

chem 5390

# ***Advanced X-ray Analysis***



## **LECTURE 7**

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**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

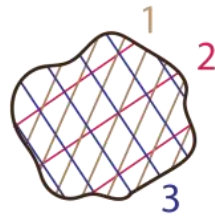
**Grinding - cause amorphism, strain, decomposition, side reactions, contamination.**

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

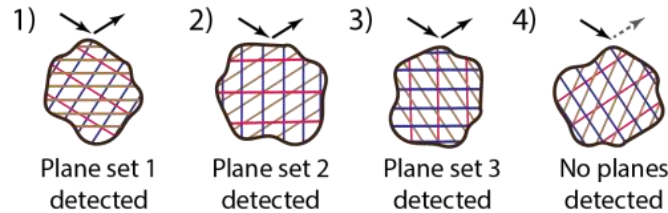
# Sample Preparation

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

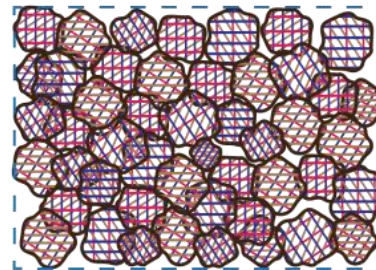
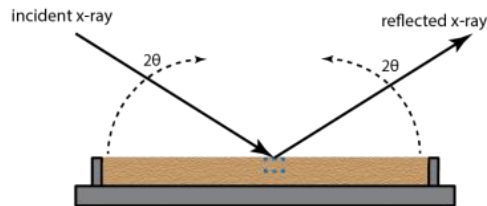
Three sets of planes



Four Possible Cases:

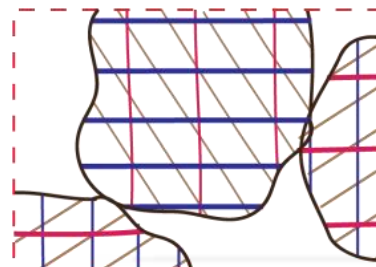
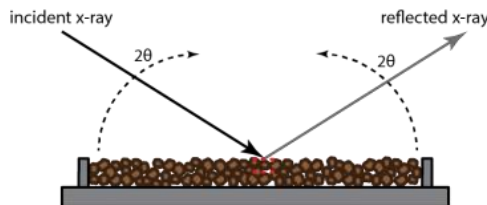


