

Introduction to X-ray Powder Diffraction. Texas A & M University.

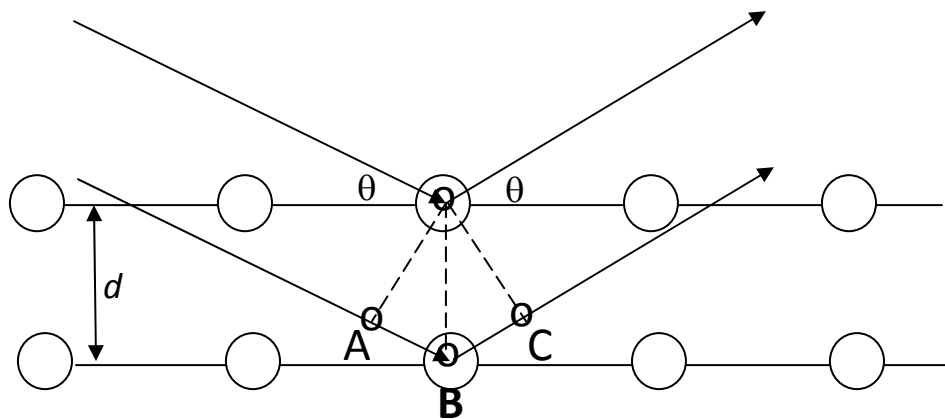
What can I use it for?

- Qualitative Identification of crystalline materials
- Quantitative determination of mixtures of crystalline materials.
- Determination of Crystalline Structure.
- Structural Analysis of crystalline materials (Stress, Strain etc.)
- Determination of Crystallite Size (not particle)
- Percent Crystallinity Determination.
- Thin film measurements.

The Basics of X-ray Powder Diffraction. A minimal-mathematical course

What is diffraction?

Diffraction arises due to the manner that waves propagate in space. Two sets of wavelets generated by point sources will interfere constructively if those two waves are in phase. If those two point sources are atoms (electrons) and the distance between them is d then the angle that the waves will constructively interfere is **theta**. It can then be shown that the wavelength (of the wave) will equal $2 \times d \sin \theta$ [$\lambda = 2d \sin \theta$] which is known as **Bragg's Law**.



$$AB = d \sin \theta \quad BC = d \sin \theta$$

$$\lambda = AB + BC = d \sin \theta + d \sin \theta$$

$$\lambda = 2d \sin \theta$$

Figure 1. Schematic of the mathematical derivation of Bragg's Law.

Notice for diffraction to occur that atoms must be aligned in long range orderly arrays. Materials composed of atoms (and therefore molecules) that have internal long range order are called **crystals**. Many materials are crystalline or polycrystalline (table salt, sugar, steel etc.) however it is possible to have materials with a full range of crystallinity, from perfect order to none. Materials with no long range order are **amorphous**. Amorphous materials will scatter X-rays (as does liquids and gases), but distinct patterns arising from conditions that fulfill Bragg's Law will not arise in the experimental results.

X-ray Diffraction Instrumentation.

X-ray Diffraction is a basically simple procedure based on a very complex mathematics. The

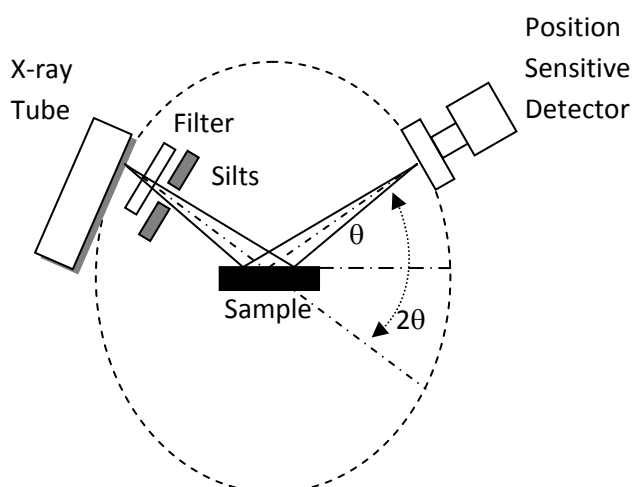


Figure 2. Schematic view of a Bragg-Brentano X-ray Powder Diffractometer.

experimental apparatus is shown in Figure 2. It consists of an X-ray Tube, a filter, slits, a sample and a detector.

