Lab 1: Introduction to X-Ray Diffraction Kelsey Lawson, 41602126

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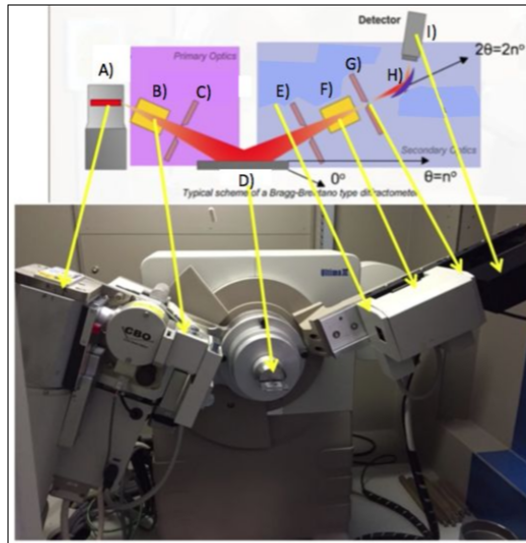
1) Basic XRD system configuration and the operational control system

a) What are the main components of an XRD system?

The main components of an XRD system can be categorized into 5 sections: The source, the primary optics, the sample holder and sample stage, the secondary optics and then the detector. For the source, an X-Ray Tube is used. This then shifts into the primary optics that condition the x-ray beam before it hits the sample using soller slits and divergence slits. The sample holder and sample stage contain the sample that is undergoing the XRD diffraction process. Next, in the secondary optics which retrieve the x-rays from the sample using an anti-scatter slit, soller slits, receiving slit, and then a single-crystal monochromator. Lastly, is the detector.

b) Label each of the XRD components in the figure below and briefly describe the purpose of each component.



A: X-Ray Tube - produces an x-ray beam to analyze the sample

B: Soller Slits - corrects angular divergence

C: Divergence Slit - controls beam spread

D: Sample - a piece of material being investigated

E: Anti-Scatter Slit - reduces the diffusion or scattering of the x-rays that occurs due to amorphous/air scattering

F: Soller Slits - limits the beam height

G: Receiving Slit - height divergence limiting slit that removes diffused scattered x-rays

H: Single Crystal Monochromator - filters Kβ rays and white radiation out

I: Detector - allows the diffracted x-rays to be detected

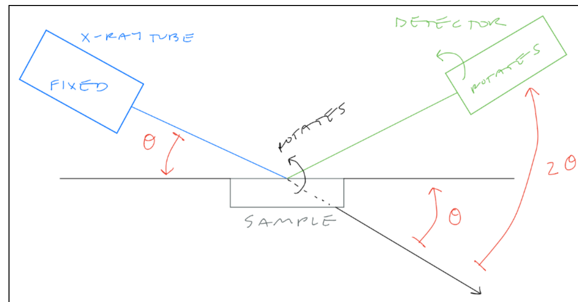
c) How are source x-rays produced? What are the main x-rays used for XRD (along with their wavelengths)?

The source of x-rays is normally from an x-ray tube. Within the x-ray tube, there is either a ceramic or glass container that has a tungsten filament to act as a cathode. The cathode emits electrons through a series of nuclear cores to accelerate them, also known as the white radiation effect. After being accelerated, the electrons travel to a designated anode material in order to bombard the element's atomic structure so that the secondary electrons are kicked out to promote an unstable state. The higher-order electrons are then moved down to fill in the lower orbital causing an energy release. The energy released during this process is x-rays and the amount of radiation produced is characterized depending on the type of anode used as well as the energy level of the atom. The most common materials are cobalt and copper. For cobalt, the average wavelength, $K\alpha_{avg}$, is about 1.790 and for copper, the average wavelength, $K\alpha_{avg}$, is about 1.542.

d) How are X-rays detected in a modern XRD system? What types of detectors are commonly used?

In modern XRD systems, the x-rays are detected through absorption by a scintillation compound that then emits visible light. This visible light is run through a Photomultiplier (PMT) that detects the visible light from scintillations and uses the photons to produce a proportional electrical voltage. The voltage then becomes the source for the computer to create the output graph. The most commonly used detector is a scintillation counter because it has high sturdiness and relatability.

e) Draw a schematic diagram of the angle between the x-ray sources, the sample and the detector for Bragg-Brentano Θ-2Θ measurements. Label Θ in these schematics. Why is a 2Θ value reported and not just the Θ value in the spectrum?