Well Ground, <math><40 \mu\text{m}</math>



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

Underground



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



# Sample Preparation

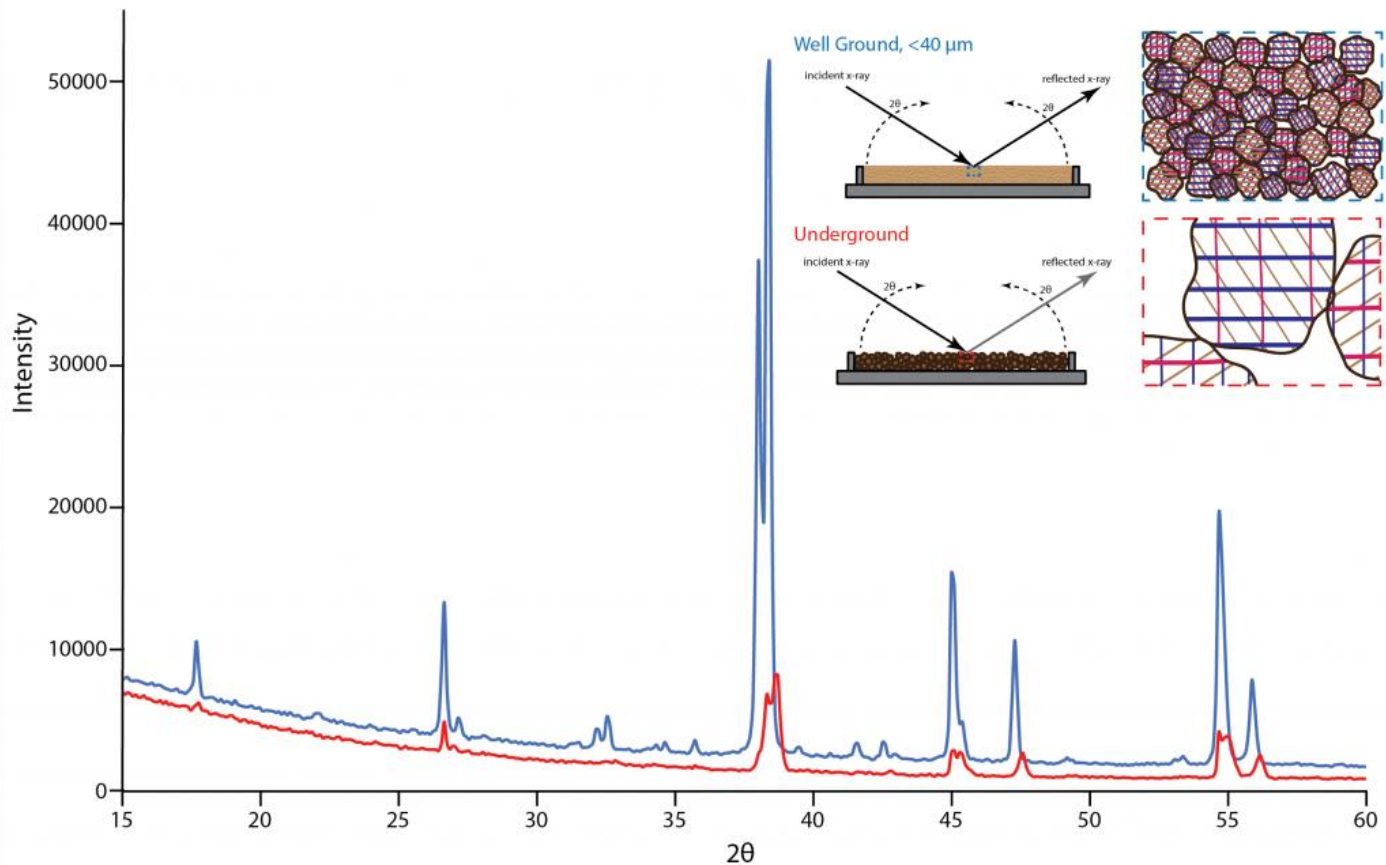
**Grinding - The figure below illustrates this relationship for a single phase sample prepared correctly and poorly.**

**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

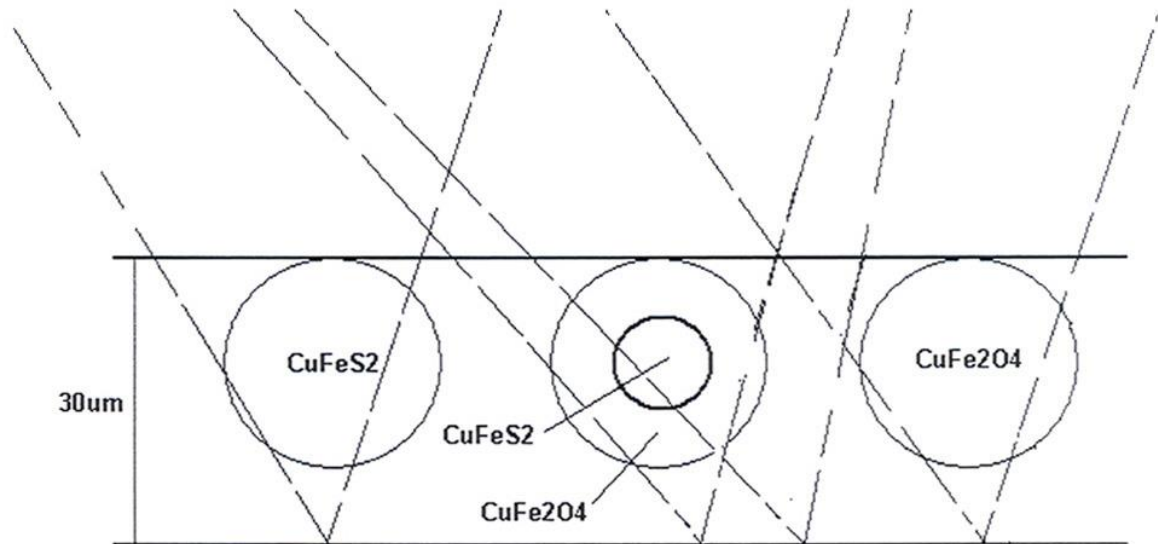
As mentioned before, even the sample thickness and  $\mu/\rho$ , mass-attenuation coefficient, affect the resulting x-ray diffraction pattern.

