SHIMADZU XRD-7000 X-RAY DIFFRACTOMETER

"The Fridge"

Operating Instructions

Table of Contents

Introduction

T he Shimadzu XRD-7000 Maxima is a state-of-the-art, multipurpose x-ray diffraction system that is optimized for powder diffraction studies of crystalline materials. The system is outfitted with a high-precision theta-theta goniometer (this is good) and a large sample stage. The software system includes a powerful search/match tool and the full International Center for Diffraction Data (ICDD) reference database of over 148,000 material phases. Many hardware upgrades – environmental chambers, fiber analysis fixtures, automatic sample loaders, etc. – and software upgrades are available for the XRD-7000 system. When some of you graduate, start companies, get rich, and throw some money back at Olin, we may be able to afford a few of the cool upgrades.

1

Radiation Safety[1,2]

X-rays produced by the diffractometer pose a very real danger. Human tissue can be severely damaged if exposed to the x-rays used in x-ray diffraction. Long-term, chronic exposures at moderate levels can directly cause a variety of skin disorders, and chronic relatively low- level exposures may be a factor resulting in increased cancer risk in exposed personnel. Although modern XRD equipment includes safeguards designed to minimize or eliminate radiation in the work environment, an awareness of the dangers of radiation exposure and associated safety issues is required for anyone using the x-ray diffractometer.

Interaction of X-Rays with Matter

X-rays are a type of electromagnetic radiation that interacts with matter. That interaction takes place as either absorption (transfer of energy from the X-ray photon to the absorbing material) or scattering (in which the X-ray photon is "redirected" by interaction with the scattering material). The process of scattering is primary in producing diffraction data from test specimens, but both processes result in the production of a variety of potentially damaging secondary radiation that can produce significant short- and long-term health effects in the event of exposure of human tissue.

The X-rays produced for diffraction analysis consist of characteristic radiation dependent on the anode target plus the continuous spectrum. Recall that the energy of X-rays and their wavelength are inversely proportional (higher energy = lower wavelength), and that the continuous spectrum minimum wavelength decreases as the accelerating voltage (kV) of the X-ray source increases. Also important to understand is that an increase in filament current (ma) and kV (beyond the minimum value required to produce characteristic radiation for the target) will result in an increase in the intensity of the generated X-rays but will not change their energy.

Radiation Sources in the X-Ray Diffraction Laboratory

The x-ray diffractometer is a source of very intense radiation, and exposure of any part of the body to the primary beam can deliver hundreds of times the maximum permissible yearly dose in a second, and an hour of exposure to the diffracted beam can result in a year's worth of permissible exposure. Whereas a primary beam exposure will produce noticeable skin damage very quickly, a diffracted beam exposure might not be physically noticed at all.

---

[1] http://epswww.unm.edu, University of New Mexico, Department of Earth and Planetary Sciences
[2] R. Jenkins and D. J. Haas (Philips Electronic Instruments), Hazards in the Use of X-Ray Analytical Instrumentation, *X-Ray Spectrometry*, Vol. 2, No. 3, July 1973

Working Safely with X-rays

It is imperative that anyone working with the x-ray diffractometer be properly trained and knowledgeable of its use in order to prevent injuries. If you do not feel you are properly trained to use the diffractometer, seek appropriate assistance from a competent and experienced user.

To minimize (and hopefully eliminate) the likelihood of exposed to radiation in the laboratory, our x-ray diffractometer includes many safety-related features, including
- Complete shielding of the X-ray source and diffracted beam such that all radiation is contained within an enclosed area.
- Fail-safe safety interlocks installed on the x-ray chamber that prevent accidental opening of the chamber door. If the door is forced open, the X-ray source is turned off. The x-ray source will not operate if the door is open.
- A fail-safe indicator light should be present which is illuminated when the x-ray source is turned on.
- Sealed openings of the chamber to eliminate any possible leakage.

Under no circumstances should anyone attempt to override any of the safety features of the x-ray diffractometer.

The system should be checked for leakage periodically with the system at operating conditions using properly calibrated survey equipment. The system should also be checked if any of the following conditions exist:
- Any change in the components of the system (with the exception of minor components such as scattering and receiving slits).
- Prior to and after any maintenance requiring the disassembly or removal of a component in the system
- Anytime a visual inspection of the system reveals an abnormal condition.

For routine operations of modern X-ray powder diffractometers, the radiation exposure in routine operations should be virtually nonexistent.

2

Background Information

NOTE: The following background text is taken directly or adapted from the *Diffraction Methods* section of ASM Handbook, Volume 10 Materials Characterization.

X-ray diffraction techniques are some of the most useful in the characterization of crystalline materials, such as metals, intermetallics, ceramics, minerals, polymers, plastics, or other inorganic or organic compounds. X-ray diffraction techniques can be used to identify the phases present in samples from raw starting materials to finished product and to provide information on the physical state of the sample, such as grain size, texture, and crystal perfection. Most x-ray diffraction techniques are rapid and nondestructive; some instruments are portable and can be transported to the sample. The sample may be as small as an airborne dust particle or as large as an airplane wing. In general, x-ray analysis is restricted to crystalline materials, although some information may be obtained on amorphous solids and liquids. XRD samples are acceptable in many forms, depending on the availability of the material and the type of analysis to be performed. Single crystals from a few microns to a few inches in diameter or loose or consolidated aggregate of many small crystals can be used. Although the overall size of the sample may be large, the actual area of the sample examined in a given experiment rarely exceeds 1 cm^2.

The type of information obtained from x-ray diffraction studies ranges from sample composition to details of the crystal structure or the state of orientation of the crystallites. Phase identification can be conducted on virtually all single crystal or powder samples. Also useful are measurements of the physical state of a sample that detect differences from the ideal crystal (presence of defects, strain, etc.).

X-ray Powder Diffraction

X-ray powder diffraction techniques are used to characterize samples in the form of loose powders or aggregates of finely divided material. These techniques cover various investigations, including qualitative and quantitative phase identification and analysis, determination of crystallinity, microidentification, lattice-parameter determinations, high-temperature studies, thin film characterization, and, in some cases, crystal structure analysis. The powder method is perhaps best known for its use as a phase characterization tool partly because it can routinely differentiate between phases having the same chemical composition but different crystal structures (polymorphs). Although chemical analysis can indicate that the empirical formula for a given sample is $FeTiO_3$, it cannot determine whether the sample is a mixture of two phases (FeO and one of the three polymorphic forms of TiO_2) or whether the sample is the single-phase mineral $FeTiO_3$ or ilmenite. The ability of x-ray powder diffraction to perform such identifications more simply, conveniently, and routinely than any other analytical method explains its importance in many industrial applications as well as its wide availability and prevalence.

In general, an x-ray powder diffraction characterization of a substance consists of placing a powder sample of a crystalline material in a collimated monochromatic beam of x-radiation. *Chapter 3 of your textbook describes the process of x-ray diffraction, and how the XRD finds the diffraction pattern for your material.* The diffraction pattern is recorded on film or using detector techniques, then analyzed to provide x-ray powder data.

In x-ray powder diffraction analysis, samples usually exist as finely divided powder (usually less than 44 μm in size) or can be reduced to powder form. The particles in a sample comprise one or more independently diffracting regions that coherently diffract the x-ray beam. These small crystalline regions are termed crystallites. Consolidated samples, such as ceramic bodies or as-received metal samples, will likely have crystallites small enough to be useful for powder diffraction analysis. The size limitation is important in x-ray powder diffraction because most applications of powder diffraction rely on x-ray signals from a statistical sample of crystallites. Bragg's Law (Equation 1) states that the angular position, θ, of the diffracted x-ray beam depends on the spacing, d, between planes of atoms in a crystalline phase and on the wavelength, λ, of the x-ray.

$$n\lambda = 2d \sin \theta \qquad [1]$$

The intensity of the diffracted beam depends on the arrangement of the atoms on these planes.

