

## GEOL3010 Lecture 10

### Factors that affect d's and I's.

XRD data are sensitive to as many as 35 different factors. These factors can be grouped in to three general sources of "error".

- Instrument sensitive
- Sample sensitive
- Specimen sensitive

Theoretical d-value ( $n \lambda = 2d \sin\Theta$ )

vs.

Practical d-value (theoretical + inherent aberrations)

vs.

Experimental d-value (practical + inherent sample aberrations + errors)

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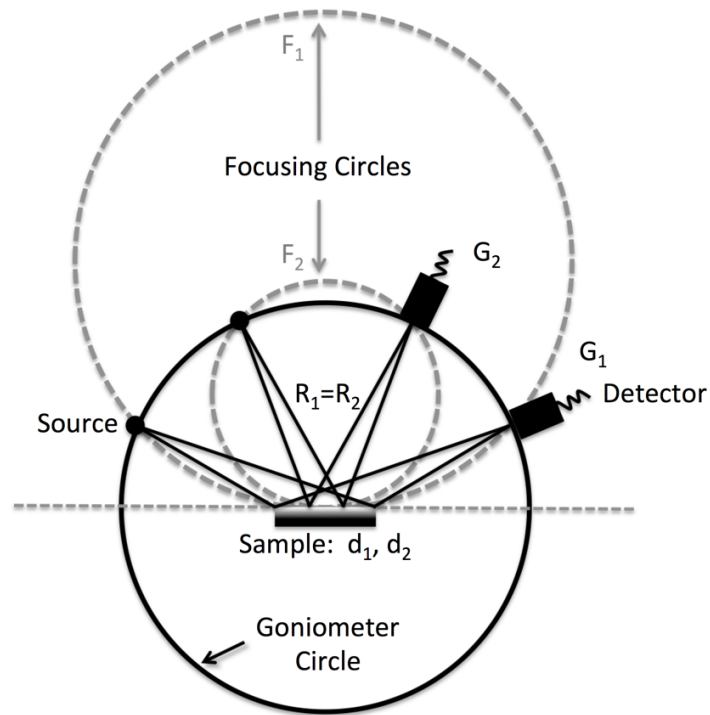
### Geometry of the powder diffractometer

The Debye-Scherrer Camera provides a visual aid for understanding the X-ray diffraction powder method.

The essential features of the powder method include a narrow beam of monochromatic X-ray radiation impinging upon a randomly oriented powder where all possible crystallographic planes are available for Bragg reflection.

### Geometrical Principles of a Bragg-Brentano Para-focusing Diffractometer

1. X-rays diverge from source
2. The "reflected" X-rays from the samples on the focusing circle are directed to their respective places back on the circle
3. The spots labeled G1, G2, G3 are the respective reflections of d-spacings d1, d2, d3.



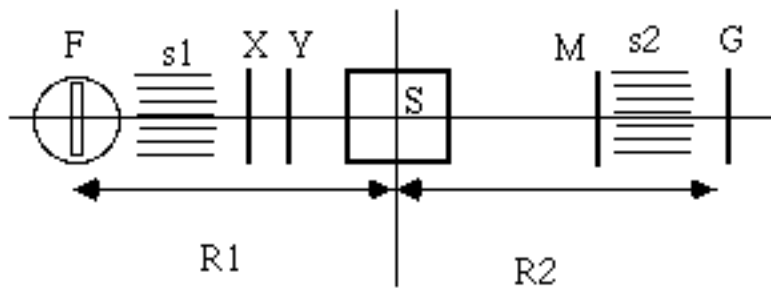
The Bragg-Brentano geometry allows for a constant distance between the sample and the detector.

It essentially requires that distance from the source to the sample and the sample to the detector (i.e.,  $R_1 = R_2$ ) and that the sample is kept on the tangent of the focusing circle.

In order to keep the detector distance constant, the sample must rotate at  $1/2$  the angular velocity of the detector. As the angle of incidence ( $\Theta$ ) changes, the detector must move  $2\Theta$ . This is called 2:1 motion.

