



CHEMISTRY 5570

Advanced Analytical Chemistry

X-ray Diffraction

Lecture 4

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Department of Chemistry

Advance X-Ray Diffraction

Class Website:

https://sites.chemistry.unt.edu/~tgolden/courses/course_downloadsFall24.xhtml

Readings:

Given at the end of each powerpoint lecture. The books are on reserve at the Willis library under CHEM 5390 (X-ray Diffraction).

Homework Assignments:

Given at the end of each powerpoint lecture. I do not accept assignments by email – all assignments must be turned in during class.

Exams:

There will be an exam in class on Tuesday, December 10th, 8:00 - 10:00 a.m.



Important for Calculations

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

where n is an integer

λ is the wavelength of the x-rays

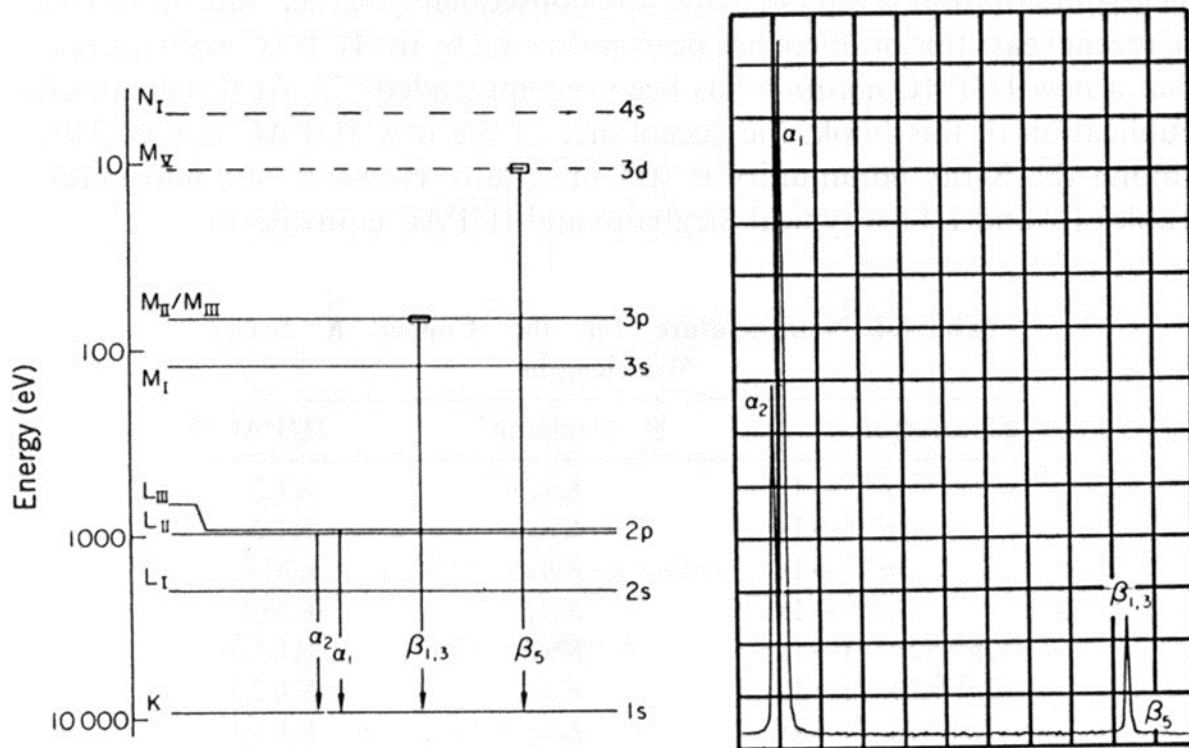
d is the interplanar spacing in the specimen

θ is the diffraction angle

Bragg Equation

Properties of X-rays

The Copper K Spectrum



The copper $K\alpha$ spectrum.

- The diagram at left shows the 5 possible Cu K transitions
- L to K “jumps”:
 - $K\alpha_1$ (8.045 keV, 1.5406Å)
 - $K\alpha_2$ (8.025 keV, 1.5444Å)
- M to K
 - $K\beta_1$ $K\beta_3$ (8.903 keV, 1.3922Å)
 - $K\beta_5$

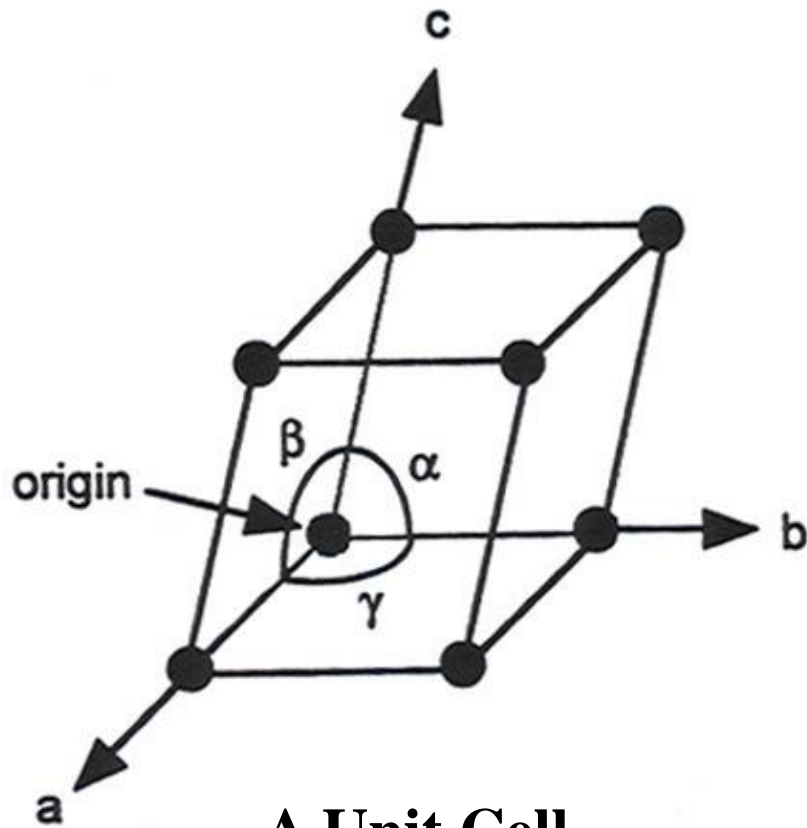
Crystallography

The size and shape of the unit cell can be described by three vectors, a , b , and c (called the crystallographic axes of the cell).