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 ( $\text{CuFeS}_2$ ) - mining ore

Can oxidize in air, if the average particle size is  $20\ \mu\text{m}$  and x-ray beam depth is  $30\ \mu\text{m}$ ,  $\mu/\rho$  of  $\text{CuFeS}_2 = 143.2$  and  $\mu/\rho$  for  $\text{CuFe}_2\text{O}_4$  is  $116.1$  for  $\text{Cu K}\alpha$  radiation. The measured x-ray pattern will be different for each particle - inhomogeneity effect.



# 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 $\mu\text{m}$	5–50 $\mu\text{m}$	5–15 $\mu\text{m}$	< 5 $\mu\text{m}$
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  $\sim 5\mu\text{m}$ , the relative standard deviation is only a few %, but statistical error increases as particle size exceeds  $10\mu\text{m}$ .

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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

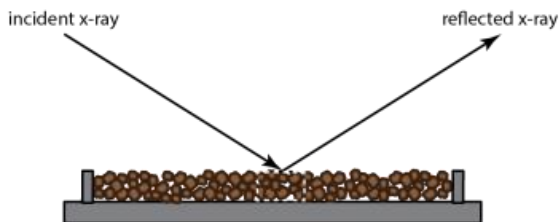
Preferred orientation occurs the samples crystallites are not randomly orientated.

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.

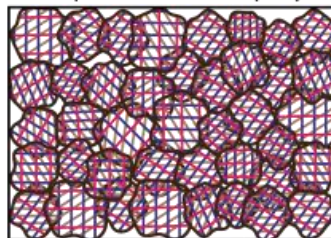
# Sample Preparation

## Preferred Orientation

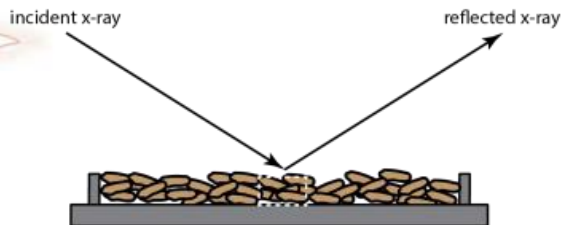
No Preferred Orientation



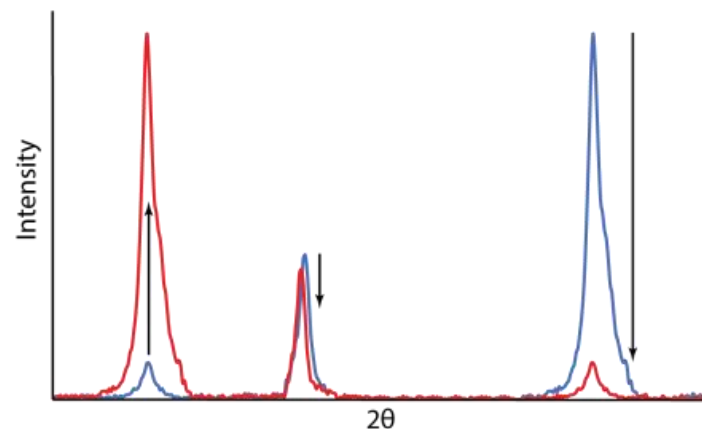
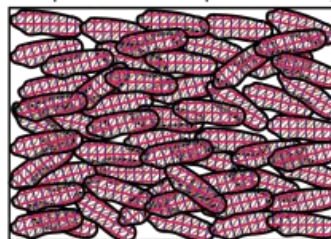
All planes detected equally



Preferred Orientation



One plane detected preferentially



No preferred orientation - correct intensity ratios

Preferred orientation - highly skewed intensity ratios

# 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 $\mu\text{m}$	10 $\mu\text{m}$	1 $\mu\text{m}$
Diffracting particles	12	760	38,000

