

## **Preparation of Whole Rock Materials for the Acquisition of Semi-quantitative X-ray Powder Diffraction Patterns**

### **1. Introduction**

Semi-quantitative mineralogy of rocks is a valuable analysis for many geologic investigations. Quantification of mineral phases present in bulk rock material, by means for X-ray Diffraction (XRD), allows for a numerical reference of geochemical variation among samples. To obtain reliable results, precise and rigorous preparation techniques are required. Quantification of crystalline components may be directly measured on unamended samples. In addition, an internal standard can be added to the sample, which allows for quantification of crystalline components as well as a means to estimate the amorphous (either organic or inorganic) content.

The ultimate goal of the preparation method is to reduce a representative split of a whole- rock specimen to a particle size less than 5  $\mu\text{m}$  (microns) and then create small aggregates of randomly oriented particles. These aggregates must then be reproducibly packed into an X-ray diffraction mount while minimizing preferred orientation of the crystallites. Depending on the rock type, organic content, and clay content, the basic methods of sample disaggregation described below are modified slightly to produce the desired results. For example, jaw crushers may not be effective in reducing chip size of organic-rich shale. Wet rocks may require drying prior to processing. In general, the most gentle method that will reduce particle size should be employed, including evaluating freeze/thaw chambers, hand grinding, ultrasonic disaggregation, micronizing mills, ceramic plate crushers, mixer mills, ring pulverizer and if necessary employing more severe grinding methods. Unnecessarily aggressive grinding methods may cause changes in the mineral phases, impart strain in the crystal lattice, or even convert crystalline materials into amorphous phases (Buhrke et al., 1998).

The basic procedure here-in follows methods described by Eberl (2003) for the preparation of randomly oriented powder mounts to determine mineral phase abundances as weight percent. The advantage of the wet McCrone milling employed in this method is that both hard and soft minerals are simultaneously reduced in particle size, rather than preferential grinding of soft minerals relative to harder constituents. Numerous alternative preparation methods and their advantages and disadvantages are described in A Practical Guide to Preparation of Specimens for X-ray Fluorescence and X-ray Diffraction (Buhrke et al., 1998).

### **2. Interfaces with Other Methods**

This method interfaces with EGL Work Instruction 05, 06, and (or) 07 for scanning samples on the Panalytical<sup>1</sup> X'pert Pro, Scintag X1, Siemens D500 X-ray diffractometers respectively, and with EGL Work Instruction 01 and 02 for loading samples into holders.

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<sup>1</sup> Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

- EGL Work Instruction 01 X-ray Diffraction SOP – Side Loading Sample Powders for the Panalytical #1812 holder for the Autoloader
- EGL Work Instruction 02 X-ray Diffraction SOP - Backpack Mounting for the PANalytical X'pert Pro using the #1181 holder for the autoloader
- EGL Work Instruction 05 - Operation of the Siemens X-ray Diffractometer
- EGL Work Instruction 06 - Operation of the PANalytical X-ray Diffractometer
- EGL Work Instruction 07 - Operation of the Scintag X-ray Diffractometer

### 3. Materials and Equipment –

- a. Small jaw crusher with ceramic corundum plates
- b. Spex 8000 Mixer/Mill with zirconia vial and grinding media
- c. McCrone Mill with zirconia grinding media (agate media can be substituted if zirconia is not available).
- d. Corundum standard – American Elements - aluminum oxide powder AL-OX-03-P with nominal grain size of 3.5  $\mu\text{m}$  or similar such as NOAH Technologies Corporation 1  $\mu\text{m}$  corundum.
- e. Methanol - Baker Ultra RESI-ANALYZED\*. 99.8% min. (by GC) or reagent grade 2-propanol.
- f. Vertrel – Miller Stephenson – Vertrel® XF specialty fluid
- g. 1.7 mm (10 mesh US. Standard Sieve) and 420- $\mu\text{m}$  (40 mesh) stainless steel sieve
- h. Teflon cups (100 ml or larger)
- i. Drying oven
- j. Agate mortar and pestle
- k. Scintillation vials (20 ml) with polyethylene cone cap liners

### 4. Procedure –

- a. Rock chips from core or outcrop are submitted by project scientists to the lab, labeled, and entered on a sample spreadsheet following EGL Method 25.
- b. Rock chips are broken down in a small jaw crusher to reduce chip size to approximately 2 mm (material will pass a 10 mesh US. Standard Sieve). Crushed material, approximately 10 grams, is then ground in a Spex zircon ball mill for 5 minutes. Pass the material through a 420- $\mu\text{m}$  (40 mesh) sieve. Material which does not pass the sieve is returned to the ball mill for another 5 minutes of grinding. Repeat this process until all material passes through the 420- $\mu\text{m}$  sieve.
- c. Split the material based on the analytical instrument requirements and sample mount to be used. Both 3.75 g or 1.25 g mounts are available:
  - i. Panalytical XPert Diffractometer - 3 or 1 g split
  - ii. Siemens D500 or Scintag X-1 Diffractometer - 1 g split only.
- d. Weigh out the sample and add a 20%, by weight, internal corundum standard. For the 1.25 g mounts, 1 g of <420- $\mu\text{m}$  ground material and 0.25 gram of standard, or for the 3.75 gram mounts, 3 g ground material and 0.75 gram standard, are weighed on a balance to the third decimal place, weights of the sample and standard are recorded and material is added to a McCrone

Micronizing Mill vial. Ten ml of methanol is added and the sample is ground for 5 minutes.