The unit cell can also be described in terms of lengths (a , b , c) and the angles between them (α , β , γ).

The lengths and angles are the lattice constants or lattice parameters of the unit cell.

Notice that the entire point lattice can be built by translating the unit cell.



A Unit Cell.

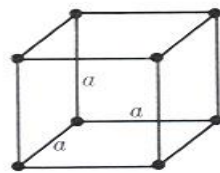
Axis	a	b	c
Lattice Parameters:			
Lengths	a	b	c
Inter-axial angle	α	β	γ

(The symbol \neq means that equality is not required by symmetry. Accidental equality may occur, as shown by an example in Sec. 2-4.)

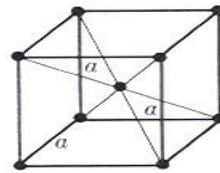
System	Axial lengths and angles	Bravais lattice	Lattice symbol
Cubic	Three equal axes at right angles $a = b = c, \alpha = \beta = \gamma = 90^\circ$	Simple Body-centered Face-centered	P I F
Tetragonal	Three axes at right angles, two equal $a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	Simple Body-centered	P I
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	Simple Body-centered Base-centered Face-centered	P I C F
Rhombohedral*	Three equal axes, equally inclined $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	Simple	R
Hexagonal	Two equal coplanar axes at 120° , third axis at right angles $a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	Simple	P
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta$	Simple Base-centered	P C
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	Simple	P

* Also called trigonal.

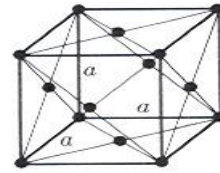
7 Crystal systems and 14 Bravais lattices.



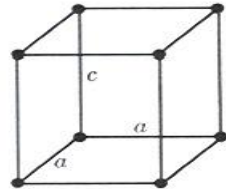
SIMPLE CUBIC (P)



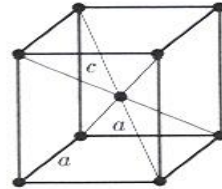
BODY-CENTERED CUBIC (I)



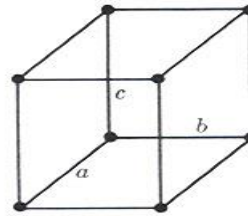
FACE-CENTERED CUBIC (F)



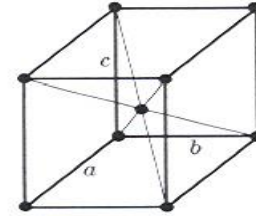
SIMPLE TETRAGONAL (P)



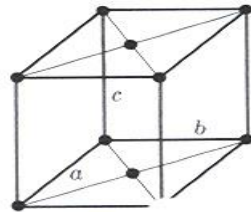
BODY-CENTERED TETRAGONAL (I)



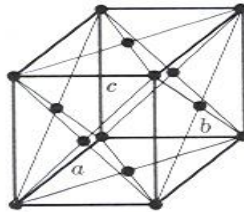
SIMPLE ORTHORHOMBIC (P)



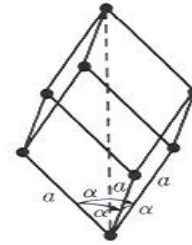
BODY-CENTERED ORTHORHOMBIC (I)



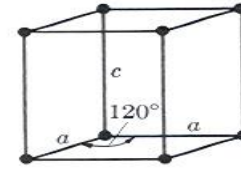
BASE-CENTERED ORTHORHOMBIC (C)



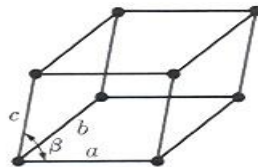
FACE-CENTERED ORTHORHOMBIC (F)



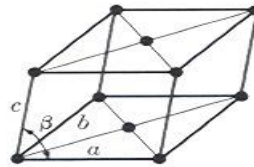
RHOMBOHEDRAL (R)



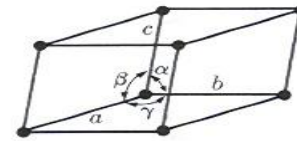
HEXAGONAL (P)



SIMPLE MONOCLINIC (P)



BASE-CENTERED MONOCLINIC (C)



TRICLINIC (P)

The fourteen Bravais lattices.

Crystallography

Geometry and the structure of crystals

Vectors and Planes

Miller Indices

A notation used to describe various planes within a crystal lattice.

Steps to determine Miller Indices

- 1) Identify the points at which the plane intersects the a, b, c axes. Intercept is measured in terms of fractions or multiples of the lattice parameter.
- 2) Take reciprocals of the intercepts. (Get rid of infinity)
- 3) Multiply to get a whole number (Clear the fractions)
- 4) Enclose numbers in (). Represent negative numbers with a bar (bar one).

Crystallography

Geometry and the structure of crystals

Vectors and Planes

In the cubic system there are six faces equivalent to $(1\ 0\ 0)$.

This set is related and denoted by $\{1\ 0\ 0\}$ - this set is called a family of planes.

