

CLAY MINERAL SEPARATION AND PREPARATION FOR X-RAY DIFFRACTION ANALYSIS

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CLAY MINERAL SEPARATION FOR X-RAY DIFFRACTION ANALYSIS

1. PURPOSE

The purpose of this procedure is to describe separation of clay minerals from bulk rock samples and preparation of oriented sample mounts of clay minerals for analysis by x-ray diffraction.

2. SCOPE

The procedure applies to separation and x-ray diffraction investigation of clay minerals for the Yucca Mountain Project.

3. PRINCIPLES

This procedure is based on Stokes Law settling of particles in a solution.

4. DEFINITIONS

None Applicable.

5. RESPONSIBILITIES

The principal investigator (PI) has the responsibility to assure implementation of this procedure for clay mineral separations being conducted for the Yucca Mountain Project. The PI may delegate performance of the procedure to any duly certified individual.

6. PROCEDURE

6.1 Overview

6.1.1 Equipment and Software Used

- o Shatterbox (or large ball mill) -- most all acceptable.
- o Ultrasonic probe capable of ~200 W.
- o Centrifuge capable of 8000 RPM with a Sorvall GSA head.
- o Sorvall GSA centrifuge head.
- o Sorvall SS-34 centrifuge head (optional).
- o Spray Drier (optional).
- o 1000 ml beakers.
- o No software is used.

6.1.2 Critical Laboratory Setup Parameters

None Applicable.

6.1.3 Special Environmental Conditions

The use of de-ionized or distilled water to wash and disaggregate the samples is necessary to ensure that no chemical alteration of the clays occurs due to cation exchange.

6.2 Cleanliness

Thoroughly clean all sample preparation equipment and work areas before use.

6.3 Traceability

6.3.1 Complete records shall be kept in a controlled YMP notebook, including full sample identification, date of preparation, and signature of person preparing each sample.

6.3.2 Great care shall be exercised not to mix or contaminate samples. All subsequent analyses rely on this procedure.

6.3.3 Carefully label containers into which the pulverized sample will be placed and keep rocks with their labeled bags and containers. Label side and top of each container so that tops cannot be switched.

6.4 Set Up for Separation

6.4.1 Obtain approximately a one-to-two-inch slice of drill-core or an equivalent amount of drill cuttings or bulk-rock.

6.4.2 Rid the sample of surface contamination using one of the following:

- o Brisk strokes of a clean, dry bristled brush.
- o Rinse with de-ionized or distilled water and dry thoroughly -- preferably at room temperature.

6.4.3 Break the bulk sample down into smaller pieces (less than 0.25 inch in diameter using:

- o A Platiner mortar and pestle or,
- o A mortar and pestle/hydraulic press apparatus.

6.4.4 Powder sample using either a shatterbox or large ball-mill.

6.4.5 Combine the entire powdered sample and mix thoroughly to ensure homogeneity. Place in a bottle properly labeled with the sample identification.

6.5 Separation

- 6.5.1 Take approximately 20-30 grams of the powdered sample and suspend it in approximately 500 to 700 ml of deionized or distilled water contained in a large plastic (~1000 ml) beaker. Disaggregate the sample for approximately 10-20 minutes at ~200 W using an ultrasonic probe.
- 6.5.2 Remove the beaker containing the suspended sample from the ultrasonic probe enclosure and cover the beaker. Place the beaker on a vibrationally stable surface and allow the sample to settle gravitationally without interruption ideally for a time equal to 47 minutes per cm depth of water. This will allow sedimentation of all particles greater than 2 μ m diameter. For a typical 14 cm water depth, total settling time should be about 10.9 hours. Overnight settling using a water depth of 14 cm will result in sedimentation of slightly smaller particles, e.g., 15 hours settling will sediment particles >1.75 μ m and 20 hours settling will sediment particles >1.5 μ m.
- 6.5.3 Decant or syphon the supernatant from the beaker into large centrifuge tubes, taking care not to disturb the sediment at the bottom of the beaker. The sediment in the beaker may be discarded.
- 6.5.4 Place the centrifuge tubes in the centrifuge and separate the ~2.0-0.35 μ m size fraction from suspension at a centrifugation speed of ~5000 revolutions per minute for a spin time of ~5 minutes. (Refer to Sorvall Centrifuge Instruction Manual for Superspeed Angle Rotors: GSA and SS-34.)
- 6.5.5 Remove the centrifuge tubes from the centrifuge and decant the supernatant into large receiving centrifuge tubes, taking care not to disturb the sediment (>0.35 μ m in diameter) at the base of the tube. Save this sediment fraction if needed.
- 6.5.6 Place the centrifuge tubes containing the cloudy supernatant in the centrifuge and separate the fine clay fraction (~0.35-0.10 μ m in diameter) at a centrifugation speed of ~8000 revolutions per minute for a spin time of 40 to 60 minutes.
- 6.5.7 Remove the centrifuge tubes from the centrifuge and decant the supernatant into labeled beakers.
- 6.5.8 Remove the fine clay sediment fraction (~0.35-0.10 μ m in diameter) from the base of the centrifuge tubes using a spatula and, if necessary, a small amount of deionized or distilled water. Save in a properly labeled sample bottle.

