IMPORTANT NOTICE: The current official version of this document is available via the Sandia National Laboratories WIPP Online Documents website. A printed copy of this document may not be the version currently in effect.

ACTIVITY/PROJECT SPECIFIC PROCEDURE

SP 12-8
USE AND MAINTENANCE OF BRUKER ANALYTICAL X-RAY SYSTEMS
D8 ADVANCE X-RAY DIFFRACTOMETER
Revision 3

Effective Date: June 27, 2013

Author:	Yongliang Xiong	*Original signed by Yongliang Xiong*	*June 26, 2013*
	(printed name)	(signature)	(date)

1.0 Purpose and Scope

This procedure provides for the operation and maintenance of the BRUKER ANALYTICAL X-RAY SYSTEMS D8 ADVANCE X-RAY DIFFRACTOMETER as part of the laboratory geochemistry research activities in support of the Waste Isolation Pilot Plant (WIPP) Project.

This procedure is applicable only for the BRUKER ANALYTICAL X-RAY SYSTEMS D8 ADVANCE X-RAY DIFFRACTOMETER.

This document is not meant to substitute for the manufacturer's instruction manuals for the BRUKER ANALYTICAL X-RAY SYSTEMS D8 ADVANCE X-RAY DIFFRACTOMETER. The user is responsible for reading and understanding these manuals (see section 2-8).

Acronyms and definitions for terms used in this procedure may be found in the Glossary located at the Sandia National Laboratories (SNL) WIPP Online Documents web site.

2.0 Implementation Actions

2.1 Responsibility

The Principal Investigator (PI), or designee, whose activities warrant the use of this procedure is responsible for implementing the requirements of this procedure.

The Project Scientist, or designee, is responsible for performing the measurements, following the requirements of this procedure, documenting the results, and assuring that the use of the latest revisions of this document is followed.

© 2013 Sandia Corporation

2.2 Safety

The activities described in this SP shall conform with SNL Environmental Safety and Health programs (ES&H). This document does not address ES&H issues. Laboratory ES&H procedures described in the SOPs of the laboratory in which the equipment is used shall be adhered to.

2.3 Qualified Users

A user of the BRUKER ANALYTICAL X-RAY SYSTEMS D8 ADVANCE X-RAY DIFFRACTOMETER (XRD) shall have the GENERAL EMPLOYEE RADIOLOGICAL TRAINING, RAD 102, when the user does not open the gate of the XRD for loading samples onto the sample magazine or unloading samples from the sample magazine. In such situation, the user can use the computer to execute the analysis if an operator who has the proper training (see below) loads and unloads samples for him/her.

Operator shall have at least RAD 214 Radiation-Generating Device Training or RAD 210, and shall have the respective Sandia Radiological Worker Qualifications badge, before loading samples onto the sample magazine or unloading samples from the sample magazine. A qualified technician from Bruker AXS, Inc. performing the maintenance or repair for the machine is exempt from this requirement.

2.4 Alignment Standard(s)

2.4.1 Alignment

Annual alignment for the parameters of measurement electronics of the diffractometer will be verified using the quartz standard slide supplied with the machine. A qualified technician from Bruker AXS, Inc., will perform annual alignment for the parameters of measurement electronics of the XRD, as Sandia National Laboratories has a service contract with Bruker AXS, Inc. for the XRD. The annual alignment is necessary to ensure best performance of the diffractometer system. In the process of the alignment, a quartz standard will be used to measure the 100% reflection of quartz at $2\theta = 26.64 \pm 0.05^{o}$ (Cu Kα radiation). If the operator needs to perform the alignment, detailed instructions on pages 3-185 to 3-189 of Bruker Analytical X-Ray Systems: D8 Advance/D8 Discover X-Ray Diffractometer User's Manual, Vol. I should be strictly followed to avoid any potential damage to the detector. The annual alignment will be documented in the Bruker AXS D8 X-Ray Diffractometer Log Book.

2.4.2 Standard(s)

A quartz solid standard with no expiration date supplied by the manufacturer, Bruker AXS, Inc., will be used for annual alignment, and the quarterly verification (Section 2.4.3).

2.4.3 Frequency

The instrument will be realigned annually (Section 2.4.1), and this is done by a qualified technician from Bruker AXS, Inc. The instrument's alignment shall be verified quarterly (every three months) with a performance test. However, if the system is not available for analyzing samples because of the need for repair, or because of the repair in process, the time of verification may deviate from the

quarterly schedule. The XRD pattern of quartz from the quarterly performance test will be included in the BRUKER ANALYTICAL X-RAY SYSTEMS D8 ADVANCE X-RAY DIFFRACTOMETER log book.

