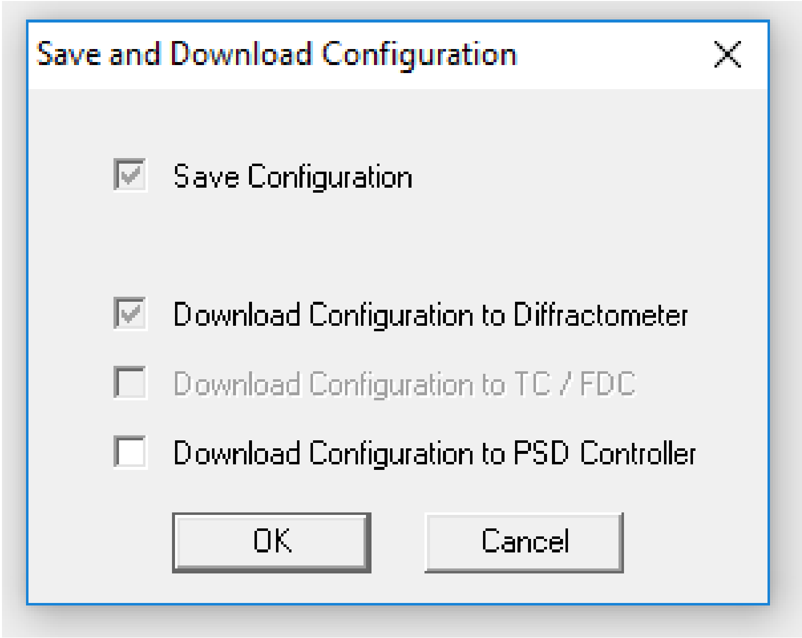


Figure 30. Save and Download Configuration page. Correct settings to save

Now that the scan is complete put the Anti Air Scatter Screen back on. Move the y drive to the 350 position and open the front door (instructions above **Removing the Anti Air scatter Screen** section). 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. Turn the XRay generator back on with the Key on the front of the instrument.

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 µSv/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.

Maintenance and Troubleshooting

Maintenance

Tube Conditioning

If X-rays have not been turned on in longer than 4 days you must complete a cycle of tube conditioning to avoid damaging the X-ray tube. In D4 Tools select the icon with the computer and plug. This connects the program to the instrument. Click on the X-RAY generator green button on the status screen, this will show the screen in *Figure 31*. Or Select "X-RAY" under the Instrument tree. Then select Utilities -> X-Ray Utilities -> Tube Conditioning ON/OFF (*Figure 31*). The "X-RAY" screen also shows the "Cooling water flow" rate (L/Min) for reference.

