

X-Ray Lab Cookbook

X-Ray Diffraction Procedures

Overview

Grind sample
Prepare a slide
Mount slide in XRD
Measure sample
Determine peak positions and intensities; print results
Remove alpha-2 pks
Match peak files with reference patterns; print results
Convert scan and peaklist files to ASCII format
Copy to Drakeshare
Further work with MacDiff

Grinding Samples to a Powder

Options: Agate mortar and pestle, Spex Shatterbox (tungsten carbide or hardened steel, large or small size; instructions on its use are given in the XRF Powder Prep notes), Spex Mixer Mill (tungsten carbide, hardened steel, agate, or alumina ceramic), Rock Labs hardened steel “masher.”

Freeze-dry sample(s) for 12 hours or more in the Labconoco freeze drier located next to the Shatterbox.

Grind dried material to a fine powder using one of the above options and then transfer to a 16 mL Wheaton glass bottle.

Transfer the ODP sample label from the plastic sample bag to the glass bottle.

Preparing Bulk Rock and Sediment Samples

Aluminum sample slides and steel backing clips are located in the desk under the ScienTech balance (second drawer down, on the left).

Clip a steel backing plate on to the back of an aluminum slide.

Transfer enough sample powder into the rectangular sample "well" to slightly over-fill it.

Note: For excessively small sample volumes, glass inserts can be added to the sample well, lowering the amount of sample needed to fill the sample slide. Although not

generally recommended due to the reduction in diffracted X-ray intensities, the bottom can be raised until it is little more than a "smear slide".

Distribute the sample powder evenly in the sample well using a clean spatula or glass slide. Add more if necessary, or remove any excessive amounts.

Using a clean glass slide or the rectangular brass plunger, gently press the sample powder flat and flush with the upper surface of the aluminum slide. If the surface of the sample is not flush, significant shifts in peak positions will result.

Wipe the aluminum surfaces of the slide with your finger or a Kimwipe and alcohol to remove any excess sample dust.

The sample is now ready to be loaded into the automatic sample changer.

Optional Chemical Treatments Prior to Clay Separation

Modification of the M.L. Jackson (1956) "SOIL CHEMICAL ANALYSIS - ADVANCED COURSE" by Hsueh-Wen Yeh, Hawaii Institute of Geophysics, 1980.

Compiled by Russell Skirrow.

Salt Removal

- 1) Thoroughly wash samples in tap water and suspend by means of a rubber-tipped stirring rod. To aid flocculation the samples are then centrifuged, and the water decanted.
- 2) This procedure is followed for at least 4 washings - the last two being carried out with distilled water. After decanting the excess water and transferring the sediment to a glass beaker in a relatively dry state, the sample is ready for step B.

Ferric Oxide Removal

Theoretically, the percentage of iron should be determined by chemical analysis, then the appropriate amounts of citrate and bicarbonate solution added to the sample (8/9 0.3M Na-citrate and 1/9 1M NaHCO₃).

- 1) For approximately 10 g samples, 80 cm³ citrate and 10 cm³ bicarbonate was found to provide a workable amount of reagent.
- 2) The glass beakers with suspended samples were mixed and heated in the water bath for at least 30 min, at a temperature between 75°C and 80°C, but NEVER exceeding 80°C as this would result in precipitation of iron sulfide. Periodically, 0.5 g portions of sodium dithionite were added until the brown coloration of the sample became a blue/green color and the material remained spongy and suspended. It was found that if a stirring rod pushed against the side of the vessel could not smear the sample against the glass, the reaction had ceased. At this point, all the ferric oxide is reduced, liberating the iron as Fe²⁺ ions to be chelated by the citrate solution.
- 3) After reaction, 20 cm³ of a 1:1 solution of acetone and saturated sodium chloride solution were added to the sample to increase flocculation. The sample and solution is warmed for 5 min.
- 4) The samples were centrifuged for 15 min and the supernatant liquid decanted, at least 4 times. If a brown/red color persists, the treatment is repeated.

Notes:

- a) An ultrasonic prop would be of great assistance in disaggregating the sediment samples - allowing quicker and more efficient ferric oxide removal.