A powder pattern from a single-phase material will have maxima at positions dictated by the size and shape of its unit cell and will increase in complexity as the symmetry of the material decreases, as shown in Figure 1. For example, many metal patterns and those from simple compounds that tend to be mostly of cubic symmetry and have small unit cell edges will produce powder patterns having fewer lines or maxima than would be expected from a compound of lower symmetry or one having a very large unit cell. A pattern of a mixture of phases in which all the individual patterns are superimposed will produce a complex experimental pattern, especially when the number of phases present in the mixture exceeds approximately three or when the phases constituting the mixture are all of very low symmetry or have very large unit cell dimensions.
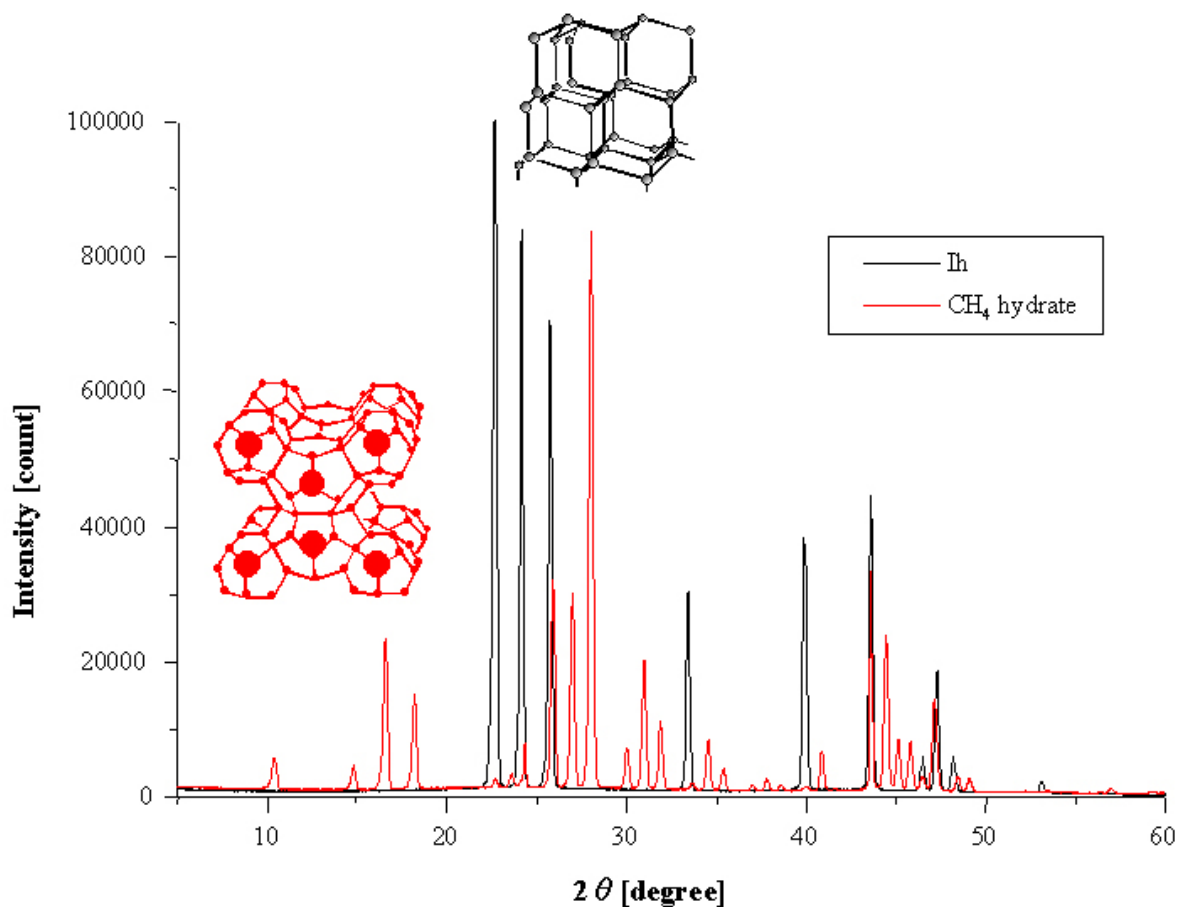
Figure 1. Two superimposed XRD graphs. Note that the CH₄ hydrate has distinctly more peaks than Ice (Ih), since it has a much more complex crystalline structure.

Phase identification using x-ray powder diffraction is based on the unique pattern produced by every crystalline phase. Much as a fingerprint is unique for each person, the diffraction pattern can act as an empirical fingerprint for that phase, and qualitative identification of phases can be accomplished by pattern-recognition methods that include established manual techniques and the newer methods that use computers, most of which implement programs based on heuristic algorithms. All of these methods make use of the database maintained by the JCPDS International Centre for Diffraction Data.

The Conventional Powder Diffractometer

Although film techniques have been in use since the inception of x-ray diffraction, the advent of powder diffractometer has been more recent. Powder diffractometers have been in use as a laboratory tool since the late 1950s and early 1960s.

The Bragg-Brentano geometry is used most commonly for powder diffractometers. Figure 2 shows this geometry as used for vertical diffractometers. In the vertical geometry, the axis A is horizontal.

In the variation of the Bragg-Brentano geometry that the Olin XRD system uses, termed the θ-θ diffractometer geometry, the sample is held stationary with its surface in a horizontal plane as the x-ray tube and the detector move.
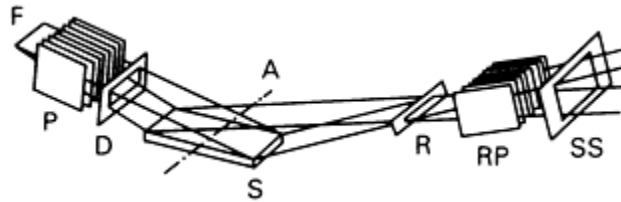

Figure 2. Geometry of the Bragg-Brentano diffractometer. F, line source of x-rays from the anode of the x-ray tube; P, soller slits (collimator); D, divergent slit; A, axis about which sample and detector rotate; S, sample; R, receiving slit; RP, receiving soller slits; SS, scatter slit.

See the ASM Handbooks, Volume 8 → Residual Stress Measurements → Nondestructive Procedures for additional information on XRD instrumentation.

References

- Callister 3.16 (on the CD)

- Askeland Section 3.9

- ASM Handbooks Online, Volume 10 Materials Characterization, Diffraction Methods.

- http://unit.aist.go.jp/eutech/euhydrate/image/X_ray.jpg - XRD Graph

3

Sample Preparation

Preparation of **Powder** Samples

1. Use fine powder if possible. If your powder is coarse (>240 grit or xxx microns), grind it with a mortar and pestle or a ball mill.
2. If only a small quantity of powder is available, skip to Step 3. If a large quantity of powder is available, fill the recess of an aluminum sample holder with powder and use a flat object, e.g., a glass slide, to level the powder with the top face of the sample holder. Skip to step 4.
3. If you don't have enough powder to fill the recess of an aluminum sample holder, you'll need to deposit some of your powder onto a glass slide. Mix a few drops of amyl acetate, acetone, or methanol with some of your powder to create a paste. Spread a thin, even layer of the paste onto the middle of a glass slide. It's important to maintain a fairly flat sample surface, so try to avoid bumps and chunks. When you're satisfied with the deposited layer, wait for the solvent to dry.

