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

Introduction

Specimen preparation is probably the single most important determinate of the quality of XRD data obtained from a powder sample. To be able to see all of the diffraction peaks, your powder must present a large number of crystallites in a random orientation to the incident beam. How you actually do that will be a function of the purpose of your analysis, the characteristics of the sample you are analyzing, and the time available to achieve that purpose.

It is important to maintain the distinction between *sample* and *specimen*. The sample is the material supplied for analysis. The specimen is the portion of the sample as prepared and presented to the instrument. How that specimen is prepared will determine whether it is representative of the sample as a whole, and if the resultant data is similarly representative.

This section will be concerned with methods of preparing specimens for analysis and systematic data errors associated with sample preparation. Different specimens will produce different kinds of analytical errors, and it is important to understand these errors and how they can be minimized.

Material in this section is derived several sources: Much of what is presented here is from the ICDD short course that the author attended in the Summer of 2002. Chapter 9 from Jenkins and Snyder (1996), "Specimen Preparation" is probably all that is needed for most diffraction work. Buhrke, et. al.'s (1998) volume on "Preparation of Specimens for XRF and XRD Analysis" is very comprehensive and includes a substantial treatment of analytical statistics. Moore and Reynolds' (1997) Chapter 6 is everything you will ever need to know about preparing clay minerals for XRD analysis.

Goals of Specimen Preparation

The goal of specimen preparation is prepare material to be analyzed in a diffraction experiment in a way that makes it possible to answer specific questions about the sample. There is no "standard" way to prepare a specimen for powder diffraction, and the most important consideration is the objective of the experiment. The general rule of specimen preparation is that the time and effort put into it should not be more than is required by the experiment objective.

As will be discussed subsequently, different methods of grinding, sieving and mounting are used depending on the amount of sample available and what data is needed about it. If the work is being done for someone else, it is important the "client" and the analyst have a clear understanding of what can and cannot be done, and the level of effort required. "I need to know what is in this sample" can be a request for a simple identification of phases present, or a complete quantitative analysis. Communication and understanding on both sides are critical here. In many cases it will be up to the analyst to educate the client on what and cannot be done, and at what expense.

The three parameters of special interest in a diffraction pattern are:

- The position of the diffraction peaks
- The peak intensities

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• The intensity distribution as a function of diffraction angle

In many ways, how close these experimental results come to representing the sample in terms of these parameters determine whether the results are useful for phase identification, or for more detailed analyses like crystallite size and distribution, stress and strain analysis or quantitative determination of different phases in a multi-phase sample. How you prepare your sample will depend on the purpose of your analysis.

Specimens and Experimental Errors

Many systematic diffraction errors may be directly related directly to specimen conditions. In the interest of treating all systematic diffractometer errors in one place, several that are not directly related to specimens are also included here. These are listed briefly below and discussed in more detail in this section.

Axial Divergence: Occurs because the X-ray beam diverges out of the plane of the focusing circle.

Flat Specimen Error: Occurs because the surface of the specimen is flat, and does not conform to the curvature of the focusing circle.

Compositional Variations between Sample and Specimen: May be related to grinding, environmental interaction or irradiation effects.

Specimen Displacement: The geometry of the sample mount causes a positional deviation on the focusing circle.

Specimen Transparency: Penetration of the beam into a "thick" specimen changes the location in which diffraction occurs.

Specimen Thickness: Thin specimens tend to produce accurate peak positions; thicker specimens tend to produce more accurate peak intensities.

Particle Inhomogeneity: Inhomogenities in particles can significantly alter diffraction intensities and peaks seen.

Preferred Orientation: Non-random orientation of crystallites can produce large variations in intensity and limit the peaks seen.

Axial Divergence

X-ray beams are, like light beams, divergent. The typical x-ray source is a horizontal line



parallel to the specimen surface. The divergence slit (D5 at left) limits the width of the beam in the plane of the specimen. The receiving slit (RS) and scatter slit (SS) do the same

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Figure 7-10

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for the diffracted beam. The soller slits (SS1 and SS2) are closely spaced parallel "blades" (usually molybdenum) designed to limit divergence in the plane perpendicular to the specimen.







divergence error occurs as shown at left. The detector "sees" signal from an arc of the Debye diffraction ring, not just an arc along the diffractometer circle. The effect a notable peak asymmetry that is most pronounced at low 2θ . This asymmetry is illustrated in Figure 7.14 (Jenkins and Snyder, 1996) with data from silver behenate.