- e. After grinding is complete, the slurry is poured into a Teflon cup using the pouring cap on the grinding vial. Add about 20-ml methanol into the grinding vial, swirl, and pour the slurry into the Teflon cup. Repeat two more times (or more if necessary) until the methanol slurry is nearly free of ground materials. Place the Teflon cup in a drying oven and dry at 50°C.
- f. After the sample is dry, lightly disaggregate the material with an agate mortar and pestle, sieve to pass a 420- $\mu\text{m}$  screen and store the material in a scintillation vial.
- g. Add 0.5-1.0-ml of Vertrel to the scintillation vial along with two glass beads (3 mm diameter) or three methyl acrylate balls (10 mm diameter) and shake the slurry in a Spex mill for 3-minutes in the scintillation vial. The amount of Vertrel will vary depending on the smectite content of the powder. The purpose of the Vertrel is to create a lubricating volatile liquid? in which to mix the dry powder and allow small aggregates of particles to form. When removed from the vial, the powder should be dry and have a “fluid” nature when transferred. If too much Vertrel is added the powder will clump in the vial and pack into corners like a mud. If this happens, simply allow the powder to vent to atmosphere for a few minutes, break up the clumps in the vial and shake with the mixing balls again. In extreme cases the solidified mud may have to be hand ground in a mortar and pestle to pass 420  $\mu\text{m}$  and then returned to the mixing vial and repeat this step using less Vertrel.
- h. Sieve the material once more to pass 350  $\mu\text{m}$  screen. Clumps which do not pass through the screen can be returned to the scintillation vial with the glass balls and mixed for a few more minutes. Repeat until all the powder passed the 350  $\mu\text{m}$  sieve. Store the powder in the scintillation vial (balls removed) for use in XRD analysis.
- i. Sieves should at minimum be cleaned with compressed air and wiped with a damp Kimwipe. If any particles are visible in the screen, place the screen in a ultrasonic bath and sonify for 5 minutes and then blow dry.

## **5. Calibration and Quality Control Samples**

Depending on the rock type, duplicate samples and(or) in-house reference materials are analyzed with each job. NIST reference materials or instrument manufacturer’s standard may be scanned to demonstrate instrument alignment.

## **6. Limits, Precautions, and Interferences**

None

## **7. Acceptance of Data**

Quality assurance will be verified via blind standards and duplicate samples.

## **8. Data Handling and Transfer**

None

## **9. References**

- Brown, G., and G.W. Brindley. 1980. X-ray diffraction procedures for clay mineral identification. In G.W. Brindley and G. Brown (ed.) *Crystal structures of clay minerals and their x-ray identification*. Min. Soc. London, London.
- Buhrke, V.E., Jenkins, R., and Smith, D.K, (eds) 1998. *A practical guide for the preparation of specimens for X-ray fluorescence and X-ray diffraction*. Wiley-VCH 333 p.
- Chung, F.H. 1974. Quantitative interpretation of x-ray diffraction patterns of mixtures: I. Matrix flushing method for quantitative multicomponent analysis. *J. Appl. Crystal.* 7:519–525.
- Drever, J.I. 1973. The preparation of oriented clay mineral specimens for x-ray diffraction analysis by a filter-membrane peel technique. *Am. Mineral.* 58:553–554.
- Eberl, D.D. 2003. User's guide to RockJock: A program for determining quantitative mineralogy from powder x-ray diffraction data. Open-File Rep. 03–78. USGS, Reston, VA.
- Moore, D.M., and R.C. Reynolds, Jr. 1997. *X-ray diffraction and the identification and analysis of clay minerals*. 2<sup>nd</sup> ed. Oxford Univ. Press, New York
- Pollastro, R.M. 1982. A recommended procedure for the preparation of oriented clay-mineral specimens for x-ray diffraction analysis: Modifications to Drever's filter membrane peel technique. USGS Open-File Rep. 82-71. U.S. Gov. Print. Office, Washington, DC.
- Shang, C., and L.W. Zelazny. 2008. Selective dissolution techniques for mineral analysis of soils and sediments. p. 33–80. In A.L. Ulery and L.R. Drees (ed.) *Methods of soil analysis*. Part 5. Mineralogical methods. SSSA Book Serv.5. SSSA, Madison WI.
- Smith, D.K., G.G. Johnson, Jr., W. Scheible, A.M. Wims, J.L. Johnson, and G. Ullmann. 1987. Quantitative x-ray powder diffraction method using the full diffraction pattern. *Powder Diffraction* 2:73–77.
- Soukup, D.A., B.J. Buck, and W. Harris. 2008. Preparing soils for mineralogical analysis. P. 13-31. In A.L. Ulery and L.R. Drees (ed.) *Methods of soil analysis*. Part 5. Mineralogical methods. SSSA Book Serv.5. SSSA, Madison WI.
- Srodon, J., V.A. Drits, D.K. McCarty, J.C.C. Hsieh, and D.D. Eberl. 2001. Quantitative x-ray diffraction analysis of clay-bearing rocks from random preparations. *Clays Clay Miner.* 49:514–528.

## **10. Attachments**

None

## **11. History of Changes**

R0: Initial Issue