Preparation of **Solid** Samples

1. Prepare a flat sample with approximate dimensions of 1" wide x 2" long x 3/16" (maximum) thick.
2. Remove all dirt, grease, etc. from the surface of the solid.
3. Load your sample.

4

Instrument Operation

This section will walk you through the basic operation of the x-ray diffractometer. You'll have to follow a series of tasks that includes

- Powering up the instrument,
- Loading your sample,
- Viewing system parameters and calibrating the instrument,
- Setting your testing conditions,
- Collecting x-ray diffraction data for your sample, and
- Analyzing your results.

It may seem boring at times, but it'll be worth it! Just think of yourself as a mad scientist armed with the power to identify completely unknown samples. Is it mullite (kind of like a fossilized mullet)? Is it diamond? Is it ice-nine? Only your analysis will tell.

Instrument Startup

1. Turn on the water chiller. The switch is on the right side of the front panel.
2. Turn on the XRD main power supply. The switch is on the left side of the instrument.
3. Turn on the computer and login as "guest" to the "this computer" domain (not MILKYWAY). You don't need a password.

Sample Loading

Load your sample, as follows:
1. Open the XRD chamber door. Inside the chamber, you will see a complex hardware system with a large sample area (in the middle) and two arms that rotate around the sample stage area. The x-ray source is mounted on the left arm, and the x-ray detector is mounted on the right arm. Unless you know what you're doing, you shouldn't touch anything connected to the rotating arms.
2. Locate the sample mounting fixture in the center of the stage assembly. The mounting fixture is a half cylinder with two spring clips (on the underside) that protrudes from the top center of the stage assembly.
3. With the sample facing up and toward you, slide your sample holder between the half-cylinder and the spring clips. If you are using an aluminum sample holder, you should center the holder (left and right edges flush with the half cylinder) and slide the holder all the way back.
4. Be careful not to get any of your powder on the XRD hardware. If you do, please wipe it off with a soft tissue or paper towel.

System Parameters Setup

1. To open the XRD hardware status software, double click the **1-Display System Parameters** icon on the desktop.
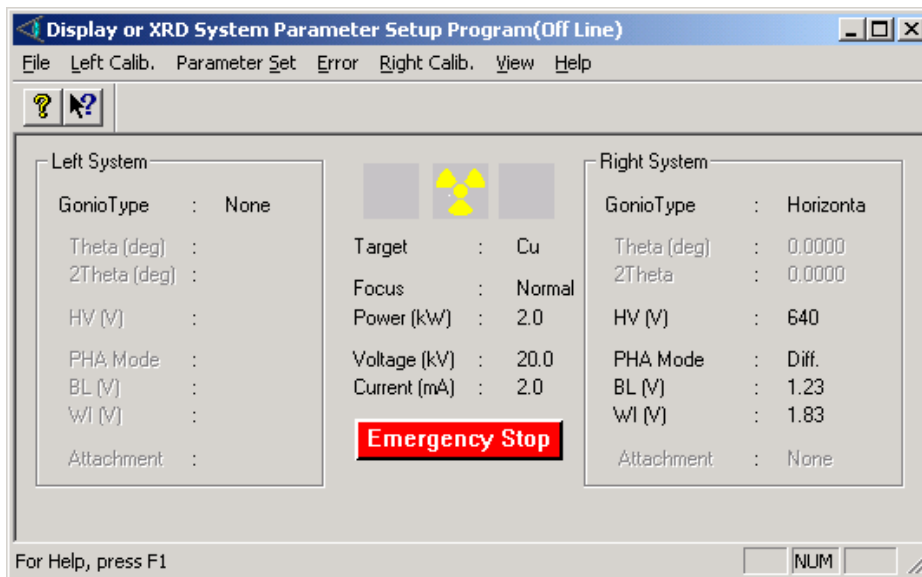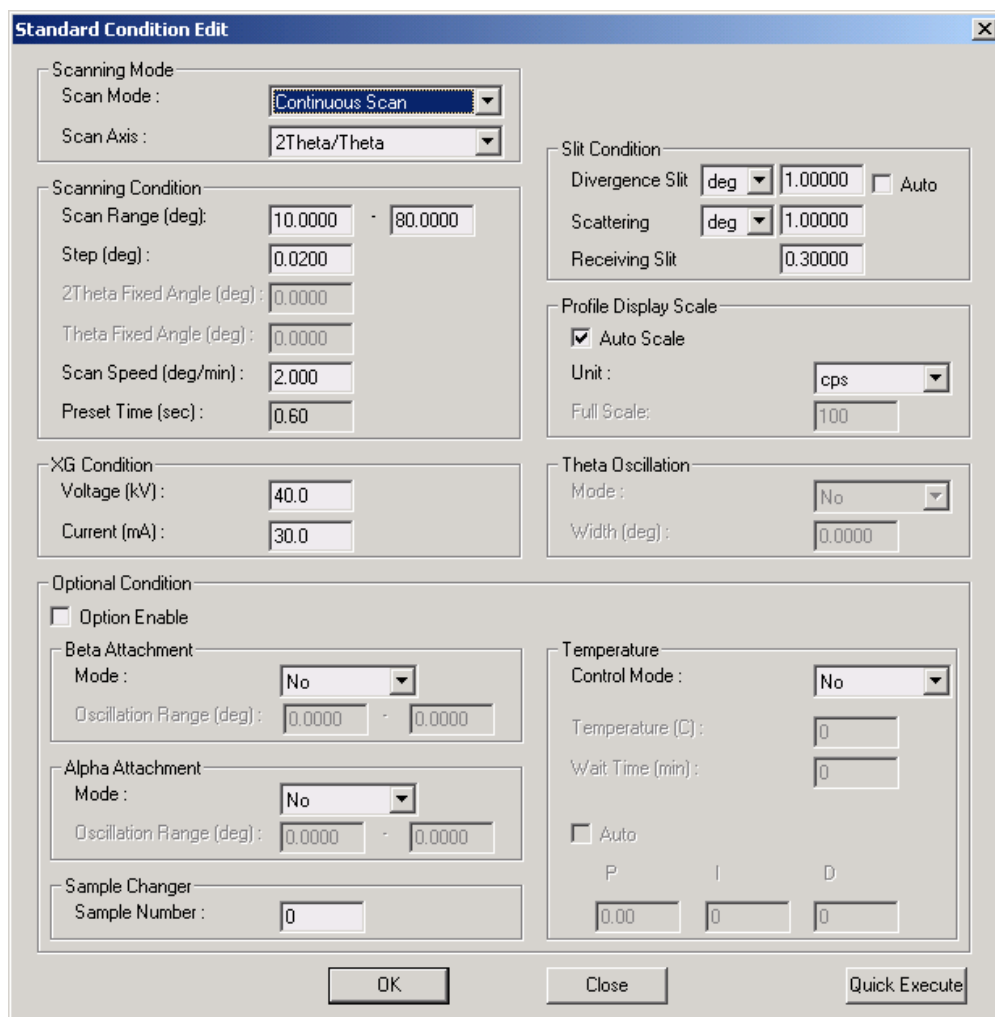

   a. When asked to open and close the XRD chamber door, do it. This step checks the safety interlocks on the XRD chamber.
   b. When asked to calibrate, answer yes. This step calibrates the goniometer position. When this step is complete, you should see some numbers appear next to the "Theta (deg)" and "2Theta" items under the "Right System" heading.