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

# Sample Preparation

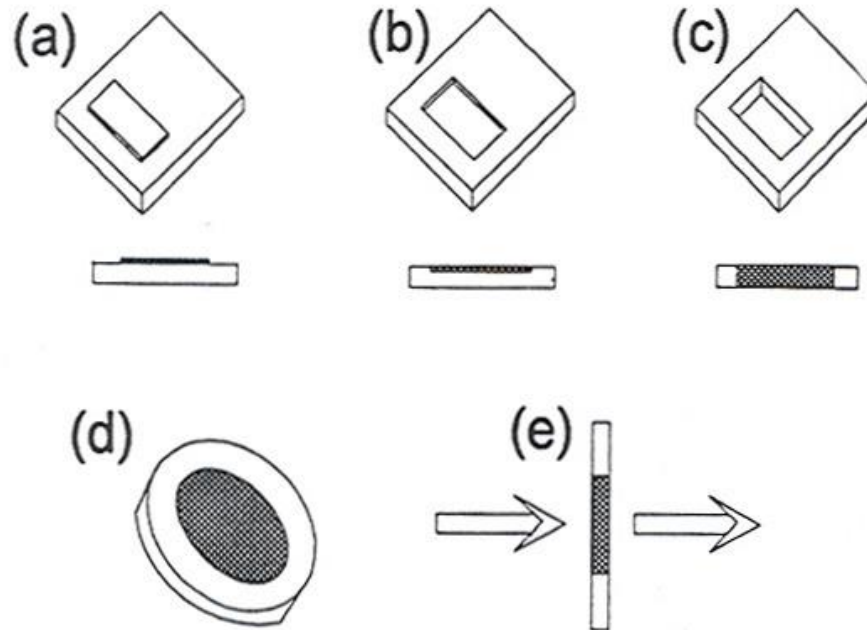
## Quartz in different particle diameter in a conventional Bragg-Brentano diffractometer

Particle size fraction /microns	15-50	5-50	5-15	<5
Standard deviation of I quartz <sub>101</sub> /%	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  $\mu\text{m}$ .
- This is necessary to get reliable results of Rietveld structure analysis, too.