$\{ \quad \}$ - denotes a family of planes

(\quad) - denotes an individual plane

The six planes in the $\{1\ 0\ 0\}$ family are:

$(1\ 0\ 0)$ $(0\ 1\ 0)$ $(0\ 0\ 1)$ $(\bar{1}\ 0\ 0)$ $(0\ \bar{1}\ 0)$ $(0\ 0\ \bar{1})$

Crystallography

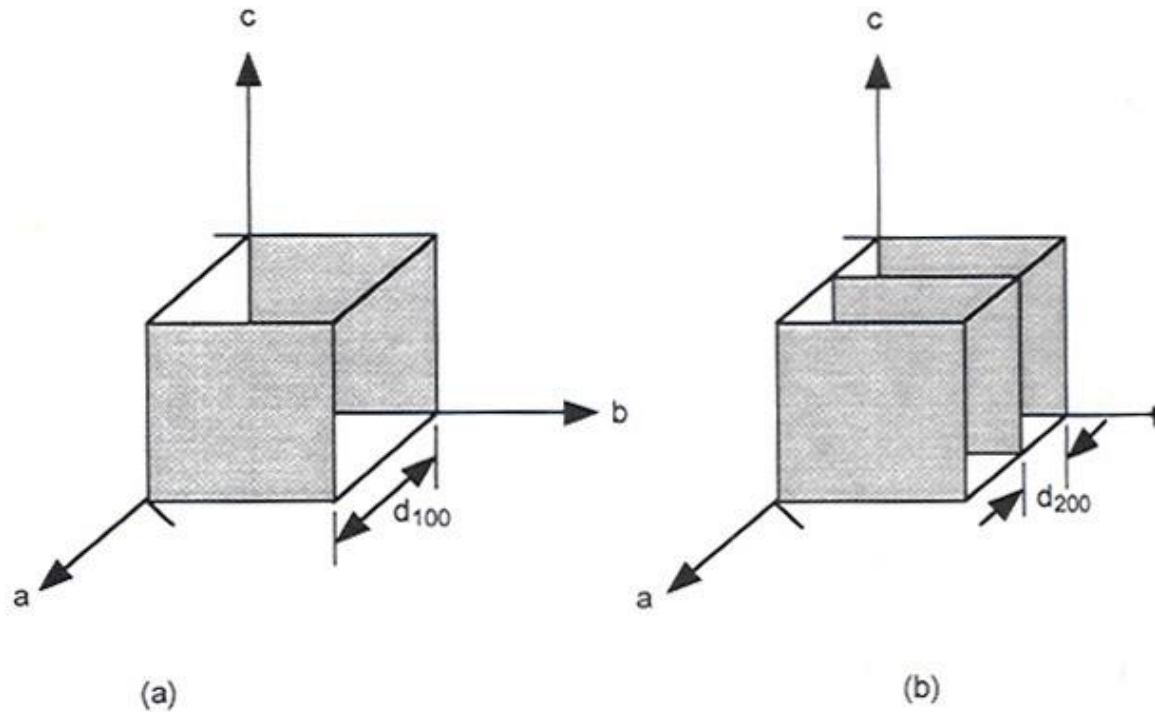
Geometry and the structure of crystals

Interplanar Spacings

The distance between an equivalent set of planes is defined as d_{hkl} - the interplanar spacing.

The interplanar spacing, d_{hkl} , measured at right angles to the planes, is a function both of the plane indices (hkl) and the lattice constants (a,b,c, α , β , γ).

The distance can be directly determined by x-ray diffraction.



The d_{hkl} interplanar spacing.

For a cubic system:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

The d_{hkl} interplanar spacing.

Cubic:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Hexagonal:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

Rhombohedral:

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)\sin^2 \alpha + 2(hk + kl + hl)\cos^2 \alpha - \cos \alpha}{a^2(1 - 3\cos^2 \alpha + 2\cos^3 \alpha)}$$

Orthorhombic:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Monoclinic:

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$$

Triclinic:

$$\frac{1}{d^2} = \frac{1}{V^2} (S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

V = volume of unit cell

$$S_{11} = b^2c^2\sin^2 \alpha,$$

$$S_{22} = a^2c^2\sin^2 \beta,$$

$$S_{33} = a^2b^2\sin^2 \gamma,$$

$$S_{12} = abc^2(\cos \alpha \cos \beta - \cos \gamma),$$

$$S_{23} = a^2bc(\cos \beta \cos \gamma - \cos \alpha),$$

$$S_{13} = ab^2c(\cos \gamma \cos \alpha - \cos \beta).$$

Diffraction Theory

Diffraction

Factors that affect the Intensity of the diffracted beam:

- 1) Structure factor
- 2) Polarization factor
- 3) Lorentz factor
- 4) Multiplicities
- 5) Temperature factor
- 6) Absorption factor - absorption of x-rays by the sample
- 7) Preferred orientation
- 8) Extinction coefficient - applies to single crystals - not applicable to powders

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

Powder XRD

Sample Preparation

Sample-related problems

Graininess

Micro-absorption

Texture

Sample height displacement

Surface roughness

Sample transparency

Sample Preparation

There are many different types of samples:

Rock material

Powder material

Single Crystal

Metal

Liquids

Coatings





Sample Preparation

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

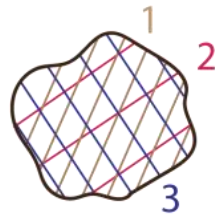
Grinding - cause amorphism, strain, decomposition, side reactions, contamination.

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

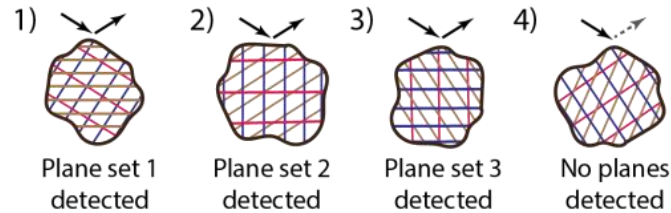
Sample Preparation

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

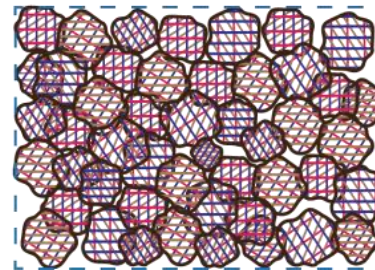
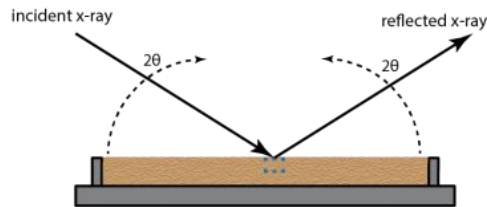
Three sets of planes



Four Possible Cases:

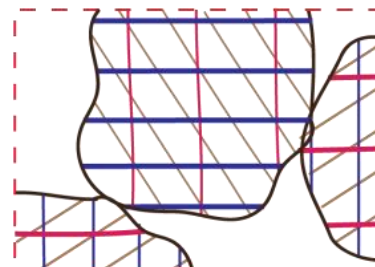
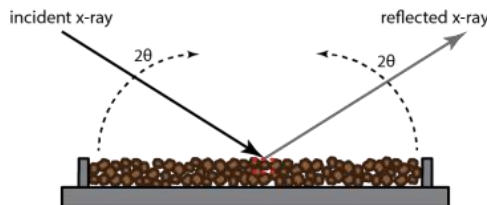


Well Ground, <math><40 \mu\text{m}</math>



- 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

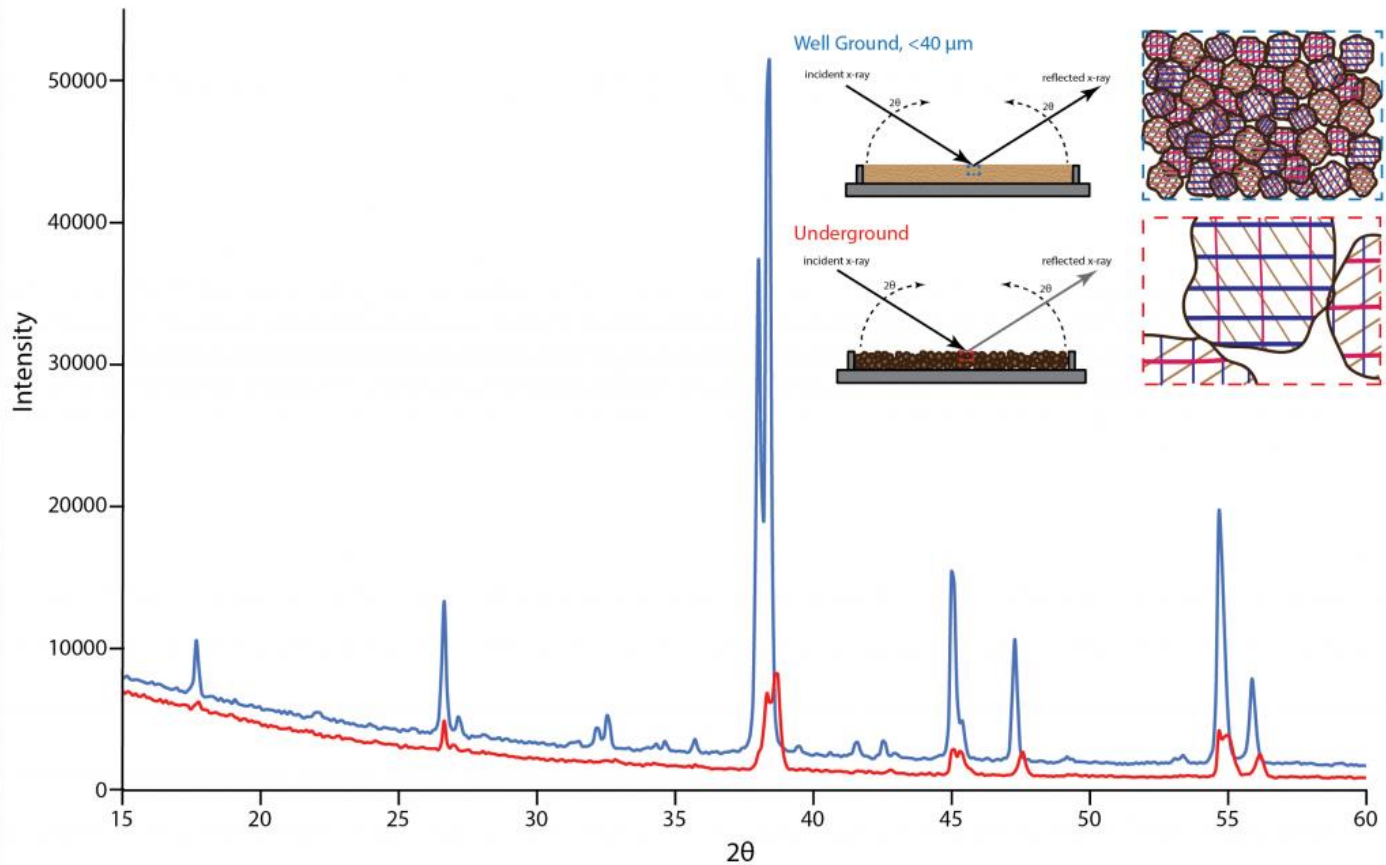
Sample Preparation

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.

For a poorly ground sample you would be able to distinguish individual grains 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

Micro-absorption

Micro-absorption occurs in samples with large particles (not crystallites) or phases with large contrast in absorption coefficients