2. Minimize the **Display or XRD System Parameter Setup Program** window or move the box to the bottom right of the screen (it's sometimes nice to leave the window visible while you're testing).

Test Conditions Setup

1. Double click on the **2-Set Test Conditions** icon on the desktop to open the **Untitled-Right Gonio System: Analysis Condition Edit Program** window. This will open a box like this:
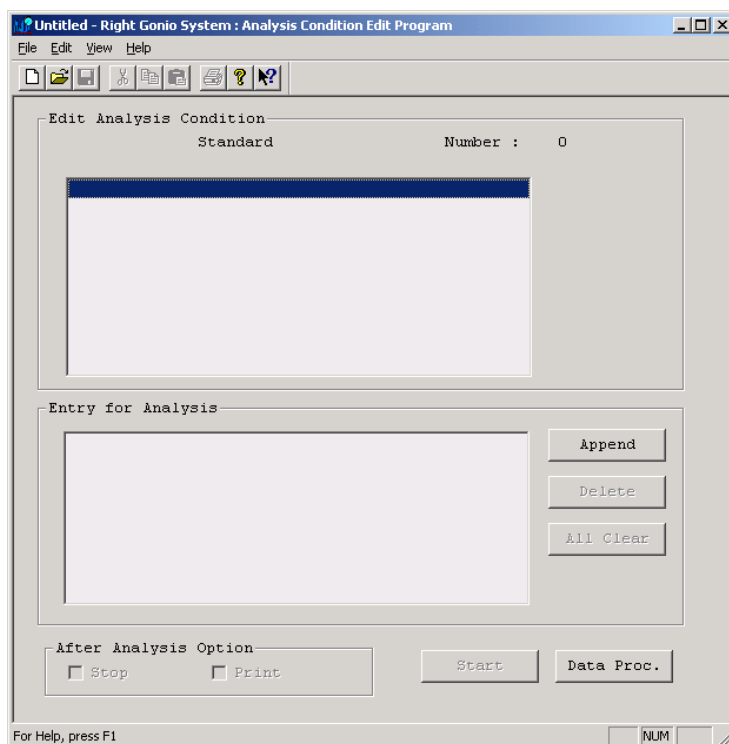
2. To open a new test parameters window, double click on the highlighted (blue) box under Edit Analysis Condition. This will open a large dialog box with lots of adjustable test parameters. The default parameters (shown below) are fine for a typical scan (35 min.), but if you'd like to speed things up a bit, try changing the Scan Speed to 4 deg. per minute.

**3.** When you hit "OK," the following dialog box opens. Type in a filename, sample name, etc., and hit "New" to create a new folder for your data.


4. Hit "Close" to close the Standard Condition Edit dialog box. This will send you back to the **Untitled-Right Gonio System: Analysis Condition Edit Program** window. Don't close the window.

Testing

1. Now you need to do something weird to satisfy the quirky (or should I say lousy) software. You need to minimize all your windows and double click on the **3-Run Test icon** on the desktop. This will open the **Right Gonio System: Analysis and Spooler Program** testing window, and for some mysterious reason, opening this window is required at this point. Minimize the new window that appears.

2. Return to your **Untitled-Right Gonio System: Analysis Condition Edit Program** window, which should still be open from the previous steps.

3. Click on your test method (in blue below) and hit the Append button.
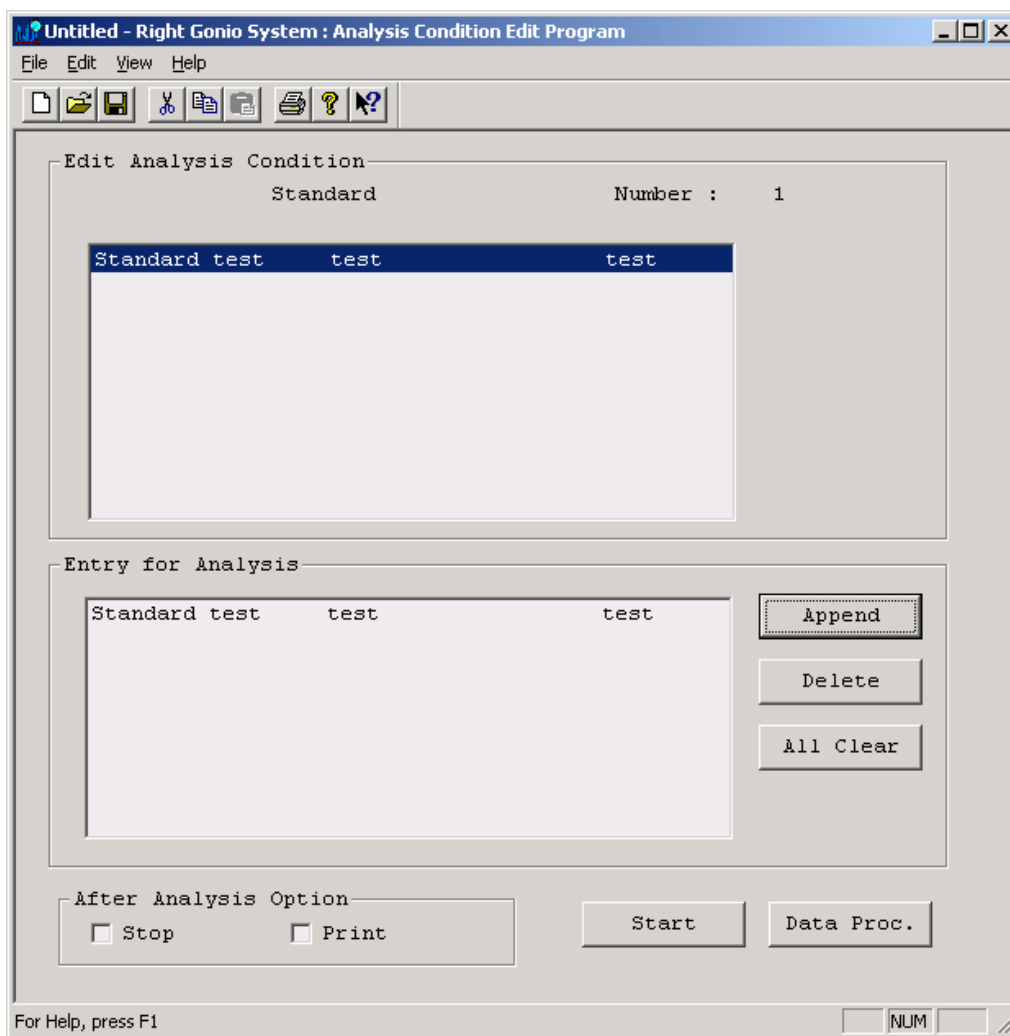
4. Click the Start button. This may or may not start your test (depending on whether it's the first test to be run since the machine was turned on). You can tell that the test has started if the x-ray source clicks on and the goniometer parts start moving.

