chem 5390

Advanced X-ray Analysis

LECTURE 6

Dr. Teresa D. Golden
University of North Texas
Department of Chemistry

Powder XRD

Sample Preparation

Problems with the sample can lead to the largest errors in the diffraction pattern, therefore it is important to be extremely careful with the sample.

Powder XRD

Sample Preparation

Proper sample preparation is essential to getting highly quality XRD data.

Need to achieve three conditions in order to have good data:

-Total randomness of crystallite orientations

-Sufficient number of crystallites to get a representative intensity distribution for the sample

-Sufficient diffraction intensity to meet satisfy counting statistics

Sample Preparation

There are many different types of samples:

- **Rock material**
- **Powder material**
- **Single Crystal**
- **Metal**
- **Liquids**

Sample Preparation

Several problems can arise during sample preparation and running of the experiment:

Grinding - cause amorphism, strain, decomposition, side reactions, contamination.

Irradiation - polymerization, decomposition, amorphism.

Special techniques - loss of water in vacuum, high temperature decomposition.

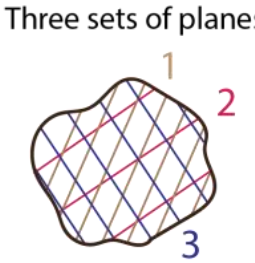
Sample Preparation

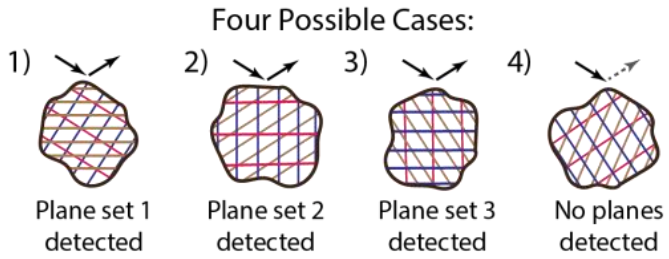
Grinding - cause amorphism, strain, decomposition, side reactions, contamination.

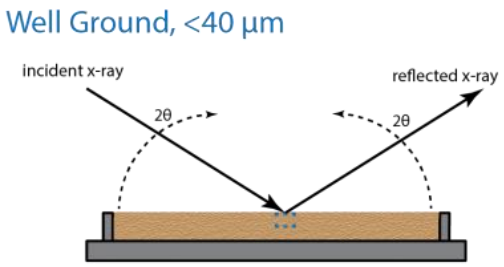
Also particle size is inversely related to both the degree of randomness of the crystallites and the measured intensity.

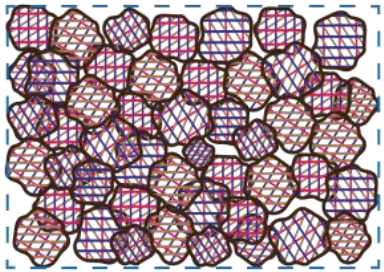
Sample Preparation

Grinding - The figure below illustrates this relationship for a single phase sample prepared correctly and poorly.

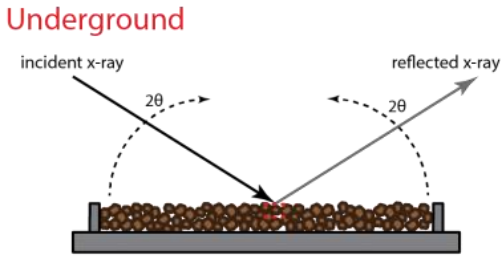


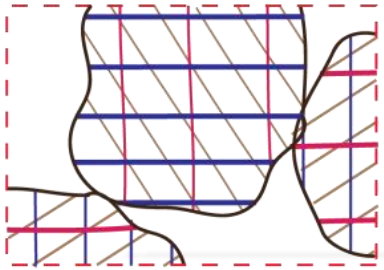






- All plane sets dectected
- Enough crystallites to get accurate intensity ratios
- Enough crystallites to get a good signal





- Not all plane sets dectected
- Not enough crystallites to get accurate intensity ratios
- Not enough crystallites to get a good signal