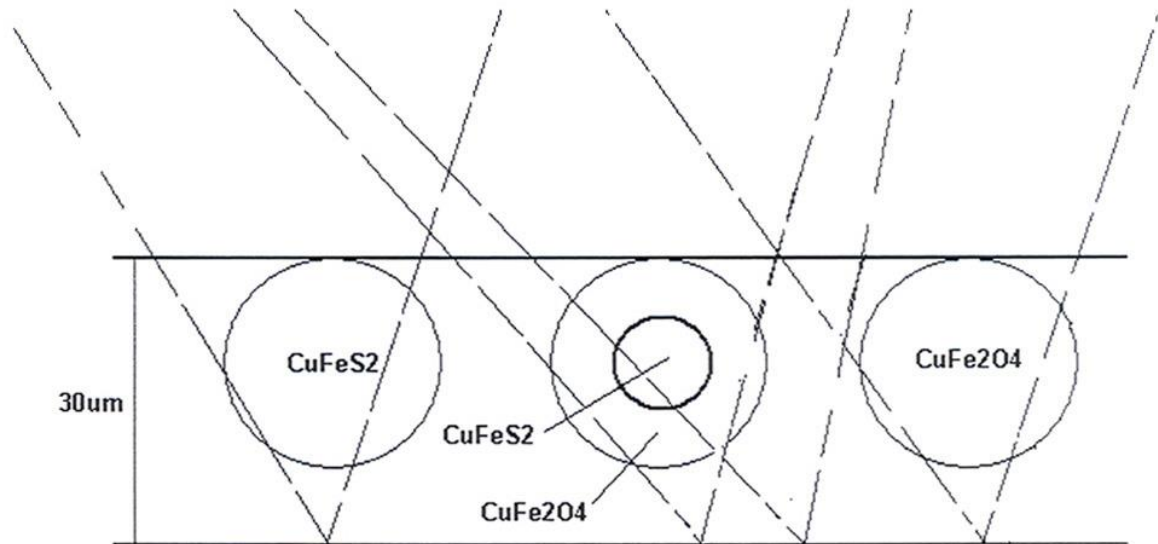
Leads to biased phase quantifications

Can be reduced by grinding / milling

Sample Preparation

Example: Chalcopyrite (CuFeS_2) - mining ore

Can oxidize in air, if the average particle size is $20\ \mu\text{m}$ and x-ray beam depth is $30\ \mu\text{m}$, μ/ρ of $\text{CuFeS}_2 = 143.2$ and μ/ρ for CuFe_2O_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 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].

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 $10\mu\text{m}$.



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 when the sample crystallites are not randomly orientated.

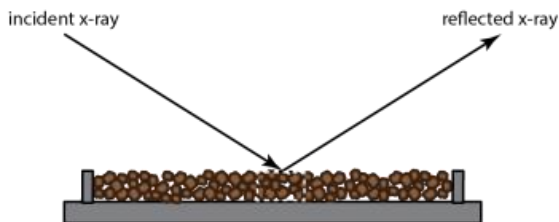
Samples that are fibrous or plate-like (ex. Clays) will orientate in a preferred direction due to their shape, causing some lattice planes to be detected more than others and therefore skewing the intensity ratios.



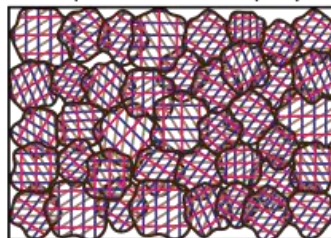
Sample Preparation

Preferred Orientation

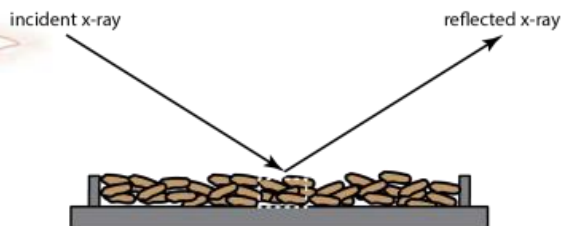
No Preferred Orientation



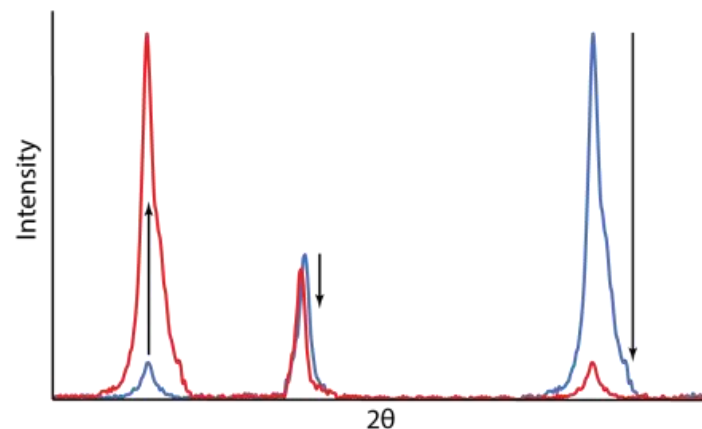
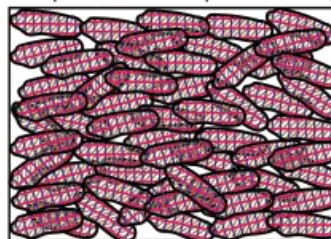
All planes detected equally



Preferred Orientation



One plane detected preferentially



No preferred orientation - correct intensity ratios

Preferred orientation - highly skewed intensity ratios



Sample Preparation

Preferred Orientation

Sometimes can avoid orientation by:

Shaving the top layer off the sample

Using back-loading sample holder

Disorder the surface with textured stamp

**Other various creative solutions can be found on the
(involving Vaseline, hair spray, ...)**

Sample Preparation

Sample Height Displacement

On the Instrument: (cause)

Focus of diffracted beam is displaced

Detector is out of focus

Diffracted beam blocked by apertures

In the XRD pattern: (effect)

2θ shift of peaks

Diffuse / broad peaks

Distorted peak profiles

Poor Rietveld fits

Sample Preparation

Surface Roughness

On the Instrument: (cause)

Focus of diffracted beam is partially displaced

Detector is out of focus

Diffracted beam blocked by apertures

In the XRD pattern: (effect)

2θ shift of peaks

Diffuse / broad peaks

Distorted peak profiles

Poor Rietveld fits

Sample Preparation

Sample Transparency

On the Instrument: (cause)

Focus of diffracted beam is partially displaced

Detector is out of focus

Diffracted beam blocked by apertures

In the XRD pattern: (effect)