5. Click on the **Right Gonio System: Analysis and Spooler Program** window to see a live view of the data collection. If the test started in Step 4, you'll see some action. If the test did not start in Step 4, hit the Start button now, and the test should begin.
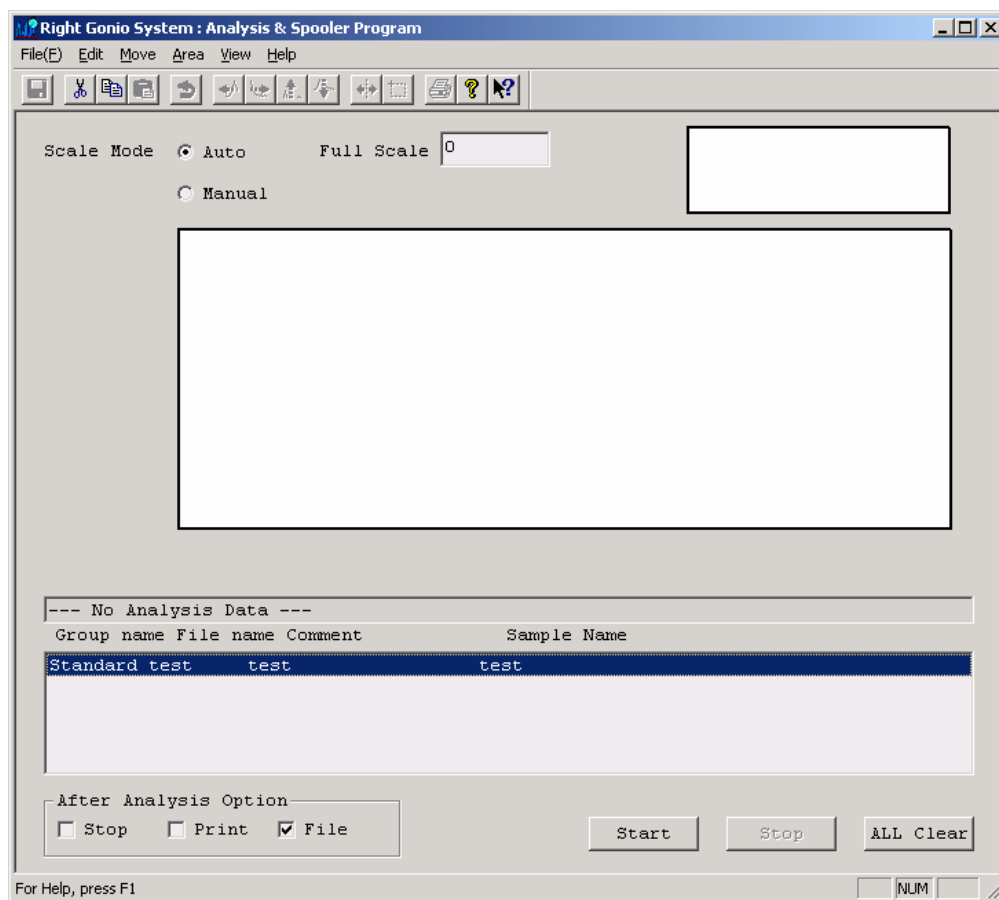
6. Once the test has started, sit back and enjoy the show. The entertainment value of live x-ray diffraction data collection lies somewhere between Star Wars: Episode I and Star Wars: Return of the Jedi. For those who aren't Star Wars fans, the live data collection lies somewhere between watching paint dry and watching lead oxide-laden rain water fall from our buildings.

Cleanup

1. If you were testing one of the powders used in the materials science courses, return the powder to the vial. Otherwise, dispose of your powder in an appropriate manner.
2. Rinse the sample holder with DI water. You may need to use a cleaning brush to remove all the powder from the aluminum sample holders. Return the aluminum sample holders to the XRD desk.

Hardware Shutdown

1. Turn off the main XRD power (left side of the instrument).
2. **Wait approximately 20 minutes** to allow cooling of the x-ray source, then turn off the water chiller.

5

Data Analysis

This section will walk you through basic data processing and x-ray pattern analysis. It should be noted that analysis of x-ray diffraction data is not always easy or straightforward, particularly when dealing with samples that contain multiple crystalline phases. This section presents a simplified look at data processing and analysis; there are a lot of little analytical tricks that are not presented here. You should seek help from experienced users if you have trouble analyzing a pattern.
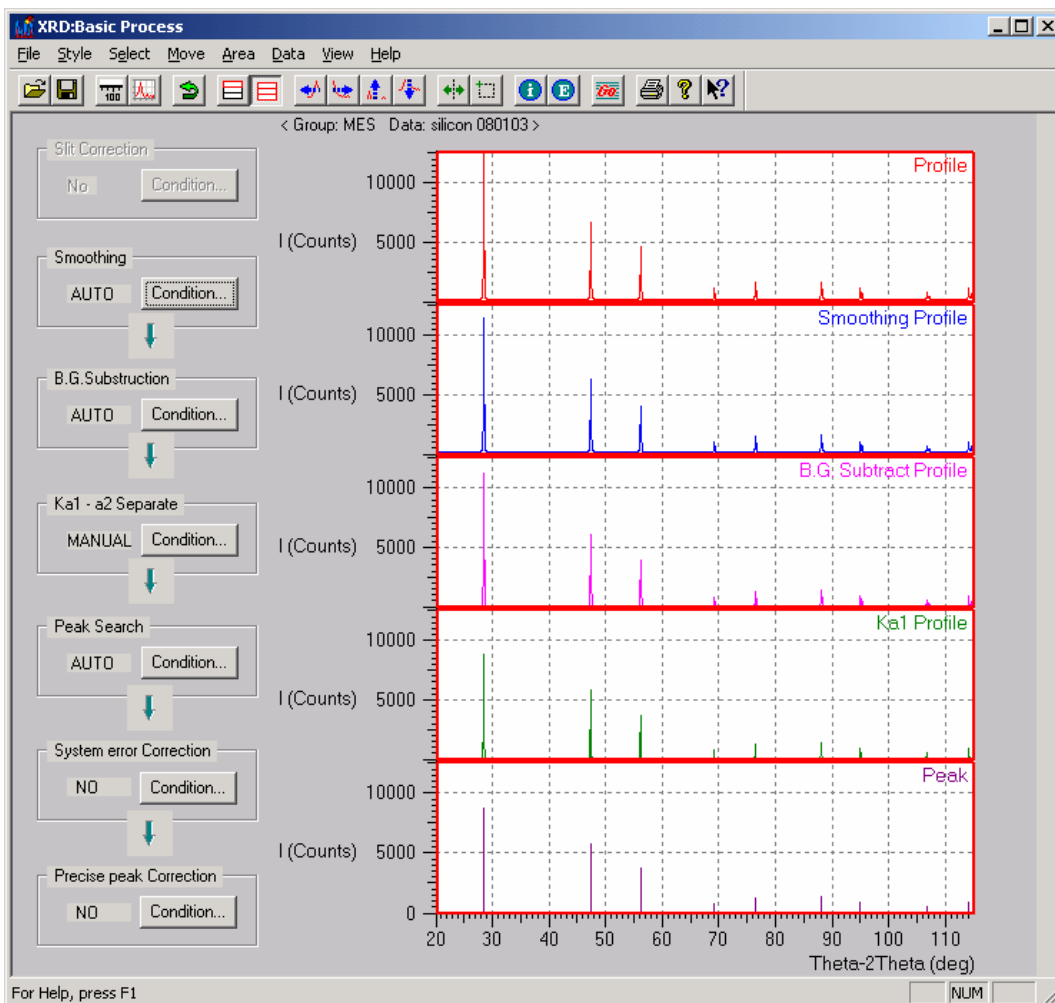
Processing Data