X-rays are generated at the home laboratory, by the collision of electrons with a specific target metal in an **X-ray Tube**. As the electrons collide with the metal atoms they ionize the metal. The empty metal orbital "shells" that are created are immediately filled by electrons from the upper metallic orbitals which results in the production of photons of electromagnetic radiation.

Very low lying orbitals produce very high energetic photons of a singular wavelength. For all metals this wavelength is in the X-ray region of the electromagnetic spectrum and because each orbital is fixed (quantized) the wavelength produced by that orbital is monochromatic.

The apparatus to produce X-rays is thus quite simple (see Figure 3). Build a device that will produce electrons (a filament) and place a metal target in close proximity to it. Enclose both the filament and the target in a vacuum chamber and pump out all of the air. When a good vacuum has been obtained then apply a large voltage potential between the filament (cathode) and the target (anode) so that electrons will jump the distance between the two and collide with the metal. The X-rays that are produced can exit the vacuum chamber through windows built from low absorption materials (e.g. Beryllium). Finally since the collision of electrons with a metal will produce heat, a good heat dissipation method (i.e. circulated chilled water) is needed to keep the metal from melting.

The most intense X-rays that are produced by this method are from the transition of the inner most electrons in the metal and are named the K-alpha X-rays. The target metal is thus chosen to produce a particular wavelength of radiation desired. For example Copper metal will produce K-alpha radiation of 1.54\AA (1.5×10^{-10} meters). Other X-ray wavelengths are also produced in the collision, but they are much weaker than the K-alpha and they can be “filtered off” by passing the X-rays through a thin metal foil (**filter**) that will absorb all X-ray radiation except for the K-alpha X-rays. The foil is made from a metal that is just before the target metal in the periodic table, thus for Copper radiation a Nickel foil can be used for a filter.

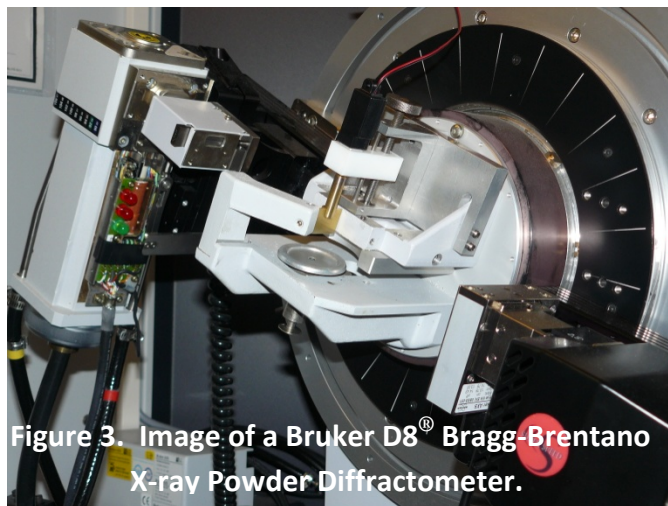


Figure 3. Image of a Bruker D8[®] Bragg-Brentano X-ray Powder Diffractometer.

Since the X-rays are diverging from the source it is a good idea to block most of the radiation from reaching the sample. We want to only illuminate the sample area and not the surrounding instrument and sample holder. To block unwanted radiation the sample is passed through **slits**. The slits are narrow 0.1 to 5 mm and only a fine narrow diverging beam of X-rays is allowed to pass to the sample. Normally these slits are kept fixed at 1 to 2 mm, which is optimum for most experiments; however if low angle data is only required slits smaller than 0.5mm are preferred (at the expense of lower X-ray flux reaching the sample).