Sample Preparation

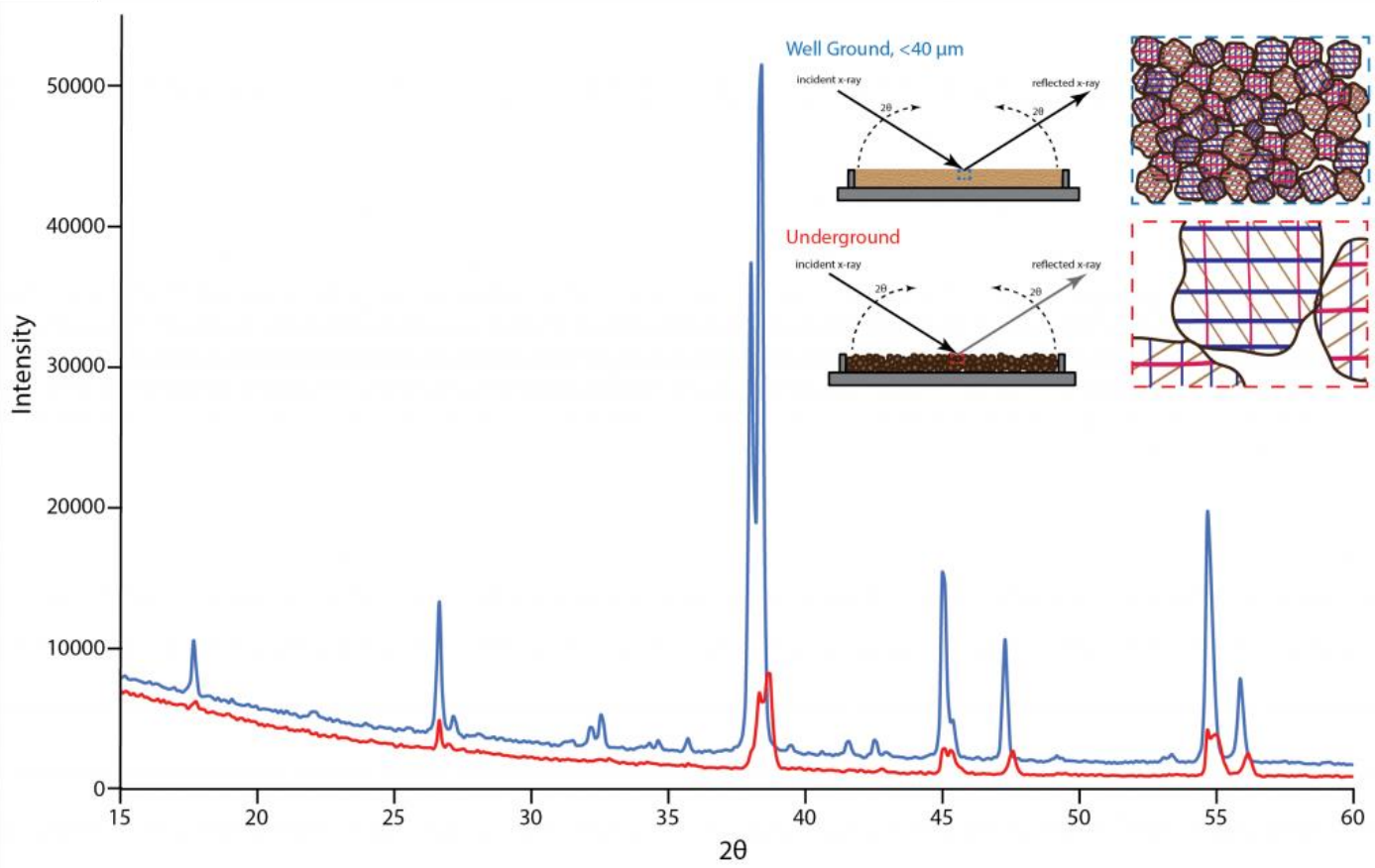
Grinding - The figure below illustrates this relationship for a single phase sample prepared correctly and poorly.

Well ground samples resemble the texture of flour such that if you were to rub the sample between your fingers you would not be able to feel the individual grains.

An under ground sample you would be able to distinguish individual grain not only by feel but sight as well.

Sample Preparation

The resulting diffraction patterns of the two samples are shown below.