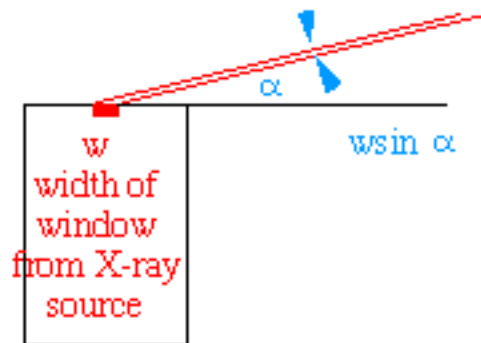
**Instrument alignment.** Principle steps all rely on the fact that the sample is always equally distant between the source and detector. (e.g.,  $R_{\text{incident}} = R_{\text{reflected}}$ )

a. Axial alignment

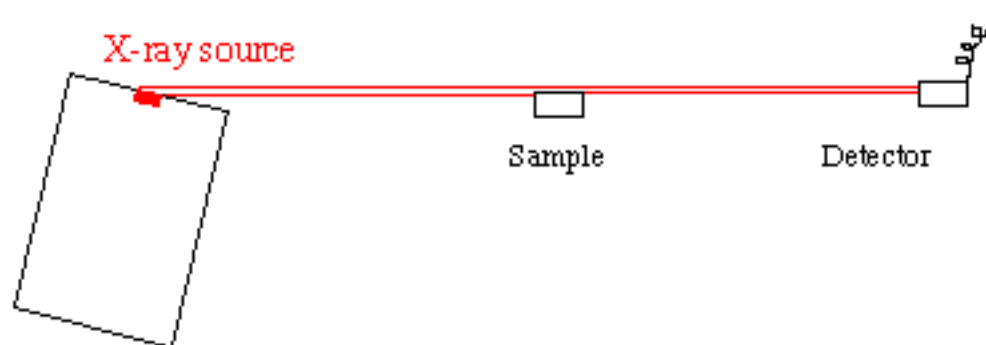


- F = source
- s1 = soller slit
- X = divergent or primary slit
- Y = primary scatter slit
- S = sample
- M = receiving scatter slit
- s2 = soller slit 2
- G = receiving slit.

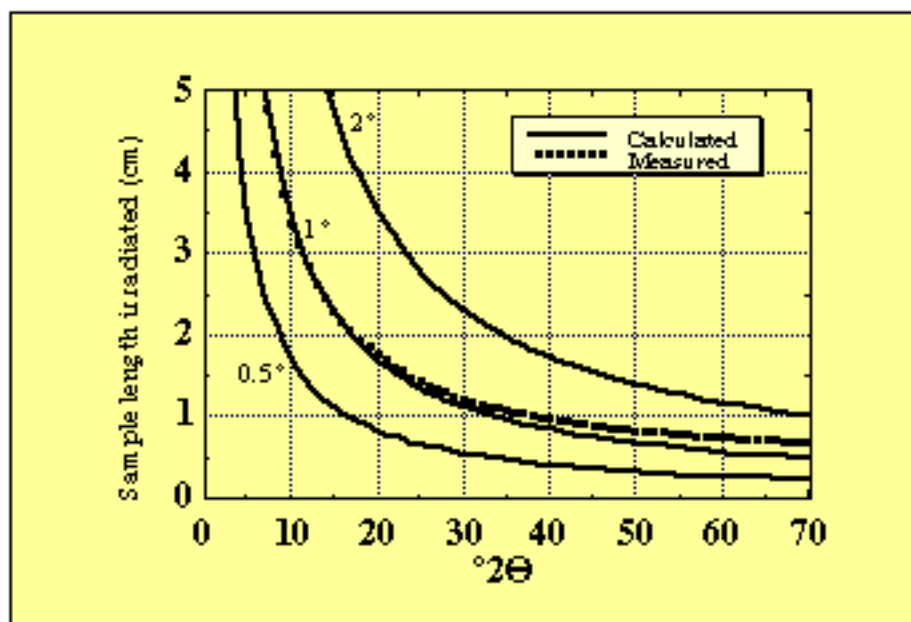
b. Set take-off angle ( $6^\circ$ )



c. Zero alignment



d. Alignment of slits. The divergence slit limits the total irradiation area of the sample. The aperture of this slit hardly affects relative peak intensities if the slit is fixed and the specimen completely intercepts the X-ray beam. Sample mounts are typically hold material in 2.5 cm wide by 2.5 cm long holder.