# Sample Preparation

## 1. Sample Holders

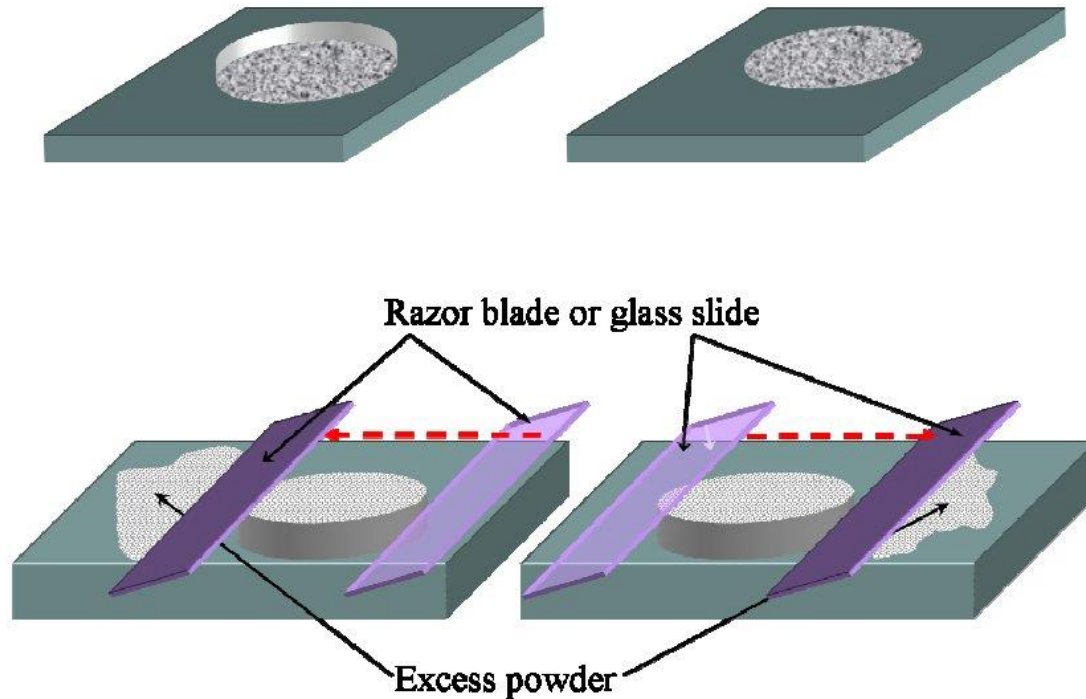


**(a) Zero-background, (b) top-loaded, (c) back-loaded, (d) circular, (e) press mounts**

# 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

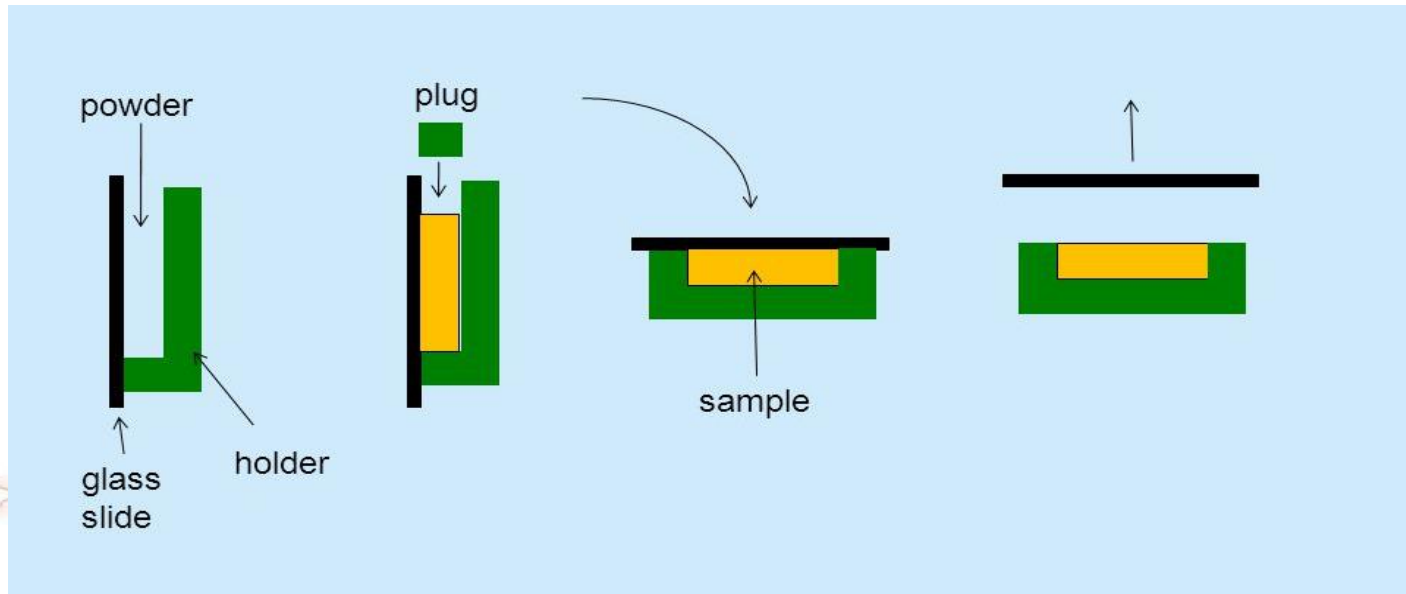
### Back Loading

**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  $\mu\text{m}$ .**



# 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.

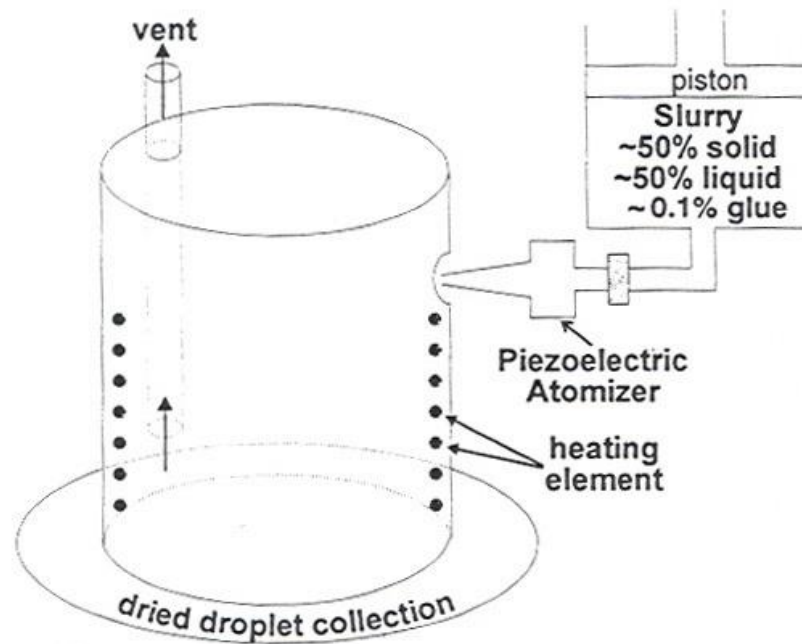
Atomize the slurry into a hot chamber so the droplets dry before hitting the walls.