- b) The water bath temperature should be constantly monitored as it can and does fluctuate.
- c) This treatment removes amorphous coatings and crystals such as hematite and goethite.

Calcium Carbonate Removal

- 1) Prior to reaction, samples are sieved (38 μ mesh size) to remove excess foraminifers.
- 2) Approximately 50 cm³ of pH 5 Na-acetate buffer solution is added to each 5 g sample. With continual stirring, the sample is suspended and reacted at boiling point in the water bath for at least 30 minutes. Samples rich in calcium carbonate may need to be centrifuged, decanted, and re-reacted.
- 3) After centrifuging and washing for at least four times, the wet sediment was made into smear slides for preliminary X-ray diffraction, and glycolation.

Notes:

- a) Rhodochrosite may persist, even after this treatment.
- b) Several East Pacific Rise samples still gave highly calcite-rich diffractograms suggesting that the sodium acetate solution may not be totally effective in removing this mineral - possibility of using 10% hydrochloric acid?

Manganese Dioxide Removal

After the samples were relatively dry they were reacted with 30% hydrogen peroxide solution.

- 1) A small amount of peroxide is squirted onto the samples, While the analyst is constantly armed with a nearby water bottle as reaction is violently exothermic. Water cools down the beaker and slows down the reaction.
- 2) The samples are left to react overnight after being thoroughly dowsed in water to stop violent reaction.
- 3) Next day the samples can be centrifuged and the supernatant liquid decanted, at least four times.
- 4) The sediment should now resemble a clay mineral assemblage, hopefully of greenish hue. If this is not the case, then the sediment is dried, powdered with a pestle and mortar and re-reacted with hydrogen peroxide.

Clay Separation Methods

Supplies

1% Calgon solution is kept in a 5-gal Nalgene container over the sink in the back of the Paleo Lab (opposite the fume hoods).

Centrifuge and centrifuge tubes are located in the Paleo Lab.

There are several methods to separate the $<2\ \mu$ particle size fraction:

1. A Quick And Dirty Clay Separation Method - Not For Quantitative Analysis (Legs 103, 116)

- 1) In a xx mL centrifuge tube, mix 5 mL of bulk sample (fresh, not dried) with xx mL of 1% Calgon solution. Use an ultrasonic bath or dismembrator if necessary.
- 2) Centrifuge the Calgon solution/sample mix at 1000 rpm for 5 min. to remove the $>2\ \mu$ particle-size fraction.
- 3) Decant the Calgon solution (containing suspended clays) into a new centrifuge tube, and spin it at 1500 rpm for 15 min. to remove the $<2\ \mu$ clay-size fraction.
- 4) Decant the Calgon solution and wash the clay residue with distilled water.
- 5) Spin-down again at 1500 rpm for 15 min. (Repeat steps 4 & 5 as necessary to remove the Calgon)
- 6) Make an oriented clay mount by placing xx drops of solution onto a xx slide and let dry for xx hrs (at xx°C).

2. A slightly more involved method. Removes carbonates first (Kitty Milliken, UT-Austin)

- 1) Remove carbonate by putting approximately $2\ \text{cm}^3$ of undried sample into a centrifuge tube with 25 mL of acetic acid (10% solution). Mix well, and let sit overnight.
- 2) The next day, shake well again to assure the reaction has stopped.
- 3) Wash the samples by spinning them in the centrifuge (15 min. at 1500 rpm), decanting the acetic acid solution, refilling with 25 mL of distilled water, and centrifuging again for 15 min. at 1500 rpm. Decant the clear water and repeat the "wash cycle" with distilled water.
- 4) Place washed sample in 50 mL beaker with 25 mL of distilled water and xx mL of 1% Calgon solution.
- 5) Put the clay material in suspension by placing the beaker under the sonic dismembrator for approximately 1 min. (do not let the sample heat-up "excessively").
- 6) Transfer the sample to a clean centrifuge tube and spin for 5 min. at 1000 rpm to remove the >2 micron size fraction from suspension.
- 7) Remove the $<2\ \mu$ size fraction by collecting the top 1 cm of solution with an eye dropper.
Note: If it is necessary to re-suspend flocculated clay particles using the dismembrator and more Calgon solution, the standard 15 min. at 1500 rpm in the centrifuge may not be enough to settle the $<2\ \mu$ particle size. You may need to increase the speed to as much as 5000 rpm to effectively remove the clay material from the Calgon solution.
- 8) Make an oriented clay mount by placing xx drops of solution onto a xx slide and let dry for xx hrs (at xx°C).