2.5 Performance Test Criteria

The performance test for the XRD involves measuring the actual position of the main quartz peak using the quartz standard slide. This peak should appear at 26.64 degrees (2θ, Cu Kα radiation, p. 3-186 of User's Manual Vol. I). If this measurement is off by more than 0.2 degrees then the instrument must be realigned. A performance test will be done immediately after realignment.

2.6 Qualification of Rietveld Analysis Procedure

Rietveld analysis does not require any calibration of the instrument. However, the test procedure should be verified as described in this section before any quantitative X-ray analysis.

2.6.1 Standard(s)

Prepare standards with the purest grade of chemicals commercially available. Chemicals that are not commercially available can be synthesized, provided that they are sufficiently pure. The synthesis procedures shall be documented in the scientific notebook for WIPP related projects. An internal standard, such as zincite or corundum, is recommended. A ratio of 0.1-0.2 g of internal standard is recommended for every gram of standard/sample.

2.6.2 Frequency of Verifying Test Procedure

Prior to performing quantitative X-ray analysis, verify the annual alignment and quarterly performance test are current (see section 2.4.3 and 2.4.4). It is recommended to qualify the test procedure using 3 standards that covers the range of expected measurement. Each standard shall be analyzed at least twice (two scans). At a minimum, verify the procedure using standard(s) containing 80 wt% of phase of interest and 20 wt% internal standard. For minor phases that are less than 5 wt%, assess the uncertainty by analyzing a standard contains 5 wt% of the minor phase (s) of interest and report the uncertainty in notebook. Each standard shall be analyzed at least twice (two scans). After the test procedure is verified, one of the qualification standards should be tested every month as a qualification check. The test procedure should be re-verified after major instrument modification including changing the X-ray tube, changing a detector, adding or removing monochromater, and realignment.

It is the operator's responsibility to properly label and store the standards. Clearly label the expiration date on the standard when it is applicable.

2.6.3 Qualification test criteria

For minor phases that are less than 5 wt%, assess the uncertainty by analyzing a standard that contains 5 wt% of the minor phase(s) of interest and report the uncertainty in notebook. Otherwise, the maximum permissible difference between the mean value by Rietveld analysis and the known gravimetric value should be within ± 6 wt %. The maximum permissible difference between Rietveld analyses of replicate scans should be within ± 2 wt %. Certain materials, such as clay, can be very difficult to do quantitative analysis on. Deviation from the above criteria is permissible and should be documented in the scientific notebook.

2.7 Procedure: Obtaining An X-Ray Diffraction Pattern

2.7.1 Sample Preparation

Plastic slides may be used for samples. Samples should be well ground before their loading on sample slides. Samples should be labeled using paper tape, and will be documented in a scientific notebook. As XRD analyses are non-destructive, samples will be put back to original sample containers.

Sample slides have two sides. One side is flat, and the other side has a depression. If there is enough sample to fill the depression of the sample slide, it is preferred to load the sample on the depression side of the sample slide. To load the sample, simply put enough sample into the depression then, use a glass slide to press the sample to make it even with the surface of the sample slide. After that, if there is excess sample on the surface of the sample slide, wipe it off with a KIM WIPE paper wetted with DI water.

If there is only small amounts of a sample, create a slurry of the sample in question. This may be done by placing a few drops water or alcohol on the slide and then stirring in a small amount of the sample or, alternatively, the sample-fluid mix may be prepared in a small beaker or mortar and transferred to the slide. If the sample is not free of soluble salts (gypsum, halite) diffraction patterns for these materials will dominate in the scan results. These salts must be washed out and the pattern rerun.

Allow the slide to dry at room temperature in the air. Be sure that the sample covers the area where the X-rays will impinge.

For Rietveld analysis it is recommended to finely grind the standards and samples. The recommended particle size for Rietveld analysis is 1 - 10 µm. This particle size can minimize preferred orientation, peak extinction, and avoid the loss of X-ray intensity. The recommended procedure is to grind each standard/sample in McCrone microsizing mill for approximately 10 - 20 min with 7 ml of non-aqueous solvent, such as ethanol, methanol or 2-propanol. Standard and sample should be ground in the same way.

Side-loaded sample slides are recommended for samples prone to preferred orientations. To load the sample in the side-loaded sample slide, first cover the cavity with a piece of filter paper, and cover the filter paper with a glass slide; then secure the filter paper and glass slide with a small clamp (a black-triangle-spring-paper clamp will work); load the powder into the cavity via the little opening on the side edge of the slide and tap down the powder into the cavity; repeat loading and tapping many times until the cavity is filled. It takes 15-20 min to load one sample.

When non-routine processes are carried out the details will be noted in the scientific notebook.

2.7.2 Operating the BRUKER ANALYTICAL X-RAY SYSTEMS D8 ADVANCE X-RAY DIFFRACTOMETER

Precautions:

- Know the location of, and be familiar with the Standard Operating Procedure (Analytical Instrument Laboratory in Building B at Sandia National Laboratories Carlsbad Programs Group Facility).