2θ shift of peaks

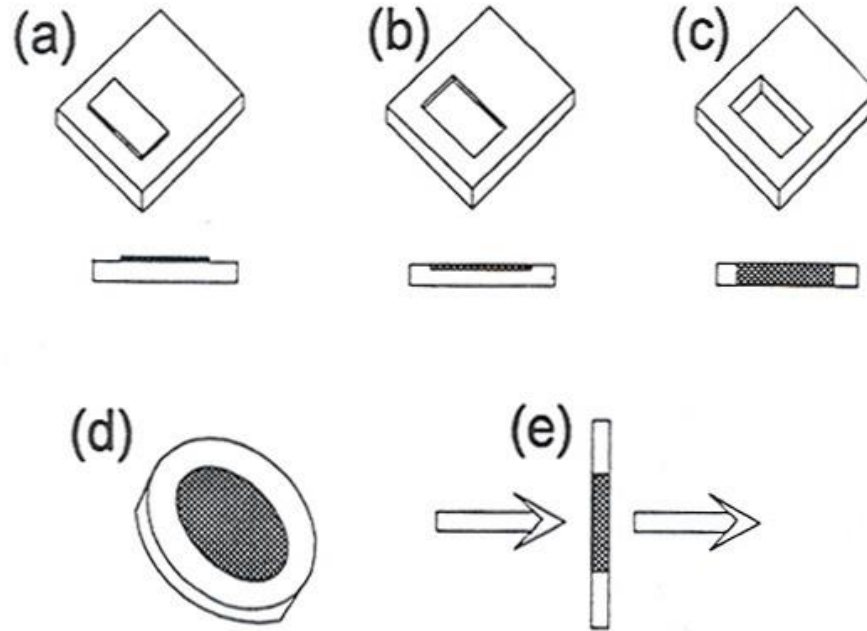
Diffuse / broad peaks

Distorted peak profiles

Poor Rietveld fits

Sample Preparation

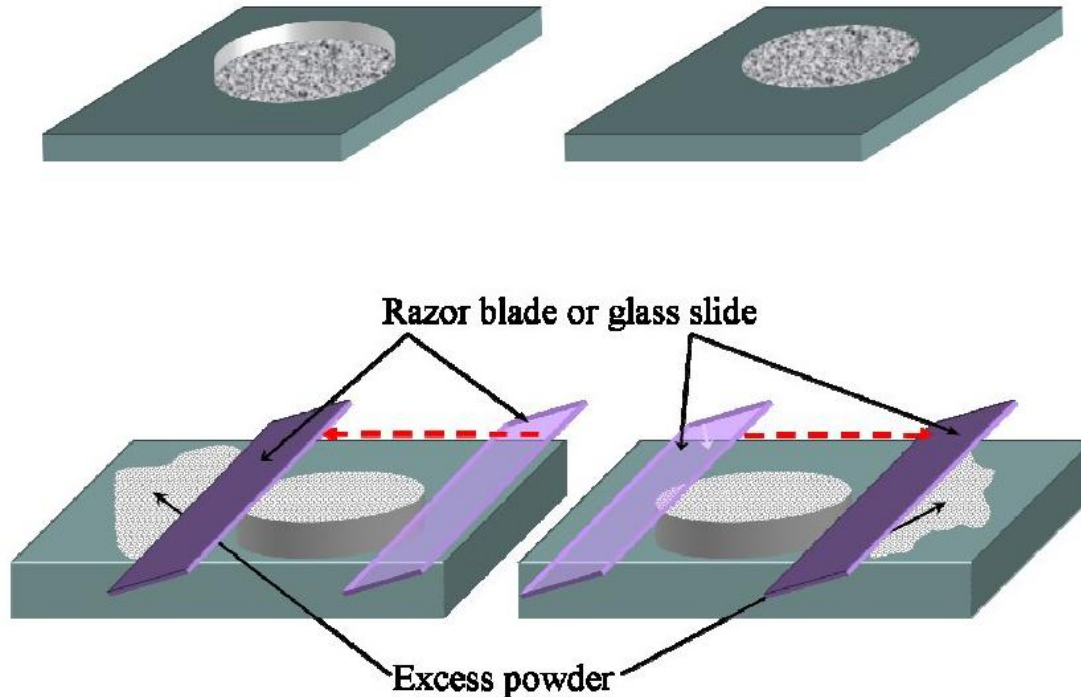
Sample Holders



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

Sample Preparation

Sample Holders Top or Front Loading



Advantage - easy preparation.

Disadvantage - may have preferred orientation.