Sample Preparation

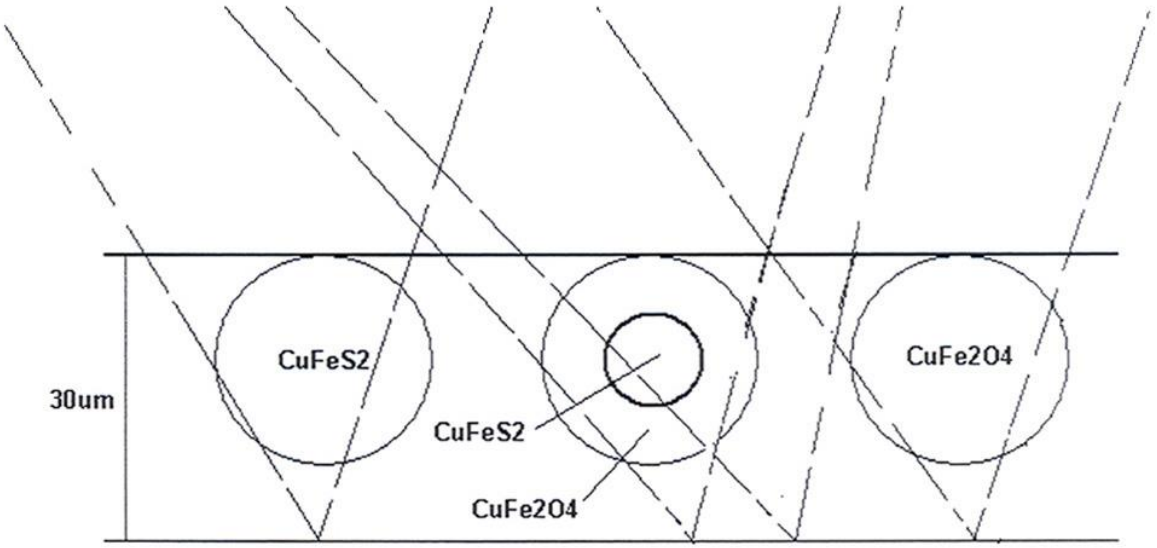
As mentioned before, even the sample thickness and μ/ρ, mass-attenuation coefficient, affect the resulting x-ray diffraction pattern.

Since the x-ray beam penetration depth is small in many samples, problems can occur when the individual particles are large relative to x-ray beam depth.

Sample Preparation

Example: Chalcopyrite ($CuFeS_2$) - mining ore

Can oxidize in air, if the average particle size is 20 μm and x-ray beam depth is 30 μm, μ/ρ of $CuFeS_2$ = 143.2 and μ/ρ for $CuFe_2O_4$ is 116.1 for Cu Kα radiation. The measured x-ray pattern will be different for each particle - <u>inhomogeneity effect</u>.



Sample Preparation

Shown are 10 fractions of a powder with each run on a diffractometer.

Table 9.4. Intensity Measurement on Different-size Fractions of < 325 Mesh Quartz Powder

Specimen No.	15–50 μm	5–50 μm	5–15 μm	< 5 μm
1	7,612	8,688	10,841	11,055
2	8,373	9,040	11,336	11,040
3	8,255	10,232	11,046	11,386
4	9,333	9,333	11,597	11,212
5	4,823	8,530	11,541	11,460
6	11,123	8,617	11,336	11,260
7	11,051	11,598	11,686	11,241
8	5,773	7,818	11,288	11,428
9	8,527	8,021	11,126	11,406
10	10,255	10,190	10,878	11,444
Mean area	8,513	9,227	11,268	11,293
Mean deviation	1,545	929	236	132
Mean % deviation	18.2	10.1	2.1	1.2

Source: Data from Alexander and Klug [6].

Sample Preparation

Notice that at small particle size ~5μm, the relative standard deviation is only a few %, but statistical error increases as particle size exceeds 10 μm.

Table 9.4. Intensity Measurement on Different-size Fractions of < 325 Mesh Quartz Powder

Specimen No.	15–50 μm	5–50 μm	5–15 μm	< 5 μm
1	7,612	8,688	10,841	11,055
2	8,373	9,040	11,336	11,040
3	8,255	10,232	11,046	11,386
4	9,333	9,333	11,597	11,212
5	4,823	8,530	11,541	11,460
6	11,123	8,617	11,336	11,260
7	11,051	11,598	11,686	11,241
8	5,773	7,818	11,288	11,428
9	8,527	8,021	11,126	11,406
10	10,255	10,190	10,878	11,444
Mean area	8,513	9,227	11,268	11,293
Mean deviation	1,545	929	236	132
Mean % deviation	18.2	10.1	2.1	1.2

Source: Data from Alexander and Klug [6].