1. Double click on the **4-Process Data** icon on the desktop to open the **XRD: Basic Process** window (shown below).
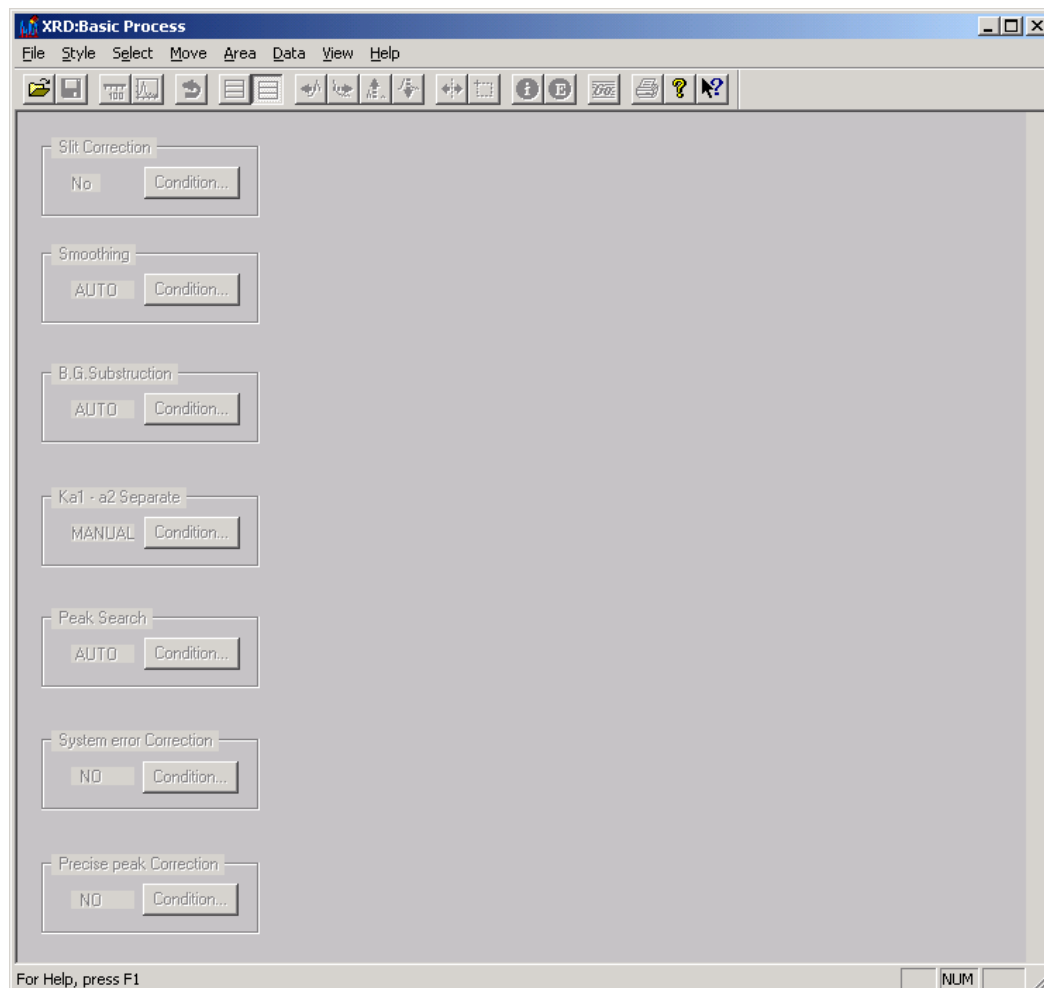
2. Open Windows Explorer and find your raw data file in the c:/xddata/Standard *xxx*, where *xxx* are some numbers. The last Standard *xxx* directory should contain a folder with your sample name followed by some numbers. Open the folder with your sample name.

3. Drag and drop the *.raw data file into the background of the **XRD: Basic Process** window. An XRD pattern should appear, as shown below.
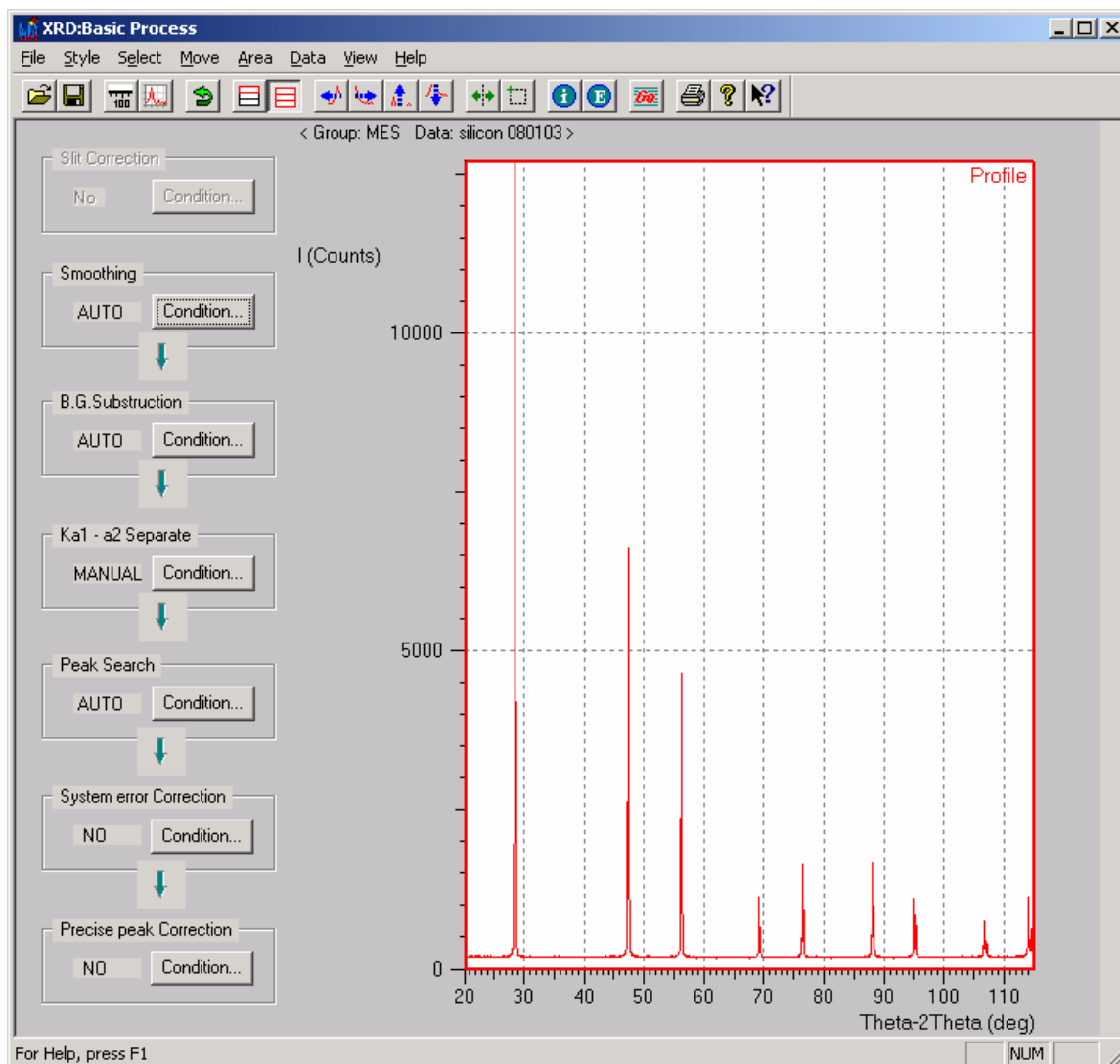

4. Click on the "*Go*" button on the toolbar to process your data with the standard parameters. This step will smooth your pattern, subtract background noise, separate overlapping peaks, and search for peaks.