The **sample** is held in a flat holder that can rotate normal to the sample in the plane of instrument, that is the axis of rotation is normal to the diffraction vector (the imaginary line that is normal to the plane of the sample). The angle of this rotation is called theta (θ) and is used to measure the diffraction angle (see Bragg's Law above). Theta is measured from a vector that is parallel to the plane of the sample and the plane of the **detector**.

The **detector** is mounted on a swing arm that can be moved around an axis that is normal to the diffraction axis. The angle of the rotation is measured in increments of twice theta or two-theta (2θ). The **detector** is an electronic device for counting X-ray photons and is connected to a computer which records the counts and controls the diffractometer.

The instrument diagramed in Figure two and three is known as a *Bragg-Brentano* para-focusing X-ray diffractometer. The para-focusing describes the method that the divergent X-ray from the source irradiates a flat specimen of width larger than the width of the divergent X-ray beam (at the sample). The X-rays are then diffracted (at the angle 2θ from the divergent beam)

towards the detector. Because of the geometry (see Figure 1) the diffracted X-ray beam will now converge at the detector. This results in a high intensity diffracted X-ray beam and a diffracted X-ray pattern of high resolution (see Figure 5). As long as the sample and detector are locked in a θ (sample) : 2θ (detector) geometry the requirement for para-focusing is met.

Sample Preparations

Preparation of your sample before the X-ray Diffraction experiment is the most important step that the average user makes in the production of a high quality powder pattern. An ideal sample contains a very large number of randomly oriented particles (crystallites) of size less than 10 microns. The sample is mounted in such a manner as to display no preferred orientation of the particles.

Step one, grinding your sample.

It is important to reduce the particle size of your powder to at least 30 to 40 microns. This normally involves crushing and grinding your sample in a mortar with a pestle. Place about a gram of your material in the mortar and with the pestle press down until all of the powder is crushed. Now begin to grind the powder by tracing small circles with the pestle pressed against the mortar starting from the center and working outward. Slowly work your way to the edge of the mortar then return to the center and start again. Repeat this procedure for about 15 mins. In general the better you grind your material the better your results will be. Be careful and do not over grind the material (hard to do by hand, easy to do with a machine). When finished move the powder to a weigh boat (or paper). You are now ready to pack the powder into the sample holder.

Step two, packing the powder into the sample holder.

Choose a top loading sample holder with a well deep enough to hold most of the powder, but not too deep as to leave room for more powder. For small samples (<100mg) a zero background holder may be necessary. For samples between 100mg and 1 gram a shallow "divoted" holder made from quartz glass can be used. For samples over 1 gram a stainless steel medium depth well holder is ok.

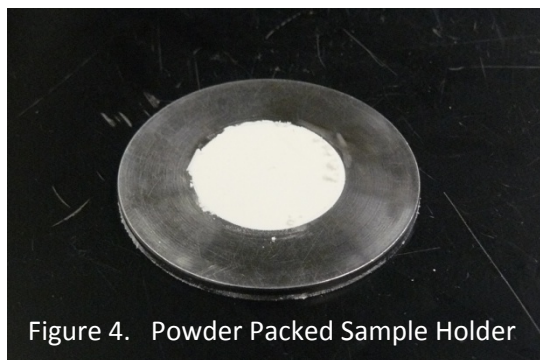


Figure 4. Powder Packed Sample Holder

Whatever holder you choose you must take care that the top of the sample is flat and level with the top of the sample holder. To do this, add the powder to the sample holder well until it spills over onto the top. With a clean glass slide, gently press the sample into the well until the glass slide touches the top of the sample holder. If there is a gap

between the slide and the powder surface, add more powder. If there are gaps in the powder coverage of the well add powder in those gaps and repeat the press.

Once you are satisfied that the powder is packed into the well as tight as possible then gently slide the glass toward the edge of the holder while continuing to press the glass against the powder. When you are finished a flat unbroken surface of the powder that is parallel to the top of the holder will be produced. (See Figure 4).

You are now ready to place the sample holder on the instrument and begin your data collection. To learn how to collect data see the next handout in this series.