3. A Real Quick And Dirty Clay Separation Method (Leg 123)

- 1) Disaggregate a bulk sample with distilled water.
- 2) Sieve sample and water mix using a 38 μ sieve.
- 3) Decant the suspension resulting from Step 2, and centrifuge for 3 min. at 1500 (?) rpm.
- 4) Decant the suspension again, and centrifuge a final time for 15 min. at 1500 (?) rpm.
- 5) Wash the final suspension through a 0.6 μ filter.

Glycolation

- 1) Prepare an oriented clay slide as above (choose your favorite method).
- 2) Glycolate the clays on the slide by placing the slide in a desiccator with glycol. The length of time necessary for complete glycolation depends on the temperature (18 hrs at 25°C, or 1 hr at 65°C).

Note: Glycolation lasts about 4 hrs without any noticeable loss of X-ray intensities or peak shifts. Depending on the scanning parameters of the XRD, you may not be able to run more than 5 to 10 samples before the glycolation is affected. Prepare your samples in small batches!

Heat Treatment

- 1) Take a non-glycolated (?) clay smear-slide and dry at the scientist's choice of time and temperature. The usual selections are 1 hr @ 375°C and 1 hr @ 500 to 600°C.

Useful References

Moore, D.M. and Reynolds, R.C. Jr. (1989) X-ray Diffraction and the Identification and Analysis of Clay Minerals. New York (Oxford University Press) 332 pgs

Loading Samples Into the XRD

Warning: the X-ray safety shutter must be closed before doing any work with the XRD.

The XRD is equipped with an automatic sample changer that carries up to 35 aluminum sample slides in a sample magazine. Unused magazines are kept in the beige steel cabinet located behind the XRD.

If a magazine is already loaded into the sample changer, remove it by reaching-up through the bottom of the automatic changer (approximately 1"); pressing the small button located on the lower part of the rack (the side furthest from the goniometer) and sliding the magazine upward until it clears the slot in the sample changer rack (approximately 10"). Remove any slides leftover from the previous run.

To load sample slides, hold the magazine vertically and load your slides starting at the bottom (position #1, as marked on the magazine), and not leaving any empty slots between samples. The irregularly-shaped end is slid in first, until it clicks gently into place and the front edge is flush with the magazine.

Replace the loaded magazine in the sample changer by positioning it into the slots on the rack, and gently lowering it until it stops, and the black plates on top of the magazine are slightly lower than the top edge of the rack.

While holding the top of the magazine, reach-up through the bottom of the automatic changer (approximately 1") and press the small button located on the lower part of the rack (the side furthest from the goniometer) to lower the magazine into the proper position.

OPEN THE X-RAY SHUTTER by pressing the "Shutters" button and the Shutter #2 "I-button" at the same time. These buttons are located on the front of the generator.

Check the operating conditions - the generator should be set at 45kV and 30mA.

After the sample magazine is properly loaded, go to the computer and double click on the APD icon. Go to the Main Menu by pressing any key when the APD title page is displayed on the screen. From the Main Menu, select **Utilities (U)**, then choose **Diffractometer Commands (D)**. At the "C=" prompt, type:

C=**MAG0** <CR> (moves the sample magazine to position zero);

C=**MAG1** <CR> (moves the sample magazine to position #1).

These commands align the sample magazine with the sample changer. Next, check to make sure the display on the control unit (interface) is in synch with the goniometer by checking the angle meter mounted on the back of the goniometer. If the angles are synchronized, continue with the analysis by pressing <Escape> twice to return to the Main menu and proceed to "Input Run Parameters" section.

If there is a discrepancy in the two angles, the problem must be rectified before continuing further.

Input Run Parameters and Sample Names

Note: At the beginning of a leg, set up the data file structure by following the directions in Appendix 1.

Select **Edit (E)** from the Main Menu, and then **Batch Program (B)** from the Edit Menu.