Sample Preparation

The best way to reduce this particle size effect is to grind the sample.

Pitfalls to avoid when grinding:

- careful not to decompose the sample

- Not to grind soft materials until the crystallinity is destroyed

- If sample is a mixture, not to let the harder component grind the softer material and destroy crystallinity.

Sample Preparation

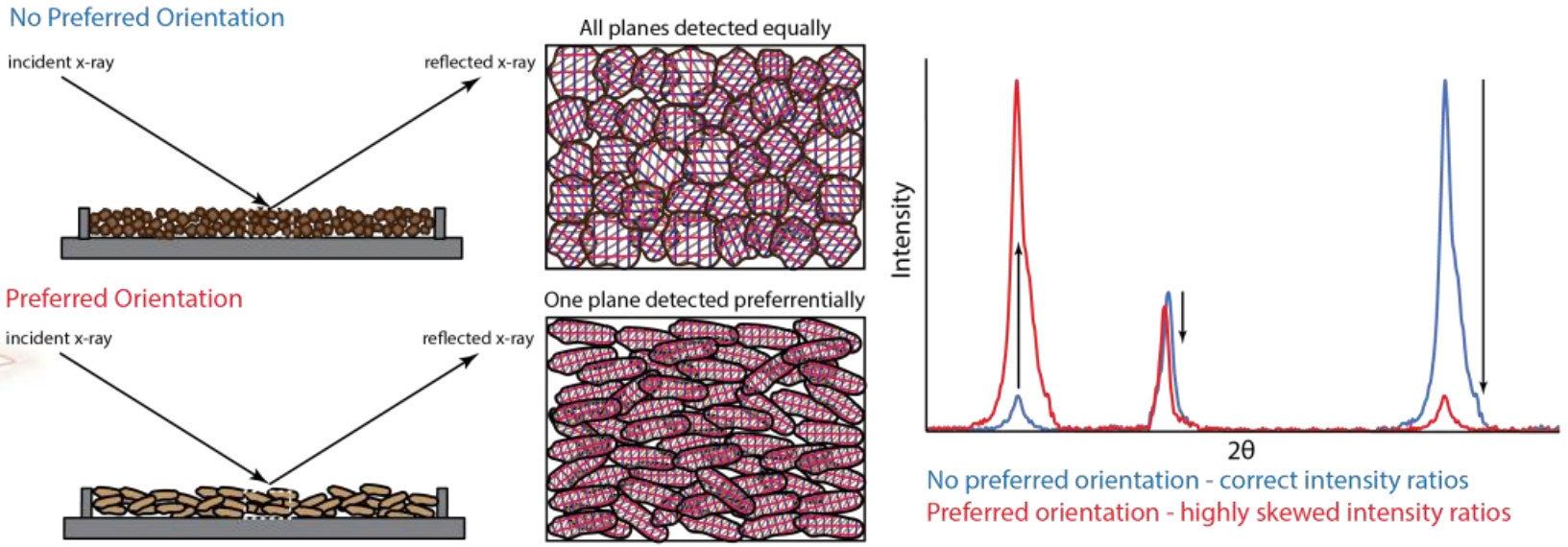
Preferred Orientation

Preferred orientation occurs the samples crystallites are not randomly orientated.

Samples that are fibrous or plate-like (ex. Clays) will orientate in a preferred direction due to their shape, causing some lattice planes to be detected more than others and therefore skewing the intensity ratios.

Sample Preparation

Preferred Orientation



Sample Preparation

The best way to reduce this particle size effect is to grind the sample.

Quartz in different particle diameter in a conventional Bragg-Brentano diffractometer

Particle diameter	**40 µm**	**10 µm**	**1 µm**
Diffracting particles	**12**	**760**	**38,000**

To achieve a standard uncertainty of < 1%, > 52900 particles would be needed.