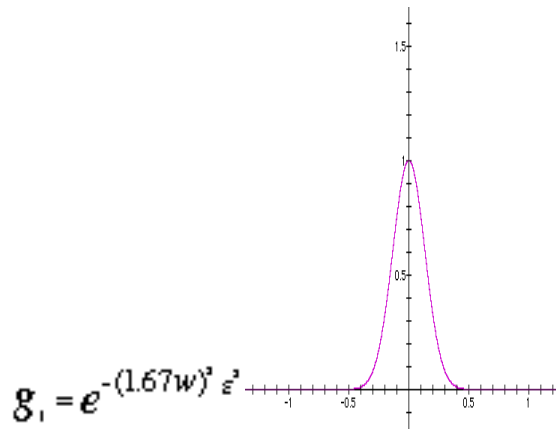
The figure above shows both the theoretical and measured the relationship between sample irradiation length versus  $2\theta$  for several different divergence slits. Modern diffractometers radii range from 180 to 250 cm. Notice that for a 1° slit that a length of 2.5 cm is reached at  $13^\circ 2\theta$ . At lower angles the sample intercepts only part of the beam resulting in reduced beam intensity per unit area of sample surface and increases the likelihood of background scatter from the sample holder. At higher  $2\theta$  angles less area irradiated, which would have an effect of decreasing diffraction intensity. The depth of penetration of the beam becomes commensurably deeper with higher angles. This effectively increases background as well as a sample displacement effect (see below). Theta compensating divergence slits on some diffractometers are designed to lessen high-angle intensity loss and displacement effects and low-angle background scattering. One must always recall however, that the standard form of reporting

relative intensity is with fixed-slit conditions and that variable slit data must be appropriately corrected.

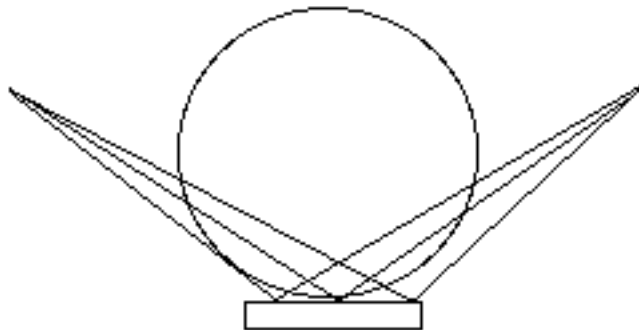
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## Five instrumental functions

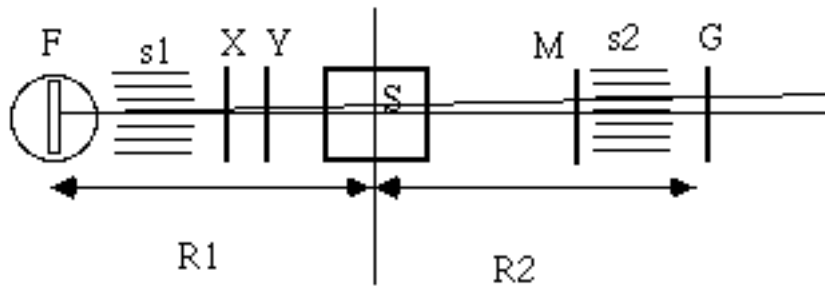
1. X-ray source - Gaussian distribution for  $K_{\alpha 1}$  radiation Early control choices of the operator are Kv and mA settings for the generator. Higher settings to increase peak (and background) intensity and counting statistics can be weighed against possible jeopardy to the tube.



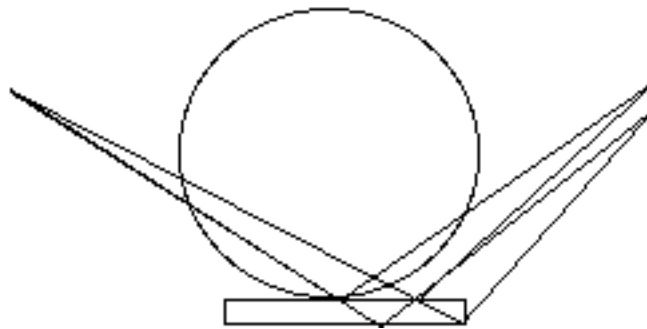
2. Flat specimen error



3. Axial divergence



4. Penetration of the beam into the sample. (Sample transparency). The more intense the incident radiation, the farther the beam penetrates the sample.