Bruker_D8_tutoriall.pdf. With any luck you will produce a powder pattern similar to the one

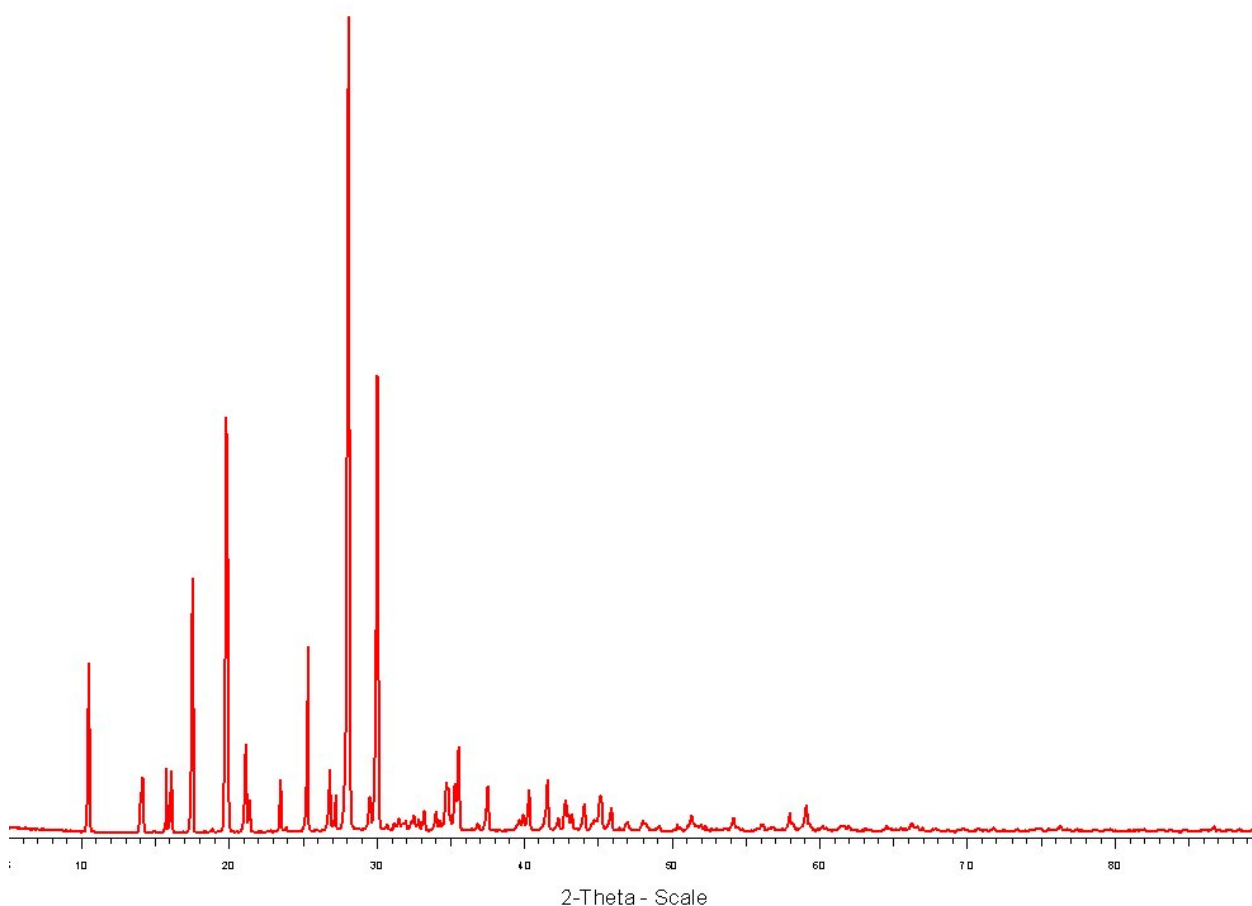


Figure 5. Powder Pattern of Ascorbic Acid.

shown in Figure 5. For more information see Ian Langford's and Daniel Loüerz's manuscript [Rep. Prog. Phys. 59(1996) pages 131-234]. (*langford_louerz.pdf*)