Sample Preparation

Quartz in different particle diameter in a conventional Bragg-Brentano diffractometer

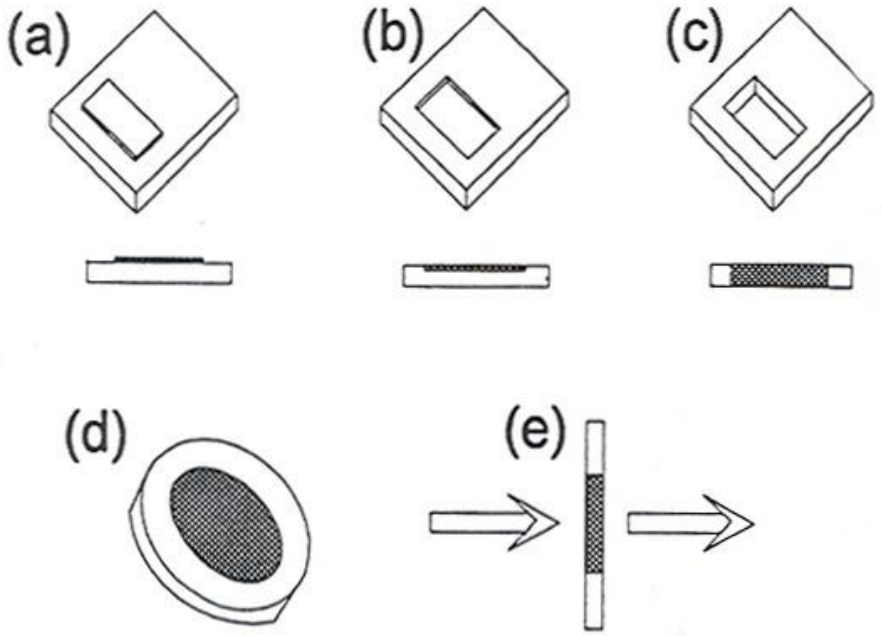
Particle size fraction /microns	15-50	5-50	5-15	<5
Standard deviation of I quartz$_{101}$ /%	18.2	10.1	2.1	1.2

-If we want to measure single peak intensities of minerals correctly, we should try to mill any samples to < 5 µm.

-This is necessary to get reliable results of Rietveld structure analysis, too.

Sample Preparation

1. Sample Holders

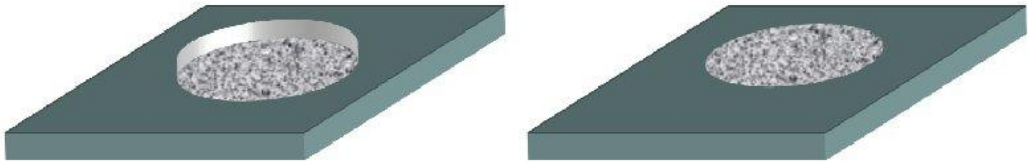


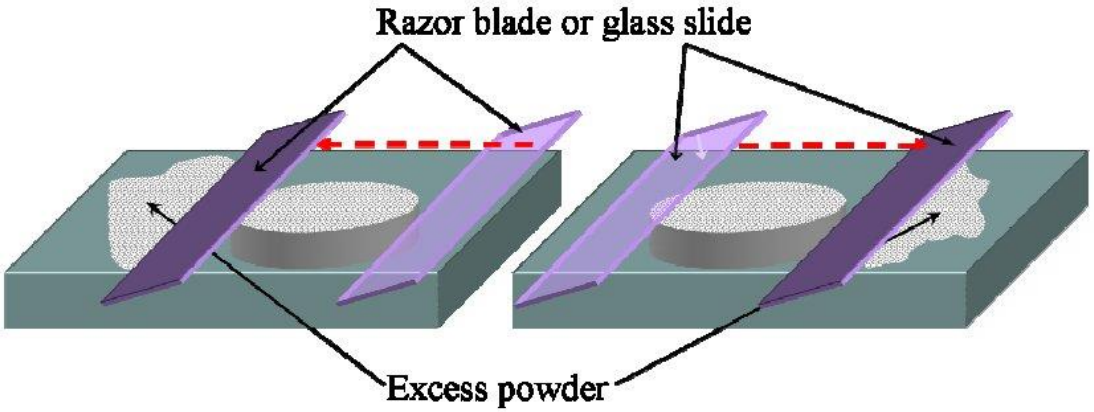
(a) Zero-background, (b) top-loaded, (c) back-loaded, (d) circular, (e) press mounts

Sample Preparation

1. Sample Holders

Top or Front Loading





Sample Preparation

1. Sample Holders

Top or Front Loading

Advantage - easy preparation.

Disadvantage - may have preferred orientation.

Sample Preparation

1. Sample Holders

   Back Loading

   Use a holder with a rectangular hole punched through it.

