

CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES		Proc. TOP-004-02
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Title PROCEDURE FOR QUALITATIVE X-RAY POWDER DIFFRACTI ANALYSIS OF GEOLOGICAL MATERIALS		DIFFRACTION
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PROCEDURE FOR QUALITATIVE X-RAY POWDER DIFFRACTION ANALYSIS OF GEOLOGICAL MATERIALS

1. Purpose

The purpose of this procedure is to describe the methods and equipment to be used in conducting qualitative X-ray powder diffraction analysis of geological materials.

2. Scope and Application

This procedure describes the equipment and techniques which may be utilized in determining the major mineralogic constituents of geological specimens by X-ray powder diffraction methods. The specimen can be a whole rock or mineral sample, an insoluble residue, a heavy mineral separate or a size fraction of any of these materials. This procedure does not apply to detailed clay mineral analysis which involves treatment of the sample to allow dispersion and concentration of the clay mineral fraction, although qualitative information on clay minerals may be derived by this procedure. Methods to analyze clay mineralogy are covered under a separate procedure. vetailed procedures for calibrating, adjusting and operating the X-ray diffractometer are given in the Operating Instructions for Siemens D-500 Diffractometer and Kristalloflex 800 X-Ray Generator. The procedures described here may vary slightly if another make or model of diffractometer is used.

2.1 Applicable Documents

The following documents form a part of this procedure, as applicable:

- (1) Center Technical Operating Procedures
- (2) Center Quality Assurance Manual
- (3) Operating Instructions for Siemens D-500 X-ray Diffractometer
- (4) Operating Instructions for Siemens Kristalloflex 800 X-Ray Generator

(5) Joint Committee on Powder Diffraction Standards

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(J.C.P.D.S.) Search Manuals

- (6) Joint Committee on Powder Diffraction Standards (J.C.P.D.S.) Powder Data File
- 3. <u>Responsibility</u>
 - (1) The cognizant Principal Investigator of the project shall be directly responsible for the implementation of this procedure. In cases where the Principal Investigator is not a member of the Center, the Project/Element Manager shall retain this responsibility.
 - (2) The Center Director of Quality Assurance is responsible for providing independent surveillance, review or audits to verify implementation of this procedure.
- 4. Equipment and Supplies

Listed below are pieces of equipment and supplies that may be utilized in the preparation of powder samples and in conducting the X-ray powder diffraction analysis.

- (1) Siemens D-500 X-ray diffractometer
- (2) Siemens Kristalloflex 800 X-ray generator
- (3) Agate mortar and pestle
- (4) Glass slide or cover glass
- (5) Aluminum specimen holder
- (6) Wash bottle
- (7) Acetone or alcohol

5. Procedures

A. Sample Preparation and Mounting

Method A:

(1) If the sample is not already pulverized, put a few crystals

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or fragments of the specimen to be analyzed in a clean agate mortar and grind with an agate pestle until all of the powdered sample passes through a 325 mesh sieve.

- (2) Invert an aluminum specimen holder (Figure 1) and place it in contact with a glass slide so that its well is sealed by the glass. The glass slide may be temporarily taped onto the aluminum holder.
- (3) Fill the hole with the powdered specimen by gently tapping in the powder from a spatula or from the sample container, and pressing it gently with a flat spatula blade or with another glass slide. Smooth off any excess powder with the edge of the blade or slide.
- (4) A second glass slide or a thin cover glass is taped on top of the powder to cover the specimen well completely.



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(5) The specimen holder, together with the glass plates, is inverted right-side-up so that the free surface of the specimen powder is exposed on top after removal of the first glass slide from the specimen holder. If the specimen surface has retained its flat smooth surface parallel to the aluminum surface, it is ready for use. The specimen powder surface may be smoothed flat if necessary by pressing the glass slide onto it before final removal. The aluminum sample holder can be labeled with the specimen name and/or number.

Method B:

A simpler and more convenient method is to smear the fine mineral powder on a glass slide and slurry it with acetone.

