Inexpensive Software for X-ray Diffraction

(prepared by James R. Connolly, for EPS400-002, Introduction to X-Ray Powder Diffraction, Spring 2005)

Introduction

Sophisticated analytical software for X-ray Diffraction (like MDI's Jade or Brukker's Diffrac+) is very powderful, very flexible and very expensive. As an example, a single workstation installation of Jade+ software will cost at least $5,000, and the ICDD Powder Diffraction file database on CD-ROM will cost $3,000 to $7,000 (depending on version purchased and other possible discounts). This type of software provides a very high level of functionality in data processing and analysis, and is essential for anyone operating an XRD laboratory.

For those without large budgets who have X-ray data they need to display and analyze, there are free or inexpensive alternatives to these commercial packages. The purpose of this document is to introduce some of this software with which the author (who is significantly spoiled by easy access to MDI's Jade) has had some experience. The programs are discussed briefly below in sections related to their function. Some software is also included for which the author has little or no experience, but that has a good reputation in the XRD community.

The programs discussed in this document are a small fraction of all that is available. By far the best source for free software (and information about commercial software packages) is the Collaborative Computational Project #14 (CCP14) for Single Crystal and Powder Diffraction. Their main address is hosted in the UK at: http://www.ccp14.ac.uk/index.html but there mirrors of the site exist in the U.S., Canada and Australia. All of the software listed in the remainder of this document may be found in the CCP14 archive. Many programs are archived by CCP14 but the index also provides links to the most authoritative source so that the most recent versions may usually be downloaded directly from their author(s).

The IUCr (International Union of Crystallographers site at http://www.iucr.org/iucr-top/ is also maintains an archive (SInCris) of free software. Their site also includes links to lots of useful crystallographic resources.

Most of the software listed below is also available on our local FTP site at in the Department of Earth and Planetary Sciences at ftp://eps.unm.edu/pub/xrd. All the XRD programs available are indexed for easy access at ftp://eps.unm.edu/pub/xrd/index.htm. These programs are provided for convenience only and will frequently not be as up-to-date as the versions on the CCP14 index.

Data Conversion Tools

MDI Jade Export/Import

Many data exchange tools do not support the MDI data format as an import or export file format, although a bit of investigation reveals that the MDI data format is very close to the "standard" data interchange format or DIF. Jade includes a conversion program which exports Jade data as a simple two column ASCII (filename.txt) format and these files may be easily converted with a simple ASCII text editor to numerous other formats readable by other programs. The MDI ASCII file includes the sample description information in the first header line followed by two columns listing sequentially listing each 2θ value and counts for each "step" of the scan. Most programs discussed below require modification of the "header" portion of the file (i.e., deleting title information, adding total # of data points in a

specific location, saving with a new filename extension, etc.) before it can be used. The format required for the program you are using will usually be part of the documentation or help information for the program. The actual editing can be done with Notepad, WordPad or any ASCII text editor.

ConvX

Simple but useful free program for converting between XRD data formats that can be very useful in translating a file that cannot be imported into a particular program into a format that can be imported. Supports conversion to/from the following data formats: Phillips RD and SD (PC and VAX versions), ASCII 2θ-Intensity, Brukker/Siemens RAW formats (DiffracPlus, DiffracAT, DiffracV1), Sietronics GPI, GSAS, DBW-type and ScanPI. Jade ASCII *.txt files may be used, but may require removal of the first line (the File description information). Users will need to experiment with what works.

Other Data Conversion Programs

Two other simple windows-based data conversion programs are POWF 2.11 and CONV 3.01. Their function and capabilities are similar to ConvX. PowDLL is the newest converter and handles a lot of different data types (including MDI's) and requires installation Microsoft's .NET framework (a free if rather large download from Microsoft). All three are available on our FTP site.

Many of the other programs discussed below include modules for importing and exporting data files and can be used for that purpose exclusively if desired. These include PowderX, WinFit, and FullProf.

General Data Processing Software

PowderX

Powder X is a freeware program from Cheng Dong of the Institute of Physics at the Chinese Academy of Sciences in Beijing. A basic tutorial for the use of Powder X can be found at http://www.ccp14.ac.uk/tutorial/powderx/index.html.

If you have unlimited access to Jade to handle your data analysis, you will probably not need PowderX (although PowderX ***will*** export to more data formats than Jade without complicated configuration changes). If you don't have Jade on your personal workstation (or the several thousand dollars needed to get it there) and want to work on your data outside of the lab, PowderX is free and can be installed where Jade is not available. The ability to easily export data to other programs (such as GSAS or FullProf) can be very useful.