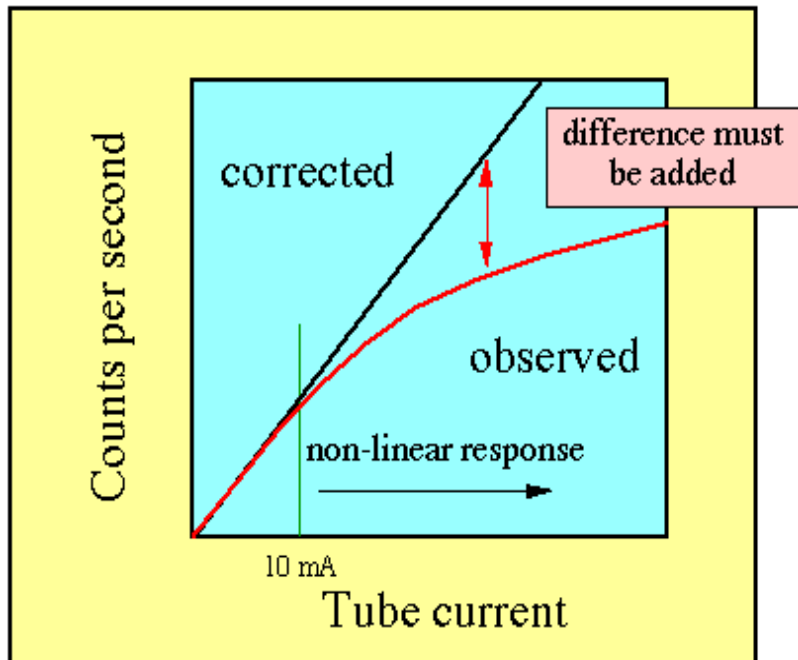


5. Receiving slit - Increasing the width of the receiving slit generally increases the peak height and width and decreases the ability to resolve peaks.

The net effect of instrument line profile modifications is to broaden and displace the theoretical line position to a lower theta angle.  $K_{\alpha 2}$  radiation will displace observed lines to higher angles.

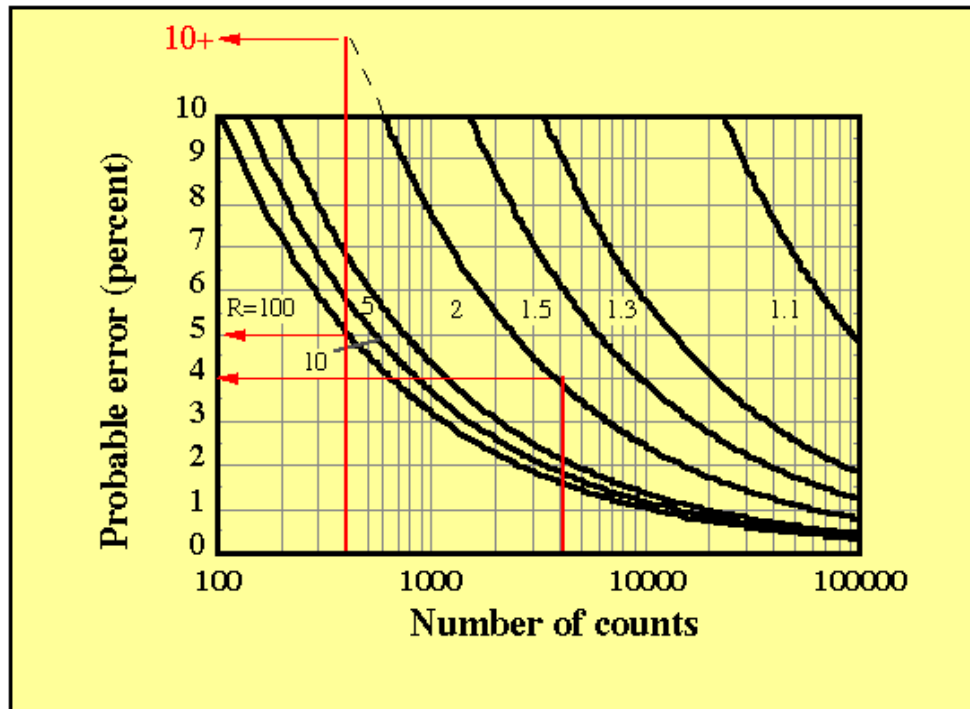
## Detector deadtime

When the measured count rate is not directly proportional to the photon rate entering the detector, the detector response is non-linear and said to have deadtime. The effect is to increase the relative intensity of the weaker peaks. Most modern detectors (with calibration and computer correction) handle count rates up to 100,000 counts per second (cps). A quick check to determine if the detector not responding in a linear fashion is to measure the intensity of the strongest line with the tube current set for the normal quantitation. Perform the measurement a second time at half the tube current. If the second measurement is more than half the first then detector deadtime is the probable cause. In this latter case the detector correction routing must be recalibrated or the observed data must be corrected accordingly.