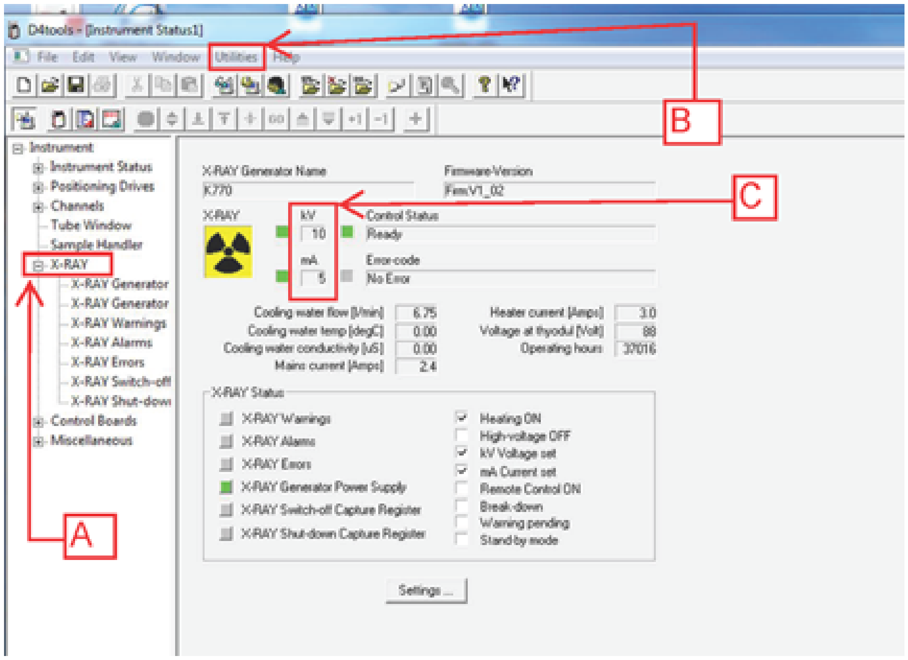


Figure 31. D4 Tools X-ray subtree window. (A) X-ray subtree button (B) Utilities command (C) Standing kV and mA

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 32*).

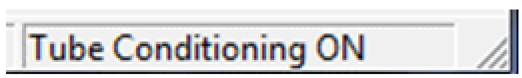


Figure 32. Tube Conditioning On Indicator

After about a minute the kV will start to increase in increments from 20kV to 55kV. The whole cycle takes about one hour and when the kV returns to 20 the cycle is complete. Once this is finished, select the 'Tube Conditioning ON/OFF' again. Note the operational status in the 'Preventative Maintenance' page of the X-Ray Lab Notebook on Confluence. To do this click on Manual Control (small head icon) in D4 Tools and type GS11. The resulting GS number is the status number. Record this value in the X-ray Tube Conditioning Log.

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, push the red mains power button, depress the high voltage button on the left side of the Bruker, and then turn off the power switch also on the left side. The Haskris chiller must remain running for **at least one hour after** turning off the XRD 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

Check the filter in the HASKRIS tank and record the flow rate every expedition. If there is a lot of debris it may be necessary to drain the tank and **refill with distilled or reverse osmosis (RO) water only - NOT Deionized.** The filter can be sprayed off in a sink taking care not to puncture the screening. If the water flow rate to the system drops to <4.5 L/min, the D4 will alarm. If it drops below 4.0 L/min, the X-ray will shut off. This may happen if 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.

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 33*).

Figure 33. 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 34*). 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.

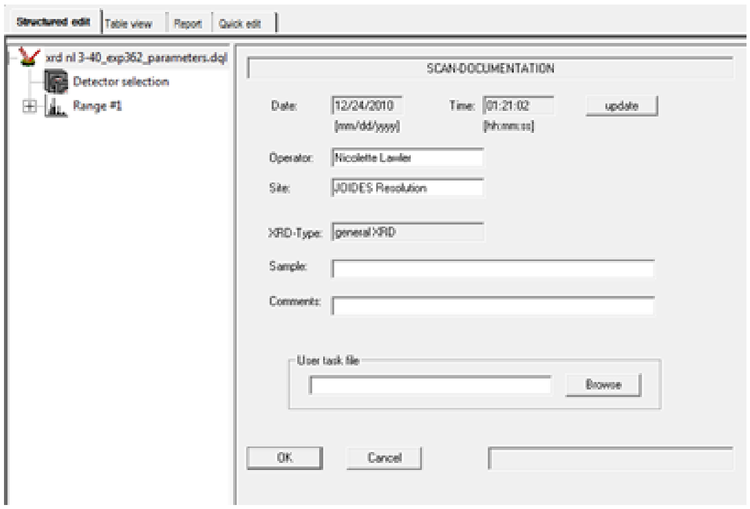


Figure 34. First page of parameter file setup.

The second page declares the detector and PSD electronic window (*Figure 35*). These settings are PSD: VANTEC-1 and 3. Do not deviate from these values. Click "OK" and continue to Scan Settings.

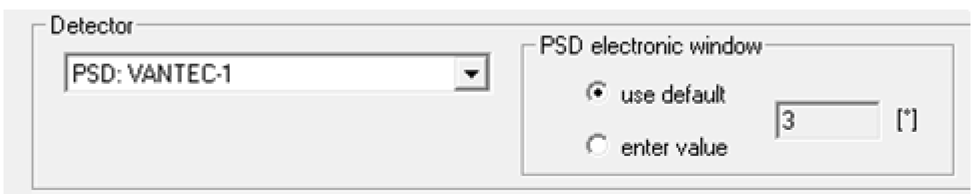


Figure 35. Detector declaration.