- (1) Prepare the specimen as in Method A, Step (1), above.
- (2) Scatter a thin layer of the powder on one-half of one surface of a glass slide.



Figure 2. Mineral powder slurry on a glass slide. Dimensions are approximate.

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- (3) From a wash bottle add enough acetone to the powder to produce a thin slurry. The powder will smear evenly and spread. Spreading may be assisted by a spatula blade. The amount of powder and acetone added should produce a layer of approximately even thickness.
- (4) Once the acetone has evaporated the powder layer will cohere. An area approximately 20 mm wide on the end of the slide surface should be wiped free of powder. The final appearance of the preparation is shown in Figure 2.
- B. Running the X-ray Diffractogram
 - (1) Turn on the cooling water supply, the goniometer, the X-ray generator, and the detector according to the Operating Instructions. Make sure the <u>K-beta</u> filter appropriate to the particular type of X-ray tube is inserted, e.g. for a Cu tube, use a Ni filter.
 - (2) Make sure the shutter is closed. Then open the lead-glass window of the radiation protection housing.
 - (3) Mount the specimen on the specimen shaft of the goniometer, and firmly hold in place with the spring-loaded clip. Make sure that the space between the clip and specimen shaft is clean and free of specimen powder. Close the shield door, then open the shutter.
 - (4) Turn the strip chart recorder power on. Determine the optimum chart scale according to the Operating Instructions.
 - (5) Set the speed selector dial on the control panel to the desired rotational direction and to the most appropriate scanning rate. If a rapid record of low angular resolution for identification purposes is desired, a fast scanning rate of 1° or 2° <u>2-theta</u> per minute may be selected. If, on the other hand, high <u>2-theta</u> precision is desired, a slow scanning rate of 1/2°, 1/4°, or even 1/8° <u>2-theta</u> per minute may be chosen.

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(6) Choose an appropriate strip chart recorder speed to suit the scanning speed of the goniometer. A slow goniometer scanning speed should always be combined with a slow recorder speed and a fast goniometer speed with a fast recorder speed. A useful goal is to achieve 2 cm per degree <u>2-theta</u> (or 1 inch per degree) for moderately slow scans of 1/2 or 1/4 <u>2-theta</u> per minute, so that peak centers can be accurately located with the eye. There is no virtue in having a long chart distance per degree; indeed 1 inch per degree (or 2 cm per degree) is normal practice at the U.S. Geological Survey and the Carnegie Institute in Washington for high-precision lattice parameter refinement. The following combinations give ideal diffractogram scales of 2 cm/1 <u>2-theta</u>:

 Goniometer speed,
 O
 2-theta/min
 1/8
 1/4
 1/2
 1

 Recorder speed, cm/min
 0.25
 0.5
 1
 2

The slowest scanning rates of $1/8^{\circ}$ <u>2-theta</u> per minute should be reserved for highest <u>2-theta</u> precision determinations, whereas the fast rate of 1° per minute would be used for normal identification purposes requiring less precision. An even faster scan of 2° <u>2-theta</u> per minute is possible, and this may be combined with 2 cm/min giving 1° 2-theta/cm on the diffractogram, which is perfectly adequate for rapid identification purposes.

- (7) Select the appropriate time constant according to the scanning rate selected; for example, a scanning speed of 1° 2-theta per minute should normally be combined with a 2 second time constant. For slower rate of 1/2° or 1/4° 2-theta per minute a longer time constant of 4 seconds may be preferable. For a 2° 2-theta per minute rate the time constant would have to be 1 second. A longer time constant gives a smoother, more easily read diffractogram. Too short a time constant of less than 1 second will show too many random changes in the detector response; hence the diffractogram will not be smooth.
- (8) Rotate the <u>2-theta</u> setting of the goniometer a few degrees below the starting value required on the diffractogram, then slowly come up to the starting

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2-theta value. The initial 2-theta value should be a whole number, for example, 27.00° .