The axial

In modern diffractometers, the combination of closely spaced soller slits on the diffracted beam and the crystal monochromator can almost eliminate axial divergence errors. This is done at the cost of decreased intensity.

Figure 7.14. The typical asymmetric diffraction profiles due primarily to the axial divergence distortion in a sample of silver behenate.

Flat Specimen Error

For diffraction to be geometrically correct, the sample should be curved and lie on focusing circle. In practical terms, this is very difficult to achieve, so flat mounts are used for specimens. This results in the flat-specimen error as illustrated in the diagram below. The specimen is tangent to the focusing circle (r_f) . The extreme edges of the specimen lie on

(prepared by James R. Connolly, for EPS400-002, Introduction to X-Ray Powder Diffraction, Spring 2005) another focusing circle (r'_f) which results in the overall diffracted intensity being skewed to



a lower value of 2θ .

Because of the distortion of the focusing circle, the decrease in 2θ takes the form of an asymmetric peak broadening towards lower angles.

The effect is most pronounced at lower 2θ angles where the beam hits more of the specimen. Reducing the width of specimen that is exposed to the incident beam can control the magnitude of the flat specimen error. This is usually accomplished by narrowing the beam by reducing the width of the beam by use of smaller divergence slits.

The flat specimen error is expressed by the

$$\Delta 2\theta = -\frac{\alpha^2 \cot \theta}{343.8}$$

where α is the angular aperture of the divergence slit in degrees. The table below lists the maximum irradiation lengths for different values of α and different anodes. These values are for a particular size diffractometer circle size, but give a reasonable idea of the effect of changing the divergence slit size. Since the radius of the focusing circle decreases with increasing 2 θ , the flat specimen error increases with 2 θ . In practical terms, however, this increase in error offset by the reduction in irradiation length at higher θ angles. In general, for most diffraction work in which low-angle (under 8° 2 θ) data is not required, a divergence slit angle of 0.50° provides a reasonable compromise between intensity and minimizing flat specimen error.

Div Slit	$2\theta_{min}$	МоКа	CuKa	CrKa
0.25°	4.6°	8.86	19.24	28.58
0.50°	9.2°	4.45	5.61	14.35
1.00°	18.4°	2.22	4.83	7.18
2.00°	37.2°	1.11	2.42	3.59
4.00°	78.0°	0.56	1.22	1.81

Maximum Irradiation Lengths (mm) with Various Divergence Slit Apertures and X-ray Wavelengths

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Compositional Variations between Sample and Specimen

These types of errors are related to three general causes:

Grinding Effects: Excessive grinding, principally when highly percussive in nature, can induce changes in your specimen. Some of these changes include induced amorphism, strain, decomposition due to local heating, or loss of volatile components. Special care should be taken when grinding samples that are particularly sensitive to low-temperature damage (i.e., some clays, zeolities, engineered materials). Over-use of ball-mills or shatterboxes can produce a "tail" of extremely fine particles that, in extreme cases, can cause particle-size-related peak broadening. Operation of this type of equipment with insufficient material can result in contamination, particularly when using a brittle grinding medium such as hardened steel or tungsten carbide.

In general, the best remedy is to use non-percussive techniques when grinding of samples to a fine particle size. Non-automated methods including grinding by hand with a mortar and pestle and sieving the resulting powder. Automated methods include use of a micronizing mill or an automated mortar and pestle. Grinding may also be done in a liquid medium (water, alcohol or acetone) to minimize percussive effects.

Irradiation Effects: Some materials react and can change composition in the X-ray beam. These effects can be significant in analysis of organic compound, but are not generally an issue in analysis of inorganics. Some inorganic compounds react to the X-ray beam by a color change or "clouding" but this generally does not interfere with the XRD pattern obtained from the specimen.

Environmental Effects: Virtually all materials will suffer some stress/strain effects as a result of elevated temperature. In most cases the thermal expansion effects are completely reversible; however in some cases the structural changes are retained.

Some materials react with particular liquids, changing the structure of the specimen. Some clay and zeolite minerals are particularly prone to interaction with water or organic liquids. These effects are usually, but not always, reversible upon drying. The environmental reactivity of clays (with water, temperature and ethylene glycol) is utilized systematically in diffraction experiments to determine the structure of these minerals.

