

X-Ray Diffraction (XRD)

EQUIPMENT

- 15 and 100-mL centrifuge tubes
- weighing balance
- centrifuge
- calculator
- mixer
- oven
- crucibles
- desiccator
- muffle furnace
- colored tape
- volumetric flasks (100, 500, 1000 mL)
- distilled water
- microscope slides 1 x 1-1/2"
- pipette

REAGENTS

- 50% methanol - Measure 100 mL TDW and add 100 mL 95% methanol.
- 95% methanol - Use Baker or Fisher analyzed reagent-grade stock.
- 95% ethanol - Use Baker or Fisher analyzed reagent-grade stock
- 1N MgCl₂ (magnesium chloride) - Weigh 102 g MgCl₂•6H₂O, dissolve, and make to a volume of one liter volumetrically using TDW.
- 1N MgOAC (magnesium acetate) - Weigh 71 g MgOAC, dissolve, and make to a volume of one liter volumetrically using TDW.
- 1 % glycerol-ethanol solution - Measure 2.0 mL glycerol and add 198 mL 95% ethanol.
- Stir the solution rigorously.
- 1N KCl (potassium chloride) - Weigh 74.6 g KCl, dissolve, and make to a volume of one liter volumetrically using TDW.
- 1N AgNO₃ (silver nitrate) - Weigh 4.5 g AgNO₃, dissolve, and make to 100 mL volumetrically using TDW.

Bulk Identification

- Use bulk sample that has been acid treated for carbonates and organic matter
- Grind with mortar and pestle until there is no grit (feels like flour)
- pour sample into large format (shallow plastic mount)
 - make sure to spread sample out evenly and to the edges to fill all the spaces
 - compress the powder with a petrographic slide (frosted side down)
 - remove any sample that remains on rim
- Place sample in machine and be gentle to not disturb the compaction of sample on mount
- Start angle at 2° (this captures clays) and stop at 65° (standard)
- Scan in continuous mode at a rate of 2°/minute
- Only one scan of each sample is necessary

Clay Identification

1. The clay saved from the centrifuge or sedimentation procedures has had calcium carbonate and organic matter removed. Removal of free iron on amorphous material may also be required.. Determine the concentration of the clay suspension by pipetting 1 mL of the liquid into a tared crucible, evaporate to dryness overnight, and weigh the clay in the aliquot. Using the equation $g \times mL = g \times mL$, calculate the amount of clay suspension needed for pipetting to obtain 50 milligrams of clay. You will need enough clay to make three slides. Example: $0.1557 \text{ g} \times 1 \text{ mL} = 0.05 \text{ g} \times (x) \text{ mL}$. (x) gives the mL to pipette for one slide.

2. Pipette twice the calculated clay suspension into three 15-mL tubes using a pipette. Prepare the three treatments needed for X-ray at the same time: Mg-saturated, air-dried; Mg-saturated, glycerol solvated; and K-saturated, air-dried. (Tip: Use different colored tape to distinguish the three different treatments)

3. Using the table below, add 3 mL of the solution needed at each step to the 15 mL tube(s), mix, centrifuge for 5 minutes at 1200 rpm, and decant supernatant.

Steps	Mg-sat. air-dried	Mg-sat., glycerol solvated	K-sat. air-dried
(1)	<i>MgCl₂</i>	<i>MgCl₂</i>	<i>KCl</i>
(2)	<i>MgCl₂</i>	<i>MgCl₂</i>	<i>KCl</i>
(3)	<i>MgCl₂</i>	<i>MgCl₂</i>	<i>KCl</i>
(4)	<i>MgOAC</i>	<i>MgOAC</i>	<i>KCl</i>
(5)	ethanol	ethanol	50% methanol
(6)	ethanol	ethanol	95% methanol
(7)	ethanol	ethanol	95% acetone
(8)	ethanol	1% glycerol ethanol	triple distilled ethanol water

COMMENTS

Mg-saturated clays tend to coagulate into uneven masses on slides and crack or peel. Check slides for cleanliness. Pre-wash slides in soapy water, rinse with TDW, rinse in dilute acid, rinse again in TDW, and oven dry. Samples high in amorphous material need to be sonified to disperse. If all fails, try diluting the amount of material being placed on the slide.

To prepare Mg-saturated, glycerol-solvated samples, 1% glycerol is used to expand smectites to 1.8 nm. Sufficient glycerol on the slides is required to solvate the clay, but if excess glycerol is applied to the slide and free glycerol remains on the surface, XRD peaks are attenuated. Some additional suggestions to dry the slides and achieve optimum glycerol solvation are: use a desiccator to dry slide (usually when the clay is thin); heat slide at 100 °C until dry; if the center of slide with thick clay appears light-colored and dry, brush slide with glycerol or add an additional drop of glycerol.

If the K-saturated, air-dried clays peel-up, check slide for cleanliness. Follow steps above to clean slides. If all these steps have been tried unsuccessfully, try diluting the clay until it does not peel.

4. Test a portion of the decanted solution after step 7 until it gives a negative (no white precipitate) test for chloride with AgNO_3 (silver nitrate).

To orient clay sample

- Set up a vacuum system for filtration
- Stir sample and filter clays through a $0.45\mu\text{m}$ millipore filter
- When filter is sufficiently covered, use tweezers to remove filter from system and apply filter onto a centrifuge tube clay side facing outward
- While filter is still damp roll the tube onto the center of the glass slide clay side down
- peel filter from slide and make sure clay has been transferred to slide

5. Let slides dry overnight undisturbed. When dry, place slide(s) in a vacuum desiccator until running XRD patterns

6. Most XRD scans should be run from $2-34^\circ 2\theta$. Run the K-saturated air-dried and heated slides from $2-15^\circ 2\theta$ to save time.

7. If a K-saturated, air-dried pattern contains a 6.2 and/or $8.8^\circ 2\theta$ ($14.2, 7 \text{ \AA}$) peak, the slide will need to be heated. Take the slide(s) and place on a smooth heat-resistant sheet or place directly on the holder in muffle furnace. Put slide(s) in order or label with a heat-resistant pen/pencil, otherwise, the high temperature will remove labels. Place heat-resistant sheet and slides into muffle. Close the muffle and turn the temperature dial to 500°C . Heat slides at 500°C for 2-1/2 hours. Turn the main switch for muffle off and crack furnace door using a wire gauze or leave in the muffle until cool. Carefully remove slides and cool the rest of the way in a desiccator until XRD can be done. Slides should be run as soon as possible to preclude resorption of water from the atmosphere. K-saturated clays will sometimes curl up on heating. If clays curl and separate from the slide, double-stick tape can be used to adhere a piece of the clay film to the slide.

8. Interpret XRD patterns for clay minerals using tables provided.

REFERENCES

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