Within the Bragg-Brentano Θ-2Θ measurement, the x-ray tube is in a fixed position while both the sample and detector rotate simultaneously. The sample's angle of rotation, Θ, is the angle between the incident beam (from the x-ray tube) and the sample's crystallographic plane represented in Bragg's law: $n\lambda = 2d\sin\Theta$. The detector's angle of rotation, 2Θ, is the angle of the incident beam to the reflected beam. Both the incident beam and the reflected beam can be observed so 2Θ's quantity is experimentally measurable whereas the crystallographic plane is unobservable. This means Θ cannot be directly determined through this experiment.

2) Sample preparation

a) *What type of samples can you measure and how should you prepare them?*

There are two types of samples that can be measured: a powder or a film sample. For powder, the top of a sample holder will be fixed atop the back loader. Before adding the powder, make sure the powder is roughly uniform in particle size. This can be achieved by grinding the larger particles in a mortar and pestle to reduce the particle size. The finer the powder, the more accurate the reading will be. The powder is then poured into the back loader with the sample holder top until full. Then taking a press, apply pressure to the powder in order to compress it into the back loader. After applying the press, take a flat edged tool to run over the top of the powder sample to ensure the surface is even and then brush any extra powder on the sample holder top away. Apply the backend of the sample holder and then flip the entire back loader with the holder over. Release the sample holder from the back loader, add nitrocellulose acid onto it to bind the powder together and then place it onto the sample rack until ready to use it for XRD. When using film, which is usually a flat piece of metal, it is already precut to a certain dimension (both length and width at a certain thickness) that will fit on the sample stage. For super-thin films, taping them to the stage is enough to keep them in place. For thicker samples, a piece of clay that is still malleable enough to form it into a pyramid is needed on the sample stage. The tip of the pyramid should be higher than the walls of the sample stage. The film sample is then placed onto the clay and is then squished down using a metal piece of equal size to the sample stage. This is then placed onto the XRD machine for testing.

b) *What properties should a sample background plate have for best results (i.e. to avoid complicating your pattern with the signal from the background plate)?*

The sample background plate should have a limited chemical makeup that only involves one element to make a single crystal. This will limit the disruption of the pattern for the sample by having a family of peaks be produced in the diffraction pattern. Knowing the pattern of the background plate can then be ignored when the sample is added and new peaks form relating to the samples diffraction.

c) *For powder diffraction, why is it important for your specimen to be finely dispersed and tightly packed?*

Having a smaller particle dimension of the powder allows a better signal to noise ratio which avoids fluctuation in intensity data. This also allows for more particle participation when it undergoes XRD for more accurate data. Further, when the powder is finely ground and then packed into a sample holder, the packing allows for the formation of different oriented planes to show various diffraction peaks in the data.

3) XRD system operational parameters and typical settings

a) What are the main operational parameters and how do they affect your scan?

The main operating parameters are: slit width, scan range, scan speed and time per step, source power, and step width. The slit width affects the resolution of the scan by opening or closing the slits at the expense of the signal to noise ratio. The scan range can be used to make optimal use of a given measurement time of the sample. The scan speed is how fast, or slow, the sample is being scanned depending on time - the slower the scan speed the better the signal to noise ratio, however there is no effect on resolution. The time per step of the scan speed is the limiting factor of the number of samples to be measured and the time available. The source power is used for the x-ray tube in kilovolts and for the best result of the scan, the maximum values should be used depending on the system. The step width involves the measurement of the sample in the 2Θ circle step by step. The higher the value of the step width within a fixed time frame for the scan decreases the amount of points measured on the sample and could increase the signal to noise ratio while reducing the resolution quality of the scan.

b) What contributes to the width of an XRD peak?

Residual stress on the sample can affect the spacing, d of the lattice structure in Bragg's Law: $\lambda = 2d\sin\Theta$. When a sample is scanned, before stress is applied, an intensity peak is given at some value of 2Θ. However, when the sample undergoes stress, the intensity peaks is held constant but at new values of 2Θ that are wider than the original. This is due to the wavelength, λ being held constant. If there is a change in atomic spacing, d, then the value of Θ has to change in order to keep the λ value fixed altering the positioning of 2Θ when plotted with intensity. Therefore, if the sample undergoes bending such that tension occurs at the top of the sample with compression on the bottom, a range of d values occur to represent the varying distances. With a range of values for d, there then becomes a range of values for Θ and hence, 2Θ. The range of possible Θ values widens the 2Θ plot in order to reference all possible d values that satisfy Bragg's equation.

c) How do you determine instrumental broadening?