Specimen Displacement

Specimen displacement can be a significant source of errors in diffraction angles measured with a diffractometer. The geometry of diffraction requires that the specimen lie on the focusing and be at the center of the diffractometer circle (see Fig 7.7 below).

Anything that causes the sample to deviate from this geometry will cause angular errors in the resulting diffraction data. Sample displacement error is quantified by the following equation:

$$\Delta 2\theta = -\frac{114.59s\cos\theta}{R}$$

where s is the displacement of the specimen from the focusing circle (along its radius), R is the radius of the diffractometer circle and $\Delta 2\theta$ is expressed in degrees. If the sample is

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the sample is "low" (s is positive), $\Delta 2\theta$ will be negative (and calculated d-spacing high).

Sample displacement errors can be the result of a deviation from planar geometry of the specimen in its mount. This will occur if the specimen is higher or lower than the sample mount surface, and will produce a systematic error. It can also be

related to improper alignment of the diffractometer. As is shown by the cosine function, this error will be more pronounced at lower 2θ angles.

It is difficult to prepare a specimen which is precisely flat and uniform. For this reason specimen displacement is a significant cause of angular diffraction errors. At low angles, it will cause asymmetric broadening of the profile toward low 2θ values, and can produce about 0.01° of angular error for each 15 µm of displacement.

Specimen Transparency

Specimen transparency errors are related to the effective depth of penetration of the X-ray beam. The effect is illustrated below.



The transparency error for a thick specimen (thicker than penetration of the beam) may be defined mathematically as follows:

$$\Delta 2\theta = \frac{\sin 2\theta}{2\mu R}$$

where μ is the linear attenuation coefficient for the x-ray wavelength, R is the radius of the diffractometer circle and $\Delta 2\theta$ is in

radians.

The "working thickness" of your specimen, $t_{0.5}$, is defined by beam penetration depth:

$$t_{0.5} = \frac{1}{\mu}$$

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where μ is the linear absorption (also called linear attenuation) coefficient for your specimen. $t_{0.5}$ is the average depth in your specimen from which the diffractions are generated. The mass absorption coefficient, μ/ρ , is tabulated for different elements and is dependent on the x-ray wavelength. For SiO₂ and CuK α , $\mu = 97.6$ /cm, or approximately 100/cm. $t_{0.5}$ thus is about 0.01 cm or 100 μ m. For high-density, high μ/ρ materials (metals, alloys), $t_{0.5}$ will be on the order of 10 μ m. For low-density organics, $t_{0.5}$ will be on the order of 1,000 μ m, and a thick sample will induce very significant displacement errors. For this reason, organics are usually mounted as thin films on a zero-background plate.

It should be noted that for powders which are not tightly packed, because μ will be a function of both the sample density and the air in the pore spaces, the actual displacement error will be greater than that estimated for a powder having the density of the solid material.

Specimen Thickness

From the previous discussion of displacement errors and an understanding of the geometry of diffraction, it is obvious that the most accurate data on peak position will be obtained from a thin sample. For this reason, simple mounts of a thin layer of powder on a glass slide or adhering to double-stick tape in a well-aligned diffractometer will yield accurate peak positions. As will be discussed later, these mounting methods tend to accentuate preferred orientation in most materials, so intensity information will not usually be very accurate.

A thick sample with a random orientation of crystallites will produce less accurate peak positions because of absorption/displacement effects, but can produce good intensity data. Exactly how good that intensity data is will be is dependent on the crystallite size and randomness of orientation as will be discussed later.

Particle Inhomogeneity

Many multi-phase samples are inhomogeneous in character. An example would be an ore



Figure 9.2. Effect of particle heterogeneity on X-ray intensity.

deposit consisting partially oxidized chalcopyrite (CuFeS₂) ore, illustrated schematically in Figure 9.2 (Jenkins and Snyder, 1996). This would consist of unaltered particles of ore (A), partially oxidized particles of ore (B – rimmed by CuFe₂O₃) and particles of CuFe₂O₃ (**C**). These two minerals have different mass absorption coefficients and as a consequence of

their inhomogeneous distribution in the specimen, their diffraction intensities will not accurately reflect their proportions in the sample.