Enter the name of the batch program at the bottom of the screen (no file extensions are necessary). If you wish to use an old batch file name, press <F5> to see a list of batch files. If a new name is entered, a new batch will be created.

Under the Edit Batch Program screen, press <CR> to accept the Default name for raw data files, and then enter the Sample Position number (in the auto sampler), the Identify Program name (i.e., Bulkmin, Claymin, Glycol, Heated, etc.), accept the default for Program Type (Identify), and enter the Sample Identification (normal ODP sample name). Change the Data File Name (default: the first 8 characters of the Sample ID minus spaces or dashes) so that each filename will be unique. The file extension (.RD) will be supplied by the software.

Press <Escape> twice to return to the Main Menu.

Starting a Batch Run

Select **Data Collection (D)** from the Main Menu, and **Batch Program (B)** from the Data Collection Menu.

Enter the name of the batch file which was created for the run, and press <CR>.

Press <F1> to start the batch sequence. Once the measurement sequence has started and several counts have been taken, you can display the scan in “real time” by selecting **Data Collection (D)** from the Main Menu, and then **Display scan (D)**. Be sure several data points have been collected before choosing this option. Otherwise, the program will crash.

To gracefully stop a scan that is already in progress, select **Data Collection (D)** from the Main Menu, and then **Stop measurement (S)**.

If you need to re-start a batch that is partly completed, edit the Batch file to delete already measured samples and then procede from step XX.

At the End of a Run

CLOSE THE X-RAY SHUTTER by pressing the Shutter #2 "O-button".

When running samples in Batch mode the final sample should automatically unload itself. If for some reason the last sample is still in the diffractometer at the end of a run, go to the Main Menu, select **Utilities (U)**, then choose **Diffractometer Commands (D)**. At the "C=" prompt, type:

C=USM <CR> (unload sample).

Peak Searching

From the Main Menu, Select **Pattern treatment (P)** then **Peak search (P)**. When prompted for the name of the scan file (*.RD), either type it in or press <F5> to list all scan files contained in C:\DATA\xxx\ (if it is a large list, you may need to press <F1> to move to the next page of the listing). From this list, use the arrow keys to select a file and the press <Return> to enter the Peak Search menu.

Once in the Peak search menu, begin the search by pressing <F1>. The results are displayed graphically on the screen and you can either accept those results, or press <ESC> to return to the previous page to change the search parameters and run the search again. When you are satisfied with the results, press <F9> to print a list of peak positions, intensities, widths, etc.

Press <ESC> three times to return to the Main Menu. The last results of the peak search will be stored in a *.DI file, where * is the same data file name as the raw scan.

Phase Identification

Select **Match pattern (M)** from the Main Menu. Choose **Match DI file (M)** and enter the name of the file you want to use (the default name will be the last file you did a peak search on) and press <Return> to go to the Match menu.

To begin the pattern matching routine with the standard mineral database, ODP-1, press <F1>. The typical search takes roughly one minute to sort through approximately 290 diffraction patterns (during the search, the number of patterns said to be matched is much greater than 290, but that number includes other databases not in use).

When the search routine has finished, the top 50 patterns are listed in order with the best fitting patterns at the top of the list. Press <F9> to print the list.

Notes: The matches can be visually checked by pressing <F8>. In the window that follows, you can toggle through the results list and superimpose various diffraction patterns onto the raw scan. See the APD Operator's Manual for details. (Don't print out graphics! There's a bug in the software that will screw-up the printer if you try to send it graphics.)

If you want to search other databases, go to the Search window and either toggle yes to any of the databases listed (opaques, zeolites, and metamorphic minerals), or enter the full DOS path to any database not listed. Press <F1> to start the search.

Converting Raw Scans and Peaklists to ASCII Format (*.UDF & *.UDI)

The raw scan file (*.RD) and peaklist file (*.DI) of each ODP sample must be converted from binary to ASCII format and saved as primary data (on DrakeShare). Other files such as *.PK, *.BK, or *.A2 files will not be saved.

To make the conversion, select **Utilities (U)** from the Main Menu, then choose **UDI/UDF File Format (U)**.