### Counting Statistics

The precision of intensity data can be limited more by counting statistics than any other single parameter except preferred orientation. The figure below illustrates how the probable error of peak intensity measurements can vary with both the total number of counts and the ratio of the peak to background counting rate ( $R$ ).



$R$  = ratio of peak to background counting rate

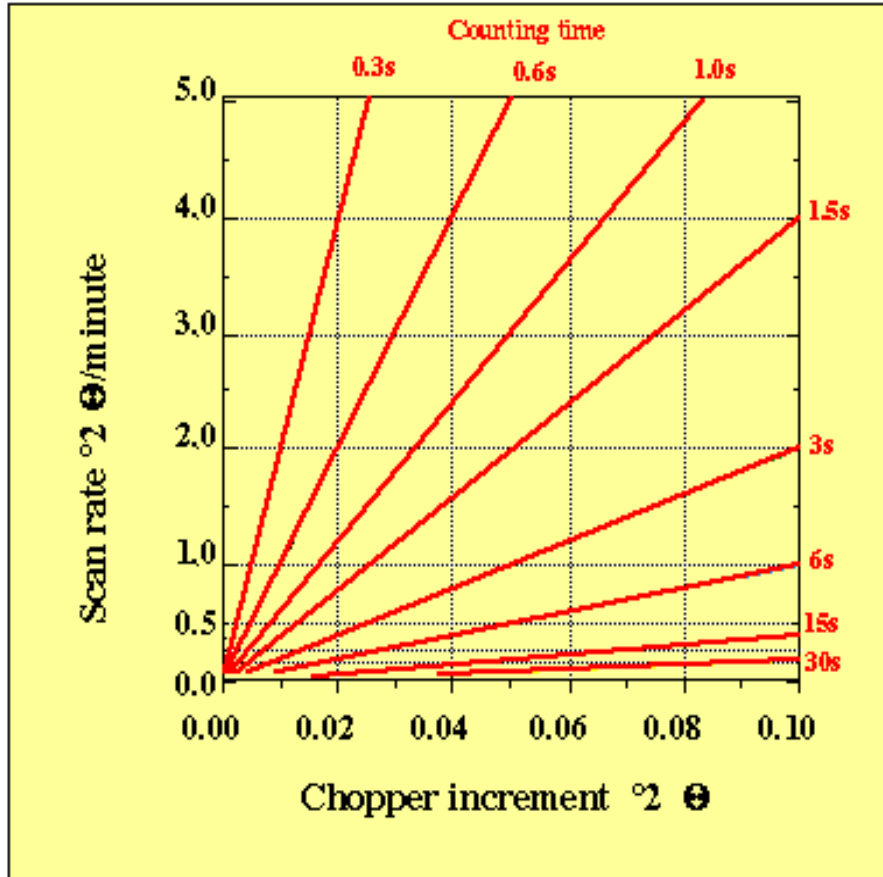
If  $R$  is large (e.g. 100), then the best precision attainable is about  $\pm 5\%$ .

If  $R$  is small (e.g. 2), then error can exceed  $\pm 10\%$ .

By decreasing the scan rate to  $0.2^\circ/\text{min}$ , then small  $R$  (e.g. 2), error drops to  $\pm 4\%$ .

Both the total number of counts and  $R$  depend upon scan rate and chopper increment. For a chopper increment of  $0.01^\circ$  and scan rate of  $2^\circ 2\Theta \text{ min}^{-1}$ , the count time per increment is only 0.3 s. If the counting rate at the peak top is 1000 cps, then the total number of counts is 300. If  $R$  is large, then the best precision attainable is about  $\pm 5\%$ . If  $R$  is 1.5, then probable error exceeds  $\pm 10\%$ . By decreasing the scan rate of  $0.2^\circ 2\Theta \text{ min}^{-1}$ , probable error drops to  $\pm 4\%$ .