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Preferred Orientation

Preferred orientation is usually the most important single cause of intensity variations in a diffraction pattern. For crystals that exhibit anisotropic shapes (or habits), there will be a tendency for the powder to develop a non-random orientation which will significantly affect the diffracted intensities from the specimen. The figure below (from Jenkins and Snyder, 1996) schematically shows the effect of preferred orientation when using the powder camera



(a) Randomly oriented specimen



(b) Specimen exhibiting preferred orientation



Figure 9.4. Random and preferred orientation.

and diffractometer.

What occurs as a consequence of preferred orientation is that the lattice planes which are oriented in the plane of the sample produce a very strong Debye ring (i.e., diffraction cone), and the planes which are in unfavorable orientations produce diffraction lines in the direction of the cones resulting in "spotty" diffraction lines in the film. The diffractometer essentially views a very narrow part of the Debye ring (much less than a powder camera film) and unfavorably oriented peaks will be severely attenuated and in many

severely attenuated and, in many cases, not seen at all.

Figure 9.4 at left (Jenkins and Snyder, 1996) schematically shows a Debye ring from one reflection from a randomly oriented specimen (a) and one with preferred orientation (b) intersecting the receiving slit of the diffractometer.

The diffracted intensity is constant around the ring with the random orientation, and very inconsistent or spotty with the preferred orientation. It is clear that the peak intensity specimen (a) will be significantly greater than that from the specimen (b).

The type of preferred orientation will depend on the crystal habit. Clay minerals have a platy habit and will orient perpendicular to (001). Others are equant cubes (NaCl), bladed (most pyroxenes

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and amphiboles) or fibrous (most asbestos minerals and some zeolites). Specialized diffractometers can be used to deal with structural analysis of some of these particular habits, but this is beyond the financial ability of most laboratories.

In laboratories such as ours in which we have a "one-size-fits-all" diffractometer, we must rely on specialized methods and tricks to force strongly dimensional materials into a (more or less) random orientation. Some of these methods will be discussed in later sections.

Severe preferred orientation in a specimen will result in "invisible" diffraction peaks, but in the majority of specimens where preferred orientation is mild to moderate, all of the diffraction peaks will be seen but their intensities will differ from that of a truly randomly oriented specimen.

Particle Statistics

Quantitative (and semi-quantitative) X-ray powder diffraction is based on the principle that quantities are proportional to intensity. Accurate intensities require:

- Random orientation of crystallites in the specimen
- Sufficient number of particles for good crystallite statistics

Powders are composed of particles. The particles may be aggregates of crystallites, single crystals, growth aggregates with a variety of boundaries, or random crystalline mosaics. Particle statistics is primarily concerned with how many particles are necessary for randomness.

We generally treat particle size as the "worst case" condition where each particle is a single crystal. While this is overwhelmingly true for synthesized or engineered powders, it is rarely true in finely crystalline rocks in which the particles are commonly random crystalline mosaics. The presence of these mosaics of fine crystallites will generally significantly improve the particle statistics.



Randomness may be described in terms of vectors representing all Bragg diffractions projected on a sphere (Figure at left). In a truly random specimen the distribution will be random on the sphere. In a specimen with preferred orientation, a non-random distribution will be seen on the sphere.

To get an idea of what particle sizes we need, we need

to know the area of the beam and volume of specimen that will diffract in the beam. Assume we are analyzing powdered quartz (SiO₂). First we calculate the volume:

- Volume = (area of beam) x (2x half-depth of penetration)
- Assume area = $1 \text{ cm x } 1 \text{ cm} = 100 \text{ mm}^2$
- $t_{\frac{1}{2}} = 1/\mu$, where $\mu =$ linera absorption coefficient
- $\mu_{SiO2} = 97.6 \text{ cm}^{-1} \text{ or } 100 \text{ cm}^{-1} = 10 \text{ mm}^{-1}$
- $V = (100) (2) (10^{-1}) \text{ mm}^3$

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• Volume = 20 mm^3

Particle Diameter \rightarrow	40 µm	10 µm	1 μm
V/particle	$3.35 \text{ x } 10^{-5} \text{ mm}^3$	5.24 x 10 ⁻⁷	5.24 x 10 ⁻¹⁰
Particles/mm ³	2.98×10^4	1.91 x 10 ⁶	1.91 x 10 ⁹
Particles in 20 mm ³	5.97×10^5	3.82×10^7	3.82×10^{10}