Choose either **Scan File (S)** or **DI File (D)**, and enter the file name in the entry field at the bottom-right part of the screen (pressing <F5> will give you a list of available files). Press <Enter>. The raw scan files (*.RD) and peaklist files (*.DI) will retain the same name, but their extensions will be changed to .UDF and .UDI, respectively.

Copy the *.UDF and *.UDI files to a 3.5" floppy (or other removable media).

Transfer both UDF and UDI files to a Macintosh computer and rename the files according to standard ODP convention (See Appendix 2).

Copy the UDF files only to the XRD folder on the DrakeShare server.

MacDiff 3.06a “Cheat Sheet”

Setting-up

Copy the folder containing the MacDiff application to your PowerPC hard drive. It'll run much faster this way than off the network.

Create a new folder on your desktop and label it “MacDiff Temp”, or something similar.

Open the MacDiff application folder and look for a file named “..... MacDiff Analysis Prog.” Move it to the MacDiff Temp folder on the desktop.

Copy all the appropriate XRD scan files from the X-ray folder on “Uservol.” The files will have a “.UDF” extension.

Using MacDiff

Start the MacDiff program by either selecting it under the Apple Menu, or double clicking on the application file.

Transfer scan files to MacDiff format by using the Open File Session command under the Files menu. For Options, select: autoload, file overwrite, peak correction, smooth counts, and find base. Do not choose print file! It takes too long.

After the files have been transferred to MacDiff format, call them up one at a time to work on them.

Print a diffractogram. Go to Page Set-up in the File menu and select options “landscape” and the the scale to 25%. Otherwise, it'll be too large to fit on one page. Click on Print.

Selecting an Analysis Program. If you are running the analysis program for the first time, select “Analysis Program” under the Analyse menu. If the program window opens with various phases and d-spacings already entered, go to the next step. If the window does not have any values, click on “Load” located in the lower left-hand corner of the window. From there, select the folder where you placed the “...MacDiff Analysis Prog,” rename it and save. The values in that program should now appear whenever you select “Analysis Program.”

Run the analysis program to identify and measure diffraction peaks.

Appendix 1

Setting-up the Computer at the Beginning of a Leg (usually one time only)

At the beginning of a Leg use the Windows application, File Manager, to create a new directory named C:\DATA\xxx\, where xxx is your Leg number. This will be the directory where all the XRD related data files will be stored. In most cases, you won't have to create another for the rest of the Leg, although you may wish to - just for easier bookkeeping.

Next, copy the files BULKMIN.IP2, CLAYMIN.IP2, HEATED.IP2, and GLYCOL.IP2 from C:\APD\DATA\ to C:\DATA\xxx\. Exit the File Manager.

In Windows, double click on the APD icon to begin, then go to the Main Menu by pressing any key when the APD title page is displayed on the screen. From the Main Menu, select **System Preparation** and then **System Parameters**.

Once in the **System Parameters** window, use the “down” arrow on the keyboard to select **Data directory**. Enter C:\DATA\xxx\, where xxx is your Leg number. Press <Escape> twice to return to the main menu.

At this point, it is also a good idea to delete any previous “Run Messages” by selecting **Data Collection (D)** from the Main Menu, and **List Messages (L)** from the Data Collection Menu. Press <F1> repeatedly until you've reached the last page of messages (could be many pages!). Press <F3> and a pointer appears at the top of the screen. Position the pointer at the bottom of the page using the down arrow, then press <F1> to delete.

Appendix 2

Naming Conventions for Sample Files

APD file names consist a sample code of up to eight characters plus a two or three character extension. Because the software automatically creates this file name from the sample ID that you enter, you must choose the sample ID with this in mind. I find that an ID that is a condensed form of the regular site/core/sect/interval name works for me. This shortened name is the last three characters of the hole number (including A, B, C, etc.) followed by the core number, core type, and the necessary number of interval characters (1 or 2) needed to fill the eight spots that are allowed. No spaces or dashes are used.

For example, sample number 1017B 11X-1, 3-5 cm would be compressed to 17B11X13.* , where "*" = file extension supplied by the software (i.e., .RD, .UDF, .UDI, etc.).

You do have to be careful that all file names are unique. You may run into problems if you have a series of closely spaced samples such as 1017B 23X-2 112-113, 115-116, etc. But I haven't had that problem yet.