6.5.9 There are several options for processing the remaining supernatant material from step 6.5.7, (this supernatant contains the $<0.10 \mu\text{m}$ fraction). The options are as follows:

- 1: If not needed, it may be discarded.
- 2: Place the beakers on a low-temperature hotplate or warm surface to evaporate/concentrate until it will fit into a labeled sample bottle.
- 3: It can be further centrifuged using the Sorvall SS-34 head at a speed of ~ 15000 RPM for ~ 1 hour to remove some of the remaining clays.
- 4: It can be run through a spray drier which evaporates the liquid and allows the clay to be collected.

6.6 Preparation of Oriented Mounts

6.6.1 Suspend a clay mineral fraction in a small amount (approximately 10 to 20 ml) of deionized water contained in a small beaker.

6.6.2 Thoroughly clean and dry a glass or quartz slide appropriately sized for the diffractometer sample holder being used, and place it on a level, stable, warm surface. The sample number is written with indelible ink on the back of the slide.

6.6.3 Drop the suspended clay sample, using an eye dropper or pipette, onto the slide using only enough sample to cover the slide. Do not overfill the slide and do not add additional suspension after the suspension on the slide has begun to dry to ensure the best orientation of clay particles possible.

6.6.4 Allow the sample to dry undisturbed on the slide.

6.6.5 The sample is now ready for x-ray diffraction analysis (refer to Siemens X-ray Diffraction Procedure, TWS-ESS-DP-16).

6.7 Data Analysis

Not Applicable.

7. QUALITY ASSURANCE

7.1 Personnel

Only those persons certified in accordance with the Los Alamos YMP Personnel Certification Procedure shall perform YMP related clay mineral separations and preparations.

7.2 Calibration

No calibration of equipment is necessary for this procedure.

7.3 Records

Full records of a clay separation, including full sample name or number, date of separation, and signature of the person separating each sample are to be recorded in a controlled YMP notebook.

7.4 Accept/Reject Criteria

7.4.1 Adherence to this procedure results in an acceptable sample for x-ray diffraction analysis. The purity of the individual samples and their size fractions are determined by x-ray diffraction. It is up to the person conducting the separation to determine if the clay fractions are of adequate purity for their work.

7.4.2 There are no real potential sources of error since this is a qualitative procedure.

7.4.3 The notebook entry for a sample shall constitute evidence that the procedure has been implemented and satisfactorily accomplished for that sample.

7.5 Procedural Deviations

Deviations from this procedure shall be fully documented in the controlled YMP notebook of the person conducting the work and shall explain the deviation and the effects it may have on the resulting work.

7.6 Storage, Shipping, and Handling

7.6.1 Samples will be tracked, handled, shipped, and stored in accordance with the procedure for Sample Identification and Control for Mineralogy-Petrology Studies (Ref 8.3).