   Attach a microscope slide to one side.

   Turn holder over and load powder into cavity.

   Place a cover over the powder surface and turn back over.

   Remove glass slide.

Sample Preparation

1. Sample Holders

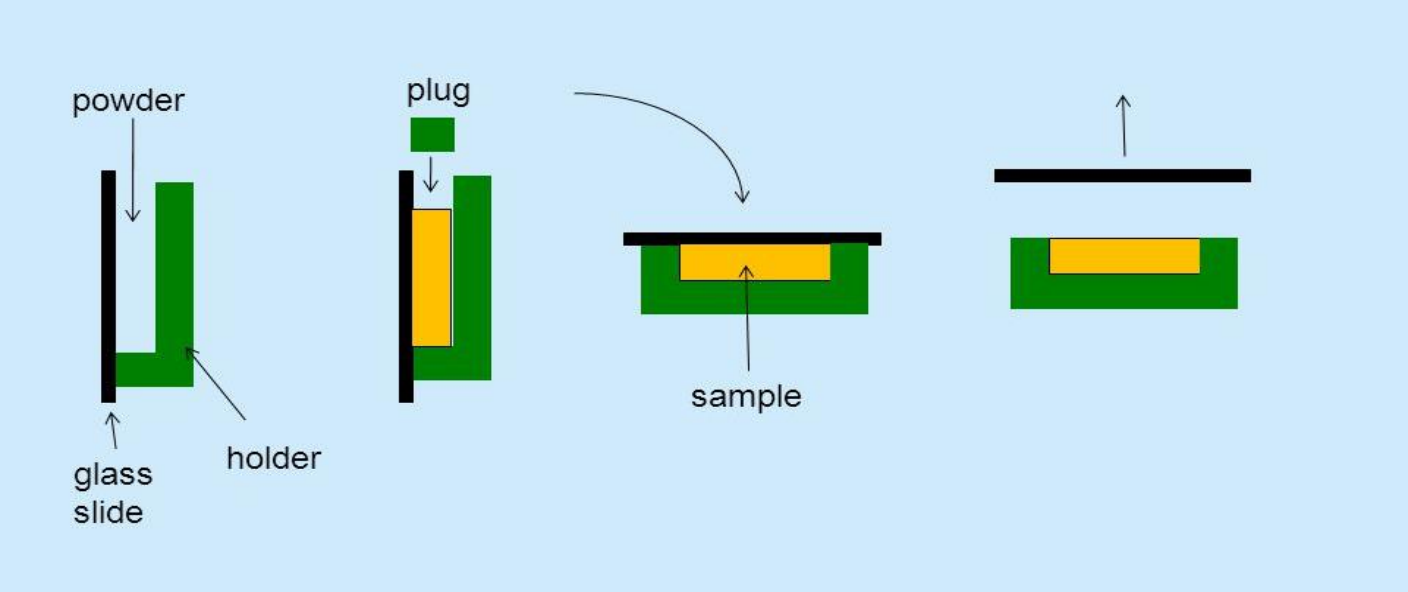
Back Loading

Advantage - gives a nice even surface.

Disadvantage - strongly enhances the (0k0) reflections of platelike materials.

Sample Preparation

Side Loading



Sample Preparation

1. Sample Holders

Side Loading

Advantage - better packing method, gives true peak intensities.

Disadvantage - difficult to do.

Sample Preparation

1. Sample Holders

Zero Background Holder

Use a single crystal that has been aligned along a nondiffracting crystallographic direction (forbidden reflection) and then polished to optical flatness.

Sample Preparation

1. Sample Holders

Zero Background Holder

- Apply a thin layer of grease to the crystal surface and wipe off leaving a monolayer.
- Grind a sample (wet or with acetone) to a dust.
- Sprinkle sample onto grease.
- Total thickness is only a few μm.

Sample Preparation

1. Sample Holders

Zero Background Holder

Advantage - very low background, small sample amounts needed.

Disadvantage - overall lower intensity makes it difficult to determine trace phases.

Sample Preparation

1. Sample Holders

   Spray Drying

   Wet grind the sample and add a binder to the slurry.