Appendix

XRD-Related Software Available Aboard the Resolution

MacDiff V3.06a -

NEWMOD 2.5 M2 - Bob Reynolds.

PCPDFWIN V1.00 - ICDD search software for reading PDF-2 CD database.

BFACTOR Vxx.x - Quantitative XRD analysis, Andy Fisher.

TADD Vxx.x - Philips Electronics.

XRDFILT - Strips-out unnecessary data in *.UDF files, Unknown author.

Appendix

Importing *.UDF Files Into KaleidaGraph

1. Open a UDF file using a PC or Macintosh word processor/editor (WordPerfect, MS-Word, EDIT, etc.).
2. Record the scan range (e.g. $2-35^{\circ} 2$) and the step size (e.g. $0.01^{\circ} 2$).
3. Create a document with a single column of numbers (X-ray intensities) by:
 - Deleting the header at the top of the document;
 - Deleting all strange characters (Hint: Use the SEARCH - FIND/CHANGE command and replace odd characters with "nothing;")
 - ?? Deleting all commas and replace with carriage returns (insert Hard End of Line).
4. Using the SAVE AS command, rename the file, and save it in TEXT EXPORT format. Choose the TEXT TYPE as MAC TEXT, soft returns to hard returns.
5. Transfer the edited text file to a Macintosh and open KaleidaGraph.
6. Open the TEXT EXPORT ?? file. Verify the format, i.e. spaces used as delimiters, greater than equal to one space, skip 0 lines, etc.
7. In a blank column, enter the appropriate 2 angles (ex. $2-35^{\circ} 2$ in 0.01° increments) one at a time, or by using the FUNCTIONS-CREATE SERIES command.
8. Graph 2 angle versus X-ray intensity. This will reproduce the diffractogram.

Note: Two or more diffractograms can easily be "stacked" on the same graph by entering a formula such as $\text{column2} = \text{column1} + 200$.

Appendix

Computer Notes

The following is a list of data files and their extensions commonly generated by the APD software.

Identify program (scan parameters)	*.IP2
Batch program (list of ID programs and sample names for multi-sample operation)	*.BP2
Raw scan data (raw intensities; binary)	*.RD
Raw scan data (raw intensities; ASCII)	*.UDF
Peak list data (raw and relative intensities, d-spacings; binary)	*.DI
Peak list data (raw and relative intensities, d-spacings; ASCII)	*.UDI
Background intensities file (binary)	*.BK
Peak data file (with background intensities subtracted; binary)	*.PK
Alpha2-stripped file (binary)	*.A2
Smoothed scan data file (binary)	*.SM

Appendix

Diffractogram Databases

An ODP specific database (ODP-1) has been compiled from several different JCPDS databases and has been installed as the APD default database. ODP-1 currently contains 290 diffraction patterns representing most of the major and minor mineral phases found in marine sediments, basalts, ultramafic, and sulfide rocks. Many of the older, JCPDS patterns have been replaced with higher quality data, and many phases that would not be expected in common rock types (tellurides, osmo-iridium compounds etc.) have been removed. As it is currently set-up, it takes roughly 60 seconds for the APD software to sort through all 290 patterns and create a list of “best-fit” phases. It is hoped that future work to install ODP-1 in a “RAM-disk” will make the matching process even faster.

More specific databases have been prepared as well. ODP-OPAQ and ODP-ZEOL are aimed at covering the more exotic minerals that may be encountered. More work needs to be done to sort out older patterns to make them more streamlined, but the databases provide an extra layer of matching support.

The general plan behind these databases is that 99% of the searching/matching will be done with ODP-1 (which contains many common zeolites, opaques, and metamorphic minerals). The other data sets will be used only when ODP-1 fails to find a match for all of the peaks.

How to transfer reference files from JCPDS database to APD-PC using TADD is briefly summarized in the Leg 143 tech report.

Manually entering ICDD files.....

Listings of ODP-1, ODP-OPAQ, and ODP-ZEOL are presented in the following pages.

Author: unknown

Version: unknown

Reviewed by: Jason Deardorf

Reviewed on: Dec. 2003

Supervisor sign off: _____