7.6.2 The equipment require no special handling, shipping, or storage considerations.

8. REFERENCES

- 8.1 SPEX 8500 SHATTERBOX/CONTAINER, instruction sheet
SPEX Industries, Inc., 3880 Park Avenue, Metuchen, NJ 08840
- 8.2 Sorvall Superspeed Angle Rotors, GSA and SS-34 Instruction Manual
DuPont Company, Biomedical Products Division, Newtown, CT 06470
- 8.3 TWS-ESS-DP-101: Sample Identification and Control for
Mineralogy-Petrology Studies.

9. ATTACHMENTS

None.

PROCEDURE FOR X-RAY FLUORESCENCE ANALYSIS

Effective Date 6/5/89

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PROCEDURE FOR X-RAY FLUORESCENCE ANALYSIS

1.0 PURPOSE

The purpose of this procedure is to describe the process for x-ray fluorescence (XRF) analysis of geologic samples.

2.0 SCOPE

This procedure applies to x-ray fluorescence analysis for the Yucca Mountain (YMP) project. This procedure covers XRF analysis of geologic samples and includes system start-up, hardware functioning, software, system shut-down, and requirements for documentation.

3.0 DEFINITIONS

ESSXRF - MicroVax II located at SM494.
XRF - X-Ray Fluorescence
System Manuals - Rigaku Manuals 1 and 2.

4.0 SAMPLE PREPARATION

Samples are prepared for XRF analysis in accordance with the following procedures:
Rock Splitting -- Operation of 50-ton Hydraulic Press (TWS-ESS-DP-55)
Crushing -- Operation of 50-ton Hydraulic Press (TWS-ESS-DP-54)
Pulverizing -- Using the Shatterbox (TWS-ESS-DP-53)
AE 100 "SCALE" Operating Procedure (X-Ray Fluorescence Analysis Sample Weighing Procedure) (TWS-ESS-DP-51)
Fusing Using the Junior Orbit Shaker (TWS-ESS-DP-52)

5.0 DESCRIPTION OF X-RAY EQUIPMENT

- 5.1 The X-ray Fluorescence Analyzer is a Rigaku 3064 sequential spectrometer with a Model 3065, 108 position sample changer. This instrument is a closed x-ray system.
- 5.2 The x-ray tube is protected by an interlock switch that prevents turn on of high voltage, and thus x-rays, if the tube is not in the machine.
- 5.3 This instrument is equipped with a fail-safe x-ray warning light, shutter open indicator light, and power applied indicator.
- 5.4 No physical means of entry into the x-ray beam is possible without removal of mechanical parts of the instrument.

6.0 SAFETY

- 6.1 This instrument is very mechanically powerful, thus extra attention should be given to staying clear of its mechanical movements.
- 6.2 No person except qualified maintenance persons shall remove panels or perform any operation not included in this procedure. Removal of any protective covers should be with x-rays off, except for calibration procedures which may require x-rays.
- 6.3 Calibration and alignment will be performed as per manufacturers published instructions (Ref., Documentation of Calibration and Alignment).
- 6.4 No modifications to x-ray limiting devices will be performed without ESS-1 group leader and HSE approval.
- 6.5 Each operator must attend an x-ray analytical instruments, radiation safety course. This course is administered by Group HSE-1 and must be retaken at three-year intervals.

7.0 START-UP

- 7.1 XRF Condition--complete shut down or power failure.
- 7.2 If any ALARM signal on the X-ray Generator Panel should light up, contact Machine Custodian.
- 7.3 Turn on the white POWER button located on the 3064 Operation Panel.
- 7.4 On the X-ray Generator Panel, turn mA and then kV knobs fully counter-clockwise. Turn on both X-Ray and Power switches.
- 7.5 Turn on the sample changer power by pushing the white switch located on the Sample Changer Panel to ON.
 - 7.5.1 Both the "power" light and the "ready" light should come on.
 - 7.5.2 At this time you should hear a pump start, which is somewhat loud at first.
 - 7.5.3 If you do not hear this pump, check on the 3064 Operation Panel to make sure that the white button marked Vac is depressed.
 - 7.5.4 If the button is not depressed, then do so. You should now hear the pump.
- 7.6 Within this cluster of buttons on the 3064 Operation Panel, make sure that the Sample Spin button is depressed and the ON Line button is depressed.
- 7.7 A bottle of P-10 gas, a water deionizer, and chiller are located against the wall to the left of the XRF.
 - 7.7.1 Check the P-10 gas flow. It should be at approximately 0.04 psig. If it is not, adjust the knob until it is.
 - 7.7.2 Turn on the water source if it is not already on.
- 7.8 Go to the left of the XRF where you will find a Water Deionizing Heat Exchanger System.
 - 7.8.1 Turn the power to ON on the Water System.