- (9) Advance the strip chart recorder so that the pen rests exactly on one of the chart lines.
- (10) Record on the strip chart the following information:
 - a) Date
 - b) Name(s) of the operator(s)
 - c) Sample identification
 - d) Starting 2-theta value
 - e) Type of X-ray tube and K-beta filter used
 - f) Operating voltage and current
 - g) Time constant and chart scale
 - h) Scan rate
 - Other pertinent information, e.g. type of specimen holder used.
- (11) Push the scan button, then the start button on the goniometer. This will start the goniometer scan and the strip chart recorder simultaneously.
- (12) After having passed the desired angular range push the stop button, or let the goniometer run to the maximum <u>2-theta</u> set on the instrument (determined by multiplying the values of 'step size' and 'step number' on the scan control panel). Rotate the goniometer back to the starting <u>2-theta</u> value.
- (13) If any of the peaks are offscale, the diffractogram may be rerun on a larger chart scale to identify their exact positions.
- C. Calibration of X-ray Diffractometer Using Standard Substances

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To check the calibration of a diffractometer, a diffractogram may be taken of a pure standard substance of known and highly refined structure and lacking in isomorphic substitution and lattice vibration. Pure quartz or silicon powder is the most commonly used standard, but other substances such as KBrO₃, high purity aluminum powder, tungsten powder, silver powder, and cadmium oxide powder may be used. Their respective diffraction lines are tabulated in the Joint Committee on Powder Diffraction Standards (J.C.P.D.S.) powder data file. The calibration will be conducted either before analyzing the unknown samples using Method A, or simultaneously with the unknown samples using Method B.

Method A:

- (1) Prepare a powder specimen and make a diffractogram of pure silicon or other standard substance using procedures described above. A quartz standard provided us the instrument manufacturer may be used in lies of a silicon powder specimen.
- (2) After the X-ray diffraction scan of the standard has been completed, the recorded <u>2-theta</u> positions of the 5 most intense peaks are compared with theoretical positions given in the J.C.P.D.S. powder data file. Any systematic error, either positive or negative, is noted and used to correct the <u>2-theta</u> readings on any subsequent experiment, provided that the alignment of the goniometer has not been changed and the same specimen preparation technique is used for both standard and unknown.
- (3) If the difference between the recorded <u>2-theta</u> of the standard substance differs too much from the ideal value (e.g., by as much as 0.10° or 0.20° <u>2-theta</u>), the <u>2-theta</u> drum of the goniometer shall be adjusted following the Operating Instructions for the X-ray diffractometer.
- (4) Both standard specimen and subsequent unknown should be run with <u>2-theta</u> progressing in the same direction, both from low to high or both from high to low. The goniometer may not reproduce exactly the same angles for both directions of scan because of backlash. Preferably the unknown and standard should be scanned at the same speed as well as in the same direction.

(5) The angular error in 2-theta becomes less as 2-theta

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approaches 180° ; therefore any error detected in a particular <u>2-theta</u> position must be used to correct only the lines in its vicinity. For example, any error found in the <u>2-theta</u> position of silicon 111 peak at Cu <u>K-alpha</u> 28.467° <u>2-theta</u> should be used subsequently to correct only the lines in this <u>2-theta</u> neighborhood. Likewise, silicon peak 422 should be used for correction in the 88.124° <u>2-theta</u> neighborhood. It may well be found that the errors in these two neighborhoods are not identical.

Method B:

An alternative would be to mix weighed amounts of an unknown specimen and weighed amounts of an internal standard to achieve approximately a 10:1 sample:standard ratio. The diffractogram will then contain the lines of both the standard and the unknown. Each standard line should be clearly labeled. This labeling may be facilitated by indexing the mixture by comparing it with a diffractogram of the pure standard, previouly taken and kept in the laboratory for quick reference. Any systematic error in the position of the standard line may then be used to correct the <u>2-theta</u> values of neighboring lines of the unknown. The standard so mixed should have been chosen to prevent its peaks from overlapping with those of the unknown. Some of the peaks may overlap, but it is important that the peaks of particular interest be distinctly resolved from the standard peaks.