Next we estimate the number of particles in our volume at different particle sizes:

Analyzing the particle distribution on a unit sphere (area = 4π steradians) yields a radiating sheaf of pole vectors. This yields the following:

Particle Diameter \rightarrow	40 μm	10 µm	1 μm
Area/pole, AP = $4\pi/\#$ particles	2.11 x 10 ⁻⁵	3.27 x 10 ⁻⁷	6.58 x 10 ⁻¹⁰
Angle between poles, α = $\sin^{-1}(2\sqrt{A_P/\pi})$ =	0.297°	0.037°	0.005°

The figure below shows the geometry of diffraction of a single particle.



Effect of soller slit is to limit length of source visible to the target

L = 0.5 mm

R is the range of the diffractometer radius, F the focal length of the anode (a characteristic of the x-ray tube), and α the angular divergence as shown. In the above example, L (= 0.5 mm) is the length of source visible to the target.

 N_p = number of particles which may diffract

= (area on unit sphere corresponding to divergence) / (area on unit sphere per particle)

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 $= A_D/A_P$

To determine A_D requires relating effective source area, FxL, to area on a unit sphere:

$$A_D = \frac{FL}{R} = \frac{(0.1)(0.5)}{200}$$
$$= 2.5 \times 10^{-4}$$

Calculating A_D/A_P yields the number of particles diffracting in any given unit area for our three particle sizes:

Particle Diameter \rightarrow	40 µm	10 µm	1 µm
N_P	12	760	38,000

The Bottom Line: The standard uncertainty in Poisson statistics is proportional to $n^{\frac{1}{2}}$, where n is the number of particles. To achieve a relative error of < 1%, we need 2.3 σ = 2.3 $n^{\frac{1}{2}}/n$ < 1%. This would require n > 52, 900 particles. What is clear from this extensive and occasionally confusing derivation is that easily achievable particle sizes are totally inadequate for truly random orientation. Thus not even 1 µm particles will succeed in achieving ±1% accuracy in intensity.

Several other factors will contribute to either improve or degrade these numbers:

- **Concentration:** mixed phase specimens reduce particles of a given phase in a unit area, thus increasing error
- **Reflection multiplicity:** Multiplicity in higher symmetry crystal structures give more diffraction per unit cell, improving statistics
- **Specimen thickness:** improves diffraction volume, limited to maximum penetration depth
- **Peak width (crystallite size):** uniform crystallites of smaller size than particle size can greatly improve statistics as long as crystallite orientation is random. Extremely small size, however, will result in peak broadening which will make areas under intensity curves non-proportional to amounts of the phase in the specimen.
- **Specimen rotation/rocking:** helps to get more particles in the beam. Rocking combined with rotation is best.

The conclusion here is that to expect accurate and repeatable intensity measurements from powder samples that can be used for quantitative analysis is not a reasonable expectation. The statistics of particle size distribution in powder diffraction alone make this impossible for anything except a uniformly sized powder with crystallite size under 1 μ m, and other factors related to consistency of packing and the presence of multiple phases make it unlikely that multiple runs from the same material will agree within in a margin of ± several percent. Careful specimen preparation can reduce these errors somewhat, but will never eliminate them.

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Sample Preparation Methods

Most of the equipment below requires specific instructions in its use. There are written procedures for the use of the Jaw Crusher, the Spex Shatterbox and the Retch-Brinkman Mill. These are mentioned below and links to them will be included on the XRD Lab web pages. Other equipment is part of the Analytical Geochemistry Laboratory in E&PS and Dr. Abdul Mehdi-Ali should be contacted regarding use.

From Rock To Specimen

(The equipment below is listed in the approximate order in which you would use it to reduce a sample from a fist-sized hand specimen to a powder suitable for XRD analysis. All of this equipment is available for use in the Department of Earth and Planetary Sciences.)

- Bico Jaw Crusher (Located in Room 110 on first floor): This is a small industrial jaw crusher with hardened steel jaw used to reduce fist-size rock, ore, glass or cement samples to small-pea sized gravel. The hardened steel jaws can add minor contamination to your sample. A separate Acrobat PDF (bico-operation.pdf) document is available describing operation of the Jaw Crusher.
- Plattner Mortar and Pestle (Located in Analytical Geochem Lab, Room 213): This is a small, hardened steel piston-cylinder-plate mortar and pestle used with a small sledge to reduce small (under 2 cm) fragments to coarse powder for further processing.
- Spex Shatterbox (Located in Analytical Geochem Lab, Room 213): An automated, percussive powdering device used to reduce coarse powders to fine powders. Excessive use of the shatterbox or using the incorrect amount of powder for the particular container can result in sample damage or hardware damage so it is critical that procedures for use of the equipment be followed strictly.