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

# Sample Preparation

## 1. Sample Holders

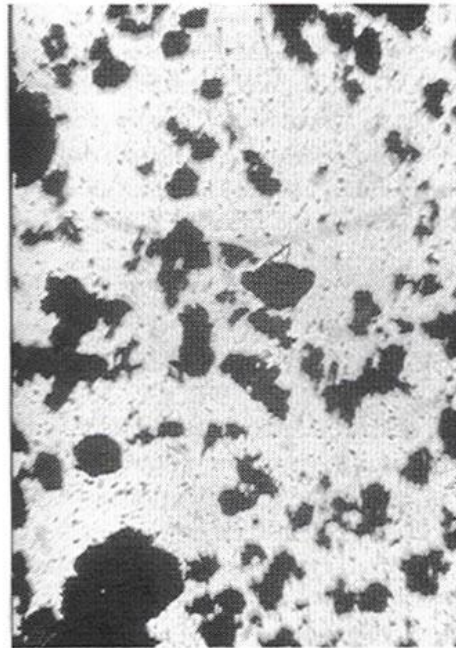
### Spray Drying



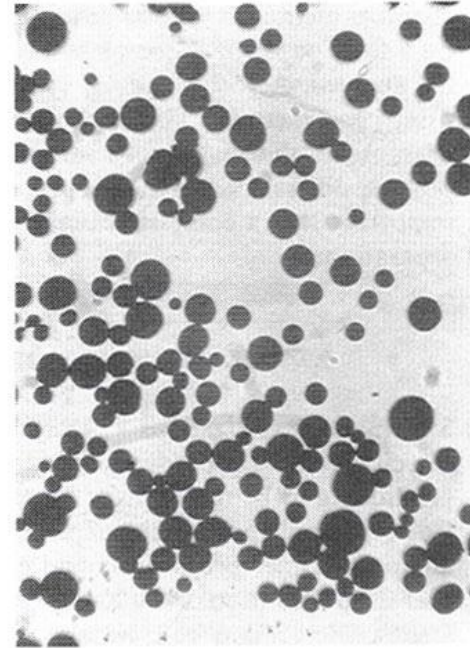
# Sample Preparation

## 1. Sample Holders

### Spray Drying



(a)



(b)

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

# Sample Preparation

## 1. Sample Holders

### Spray Drying

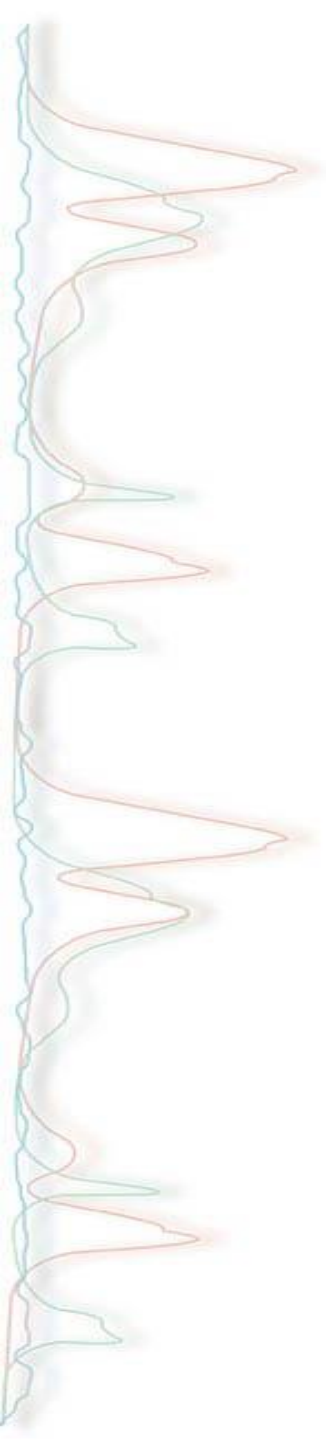
**Advantage - eliminates preferred orientation.**