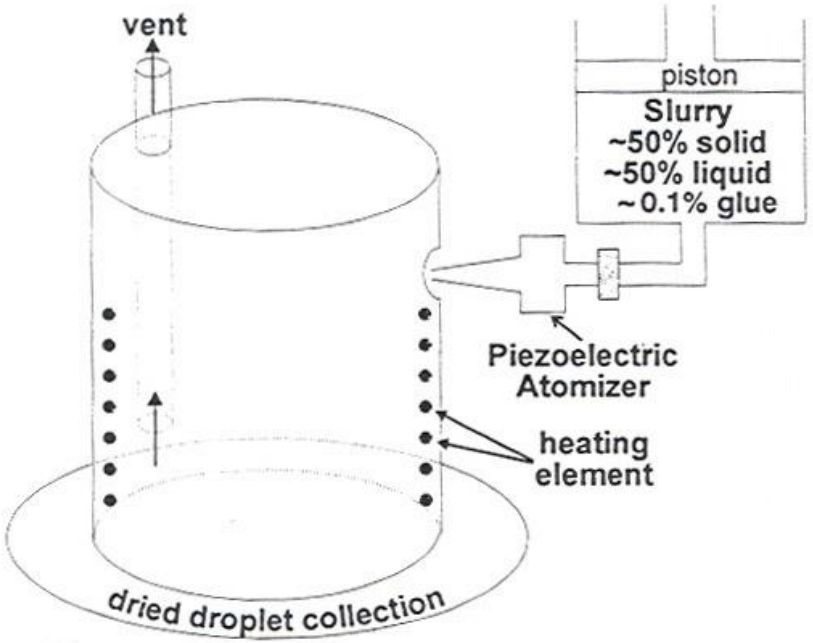
   Atomize the slurry into a hot chamber so the droplets dry before hitting the walls.

   Mostly used when the relative intensity information is critical, i.e. quantitative phase analysis or Rietveld structure analysis.

Sample Preparation

1. Sample Holders

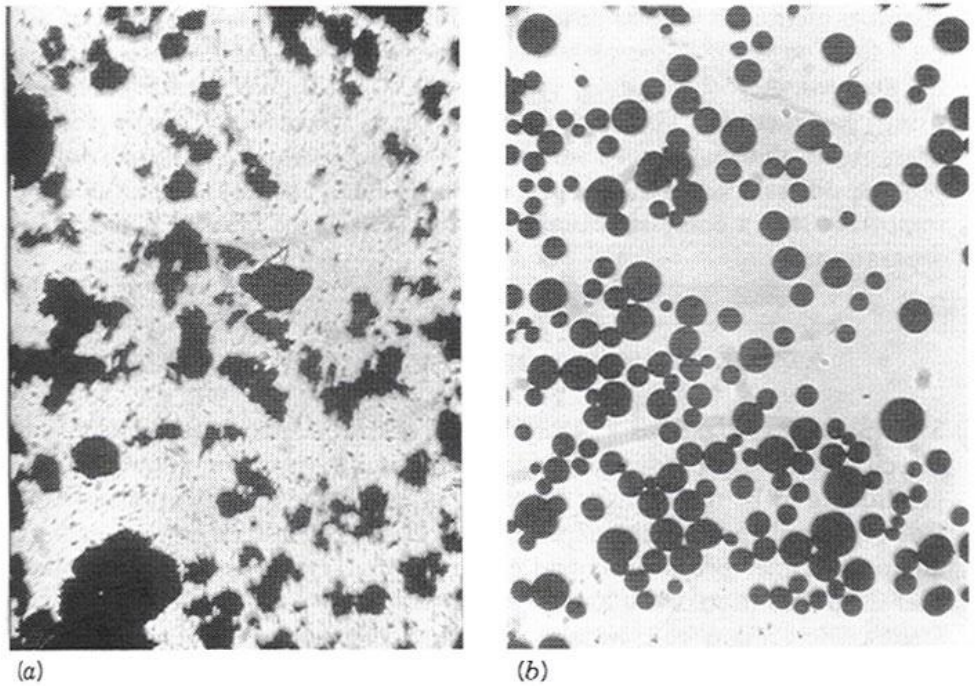
Spray Drying



Sample Preparation

1. Sample Holders

Spray Drying



SEM micrograph of a hematite powder before and after spray-drying.

Sample Preparation

1. Sample Holders

Spray Drying

Advantage - eliminates preferred orientation.

Disadvantage - requires longer sample preparation time (15-30 min).