Scan Settings includes Scan Type and Sample Rotation (*Figure 36*). 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.

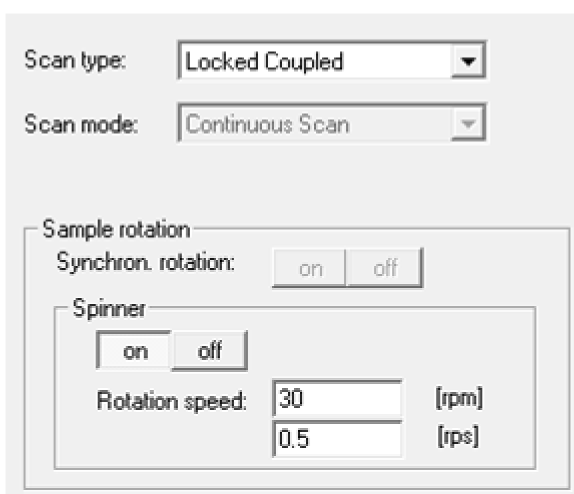


Figure 36. Scan Settings parameter window.

Scan Parameters includes the scanned angle range, angle step size, number of steps, time per step, and delay time (*Figure 37*). 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°2) there is a very sharp peak. This is caused by beam overspill onto the sample holder and into the detector.

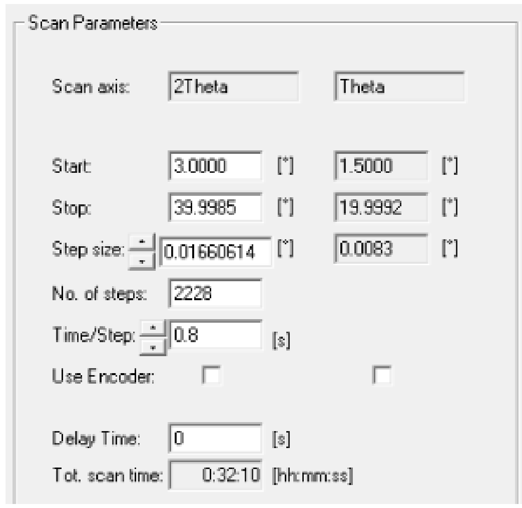


Figure 37. Scan Parameters window.

Generator Settings contains the X-Ray Tube Configuration and Generator Configuration (*Figure 38*). 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.

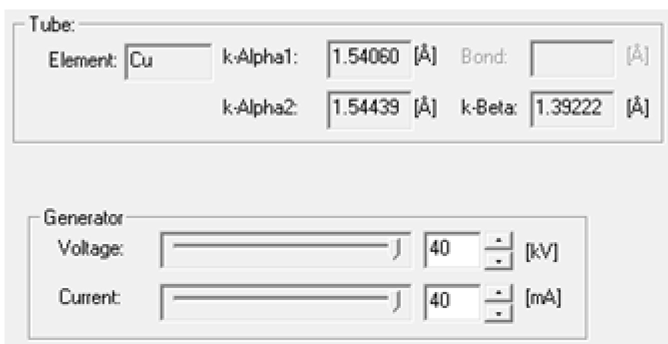


Figure 38. Generator Settings window.

The Beam Optics settings lists the Divergence Slit and AntiScattering Slit (*Figure 39*). Both of these are constant values based on our hardware setup. The Divergence Slit should be set to .300° (0.6mm). Click "OK" and you will have finished all the settings and will loop back to the first window.

Figure 39. Beam Optics window.

Save As the file under a new name to the path Local Disk C: > DIFFDAT1. 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 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

This document originated from Word document XRD_UG_375.doc (see Archived Versions below for a pdf copy) that was written by H. Barnes and K. Bronk; edited by N. Lawler and A. Armstrong. Credits for subsequent changes to this document are given in the page history.

Archived Versions

LMUG-XRDUserGuide-230220-1933-176.pdf

XRD_UG_375.pdf