5. You should end up with a series of XRD patterns like those shown in the following image. If everything looks ok, hit the save button on the toolbar to save the processed data.
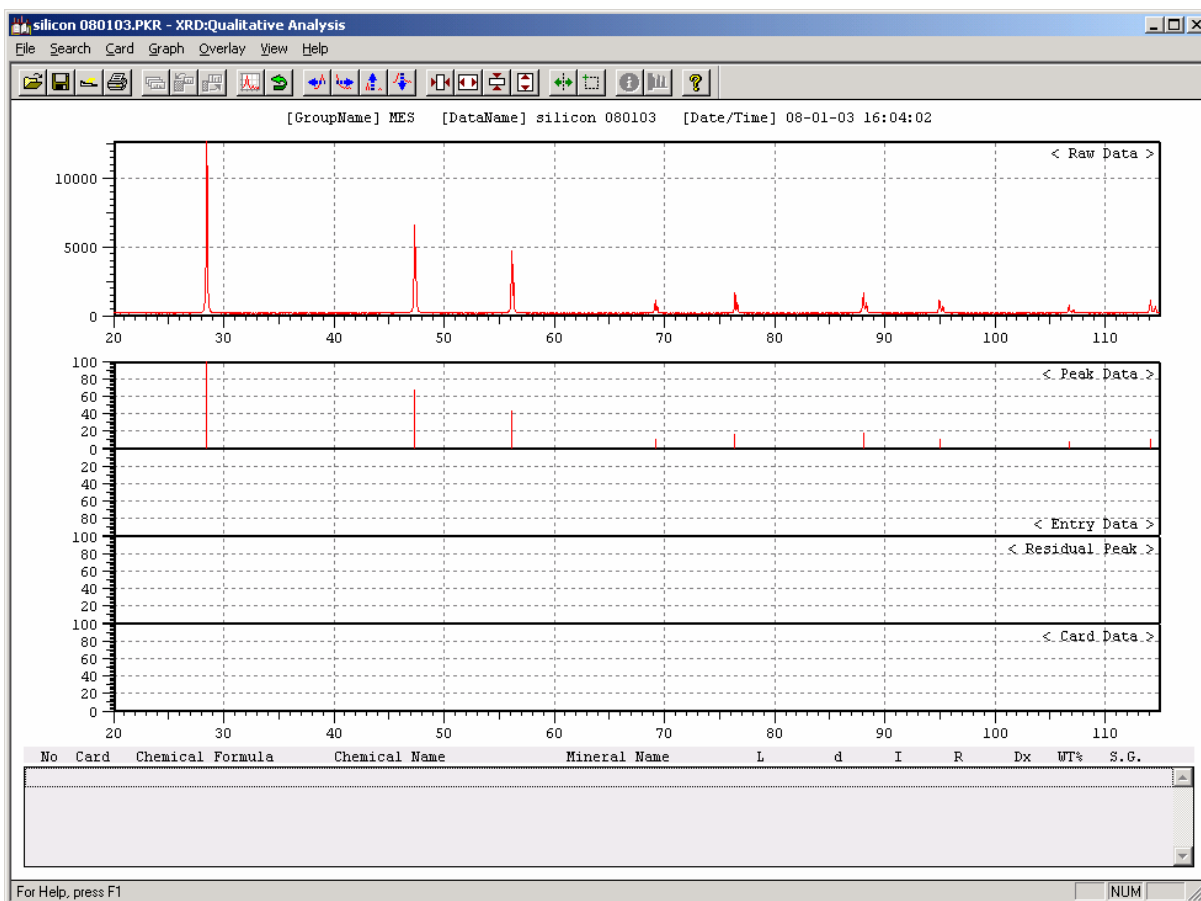
Analyzing Data

1. Double click on the **5-Analyze-Search-Match** icon on the desktop to open the **Untitled: XRD Qualitative Analysis** window.

2. Open your processed data file with the pkr extension.
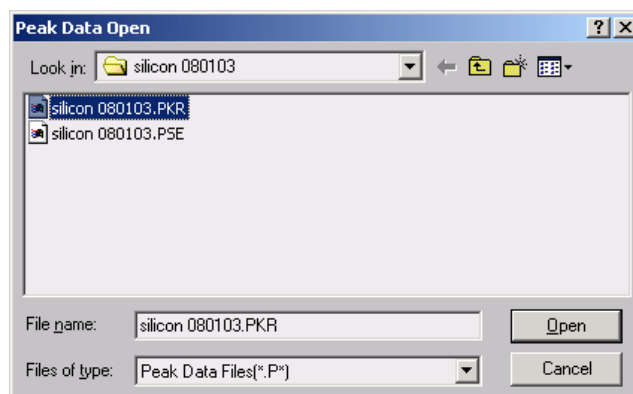
Your pattern with marked peaks should appear in the window, as follows:

3. Go to "Search…Pre-Search" in the pull-down menus. Click the search button to accept the default background parameters. You may want to increase the Background Intensity value if your pattern is very noisy and full of low intensity false peaks. The Background Intensity number is a percentage of the maximum peak intensity.
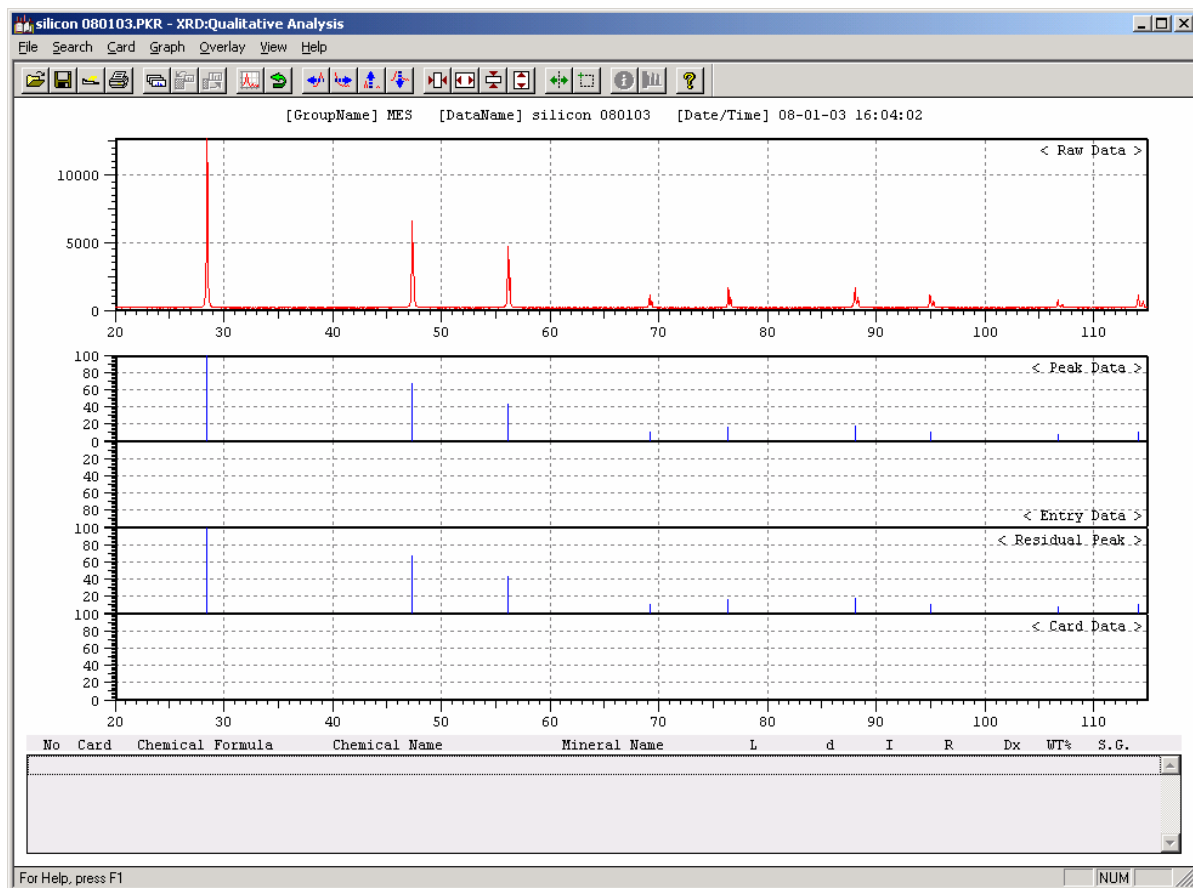
You should now see a number of blue peaks in the Peak Data and Residual Peak boxes, as shown below.