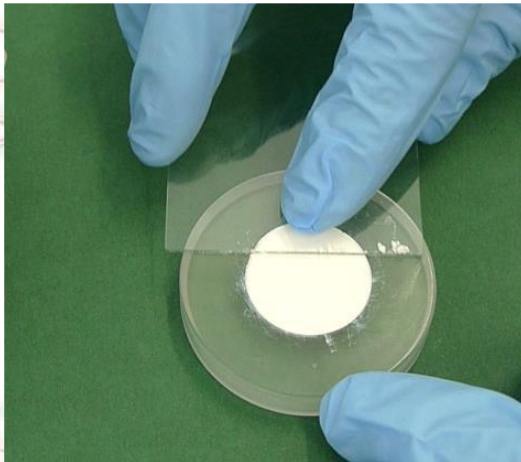
Golden XRD Lab



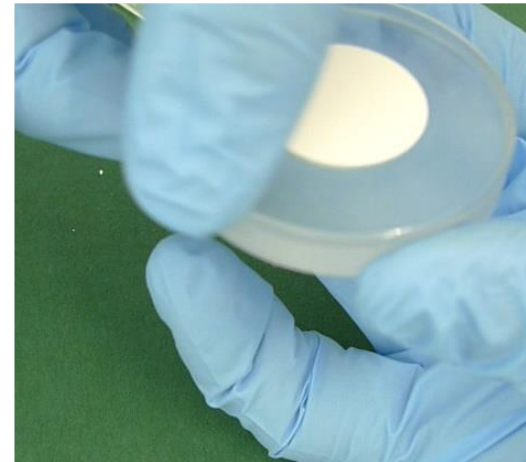
1. Fill sample holder



2. Spread and compact powder



3. Scratch off excess powder



4. Clean rim



Sample Preparation

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

Sample Holders

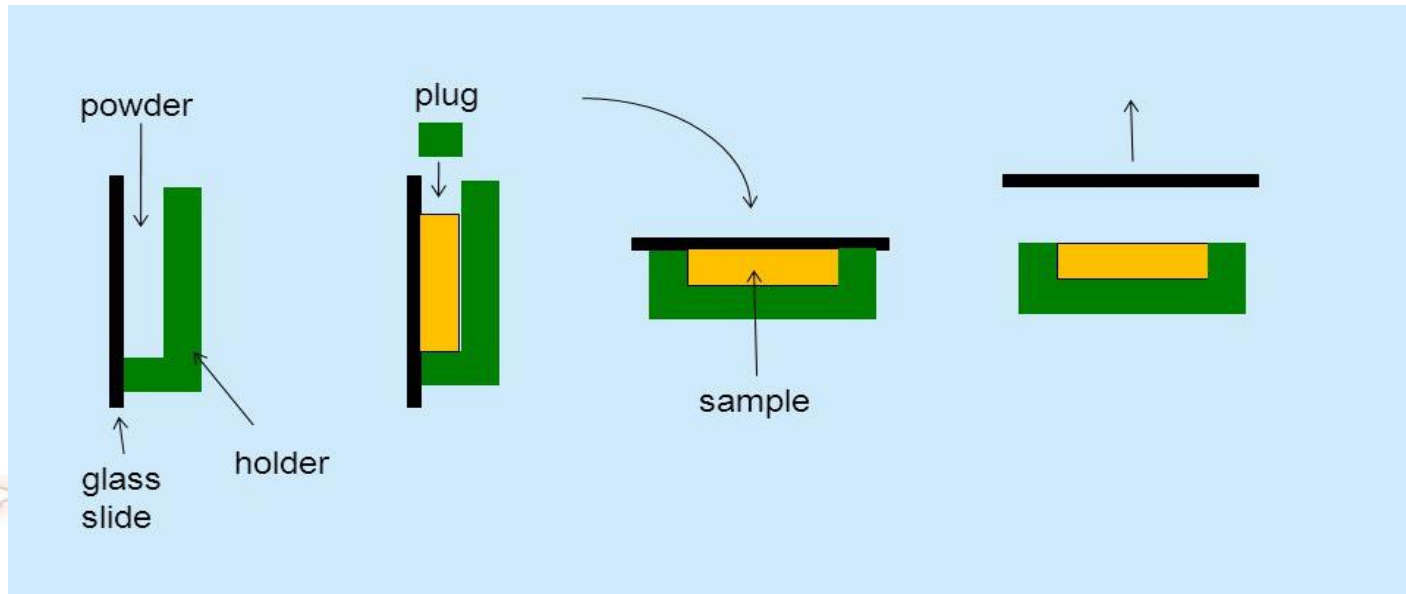
Back Loading

Advantage - gives a nice even surface.

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

Sample Preparation

Side Loading



Advantage - better packing method, gives true peak intensities.

Disadvantage - difficult to do.



Sample Preparation

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

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

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

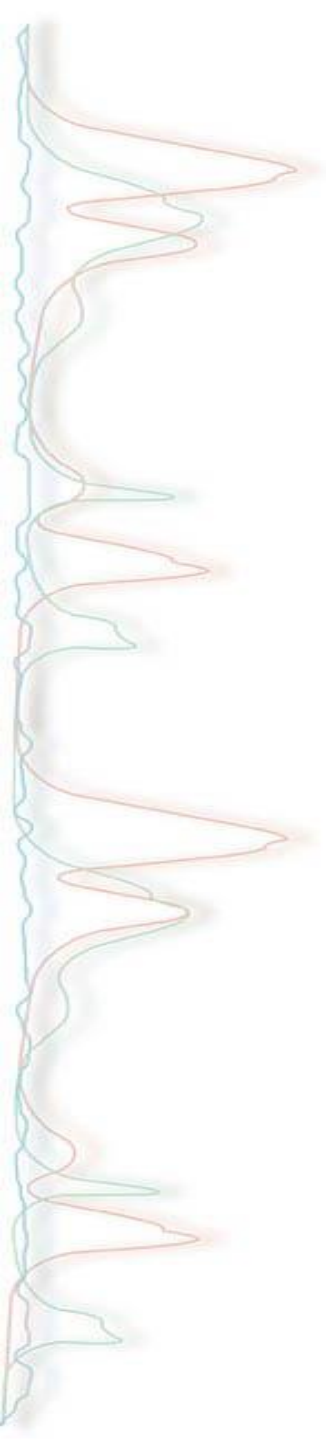
Sample Holders

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.

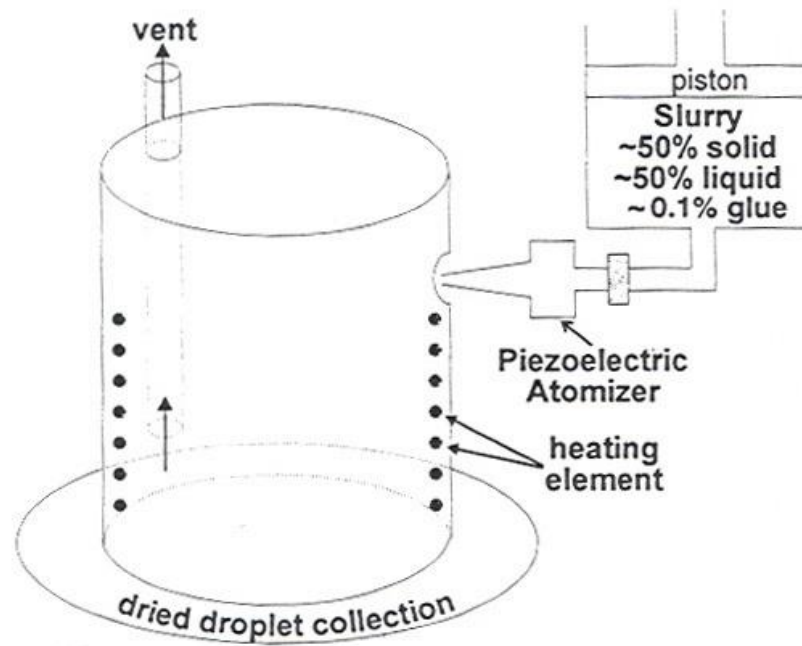
Mostly used when the relative intensity information is critical, i.e. quantitative phase analysis or Rietveld structure analysis.