In order to determine instrumental broadening a near-perfect sample that has negligible broadening is run through the system. Because of the negligible broadening, or lack of peak width, from the sample, any overlay that adds width is then associated with instrumental broadening based on the diffractometer used.

d) What do you consider when choosing your scan parameters?

Choosing scan parameters will vary depending on the quality of the sample chosen and what instrumentation is used. Because there are no set parameters, a rule of thumb is the scan range can be between 5-90° and the step width can be at 10-20 individual data points above the full width at half maximum for most cases. The scan rate however does fully rely on the material chosen due to the crystallinity but after a quick scan to see what the machine is picking up adjustments can be made to fix errors & detector position.

e) *What is the low angle limit for data collection, and why (what happens at 2Θ = O degrees)?*

The low angle limit for data collection is at 2Θ = 1 on basic XRD machines but there are specific small angle systems that can have low angle ranges from .1 < 2Θ < 5. The angle for 2Θ cannot be at zero because this would start the detection parallel to the sample plane and the beam would not reach sample.

f) *Briefly outline the main steps for collecting XRD data from specimen preparation to instrument operation.*

1) Depending on the machine being used, you may have to allow warm up time for the mirror. If so, do this before prepping the sample to save time.
2) Prepare the sample that is going to be analyzed:
    a) Powders: If the powder is not at an ideal particle size, grind it up to ensure enough particle participation for diffraction. Place the powder into a sample mold adding liquid (can use nitrocellulose acid) to ensure the powder is compacted and won't disintegrate on the machine.
    b) Thin Films: Use tape to attach the film to the sample holder and remove any bumps to have the film completely flat. When applying the tape make sure the sample has enough surface area to be detected by the beam.
    c) Solids (Bulk Metals): Adding a small amount of clay to the sample plate, place the solid sample on and push down so that it stays in place and is level. If the sample plate has raised edges, make the sample in line with the height of the plate.
3) After the sample is prepared, place it onto the sample stage and lock it in place & close the XRD door if applicable. (If using a knife edge micrometer align it so that the sample and knife edge has no gap then set it to 0.000mm. If this value moves the knife edge is hitting the sample. Raise it to 1.200mm.)
4) Open XRD program on a computer and start a new file. This is where the 2Θ range (start and stop angles), step size (increment) and time per step, and power usage is set. Add the values for each component listed and a scan time dependent on these variables will be calculated. Save the file as .DQL to your computer.
5) Open XRD Commander and select the jobs tab then the create job button. Add a position number, sample ID (description of the sample), the parameter file (the .DQL file saved in Step 4), and raw file (create filename for .RAW file and apply here). Start the job and wait until done. After the job is completed save the job file by exporting it and saving it to the computer.
6) Remove the sample by opening the doors, turning off the vacuum, releasing the sample from the stage and then close the doors.
7) Close any programs used that are no longer in use and clean the station where the samples were prepped or by the computer if needed.

4) Interpreting powder XRD patterns

a) *What features of the powder XRD patterns are important for interpreting the material information encoded?*

   The characteristics of the powder pattern at a certain wavelength in terms of peak position and peak intensity can be used to identify the substance in the sample. A database with powder diffraction files can be used to identify the specific peaks seen.

b) *What information is contained in a powder diffraction file (PDF) and how can you access this information?*

   In the powder diffraction file (PDF) a collected amount of known powder patterns are used for identification of certain sample substances. This file is provided by the International Centre of Diffraction Data and UCI offers full access to download the files.

c) *What peaks might you observe in your XRD data that are not indicative of the structure/chemistry of your sample?*

   Peaks that are not related to the structure or chemistry of the sample can occur due to the presence of the background plate which will show as background noise or as an error due to the placement of the sample being misaligned shifting the peaks forwards or back off the reference pattern.

d) *What are the common sources of error in an XRD experiment?*

   Some common sources of error within an XRD experiment are from sample displacement, axial divergence, flat specimen error, poor counting statistics and sample transparency error. Sample displacement occurs when the sample is not in the correct place - not on the focusing circle. Axial divergence is related to the x-ray beam in plane with the sample and can be minimized with the primary and secondary optics. A flat specimen error and poor counting statistics are from not prepping the sample correctly. And finally, the sample transparency error is from the diffraction beam being partially displaced causing a shift in the peaks.