- 7.8.2 On the front panel, you will find a meter that is for measuring the conductivity of the water used for cooling the x-ray tube.
- 7.8.3 Next to the meter is a toggle switch.
 - 7.8.3.1 Hold the toggle switch down to ADJ (do not release). The needle should read full scale.
 - 7.8.3.2 If the needle is not full scale, adjust the knob until the needle aligns with the last graduation mark.
 - 7.8.3.3 If you cannot align the mark, replace the "AA" batteries (consult system manuals for replacement of batteries), and repeat steps 6.8.3.1 through 6.8.3.2.
 - 7.8.3.4 Hold the toggle switch up to MEAS. The needle should be to the left of the 1.0 mark. If it is not, replace deionizing cartridge located on wall.
 - 7.8.3.5 CAUTION: If the system is turned on with water having a conductivity greater than 1.0, damage may occur to the x-ray tube.
 - 7.8.3.6 If the conductivity of the water is below 1.0, then proceed with the next step.
- 7.8.4 Open the front panel and check the water temperature (21-24°C), jacket pressure (1.2-1.6 psi), and target pressures gauges (3.6 psi). Adjust the appropriate knobs below the gauges as necessary.
- 7.9 Return to the front of the XRF and go to the upper right corner of the spectrometer where you will find the X-ray Generator Controls.
 - 7.9.1 Check the kV and mA settings to make sure they are on their lowest settings (20 kV and 2 mA, respectively). The load dial should be set at 2.7 kW.
 - 7.9.2 Note that both the "power" light and x-ray "ready" light are on. If neither light is on, contact Machine Custodian.
 - 7.9.3 If at any time during this operation an instability of either the kV or mA meter is observed or an arcing sound is heard, immediately turn off the x-ray generator by depressing the x-ray Off switch.
 - 7.9.4 Slowly increase the kV by increments of 5, one click every 3 to 5 minutes, until the operating condition of 40 kV is reached.
 - 7.9.5 Slowly increase the mA by increments of 5, one click every 3 to 5 minutes, until the operating condition of 50 mA is reached.
 - 7.9.6 Wait one hour to allow the machine to warm up before proceeding. This allows the machine to stabilize.

8.0 DRY RUN

8.1 Resolution Check

- 8.1.1 The resolution is checked on Cu K alpha x-ray line using the flow proportional counter. Resolutions <30% are acceptable. If >30%, release ON LINE, depress quantity, memory (Rigaku Instruction Manual 1, pg. 4-14).
- 8.1.2 Load the Al and Cu sample and position the sample changer to Cu sample.
- 8.1.3 On the Pulse Height Analyzer rotate the Mode knob to DIFF x 0.1.
- 8.1.4 On the PHA Setter, rotate the only knob to SCAN.
- 8.1.5 On the Ratemeter set the outer Range Knob to 10 and the inner Range Knob to x2.
- 8.1.6 Return to PHA setter and set Scan Speed switch for 10 minutes.
- 8.1.7 Pull out the Chart Recorder and turn it on by pushing the POWER Button.

- 8.1.8 Press **START** on PHA setter. The chart recorder should slowly advance and begin to draw a bell shaped curve.
- 8.1.9 When finished, push **STOP** on the PHA setter and measure resolution (FWHM). See Rigaku instructions on resolution calculations (Rigaku Instruction Manual 1, pg. 4-14).

8.2 Prepare the XRF for sample analysis by doing the following on the 3064 Operation Panel:

- 8.2.1 Remove the Cu and Al samples.
- 8.2.2 Set the priority to **ON LINE**.
- 8.2.3 Release the scanning mode quantity button.
- 8.2.4 Release the program mode memory button.
- 8.2.5 Log into ESSXRF MicroVax II.