Powder X is basically a Windows-based pattern-processing program that operates under all versions of Windows. It has many useful functions such as data smoothing, background subtraction, $K\alpha_2$ elimination, peak search, and indexing. It imports and exports data in multiple data formats[1], and includes algorithms to correct for specimen displacement and zero-angle errors. Many of the output formats are those used by a variety of pattern

[1] To be used in PowderX, MDI data must be saved in MDI ASCII Text format (with Jade) and edited: add a second header line consisting of the total number of data points, and saved with a *filename*.xrd extension.

refinement programs such as GSAS and FullProf. The program also includes a simple pattern calculation algorithm developed by the author (LAZY) that will generate a calculated pattern from input structural data.

Import of MDI data files requires starting with an ASCII export file and then editing that file to conform to the import requirements of the PowderX ASCII data. It is not difficult to do, but must be done correctly for the import to work.

The software is available from the CCP 14 site as a single large ZIP file, or a series of 5 smaller ones. The archives are password protected. There is no charge for non-commercial use of the software, but to be "legal" users must send an Email to the author, Cheng Dong at chengdon@aphy.iphy.ac.cn including the following information: Your Full Name, Title, affiliations, mailing address, telephone and Fax numbers. He will then register you as an official user of the program and send you the password to unlock the archive.

WinFit

WinFit is a free peak-fitting program from Stefan Krumm of the Institute for Geology in Erlangen, Germany. Several years ago I used WinFit to successfully resolve overlapping peaks of multi-phase rock samples in Siemens (Brukker) .RAW data files. The latest update available is dated 1997 and it doesn't support long filenames (which can make navigating your file system a bit tricky) and it is somewhat crash prone in modern versions of Windows. It is instructive as a tool for learning about peak decomposition.

The menu lists the MDI data file as one of the formats (with ???? next to it), but my experience is that attempting this import will invariably crash the program. To successfully convert an MDI data file for input into WinFit you must first save it in Jade as an MDI ASCII file (*.TXT) then edit the file removing the first line (the sample title) leaving only the two-column 2θ and counts data. That file then is saved with a *.ASC extension, and can be imported into WinFit. WinFit also supports direct input from Siemens/Brukker *.RAW and a variety of Phillips and Rigaku formats.

All of the software available through Stefan Krumm is linked on his software page at http://www.geol.uni-erlangen.de/html/software/soft.html, . Though most of what is here is pretty old, some of it (including his "Virtual Crystallographic Calculators") can be quite useful.

Microsoft Excel

Microsoft Excel may be used for display and analysis of XRD data. The main issue is getting the data into spreadsheet format so that it can be used. Excel can be setup to import a variety of parsed data, and many ASCII formats may be read, although you may find yourself having to create a specialized import routine to do so. A two column 2θ vs Intensity format is easiest to import. The easiest way to do this with Jade is to save the file as an MDI ASCII Text format and use Excel's text import Wizard (under the Data menu). Patterns may be plotted as simple X-Y "Scatter" plots for presentation, and different data formats overlaid in a common environment fairly easily.

Excel is not commonly used for sophisticated data analysis, but it can be. A look at Dennis Eberl's Excel applications Mudmaster and RockJock (discussed below) demonstrate how the analytical power of Excel's solver and other mathematical functions can be used to create

pretty amazing analytical tools. To tap some of the hidden data analysis power in Excel, you need to install the Solver and Analysis Toolpack "Add Ins" from the Tools menu.

For those wanting to pursue Excel as a serious analytical tool, there are a lot of fat computer books available about programming in VBA (Visual Basic Applications). Two highly regarded books that get high marks for readability and information are "Excel 2003 Power Programming with VBA" and "Microsoft Excel 2003 Formulas", both by John Walkenbach. Though some recent reviewers have decried the lack of the most up-to-date information (XML, SharePoint integration and InfoPath), they still are indispensable for the kind of programming done by Dennis Eberl in Mudmaster and RockJock. These are available from larger local bookstores (but not UNM's), or online from Amazon.com.

Specialized Data Analysis Tools

Mudmaster

Mudmaster is an Excel spreadsheet that is designed to determine particle size in fine-grained powders. Since it uses peak shape and size to evaluate peak broadening as related to "particle" size, it is actually measuring crystallite size rather than the actual of the particles. If each particle is a single crystal, then this is not an issue. The spreadsheets also can be used to examine peak asymmetry and evaluate strain in addition to crystallite size.

The crystallite size is equal to $(N-1)d_{hkl}$, where N is the number of hkl planes responsible for a reflection. The program makes use of this to evaluate the crystallite size in a diffraction pattern. The program consists of a main workbook (MudMastr.xls) that includes the "Peak Picker" to select the peak to be analyzed, Sheet 1 where results are calculated and shown, and Sheet 2 containing all the macro bells and whistles that do the calculations. A few other spreadsheets perform specialized functions including editing data to remove minor peaks in the "tail" of the peak of interest (PkChopr), shifting of patterns using a standard to correct for linear offsets (PkSift), modifying data to change step size (Stepcon), estimate the layer scattering intensity Lorentz polarization factor and G^2 when this is not known (CALCLPG2), and a sample data set (Samp). The program include a detailed operations manual that "walks" you through the data entry and calculation process, and includes references to papers that discuss crystallite size and strain calculations.