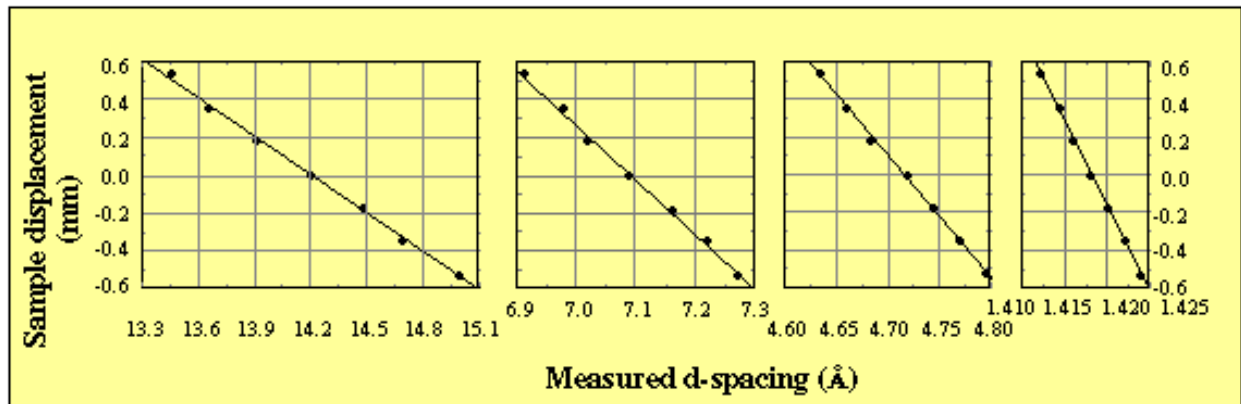


Further improvement in peak intensity precision is possible by smoothing over the peak top in small increments and also averaging background over hundreds of increments on both sides of a peak.

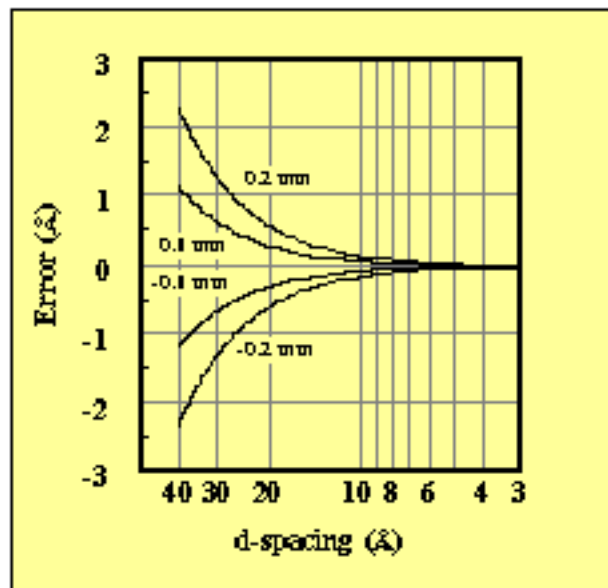
### Sample displacement

Displacement of the sample off the diffractometer focusing circle can be brought about in three ways. Firstly, there is instrumental misalignment. Often neglected is the tacit assumption that the goniometer is properly aligned before any experiment is run. This can be easily maintained with a proper alignment using manufacturer provided tools and checking with a standard material such as the U.S. National Institute of Standards and Technology Reference Material 640b.

If the sample holder is properly aligned then the second potential source of displacement error comes from way the sample itself is packed into the sample holder (see next section). The figure below shows the changes in measured d-spacings for a series of reflections as a function of displacement from the goniometer focal plane.



Displacement error increases rapidly as  $2\theta$  falls below  $20^\circ$  as see in the figure below.



Equally important is the decrease in diffraction intensity with increasing displacement. Finally, effective displacement or sample transparency can be a consequence of a low mass absorption coefficient ( $\mu$ ) or high sample porosity (see next section).