There are a variety of shatterboxes of different sizes and compositions including hardened steel, tungesten carbide steel, Alumina Ceramic (Al_2O_3), and Zirconia (ZrO_2). The shatterboxes themselves as well as the mechanical "shaking" hardware is very expensive and using them improperly can lead to serious damage.

A separate Acrobat PDF (spex-operation.pdf) document is available describing operation of the shatterbox.

- Spex Ball Mill (Located in Analytical Chem Lab, Room 213): Machine shakes small balls (plastic, hardened steel or tungsten carbide) in a small container to reduce the particle size of a coarse powder.
- Alumina Mortar and Pestle (Available in XRD Lab or Analytical Chem lab): Hand-grinding for small amounts of powder to reduce size or disaggregate. The large or small mortar may be used depending on the amount of sample. Done carefully, this will do minimal damage to a sample and is often sufficient to prepare a powder for quick phase identification. It is not useful for making very fine, uniformly sized powders for higher precision work without extensive sieving using very fine sieves.
- Sieves (Located in Analytical Chem Lab, Room 213): A variety of sieve screens (metal, teflon) are available. The table below lists the maximum particle sizes passed by a particular "mesh" of sieve screen. Theoretically sieves may be used to pass particles as small at 10 µm, however it is exceedingly difficult to actually grind particles that (Material in this document is borrowed from many sources; all original material is ©2005 by James R. Connolly)

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small by any manual means, and the electrostatic interaction between the particles and the sieve material make it all but impossible to actually get particles to pass through a sieve screen that small. Practically speaking, the 325 mesh screen is usually the smallest used on a routine basis, although 400 and 600 mesh screens can be used successfully with a lot of effort.

"Mesh" size of sieve screen	Maximum diameter of particle passed
200	74 µm
325	45 μm
400	38 µm
600	25 μm
1000	10 µm

Retch-Brinkman Automated Mortar and Pestle (Available in Lab): This specialized grinding device is designed to reduce powders to as fine as 1 µm in a non-percussive environment, producing minimal sample strain and damage and a very evenly sized powder without the "fine" tail that can produce peak broadening. This system is used in many XRD labs, including LANL, to produce powders for quantitative analysis. It uses precisely machined agate mortars and pestles, and can grind dry or wet. Wet grinding with alcohol, distilled water or acetone is recommended to minimize strain effects. An Adobe Acrobat PDF (brinkman-operation.pdf) with detailed instructions for the use of this instrument is available.

Sample Mount Methods

There are many different ways of mounting samples for analysis depending on the questions being addressed in your experiment. For rapid determination of accurate peak positions, you will want a thin sample with as much area as possible presented to the beam. For accurate intensities, you will want a thick sample of randomly oriented crystallites. In all cases, you want your specimen to be in the proper position on the diffractometer and focusing circles.

In our lab, your author routinely uses a plastic cavity mount that allows side-loading of powder against a glass slide. This produces a well packed specimen which presents a very flat surface to the beam and the side-loading helps minimize (but does not eliminate) preferred orientation. What works for you will depend on the purpose of your experiment and the nature of your sample. For quick identification of an unknown phase, sprinkling some powder onto double-stick tape on a glass slide may be sufficient. For more precise structural measurements, careful mounting of a large volume of specimen to eliminate preferred orientation may be required. The only hard and fast rule is to do only what you need to do to get the data required by your experiment.

Important note: Run an empty sample holder as a "blank": Although most materials used as sample holders (machined Plexiglas mounts, plastic mounts, deep-well aluminum or

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plastic mounts, glass slides, off-axis quartz plates, etc.) are ostensibly amorphous and do not yield a diffraction pattern, in practice this is rarely the case. For example, the Plexiglas mounts used in our lab yield a well defined amorphous "hump" in the range of 10-20° 20, and the glass petrographic microscope slides used for slurry mounts show a well defined amorphous "hump" in the 20-30° 20 range. Quartz plates cut off-axis should give no diffraction pattern and have very low background, but in practice can contribute small diffraction peaks in some orientations. To fully understand the potential contribution of your sample holder to your data, it is important to *make a diffraction run with your sample holder* (in the orientation in which it will be used for data collection) *without any specimen present* using the run parameters you expect for your actual samples and keep that pattern for reference.