Sample Preparation

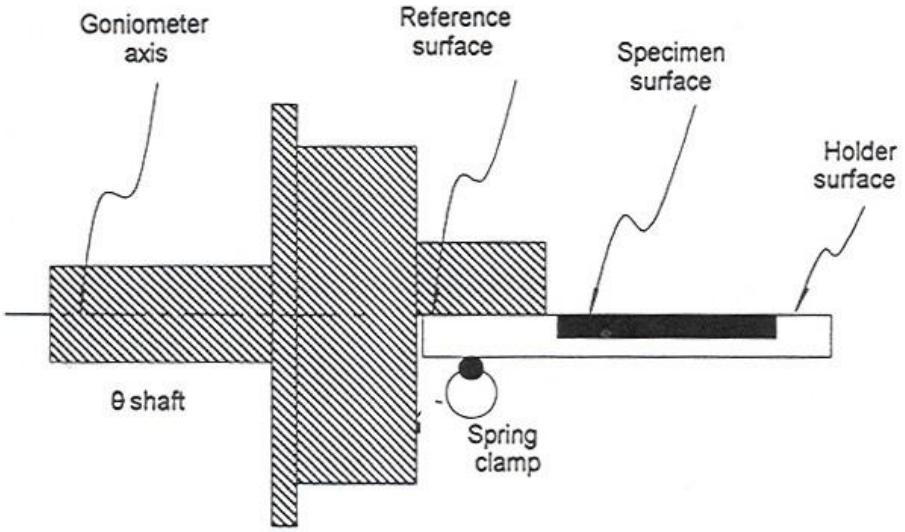
1. Sample Holders

Irregular Sample Holder

Sample Preparation

2. Measurement of Prepared Samples

Sample displacement occurs with the mechanical mechanism.



Group Assignments:

Group 1:
Samar A. (Kelber)
Kabirat B. (Kelber)
Precious C. (Kelber)

Group 2:
Cynthia A. (Yan)
Aida Y. (Yan)
Kynnedi S. (Skellam)

Group 3:
Mojgan G. (Cundari)
Kyle M. (Ma)
Changjia Z. (Ma)

Group 4:
Jennifer E. (Golden)
Marcus G. (Golden)

Crystallography

Lab Assignment:

Lab 1: Safety and Sample Preparation

Tuesday, Sept. 21st 8:00 am

Group 1

Tuesday, Sept. 21st 8:30 am

Group 2

Thursday Sept. 23rd 8:00 am

Group 3

Thursday Sept. 23rd 8:30 am

Group 4

Sample Preparation

Do UNT Bridge Module: - send certificate by this Friday

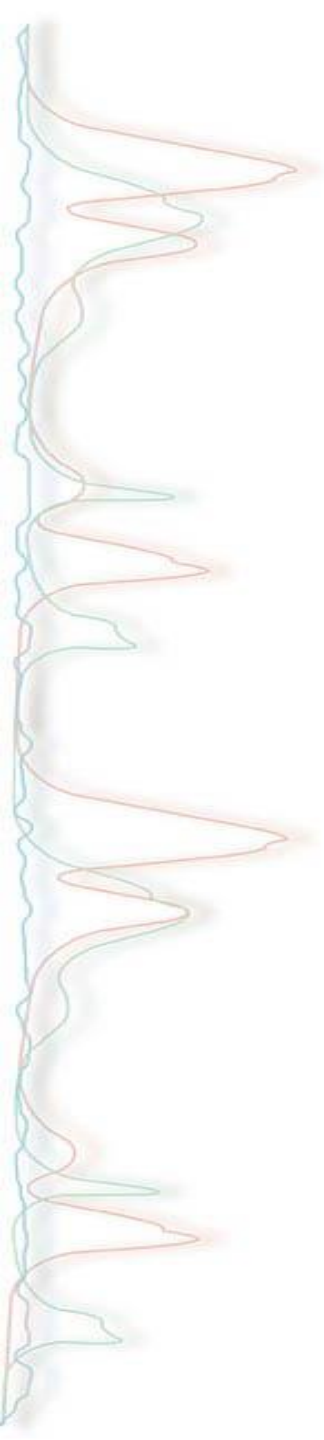
“Radiation Safety Training”

Homework 3: Due next Tuesday

- **Read Chapter 9 from:**

  -Introduction to X-ray powder

  Diffractometry by Jenkins and Synder



chem 5390

Advanced X-ray Analysis