- All operators must at least have either RAD 210 or RAD 214.

- Users shall never bypass any safety circuits, nor attempt to service the electrical components without authorization and guidance from trained repair personnel. High voltages, up to 60 kV are produced by this machine.

- The maximum setting for qualitative XRD using copper target is 30 kV and 30 mA. The maximum setting for quantitative XRD using copper target is 40 kV and 30 mA. To prevent burning out the (very expensive) X-ray tube never exceed these levels.

- In the event of an emergency push the "X-rays off" button (red button) immediately.

Turn on the cooling water for the water chiller by rotating the valve on the wall counter-clockwise so that the handle points horizontally. Then, turn on the water chiller.

Prior to turning on the power to the generator, check to make sure that the temperature of the water chiller is below 80°F and the pressure is not lower than 50 psi. If the temperature exceeds or pressure is below the above respective values, Bruker AXS, Inc. will be notified. The service contract of Sandia National Laboratories with Bruker AXS, Inc., covers the water chiller.

Turn on the power to the XRD (green button). Allow the XRD to warm up for at least 30 minutes before use. During this time, samples can be loaded onto the sample magazine.

On the main computer, open the DIFFRACplus Measurement Part Plus folder, and then double click the program XRD Commander.

In the first column of the program XRD Commander, enter the sample position in the sample magazine. In the second column, enter the sample ID. In the third column, enter the scan parameters saved as a file. In the fourth column, enter the file name for the XRD pattern to be saved. Leave the fifth column (Script column) empty. For the sixth column (Model column), select QL in drop-down button. After that, click Start button to initiate the scanning.

It is important to note that samples shall be scanned between 10º and 90º in terms of 2θ. Scanning at an angle lower than 10º is prohibited, unless the expected main peak of the sample lies in the 2θ range lower than 10º. In such cases, the custodian of the XRD shall be notified to obtain his/her approval before use. The current custodian is Yongliang Xiong.

2.7.3 X-ray Shutdown

Unless there is a problem with water supply or the water chiller, or an emergency, the instrument should not be shutdown.

2.7.4 Phase Identification

When a scan -is completed the spectrum is automatically saved as a RAW file and automatically stored in the folder C:\DIFFDAT1 on the main computer. The user can open a file to print it out as a hard copy, and then can move the electronic file into a folder created by the user.

To evaluate the phase(s) of the sample, the user's manuals for the EVA software are worth reading. The following procedure can be used.

A. Open the DIFFRAC PLUS Evaluation folder
B. Open the "EVA" icon
C. Open your RAW file
D. Hit the "F2" key to open "toolbox", used for peak searching, peak labeling, etc.
E. Hit the "F3" key to open "search/match", used for searching the database for phase identification, etc.
F. You may drag-and-drop these dialog boxes on the screen to where they do not obscure your view of the data.
G. When the phase(s) is matched to one in the database, the file can be saved as an "EVA" file. Print out a hard copy of the analysis and keep it in the scientific notebook or scientific notebook supplement.

2.7.5 Requirements for Rietveld Analysis

Rietveld analysis requires accurate powder diffraction scans. Adjust the step size so that there are at least six data points above the full half width maximum (FWHM) for peaks that you plan on fitting. Adjust the time per step so that the most intense peaks have at least several thousand counts. Rietveld analysis requires crystal structure data that are close to the actual structures found in the specimens. Perform phase identification (see section 2.6.4) and obtain (from the literature) crystal structure information for all the phases that are in the sample. Free databases for crystal structure include: American Mineralogist Crystal Structure Database (http://rruff.info), Crystallography Open Database (http://www.crystallography.net/) and Min-cryst (http://database.iem.ac.ru/mincryst/). Download the crystal structure in CIF format or STR format. Some structures in free database may require reformatting (see p. 63 TOPAS 4 Tutorial for example). Additionally the *Handbook of Mineralogy* is located in the WIPP library.

Rietveld analysis requires a model that reflects systematic errors in the pattern and peak shape. See detailed information in next section.

2.7.6 Rietveld Analysis Procedure

Rietveld analysis can be performed in a graphical user-interface (GUI) and a text based mode (launch mode). The GUI is easier to operate. Users can find out how to use the launch mode by reading the TOPAS user manual and technical reference. Users are strongly recommended to practice Rietveld analysis using the TOPAS 4 tutorial. The following procedure uses the GUI, and is an example of basic quantitative X-ray analysis.