Because of the way our Scintag PAD V system's specimen holder works, any mount that is flat, rectangular, and about 1 inch wide can be used to hold specimens. The best mounts contain machined "wells" or cavities below the planar surface that allows the specimen to be mounted exactly parallel to the planar edge of the mount so that the specimen is exactly tangent to the focusing circle. Below are described some of the different types of specimen mounts available in our lab and how they are used.

• Top-mount (plastic)

These Plexiglas mounts have small wells machined into the top surface of the mount to hold a powdered specimen. The wells vary somewhat in depth (from a fraction of a mm to about 2 mm) and dimension (from 1 x 1.5 cm to almost the full size of the mount) to accommodate different volumes of powder. These are loaded by dropping powder into the well and "leveling" it with a glass slide or other flat-edged tool. *The small-well mounts are best to use for low-volume specimens that are not susceptible to preferred orientation.* Because of the way these mounts are loaded and leveled, preferred orientation will be strong in materials that are susceptible to it.

• Side-Drifted (plastic)

These Plexiglas mounts have a 1 x 2 cm specimen well 1 mm deep machined from one edge of the mount. Samples are loaded by clamping a microscope slide to the top of the mount with a pair of small binder clips then dropping the powder into the cavity formed by the well in the mount and the glass slide. When the well is filled, the clips are removed and the glass slide carefully taken off leaving the side-drifted specimen level with the top of the mount surface. Three of these mounts are available for use in the lab.

• Glass Slides (for slurry mounts made with water, alcohol or acetone)

27 x 34 mm glass microscope slides are available for use as sample mounts in the lab. A slurry mount is made by mixing a quantity of powdered sample with liquid (typically water, alcohol or acetone) in a glass vial, agitating it to produce a suspension, dropping the suspension on a glass slide with an eyedropper and allowing it to dry. The resultant specimen is a thin layer of material that will show strong preferred orientation in materials susceptible to it. This is the preferred method for mounting clay samples where preferred orientation is used as a tool for sample characterization.

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• Double-stick tape mounts (on glass slide or Plexiglas mount)

Double-stick cellophane tape is placed in the center of a glass slide or the back (flat) side of Plexiglas mount and a small amount of fine powder is "dusted" onto the tape. Unlike other methods, the analyzed specimen is not recoverable and the analyzed volume of sample is small and particle statistics will not be very good. The sticky character of tape can reduce preferred orientation in some materials, but this is very dependent on the powder geometry and not quantifiable. In spite of the limitations, this type of mount is extremely quick to prepare and is useful for quick scans for phase identification.

• Zero-background mounts (off-axis quartz plate)

Single-crystal flat machined quartz plates cut with the c-axis at large non-vertical angle to the machined surface should (theoretically) produce no background in a diffractometer. We have several of these (home-made and not perfect) plates available in the lab that may be used for slurry mounts and one with a small ($\sim 1 \times 5$ mm) machined groove cut in the center that can be used for a small amount of powder. We expect to acquire more of both varieties from the Gem Dugout (http://www.gemdugout.com) sometime in Spring, 2005.

• Thin Film Mounts (plastic or aluminum with clay)

These mounts are deep (5-10 mm) U-shaped rectangular wells that are used in combination with Plasticine clay to mount thin-films for analysis that are too small to be placed directly in the sample holder. A small cylinder of clay is formed, placed in the bottom of the mount extending above the top edges then a thin film sample is placed on top and pressed down until the top surface is level with the top edges of the mount. Large thin-film plates (that are not too wide) may be mounted directly in the spring-mount of the diffractometer.

• **Back-packed mounts** are not available in our lab. These mounts have a hollow cavity (similar to the side-pack mounts) that is open to the back of the mount. A piece of facing material (typically a glass slide or thin stiff board) is placed against the top of the mount and the specimen loaded from the back.

