# X-Ray Diffraction (XRD): Quick User Guide

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## Introduction

The X-Ray Laboratory onboard the *JOIDES Resolution* performs diffraction analyses of minerals and rock powders using a D4 Endeavor XRD from Bruker AXS. Associated software, DIFFRACplus and TOPAS, allow for analysis of minerals and rock powders; including peak-matching and mineral & chemical compound identification. The XRD lab provides scientists with a quick and reliable tool for mineral identification; it is particularly useful for identifying fine-grained minerals or mixtures of alteration minerals that cannot be easily identified with other techniques onboard. XRD can also be used to determine the proportions of minerals present.

## Apparatus and Materials

### Laboratory Apparatus

–Haskris water-water chiller for X-ray tube
–Cahn Model 29 or 31 microbalance
–Mettler-Toledo XS204 dual-balance system
–Powdering equipment: Agate mortar and pestle, Ball mill, Shatterbox, X-Press
–Glass bottles
–Sonic dismembrator
–Glass rod
–Glass beakers
–Pastuer pipette/eye dropper
–Centrifuge and glass centrifuge tubes
–Dessicator

### Reagents

–Ethylene glycol (clay glyconation)
–$HNO_3$ (glass cleaning)
–2 M HCl: 16.4% v/v (carbonate dissolution)
–Glacial acetic acid, 10% solution (v/v) (carbonate dissolution)
–Distilled (reagent) water (DI)
–1% Calgon solution (w/v)

### Instrument Hardware

–Bruker AXS D4 Endeavor XRD with Goniometer, X-ray source, Tube housing, Mount, and Sample holders
–Vantec-1 detector with Optics and Slit systems

### Instrument Software

–DIFFRAC.EVA evaluation software
–DIFFRAC.TOPAS software for diffractogram analysis

## Sample Preparation

Sample preparation techniques may include the following:

–Drying and powdering solid samples
–Mounting smear slides for small samples
–Removing carbonate from high-carbonate samples
–Separating the clay fraction from larger grain size particles
–Expanding swelling clays with ethylene glycol

## Solid Sample Preparation

Solid samples are prepared for X-ray diffraction by grinding, which can be accomplished by several different methods. Appropriate method is dependent on sample matrix, size, and/or quantity:

–Soft clay: Agate mortar and pestle
–Hard solids: Mixer Mill
–Hard solids in bulk quantities: Shatterbox
–Hard sample too large for Shatterbox: X-Press

### Grinding Solid Samples

1. Freeze-dry sample(s) for at least 12 hr before grinding.
2. Grind solid samples to a fine talc-like powder using one of the following methods:
   –Agate mortar and pestle
   –Spex Shatterbox
   –Spex Mixer Mill (tungsten carbide, hardened steel, agate, or alumina ceramic)
   –X-Press
3. Transfer the powdered sample to an appropriate labeled glass bottle or sample bag.
4. Unless the sample material is very small (see next section); Select the steel or plastic XRD sample holder.
5. Fill an empty XRD sample holder with enough powdered sample. Gently press the powder flush with the sample holder using a glass slide.

*Note: The surface of the powder must be smooth. Remove excess powder from the sample holder edges and carefully place in the appropriate XRD slot.*

### Sample Slurry/Smear Slide Mount for Small Sample Amounts

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 a quartz disk insert. Although not useful for semi quantitative analysis, this method is useful for rapidly determining bulk mineralogy.

1. Grind the sample to a talc-like powder (<0.062 mm).
2. Place a small amount of sample in the center of the quartz disk. Two quartz disks will adequately fill the sample holder. The upper quartz disk will be used for the slurry.
3. Add 2–3 drops of acetone, isopropyl alcohol, or distilled water to the sample.
   *Note: Acetone and Isopropyl dry faster than water.*
4. Create a thin layer of sample material using a glass rod (rolling it over the sample works well).
5. Place sample in desiccator to dry.

## Removing Carbonates before Clay Separation

In some sediments, to identify clay minerals it is necessary to dissolve carbonates. The goal is to remove as much carbonate as possible in order to analyze and isolate the material contained within.

### *Hydrochloric Acid Treatment*

The simplest method for removing carbonate is treatment with HCl. However, treatment using strong acids can attack the structure of the clay minerals, particularly tri-octahedral minerals. Be aware that this treatment may affect clay crystallinity.

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

### *Acetic Acid Treatment*

A slightly more involved, but less destructive, method (from Kitty Milliken, UT-Austin) is as follows.

1. Place ~2 $cm^3$ of undried sample into a centrifuge tube with 25 mL of acetic acid (10% solution).
2. Mix well, and let sit until the reaction ceases.
3. Shake well again to ensure the reaction has stopped (i.e., no more bubbles).
4. Spin sample in the centrifuge (15 min at 1500 rpm)
5. Decant the acetic acid solution and dispose of the acid solution properly.
6. Add 25 mL of DI to the centrifuge tube and centrifuge again for 15 min at 1500 rpm.
7. Decant the clear water.
8. Repeat the “wash cycle” (Steps 5 and 6) with DI.
9. Place washed sample in a large beaker with some distilled water and a little 1% Calgon.
10. Suspend the clay material by placing the beaker in a sonic dismembrator for ~1 min.
    *Note: Do not let the sample heat up.*
11. Transfer the sample to a clean centrifuge tube and spin for 5 min at 1000 rpm to remove the >2 µm size fraction from suspension
12. Remove the <2 µm size fraction by collecting the top 1 cm of solution with an eye dropper.
    *Note: If it is necessary to re-suspend flocculated clay particles using the dismembrator add more Calgon solution. 15 min at 1500 rpm in the centrifuge may not settle the <2 µm particle size. Increase the speed to as much as 5000 rpm to remove the clay from the Calgon solution.*
13. Make an oriented clay mount by placing 2–3 drops (enough to cover the quartz disk) of clay suspension onto a glass slide and let dry in a desiccator.