4. Now the fun begins. Go to "Search…Search" in the pull-down menus to open the search Conditions dialog box.
5. Unless you know something about your sample (whether it is a mineral, organic, inorganic, metal, etc.), select the MAX search option to search all 148,000+ files in our diffraction databases. The other default parameters are usually fine, but you may want to consider changing the following:
   a. Matching Peaks: Value could be lowered if you only have a couple of peaks, or raised if you aren't having much success with the automatic search/match.
   b. B.G. Intensity: Value should match what you entered for step 3.
   c. Window Width: Value could be lowered if you have a relatively pure sample and a pattern with high intensity, narrow peaks.
   d. Exist Atom…, Major Atom…, and Absent Atom…: These buttons open a periodic table dialog box that will allow you to select atoms that you know are present or absent in your sample. You may want to use this feature if you already have chemical data from another analysis, e.g., EDS or ICP.

6. Hit the Search button and wait for the computer to search through the tens of thousands of database entries. The result of the search is a list of possible matching materials, as shown in the example figure on the next page. The software places the "matching" hits in order, starting with the best match. Scroll through the "matching" hits, and you should see the diffraction peaks from the hit appear in the **<Card Data>** graph.

In the example shown below, the first hit (SiO_2) clearly matches the collected and processed data. Take a look at the peak locations (d value) and intensities – it couldn't be much better! Your sample may correspond to one of the first few hits, or it may not.. If it does not seem to match any of the suggested compounds, don't lose hope. Try entering some different search parameters and running the search again. Also, keep in mind that many "real" x-ray diffraction samples contain multiple crystalline phases, so look for compounds that match a few but not necessarily all of the diffraction peaks.
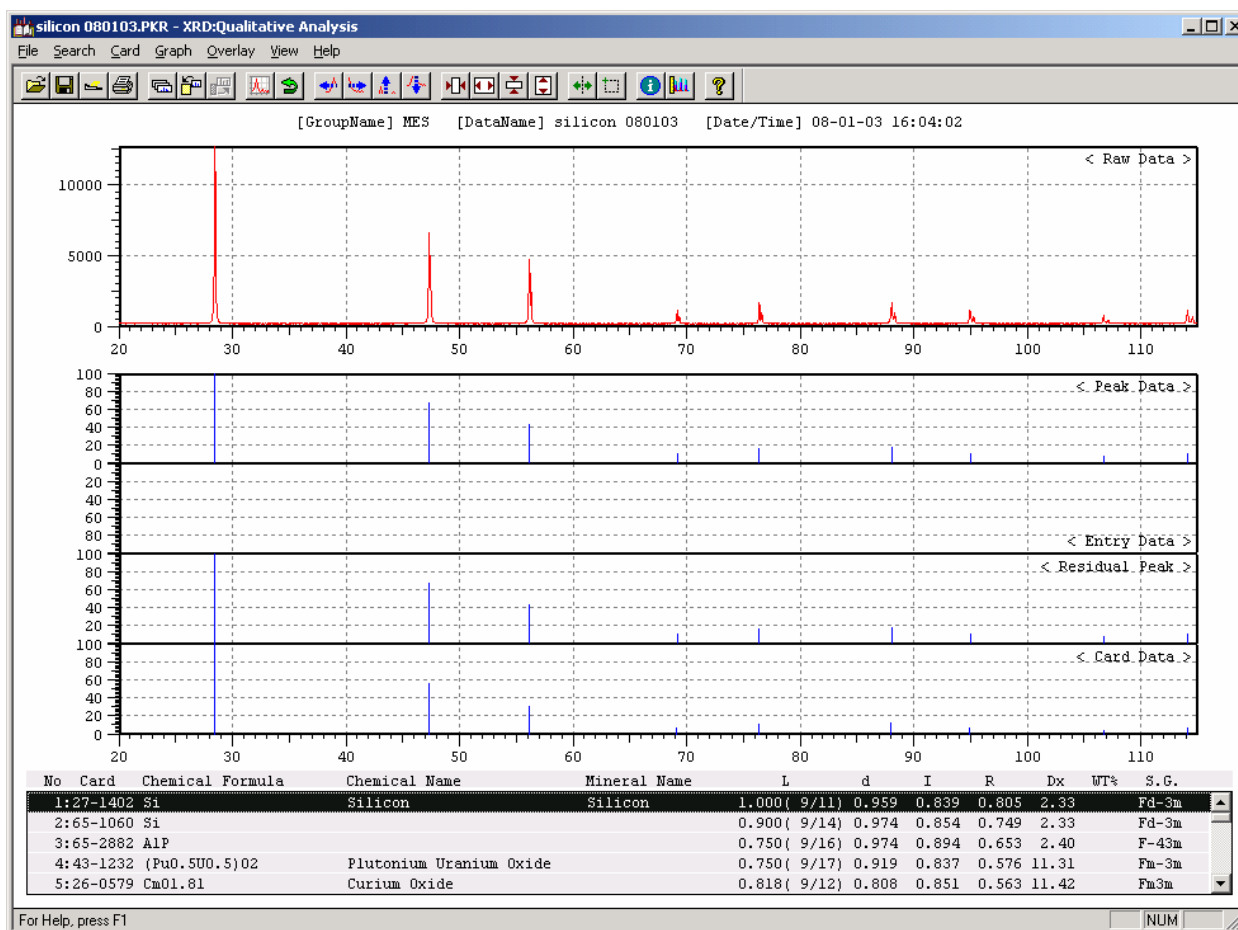
NOTE: If you do start to lose hope with the search/match program, call someone with a lot of x-ray diffraction experience.

7. **Entering Database Cards**. Once you have found a database card that seems to match your x-ray diffraction pattern, you may enter the card as a hit by clicking on the **Entry** button on the toolbar (the 6th button from the left) and clicking OK. The entry action will tag your card with a specific color, and the card peaks will appear in the **<Entry Data>** graph. You may enter as many matching peaks as you like. Each entry will be tagged with a different color. To erase entered cards, click on the **Erase** button on the toolbar (the 7th button from the left).

8. **Subtracting Found Peaks.** You may wish to re-run the search without the peaks from the matching database entries. To do so, click on the **Search…Subtract** option from the pull-down menu and click on OK. This will mark matching peaks in red on the **<Residual Peaks>** graph and leave un-matching peaks in blue. Run the search as before (see Step 6 above), and you will receive search results for just the un-matching residual peaks.