9.0 ANALYZING SAMPLES WITH THE XRF

- 9.1 The XRF is ready to analyze prepared samples after the dry run has been completed.
- 9.2 Mount the glass disks in the holders with the side to be analyzed facing up. Pass the holders under the bridge to make sure they will load properly.
- 9.3 Place the holders in the sample tray. Slot number six must always be filled. There are a maximum of six samples per tray (never fill slot number one and zero as sample changer will fail to load samples). Put an appropriate control standard in any slot, position 2-6. Record the sample positions in the tray and tray number in the controlled XRF Sample Tracking Logbook.
- 9.4 Make certain the Reference Standard (used to correct for instrumental drift) is in position 1 in the sample chamber and close the lid.
- 9.5 Place the sample tray in the left side of the sample changer tray racks. Make sure that the sample changer is full, nine trays per side.
- 9.6 Check green LED on sample changer to ensure that the first cassette is sensed by the changer.
- 9.7 Log into account XRFLAB on one of the terminals in the XRF LAB, Room 118, SM494.
 - 9.7.1 Type ESCP <CR> to start the analysis program.
- 9.8 Follow the instructions in the Rigaku DATAFLEX software manual. Explanations of commands are documented in this manual.

10.0 STANDBY CONDITION

- 10.1 This is the normal Standby Mode. If a complete shut down is required, skip to step 10.
- 10.2 The XRF should not be left at operating levels 40 kV and 50 mA when not in use. During nights or weekends when it is not analyzing, the mA and kV levels of the x-ray tube should slowly be turned down (one at a time, mA first, kV second) to the minimum value.

11.0 SHUTDOWN

11.1 On the X-ray Generator Panel:

- 11.1.1 Slowly turn down the mA dial to its minimum.
- 11.1.2 Slowly turn down the kV dial to its minimum.
- 11.1.3 Turn the x-rays off.
- 11.1.4 Allow the x-ray tube to cool for at least 15 minutes.
- 11.1.5 Turn off power switch below x-ray switches.

11.2 On the Sample Changer Operation Panel:

- 11.2.1 Switch the Manual Lid to OPEN.
- 11.2.2 When the vacuum is released (a hissing sound will be heard), turn off the power on the sample changer.

11.3 On the 3064 operation panel, turn off the power.

11.4 Turn off the Water Deionizing System.

12.0 QUALITY ASSURANCE

12.1 Personnel

Only YMP certified persons may operate the XRF using this procedure. Evidence of certification shall be documented in accordance with the YMP Procedure for Personnel Selection, Indoctrination, and Qualification (TWS-QAS-QP-02.1, R1). Training for this procedure consists of reading the written Detailed Procedure and performing the procedure under the supervision of a trained person. The preparer of this detailed procedure is considered trained to perform this procedure and to train others.

12.2 Control Standards

Analysis of internationally recognized standard reference materials (silicate rocks) will be used in each run. These standards are described in Geostandard Newsletter, Abbey (1980) (Ref.13.1), and are listed in Attachment A.

12.3 Calibration

Calibration for trace elements is accomplished by using the standards (Attachment A). Elements free of overlaps are fit to a linear least squares fit (unconstrained). Overlapped elements are fit using multiple linear least squares fits. Matrix corrections in both cases are accomplished by Rh/Compton ratioing (Harvey and Atkin, 1982).

Calibration of major elements is accomplished by updating intensities from BCR-1 (a USGS standard) in XRF-11 driver file as described in XRF-11 User Guide (Criss, 1985).

12.4 Documentation

- 12.4.1 The following are recorded on an XRF Submittal Form (Attachment B): fusing number, sample identification number, date fused, who did the fusing, rock type, type of analysis wanted, and requester.
- 12.4.2 The analysis data are recorded on magnetic tape and hard disk. In addition, a hard copy is sent to the requester.
- 12.4.3 The following are recorded in the XRF Log: notes pertaining to problems, experiments, changes in operating parameters or procedure.
- 12.4.4 A hard copy of the analyses and the associated calibration tables shall be kept in a loose leaf binder. A disk of these data are stored on the ESSXRF VAX.