## Separating Clay

There are various methods for separating clay from coarser material. Those listed below are methods used onboard. Discuss with the scientist(s) if other methods should be used.

### *“Quick and Dirty” 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% Calgon solution. Use an ultrasonic bath or dismembrator, if necessary.
2. Centrifuge the Calgon solution/sample mix at 1000 rpm for 5 min to remove the >2 µm particle-size fraction.
3. Decant the Calgon solution (containing suspended clays) into a new centrifuge tube, and spin it at 1500 rpm for 15 min to remove the remaining <2 µm clay-size fraction.

4. Decant the Calgon solution and wash the clay residue with distilled water.
5. Spin-down again at 1500 rpm for 15 min.
   *Note: Repeat steps 4 and 5 as necessary to remove the Calgon.*
6. Make an oriented clay mount by placing 2–3 drops (or enough to cover the quartz disk) of solution onto the quartz disk and let dry in the desiccator.

### Treating with Ethylene Glycol

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: Vapor treatment and Quick treatment.

#### *Vapor Treatment*

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

*Note: Glyconation may only last 4 hours after the samples are removed from the glyconation container.*

1. Find the "Glyconator" container stored in the ICP prep sink cupboard.
2. Pour ethylene glycol to a depth of ~1 cm in the bottom of the container.
3. Place the samples onto the shelf
4. Place glyconator (with samples) in oven at 60°–70° overnight.
5. Keep samples in glyconator until ready to analyze.

#### *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.
   *Note: Excess ethylene glycol may be gently mopped up with a lab tissue.*

## Running Samples

Running a regular XRD sample requires the following steps:

–Scan the samples on the XRD
–Convert the raw sample results to an .uxd file
–Print the raw scan to a png file
–Upload the raw, uxd, and png files to LIMS

### Scanning Samples

1. Open *XRD Commander* > **Jobs** tab > **Create jobs.**
2. Under *Positions*, enter the position of the sample (A1–A6 up to K1–K6).
3. Use the Text ID. Use the barcode scanner to enter the Sample ID.
4. Select the appropriate **instrument.dql** file under *Parameter*. If needed, use the *XRD Wizard* to set up a new parameter file (2θ span between 2.5°2θ and 80°2θ).
   *Note: Several .dql files are already created under C:\Documents and Settings\daq\Desktop\XRD Expedition Files\.*
5. Specify the path to save the raw results file, for example *C:\data\xrd\in.* Use the sample's Text ID as the file name.

6. Select the appropriate instrument settings:
   –Script: *measure.vbs*, located in the *DIFFPLUS* folder (should open automatically)
   –Mode: **QL** (qualitative)
   –Time Scale: **1.0**
7. Check that the samples are loaded correctly and nothing is blocking the sample handler.
8. Click **Start**.

### Converting Raw File to .uxd File

After the scan is completed, convert the .raw file into a .uxd file; the .raw file is only readable by the Eva software, whereas the .uxd file can be read by other programs.

1. Click the *Raw File Exchange* software icon on the desktop.
2. On the left panel or "Source", select the .raw file(s) of interest from the drop-down menu.
   *Note: Raw files should be stored in C:Data/in.*
3. On the right panel or "Target", select the .uxd file type from the "convert to" drop-down menu.
4. Under the "Target" panel, choose C:/Data/in for the location of the new exported .uxd files
5. Click **F9 Convert** (bottom right corner).

### Printing Scan to PDF

1. Double-click on the .raw file, which automatically opens the file in the DIFFRAC.EVA software.
2. Go to **File > Print**.
3. Export as a .PNG file.
4. In the save window, name the file with the Text_ID and **Save**.

### Uploading Files to LIMS

The XRD files are uploaded using the MegaUploadaTron 5000 (MUT) program located under the *Start* menu. There are three files for each scan (.raw, .uxd., and .pdf).

1. Open **MUT**.
2. Click **File > Open Upload Directory** to select the directory in which to save the files.
4. Ensure that all files to be uploaded are checked in the uploader window.
5. Click **Upload**.
6. Check that the files moved into the target directory and are uploaded to LIMS.

## QA/QC

The corundum standard NIST 1976 should be run with every scan for quality assurance and quality control. See the *XRD User Guide* for more information on running and evaluating this standard.

Several other standards (powdered concentrates of minerals) are located in the XRD standard drawer in the XRD laboratory. Discuss which, if any, standards the scientists would like to have measured.

## Health, Safety, and Environment

### Physical Hazard Warnings

#### *Danger: Radiation*

The direct beam of the X-ray source is very intensive. 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.

#### *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.

#### *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. 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, the 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.

#### *Calgon*

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 very dangerous. It can cause severe tissue damage on contact, is highly toxic, and the fumes present risks of poisoning and chemical burns. **Always add acid to water!** When mixed with water, large quantities of heat are liberated, so appropriate care should be taken when diluting. Nitric acid is a strong oxidizing agent, so waste should not be mixed with any organic materials.

*Note: although diluted from concentrated strength, the 10-15% 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 (~12 M) is highly dangerous. It can cause severe tissue damage on contact, is highly toxic, and the fumes present risks of poisoning and chemical burns. **Always add acid to water!** When mixed with water, hydrochloric acid liberates large quantities of heat, so appropriate care should be used when diluting this compound.

*Note: 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. **Always add acid to water!** When mixed with water, glacial acetic acid liberates large quantities of heat, so appropriate care should be used when diluting this compound. Glacial acetic acid is also a flammable liquid and should be stored away from oxidizers (e.g., $HNO_3$). 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.