Crysfire

One of the main obstacles to using powder patterns in structural analysis programs such as GSAS or FullProf is an accurate determination of the unit cell parameters for input into the modeling program. Crysfire is a Windows interface to nine different computer programs that perform pattern indexing. In a simplistic way, you input your analytical peak data in one of a number of different formats, the interface "feeds" your data to the different indexing programs, calculates unit cell parameters by a variety of methods and returns the data to the Crysfire interface. Crysfire makes use of system environment variables to exchange information between the different indexing programs and the results module; this requires careful installation to make sure the data is exchanges successfully. As described by the authors, "Hopefully it all works seamlessly together, allowing non-specialist users to perform indexing operations on their datasets with a minimum of keystrokes and effort. By non-specialist I mean non-specialists in powder indexing - they are still assumed to have some

crystallographic knowledge and are likely to be people engaged on structure determination from powder data, for whom indexing is simply a necessary but critical preliminary to the main show."

The information about the software and the download links are at http://www.ccp14.ac.uk/tutorial/crys/index.html. The online documentation on this site is a bit out of date, and it is best to download the whole crysinst.zip from one of the archive mirrors. The latest archive includes fixes and updates through January, 2005. This version is included in or XRD FTP archives at ftp://eps.unm.edu/pub/xrd/index.htm.

Quantitative Analysis Tools

GSAS

General Structural Analysis System is a very mature Rietveld program, and comes in versions to run on Windows/DOS PCs and Linux systems. Written originally for UNIX, the "port" to the Windows platform essentially links a series of DOS command windows in which the actual work is done with command line modules. EXPGUI is a graphical interface that is a bit friendlier that the command line interface. The latest version includes a windows installer (gsas+expgui.exe) that sets up most of the program for you (except that you still have to manually set the environment variables as described in the readme.txt in the c:\gsas folder). It has been developed as free open-source software and is maintained by Allen C. Larson & Robert B. Von Dreele of Los Alamos National Laboratory.

GSAS has a very good reputation and a large community that uses it, but it is an "expert's" program in that the user really needs to know what they are doing to get good results. In popular terms, the learning curve is very steep. It comes with a 231 page manual which contains surprisingly little about Rietveld refinements and is chiefly concerned with how to interact with the 37 different program modules. Initial impressions are quite intimidating, but the software gets great reviews from those who learn to put it through its paces.

GSAS information and distribution has been assumed by the NIST Center for Neutron Research. The main page linking everything connected with GSAS is available at: http://www.ncnr.nist.gov/programs/crystallography/software/gsas.html. This page also includes links to all mirror sites for various versions of the program, and an excellent tutorial about how to use EXPGUI, the graphical interface to GSAS that allows you to do much (but not all) of what GSAS can do in a "friendlier" graphical environment. We have the January, 2005 distribution available on our FTP site at ftp://eps.unm.edu/pub/xrd/index.htm.

FullProf 2000

FullProf is another profile refinement (Rietveld) system produced by Juan Rodríguez-Carvajal at the Laboratoire Léon Brillouin (CEA-CNRS) in France. The software presents an friendlier GUI interface than GSAS (through the plotting Program WinPLOTR co-written by Thierry Roisnel and the author at the LLB) but is still a complicated analytical tool requiring good data input by a user who understands diffraction data, and crystal structure analysis, and is willing to master fairly complicated input data file structures.

Unlike the GSAS manual, the 139-page FullProf 2000 manual (in Acrobat PDF format) includes a good discussion of the Rietveld procedure and suggests the best sequence of steps

to follow to produce a good refinement. It is still no substitute for the study required from the Rietveld literature referenced in the previous "Introduction to Quantitative X-Ray Diffraction" chapter. We have a recent version of FullProf on our ftp site at at ftp://eps.unm.edu/pub/xrd/index.htm. The program is distributed through the CCP14 archive at: http://www.ccp14.ac.uk/index.html.

RockJock

RockJock is a massive (40 MB) Excel spreadsheet that uses Excel (Visual Basic) Macros, Formulas and the (add-in) Solver function compare integrated intensities of phases identified in a whole-pattern with those of an internal standard to perform quantitative analysis on an XRD pattern. While not as precise as full-blown Rietveld refinements, the system holds promise for doing reasonable quantitative analyses since it does a least-squares fit on the intensities of the whole pattern that can reduce the effect of preferred orientation on the results.