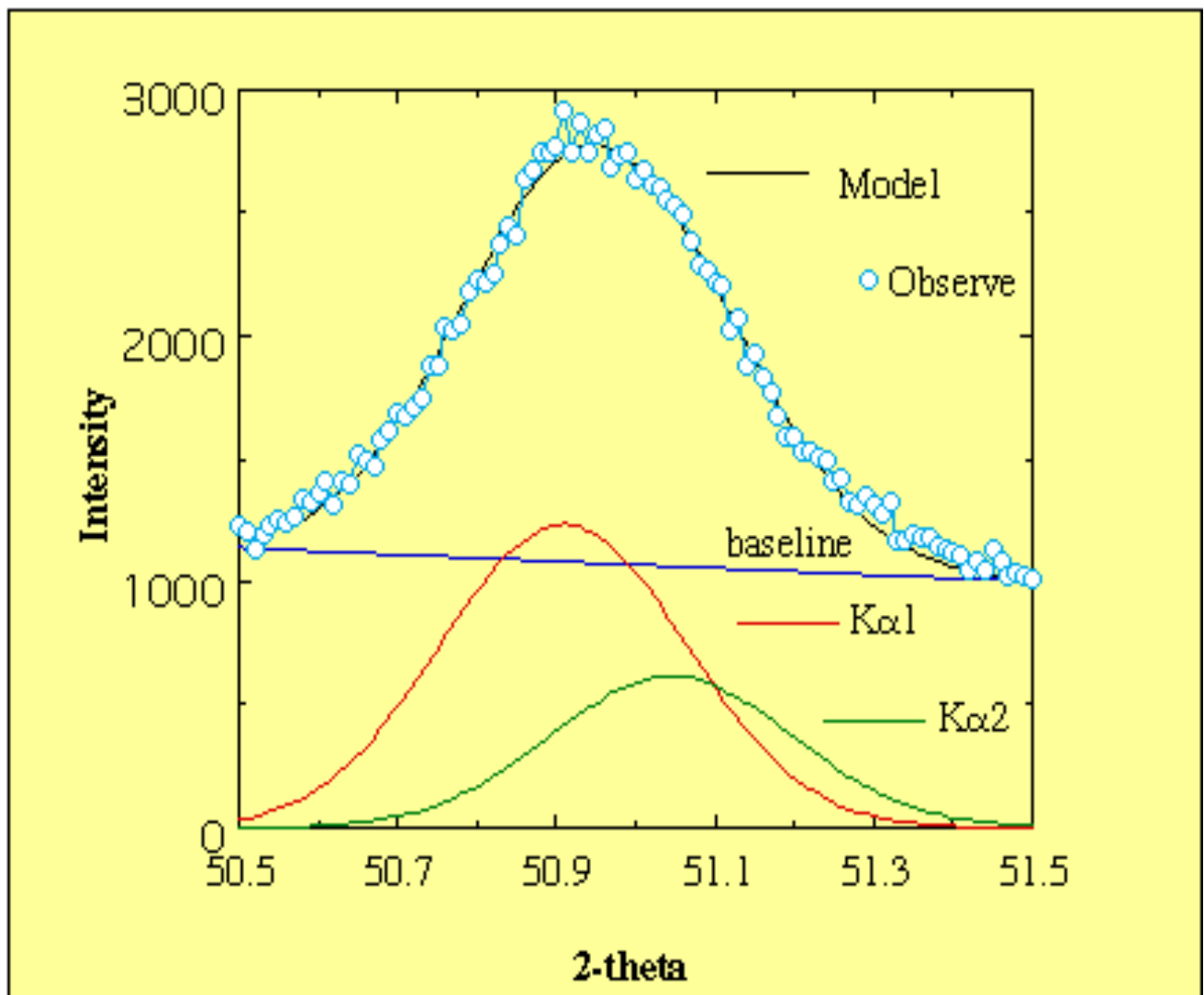
## Background

Background can be produced from several sources. These include:

1. Fluorescent radiation emitted by the specimen
2. Diffraction of a continuous spectrum of wavelengths
3. Diffraction scattering from materials other than the specimen including soler slits, specimen binder, sample mount and air.
4. Diffuse scattering from the specimen itself, including
  - Incoherent (Compton) scattering which increases as when light elements are present

- Coherent scattering:
  - Diffuse scattering due to various crystallite imperfections. Extremely short-range ordered material like glass cause intense diffuse scatter.
  - Low intensity maxima contribute to background when the number of unit repeats normal to the diffracting plane are small.
  - Temperature diffuse scattering is general small unless soft materials are involved.