Import data file
1) Start TOPAS
2) "File" → "Import Data File" → select the raw file name

Input instrument profile
1) Under the raw file name, open Emission profile. Our target material is copper and the default wave length for Cu Kα1 and Cu Kα2 is 1.540596 and 1.544493 Angstrom (see detail in TOPAS 4 Tutorial p. 6).
2) Open Background profile. Check Chebychev. Default value for Order is 3 or 4. Check 1/x Bkg
3) Open Instrument profile.
   A. Input Goniometer radii profile. The default value for Primary Radius and Secondary Radium of D8 diffractometer is 217.5 mm and is 217.5 mm.
   B. Input Equatorial Convolutions profile.
   C. Check Point detector.
   D. Input the Receiving Slit width (mm) and select "Fix".

E. Input FDS shape (angle) and select “Fix”.
   1) The FDS shape (angle) can be found by following the procedure in section 2.6.4 step A through D and then by selecting “scan” in the tool box window.
F. Input Axial Convolutions. Check Full Axial Model.
G. Input Source Length and select “Fix”. The default Source Length value is 12 mm.
H. Input Sample Length and select “Fix. The default Sample Length value is 15 mm.
I. Input RS length and select “Fix”. The default value is 12 mm.
J. Input Primary Soller slit and select “Fix. The default Primary Soller slit for the D8 diffractometer is 2.5 º.
K. Input Secondary Soller slit and select “Fix. The default Secondary Soller slit for the D8 diffractometer is 2.5 º. See p. 33 of TOPAS user’s manual for more details.

4) Open Corrections profile.
   A. Input Peak shift profile. Check Sample displacement and select “Refine”.
   B. Input Intensity corrections profile. Check LP factor and select “Fix’’. See p. 109 of TOPAS technical reference for LP factor values.
   C. Input “Sample convolutions profile. Check Absorption(1/cm) and select “Refine”.

Input crystal structures
1) Highlight raw file name
2) Select “Add structure”
3) Select “Load CIF(s)” or “load STR(s)’
4) Input the crystal structures one by one

Refine variables
1) Highlight the crystal structure.
2) Check “Use phase”.
3) Refine the lattice parameters.
4) Check “Scale” and select “Refine”
5) Check “Cry size L “and select “Refine”.
6) Check “Strain L” and select “Refine”.
7) Note: for quantitative X-ray analysis, atomic coordinates, occupancy factor and equivalent isotropic temperature factor are not refined.
8) If preferred orientation is observed, highlight “Preferred orientation” and input the hkl value and check under “Use”. Select “Refine”.
9) Hit “F6” Key

Save project file
“File” → “Save project File as ” → input project file name. The resulting project file is in Pro format. Print out a hard copy of the analysis and keep it in the scientific notebook or scientific notebook supplement. Make sure the sample name is noted on the hard copy.

2.8 Maintenance

Annual maintenance will be performed on the instrument by the qualified technician from Bruker AXS, Inc. per the service contract of Sandia National Laboratories with Bruker AXS, Inc.

2.9 References

BRUKER AXS GmbH, 1999. Bruker Analytical X-Ray Systems: D8 Advance/D8 Discover X-Ray Diffractometer User's Manual, Vol. I, Karlsruhe, Germany.

BRUKER AXS GmbH, 1999. Bruker Analytical X-Ray Systems: D8 Advance/D8 Discover X-Ray Diffractometer User's Manual, Vol. II, Karlsruhe, Germany.

BRUKER AXS GmbH, 2008. Bruker Diffrac plus TOPAS, TOPAS 4 User Manual, Karlsruhe, Germany.

BRUKER AXS GmbH, 2008. Bruker Diffrac plus TOPAS, TOPAS 4 Technical Reference, Karlsruhe, Germany.

BRUKER AXS GmbH, 2008. Bruker Diffrac plus TOPAS, TOPAS 4 Tutorial, Karlsruhe, Germany.

3.0 Records

The following QA records, generated through implementation of this procedure, shall be prepared and submitted to the WIPP Records Center in accordance with NP 17-1 (Records):

QA Record

- Scientific Notebooks
- Annual Alignment
- Data Interpretation
- Data Printout

The PI shall be responsible to the preparation and submittal of Scientific Notebook, Data Interpretation, and Data Printouts. The custodian of the BRUKER ANALYTICAL X-RAY SYSTEMS D8 ADVANCE X-RAY DIFFRACTOMETER shall be responsible to the documentation of Annual Alignment and its submittal.

4.0 Appendices

There are no appendices associated with this document.

This work of authorship was prepared as an account of work sponsored by an agency of the United States Government. Accordingly, the United States Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so for United States Government purposes. Neither Sandia Corporation, the United States Government, nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately-owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by Sandia Corporation, the United States Government, or any agency thereof. The views and opinions expressed herein do not necessarily state or reflect those of Sandia Corporation, the United States Government or any agency thereof.

Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Parties are allowed to download copies at no cost for internal use within your organization only provided that any copies made are true and accurate. Copies must include a statement acknowledging Sandia Corporation's authorship of the subject matter.