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

# Sample Preparation

## 1. Sample Holders

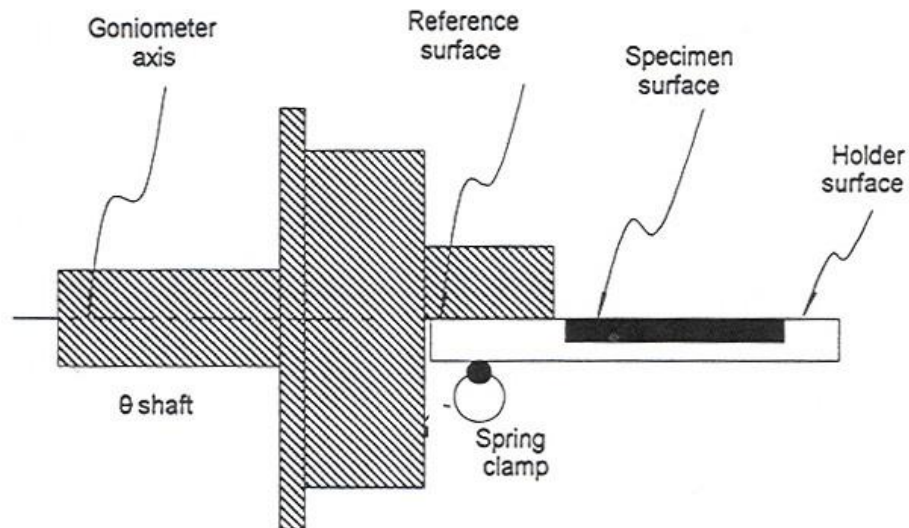
### Irregular Sample Holder



# Sample Preparation

## 2. Measurement of Prepared Samples

Sample displacement occurs with the mechanical mechanism.





## **Group Assignments:**

**Group 1:**

**Group 2:**

**Group 3:**

**Group 4:**

# Crystallography

## Lab Assignment:

### Lab 1: Safety and Sample Preparation

**Tuesday, Sept. 8:00 am**

**Group 1**

**Tuesday, Sept. 8:30 am**

**Group 2**

**Thursday Sept. 8:00 am**

**Group 3**

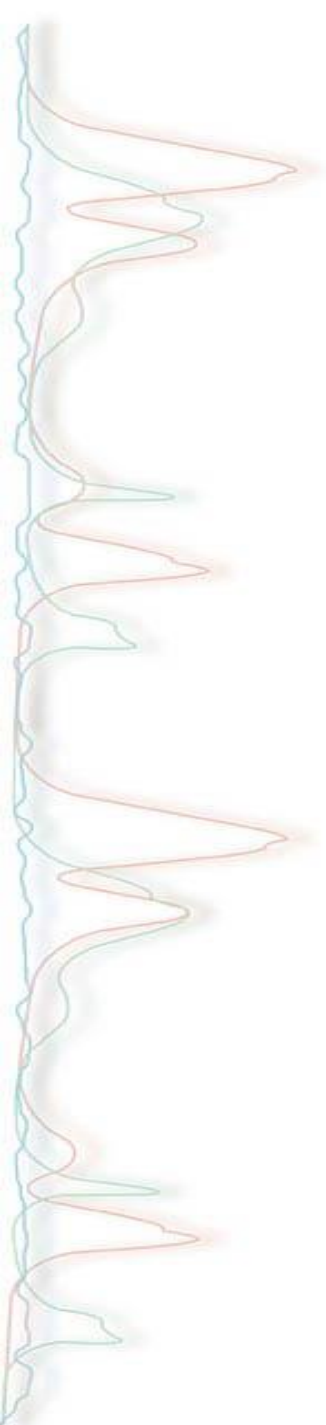
**Thursday Sept. 8:30 am**

**Group 4**

# Sample Preparation

## Homework 3: Due

- Read Chapter 9 from:
  - Introduction to X-ray powder  
Diffractometry by Jenkins and Synder



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**Advanced X-ray Analysis**