Special Methods for Reducing Preferred Orientation

The most pervasive specimen-related effect on the quality of X-ray powder data, particularly as regards intensities of diffraction peaks, is that of preferred orientation. Numerous conventional mount methods attempt to minimize this effect with varying degrees of success. The main difficulty is that for some materials (clays, minerals with very strong cleavages, etc.) the tendency to develop preferred orientation is so strong that it is virtually impossible to eliminate. Two methods discussed below create a non-oriented specimen using different types of aerosol methods. As always, the requirements of your experiment will dictate whether these methods are something you choose to apply.

Aerosol Spray Drying using Clear Acrylic Lacquer

This method, demonstrated at the ICDD Powder Diffraction School, is quick, easy to do (if somewhat unpleasant to the nose since it uses acrylic spray lacquer) and inexpensive.

(Material in this document is borrowed from many sources; all original material is ©2005 by James R. Connolly)

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

Materials required are a large piece of clean plate glass, some clear acrylic spray lacquer (Krylon works well), some clean single edge razor blades, and a well ventilated (but not windy) room. The method does not work very well with a tiny amount of powder, and any powder used will not be recoverable since it will be in a acrylic matrix. General steps are:

- 1. Prepare a quantity of powdered sample using any of the methods described earlier.
- 2. Spread the powder (typically 1-2 grams) on a small area ($\sim 5 \text{ cm}^2$) of the glass plate.
- 3. Shake the acrylic spray lacquer following directions on the can.
- 4. Spray the lacquer obliquely (at ~45° angle) at the powder using short bursts until all of the powder has been blown out of it's original position. The idea hear is to blow the powder into the air in a "mist" of spray lacquer such that the "aerosoled" powder will adhere to the lacquer droplets as they dry and fall back to the glass surface. Short bursts will maximize the interaction of lacquer with the powder while minimizing the volume of lacquer used.
- 5. Allow the lacquer to dry on the glass plate. This will take a few minutes.
- 6. Using a clean single-edged razor blade carefully scrape all of the dried lacquerpowder mix from the glass surface and allow it to dry on the surface another few minutes. .
- 7. Using the razor blade, very gently "chop" (do not grind!) the scraped lacquer-powder mix to make a mountable powder.
- 8. Mount the prepared specimen using any of the sample mounts available following normal procedures. Be gentle to the specimen so that the acrylic spherules are preserved.
- 9. Run the sample in the diffractometer normally.

While the acrylic lacquer should be amorphous, the material is likely to have some background characteristics that will contribute to your pattern. Therefore it is advisable to prepare a lacquer-only specimen and run it as a "blank" so that its background characteristics will be understood.

While this method can virtually eliminate preferred orientation, successful application will depend significantly on the ability of the person who prepares the specimen. This will have a significant effect on the amount of lacquer included in the final specimen. If operator-independent repeatability is an issue, purchase or construction of an aqueous spray-drying system described in the next section may be best solution.

Aqueous Spray Drying in a Heated Chamber

Aqueous spray drying in a heated chamber provides a method of creating a specimen that virtually eliminates preferred orientation in a consistent and repeatable manner. From Steve Hillier's 2002 article: "This method consists of spraying a sample, usually as an aqueous suspension, into a heated chamber where it dries in the form of the spherical spray droplets. The resulting dry product consists of thousands of tiny spherical granules of the sample components. Typically, the average diameter of the granules is about 50 microns. Both the arrangement of any component within the spherical granules and the random way in which

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spherical granules pack together ensure that preferred orientation is eliminated. Spray drying is therefore a method capable of producing truly random powder samples for XRPD."

The spray drying apparatus (as designed, constructed and marketed by Hillier) consists of

- a spray drying oven (3kW) and digital heating controller
- a thermal jacket to insulate the oven
- a modified air brush to spray the sample into the oven
- a heat resistant non-asbestos base stand
- a ream of paper suitable for sample collection

While considerable expense is involved in acquiring (or building) the equipment, it provides a relatively operator-independent system for creation of randomly oriented powders that produce consistent and repeatable diffraction patterns. For discussion of the method and how to acquire a spray drying system see the following references:

- Hillier, Stephen, Spray Drying for X-ray Powder Diffraction Specimen Preparation, Commission on Powder Diffraction, Intl. Union of Crystallographers, Newsletter #27, June 2002.
- Spray Drying information on the web site of the Macaulay Institute: <u>http://www.macaulay.ac.uk/spraydrykit/index.html</u>