D. Identification of Specimen Mineralogy

- (1) Mineralogical composition of geological samples will be identified by comparison of observed X-ray diffraction patterns to standard patterns of reference substances determined by the Center, and/or by comparison to the powder diffraction data file published by the Joint Committee on Powder Diffraction Standards (J.C.P.D.S.). The reference material diffractograms produced by the Center shall have been previously compared with the J.C.P.D.S. powder data file and the diffraction lines properly labeled with their respective <u>hkl</u> planes.
- (2) For comparison with the J.C.P.D.S. powder data file, the <u>2-theta</u> peak positions and intensities are read off the strip chart or other recording device. The <u>2-theta</u> values are converted to d-spacing values using the Bragg equation: d_{hkl} = <u>lambda</u>/(2 sin(<u>theta</u>_{hkl})

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where d is the interplanar spacing between <u>hkl</u> planes, <u>lambda</u> is the wavelength of X-rays giving rise to the reflection, and <u>theta</u> is the angle measured from the diffractogram (=2-theta/2). If a Cu X-ray source is used, <u>lambda</u> equals 1.541 angstroms for <u>K-alpha</u>, 1.544 angstroms for <u>K-alpha</u>, and 1.542 angstroms for <u>K-alpha</u> (weighted average). If the peak is not resolved into a <u>K-alpha</u> and <u>K-alpha</u> doublet, lambda is taken as the value for <u>K-alpha</u>. If the peak is resolved into a <u>K-alpha</u> and <u>K-alpha</u> doublet, particularly at high <u>2-theta</u> values, the <u>2-theta</u> position of <u>K-alpha</u>.

(4. After the experimental values of d, and I are tabulated, the unknown will be identified using the Hanawalt method or the Fink method. These methods are discussed in detail in the J.C.P.D.S. Search Manuals.

Note: Every mineral and crystalline substance, whether organic or inorganic, has a unique powder diffraction pattern. Minerals and other crystalline substances of fixed chemistry which are not characterized by chemical substitution and isomorphism, such as quartz and fluorite, can be readily identified by their X-ray powder patterns because of the rather constant nature of their crystal structure. Nevertheless this should not be taken to mean that any single mineral can be identified solely on the basis of its powder pattern. Isostructural compounds may have identical diffraction patterns except for intensities; the CaF₂ pattern, for example, is nearly identical to that obtained from HoF2. In addition many m. nerals have no fixed chemistry; for example, olivine, which may range from forsterite to fayalite. Each member of t. e olivine series has its own particular diffraction pattern. Although there are certain similarities between all olivine diffractograms. Feldspars also present difficulties because of their complex structural variation.

Accordingly, for many minerals it will not always be

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possible to obtain a perfect match between the X-ray pattern of the unknown and one of the powder data file cards. Interpretations and judgements will be necessary and the data file should not be used blindly. Other additional data may be sought, for example, using petrographic thin section analysis or microscopic immersion methods to complement the X-ray diffraction analysis.

The analysis of mixtures of mineral components may be complex. Interpretations of such mixtures approaches an art rather than a science and requires comparison of all the lines of the mixtures with lines of each of the assumed separate phases. If the individual phases are known, then a comparison of the mixture pattern with patterns taken of individual separate phases helps a great deal. Tentative hypotheses about the components may have to be made and confirmed or rejected by identifying all the lines of each component in the mixture. To aid in identifying the mineral components of a mixture, computerized peak matching methods may be employed.

- <u>Identification and Storage</u> According to TOP-004.
- 7. <u>Control of Samples</u> According to TOP-004.
- <u>Deviation from Procedures</u> According to TOP-004.
- 9. <u>Records</u> According to TOP-004 or Item 5.B.10 above.
- 10. <u>References</u>

Hutchison C.S. (1974) <u>Laboratory Handbook of Petrographic</u> <u>Techniques</u>, John Wiley, New York, p.132-179.

Cullity B.D. (1978) <u>Elements of X-ray Diffraction</u>, Addison-Wesley, Reading, Massachusetts, 555p.