Sample Preparation

Sample Holders

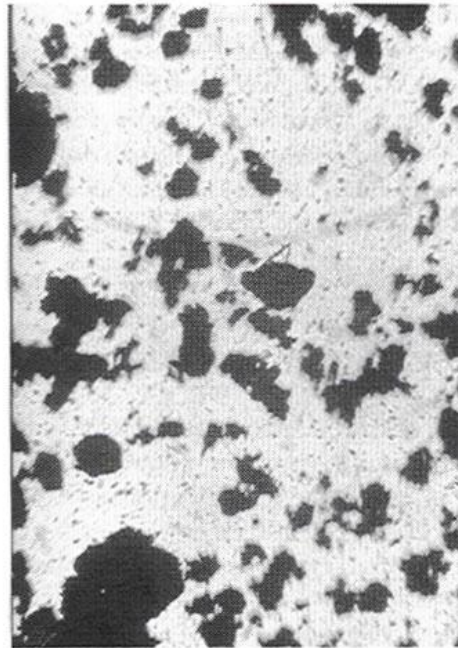
Spray Drying



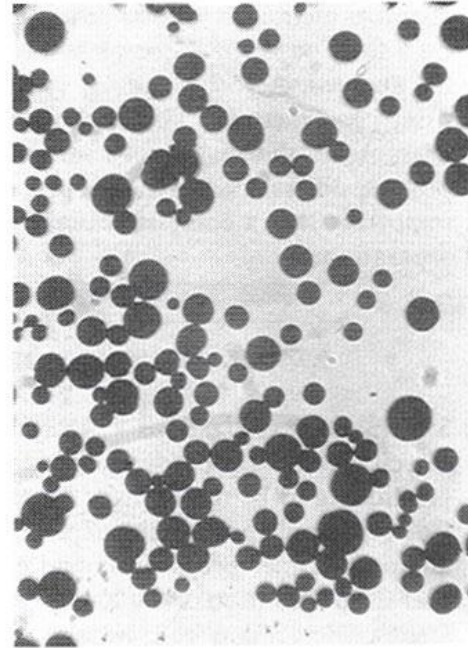
Sample Preparation

Sample Holders

Spray Drying



(a)



(b)

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



Sample Preparation

Sample Holders

Spray Drying

Advantage - eliminates preferred orientation.

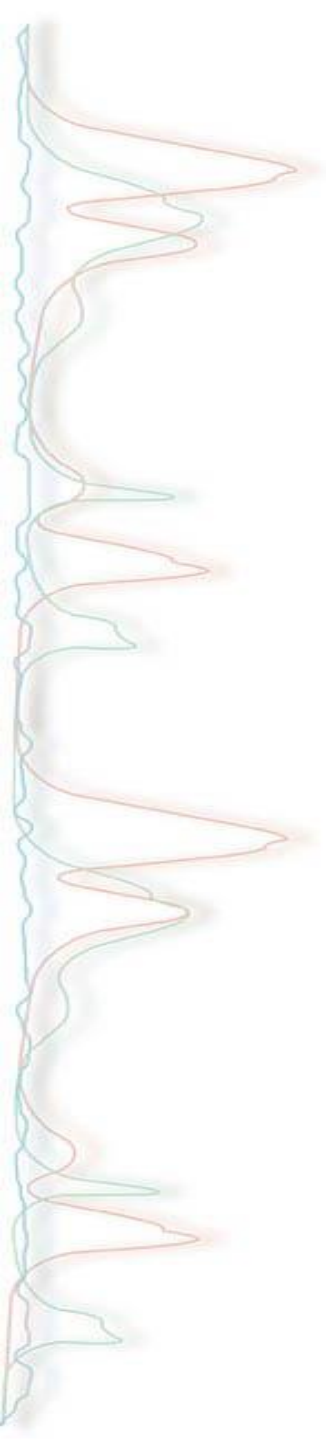
Disadvantage - requires longer sample preparation time (15-30 min).

Sample Preparation

Sample Holders

Irregular Sample Holder

Examples



Sample Preparation

Perfect sample:

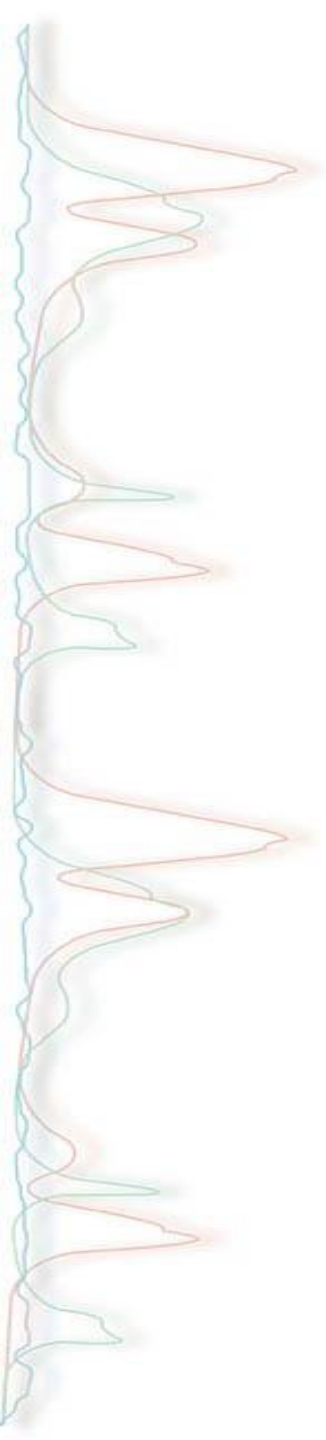
Crystallites and particles of 1-5 μm size

Perfectly random orientation

Perfectly flat surface

Surface precisely centered in the goniometer

High packing density



Assignments

Read Chapters 1&2&3 from the following textbooks:

- X-ray Diffraction, A Practical Approach by Norton
- Elements of X-ray Diffraction by Cullity and Stock
- Introduction to X-ray powder Diffractometry
by Jenkins and Synder

Read Chapter 9 from:

- Introduction to X-ray powder
Diffractometry by Jenkins and Synder