Written by Dennis D. Eberl, the software was published in 2003 as U.S.G.S. Open-File Report 03-78, "Determining Quantitative Mineralogy from Powder X-ray Diffration Data". It is available via FTP from the author at ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/RockJock; it is also linked on the CCP14 archive. The 45 page manual is well written, easy to follow and includes appropriate literature references.

Data to be analyzed in RockJock must conform to certain conditions: An internal standard of 10% ZnO (by weight mixed as 9 parts sample to 1 part standard or 3.00 g to 0.333 g), 2θ range 5 ° to 65 ° with a 0.02 step size and a count time of at least 2 seconds per step. Specific methods of grinding (using a McCrone micronizing mill) and mounting (side-drifted against frosted glass) are also indicated. The data range may be modified by changing the spreadsheet, but is not recommended. A "Peak Chopper" spreadsheet is included to modify data collected with other step sized, but this sort of conversion will invariably result in loss of data quality.

Your author's first impression of the program is that the least-squares refinements using Solver in Excel are extremely slow. Eberl recommends a 1GHz (or faster) processor, and your author's system ran at half of that speed. He states that calculation times can be ½ hour or more for many samples. It took about 10 minutes each to do the initial tests on the "Full Pattern" and "Clays" sheets (recommended in the installation procedures) and the data presented in these is fairly simple. The program continues doing "trial" fits until you interrupt it, and during the first calculations the CPU was so busy that it was difficult interrupt it to stop the calculations. It is slow, but if it does decent quantitative analyses it could be worthwhile.

Sources of XRD Standard Data

The International Center for Diffraction Data (ICDD)

The ICDD, located in Newton Square, Pennsylvania (near Philadelphia) is the main source for X-Ray powder diffraction data in the world. Founded in 1950, the ICDD database is the Powder Diffraction File (or PDF). It has grown from a few thousand patterns in its first years to over 136,000 patterns in its current release. About half of the patterns are experimental

data obtained in laboratories such as ours under the ICDD's "Grants in Aid" program. Another 35% to 40% of the patterns are calculated from data in the Inorganic Crystal Structure Database (ICSD – see below), and the balance are organic materials. The ICDD has recently added a separate organics-only database that is designed primarily for the pharmaceutical industry. Virtually every XRD software vendor writes its Search-Match software to access the PDF.

The database is expensive. The older-format PDF-2 database for a first-time purchase will cost a commercial user close to $7,000; a 20% academic discount reduces this cost to University labs (like ours) to under $5,000. Annual updates are recommended but not required for the PDF-2 at about $1,000 (with a 20% academic discount). This update cost is cumulative so that if you don't update for a few years, you need to pay for all the years you missed. The new format (PDF-4) of the database is less expensive both is cost and annual updated, but it is time-locked and must be renewed annually. A full PDF-4 license is $5,200 ($3,640 academic), and the annual renewal is $990 ($690 academic). The PDF-4 includes some good relational software for data retrieval, draws real patterns instead of stick figures for comparison with your data and is generally a better product. High-cost analytical software (like Jade) can read and use either form of the database with equal functionality, but stand-alone retrieval functions require an add-on program to the PDF-2 that is included with the PDF-4.

Since ICDD is virtually the only source for XRD data, particularly that used by automated search/match programs, those who want to use the data have little choice but to purchase it (or work in an environment in which it has been purchased for you).

The Inorganic Crystal Structure Database (ICSD)

The ICSD is the premier source for inorganic crystal structure data. This data is the required starting point for use with Rietveld-type profile refinement method(s), and most Free and commercial Reitveld programs read this database directly eliminating a lot of tedious manual entry of data. It currently contains about 65,000 entries of detailed structural data. Cost is considerably less than the ICDD products: A single commercial license is $1,736 annually, but an individual at a University can license the data for $450 annually, and academic departments can license site-wide use for $950 annually. The database is priced in Euros, so the cost in dollars varies with the exchange rate. Current information and prices are at http://icsd.ill.fr/icsd/. This is a bargain compared to the ICDD databases, but most search/match software cannot use ICSD data directly.

Mineralogical Society of America

If you want structural data for minerals for your Rietveld refinements, this free online source has structural data for every experimentally determined structure published in the Journal of the Mineralogical Society of America (2,627 of them). The following article discusses the structure of the database and how it is accessed: Downs, R.T., and Hall-Wallace, M., 2003, *The American Mineralogist crystal structure database.* American Mineralogist, v. 88, p. 247-250. The entire database is online at the following URL (which explains how to use it): http://www.minsocam.org/MSA/Crystal_Database.html.

Other Diffraction and Crystallographic Data Sources

The International Union of Crystallographers (IUCr) maintains an index page to sources of crystallographic and diffraction data at http://www.iucr.org/iucr-top/data/. There are some free sources listed here (the Mineralogical Society of America being by far the largest) but the ICDD and ICSD are clearly the dominant players in this area.