XRD Bulk Analysis

0.2 g of powdered sample is required for XRD analysis.

The powdered sample should be prepared using agate motor and pestle by hand (This procedure is done to not to harm the structures present in the sample).

Get the XRD spectra of the sample. Set the angle range 5^o-80^o, if looking for clay. Else set the range 0^o-100^o. give the step size of 20 sec. and process the data using Xpert High score software for the bulk analysis as:

Select "Treatment" → "Search peaks"

"Background"

Select "Accept"

Set the minimum significance to 0.80. Select "Search". Peaks will appear at the spectra. Select label peaks, by right clicking on the spectra to get the labels on peaks i.e., d-spacing values.

Select "Analysis"

"Search & Match option"

Enter the minerals that you want to search or just press "Search" if you don't know what minerals are present in your sample.

A list of minerals will appear on the screen. Select the mineral matching with the peaks.

For Clay analysis

Clay separation and Glycolation XRD Analysis

MATERIAL REQUIRED

- Glass slides (Round slides of 2 mm thickness and 2.5 cm diameter.
- Fine grained powdered sample[5-10g of sample]-
  - -To make sample fine grained, use RETSCH VIBRATORY DISC MILL-RS200,Start grinding for around 30 seconds, check the texture of the powder by touching it after grinding, it should feel like talc powder otherwise again grind it for some seconds (approx. 15-30 sec).
  - -For Soft samples, use agate motor and pestle to make powder.

Fig 1. Agate motor and pestle

- Beaker
- Distilled water
- Pipette or Dropper or plastic syringe
- Plastic centrifuge tube
- Tissue paper
- Centrifuge machine
- Sonic probe

Clay separation method

Step 1: Take 5-10 g of fine-grained powdered sample in a beaker. Add 50-100ml of distilled water respectively. Then shake the beaker to mix powder and water.

Note: we can do it with 3-4 g of sample if extra sample is not available.
However, prefer 5–10-gram quantity.

Fig 1: Sample mixed with distilled water prepared for sonication

Step 2: Sonication:

To mix powder and water nicely, we use sonic probe for 2-3 minutes. [In sonic probe, there is 5 sec run and 10 sec break]. After sonication, put the sample idle for some time. In addition, check whether the sample is settling in the bottom of beaker fast or not. If it is settling too fast (in 1 or 2 min), then take the pipette and took out the upper part of solution in centrifuge tube. If the settling time is very slow then leave the sample idle for some hours. Keep checking the sample accordingly. After settling of sample, again take out the upper part in another centrifuge tube.

Fig 2: (a) and (b) Sonication probe machine; (c) Result after sonication

Step 3: Centrifuge

Take the sample filled centrifuge tube and another centrifuge tube filled with distilled water (amount of distilled water should be equal to the amount of sample. e.g. If we have 20 ml of sample in one centrifuge tube, then distilled water should also be 20 ml.
Now, put these tubes in centrifuge machine at 6000-rpm speed for 15 minutes.

Step 4: After centrifuge, clay is accumulated on the wall of tube. To take out this clay from tube, leave only 0.5-1 ml of water in the tube and dissolve it nicely. Now, put this clay on glass slides with the help of pipette. (Use pipette to take out clay solution from the tube).
Note: Always make two slides of one sample

Fig 4: (a) Result after centrifuge, (b) Glass slides with sample on it

➢ Place the dessicator idle for 10-15 minutes and then check whether the slides are wet.
Note: Now, scan these glass slides usingX-ray diffractometer (XRD).

GLYCOLATION

If more than one clay mineral (Smectite/Montmorillonite, vermiculite or Illite) is present in the sample then we need to perform glycolation procedure to identify them accurately.

Material Required:
- Oven
- Ethylene glycol
- Desiccator
- Glass slides

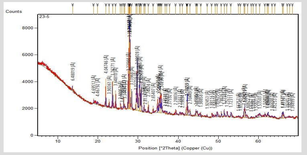
➢ **Step 1:** Prepare glass slides (step 1-5) as mentioned above.
➢ **Step 2:** Fill the desiccator with ethylene glycol (as shown in the figure below) and put the slides in desiccator.
➢ **Step 3:** Put the desiccator in oven at 90-degree temperature for one hour. (In our lab)
[Note: Don't take out the slides from the desiccator]

➢ **Step 4:** Take the desiccator with slides for XRD.
Note: If there is no change in XRD pattern before and after glycolation then put the glycolated slides in oven/furnace for 10 minutes at 400-degree Celsius temperature. (In our lab)
Now again take the XRD pattern. [If clay mineral is present in the samples then peaks will show up].
Follow the clay mineral identification flow diagram to identify the clay mineral given on USGS site [https://pubs.usgs.gov/of/2001/of01-041/htmld Now, scan these glass slides using X-ray diffractometer (XRD).

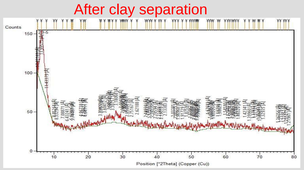
Fill the desiccator with ethylene glycol till the arrow

RESULTS

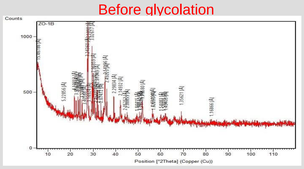
Before clay separation

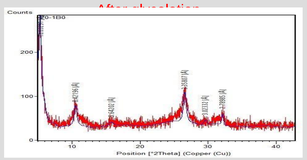


After clay separation



Before glycolation





Mineral Quantification

Rietveld refinement method: The Rietveld refinement method calculates the structure factors from atom position in a crystal structure model. There are two ways to use this technique.

Internal standard: A known amount of 100% crystalline standard base is added to the sample.

External standard: An external standard can be used to put all Rietveld quantities on an absolute scale. An "instrument intensity constant" often called K-factor is determined.

Amorphous content quantification using Rietveld refinement:

Load the external standard file into High score plus. Find the minerals present in the sample and convert pattern to phase.

Start a Rietveld refinement in automatic mode. Wait until the refinement is finished.

Switch to manual fitting mode.

Open the refinement control pane, global variable node, background polynomial sub node. Check to refine one additional background coefficient.

Change the number of **peak base width for fit** from 20 to 50 and **solver tolerance to 0.0001.**

Click to **refine the shape 1 parameter and the V parameter.**

Keep refining until the **goodness of fit (G.O.F) is less than 5.**

Right click on the derived phase data and **select Take current K-factor as standard** from the shortcut menu. This stores the K-factor for your next analysis steps

Go to the **customize menu** and open the **Fitting/Rietveld** tab under the **program setting.**

Change the "show weight percentages" mode into **External K-factor corrected** and close the dialog.