12.5 Sample Handling and Storage

Upon completion of XRF analyses, fused disks will be stored in accordance with Procedure for Sample Identification and Control for Mineralogy-Petrology Studies. (TWS-ESS-DP-101)
There are no specific storage requirements for the equipments used in this procedure.

12.6 Accept/Reject

The requester (i.e., investigator) and/or the operator shall have authority to accept or reject analyses. Acceptance or rejection shall be a matter of the investigator's professional judgement, based upon comparison of the results of analyses of standards with their published values, and upon the intended end-use of the data.

12.7 Potential Sources of Uncertainty

1. The selection of counting time for peak and background is based on the typical sample. If samples are analyzed containing far less of the element of interest, the error due to counting statistics will become large, leading to poor precision.
2. Unexpected or uncorrected elements may overlap measured elements, resulting in unexpectedly high concentrations.
3. Reporting of uncertainties in XRF Analyses is addressed in document TWS-ESS-1-1/89-8.

13.0 REFERENCES

- 13.1 Abby, S., 1980, Studies in "Standard Samples" for use in the general analysis of silicate rocks and minerals: Geostandards Newsletter, vol. 4, no. 2, p. 163-190.
- 13.2 Harvey, P. K., and Atkin, B. P., 1982, The estimation of mass absorption coefficients by Compton scattering: extensions to the use of Rh K α Compton radiation and intensity ratios: American Mineralogist, vol. 67, p. 534-537.
- 13.3 Rigaku Dataflex Software Manual
- 13.4 Rigaku Instruction Manuals 1 and 2 (X-Ray Fluorescence)
- 13.5 Criss, J. W., 1985, XRF-11 Users Guide : Criss Software Inc., 12204 Blaketon St., Largo, Maryland 20772.
- 13.6 TWS-ESS-1-1/89-8: Reporting of Analytical Uncertainties in X-Ray Fluorescence Analyses.

- 13.7 TWS-ESS-DP-101: Procedure for Identification and Control for Mineralogy-Petrology Studies.
- 13.8 Software: Rigaku Dataflex 360 as described in TWS-QAS-QP-3.1, R0.
- 13.9 TWS-ESS-DP-51, R0 Mettler H80 Operating Procedure (X-Ray Fluorescence Analysis Sample Weighing Procedure)
- 13.10 TWS-ESS-DP-52, R1 Sample Preparation for X-Ray Fluorescence Analysis: Fusing and Lapping
- 13.11 TWS-ESS-DP-53, R1 Pulverizing Using the Rocklabs 3E Shatterbox
- 13.12 TWS-ESS-DP-54, R1 Crushing: Operation of 50 Ton Hydraulic Press
- 13.13 TWS-ESS-DP-55, R1 Rock Splitting: Operation of 50 Ton Hydraulic Press
- 13.14 TWS-QAS-QP-02.1, R1 Procedure for Personnel Selection, Indoctrination, and Qualification

ATTACHMENT B

XRF SAMPLE FORM

Requestor: _____ Date Submitted _____

File ID. _____, Program Code: _____, NNWSI (Y/N): _____, No. of Samples: _____

Majors (Y/N): _____ Traces (Y/N): _____

Do you want to check samples after they are split (Y/N): _____

Comment: _____

	Date	Operator
Splitting	_____	_____
Crushing	_____	_____
Shatterboxing	_____	_____
Fusing	_____	_____
Analysis Complete	_____	_____
Data Reduction	_____	_____
Final Report	_____	_____

ANALYSIS WILL BE LISTED IN ORDER BELOW

Sample No.	Fusion No.	Description (Rock Type)
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

Analysis continued on Page 2

SAMPLE LOG SHEET

Samples received in Sample Prep Lab _____
Signature _____ Date _____

Samples distributed to _____
Signature _____ Date _____

NNWSI _____ R&D _____

All fused discs will be returned unless otherwise specified.
ESS-1 Form 2 (September 1988)