Peak fitting procedures typically need to consider removal of background. Without correction for the background much of the trace is fit with nonsensical peaks that do not provide a unique solution. Most all XRD manufacturers provide peak fitting software to allow this procedure.



The figure above demonstrates a single peak fitting approach. The form of the fit is:

Intensity = baseline +  $K_{\alpha 1}$  Gaussian (peak ht. and width) +  $K_{\alpha 2}$  Gaussian (peak ht. and width).

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## Sample Preparation

Specimen sensitive errors are most introduced while preparing the sample for presentation to the X-ray beam. Itemized below are the most profound parameters related to preparation and mounting of powder.

### 1. Coherent scattering domain.

It is possible to calculate the diffraction pattern (*i.e.*, interference pattern) for any given crystal structure given:

- The nature of the electrons that surround the atom.
- The thermal vibration of the atom center.
- The arrangement of atoms in the unit cell.
- The wavelength of the incident, monochromatic radiation.

Under ideal conditions all the diffraction takes place at the Bragg angles of reflection.

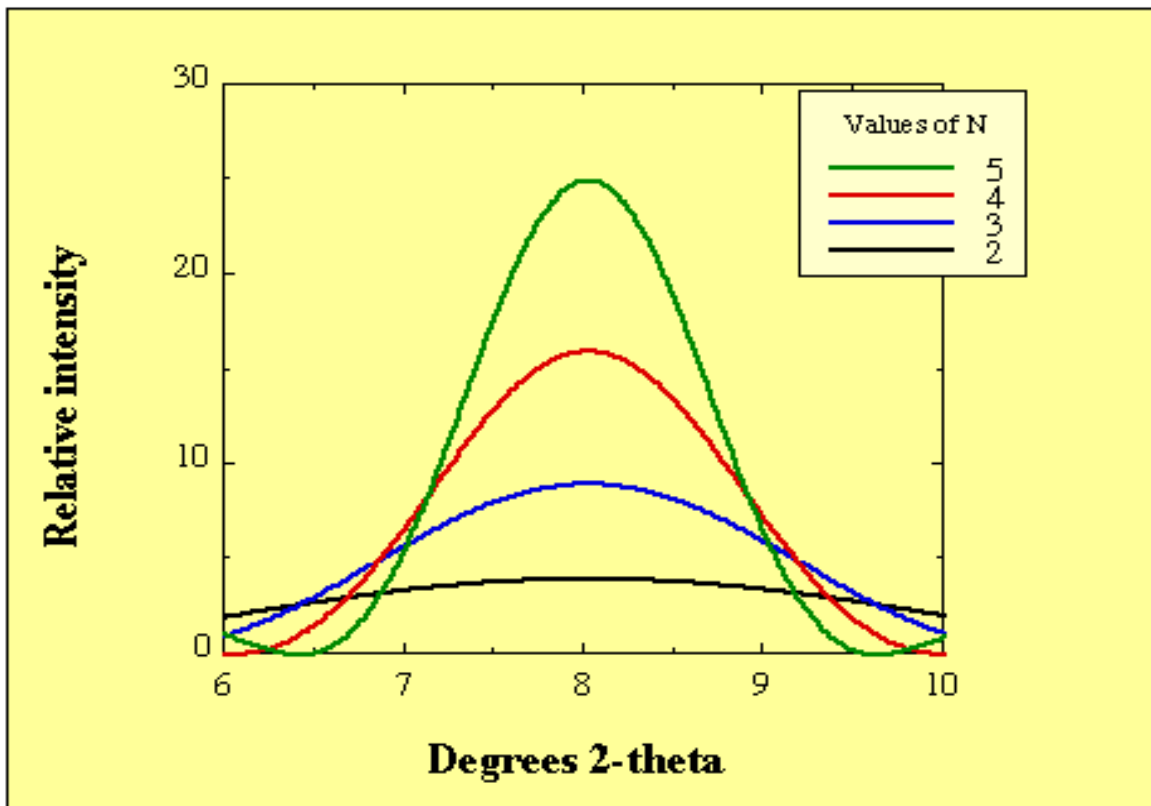
Diffraction effects (in one dimension) due to scattering from a grating can be described by an interference function:

$$\Phi = \frac{\sin^2 \left( 2 \pi N D \frac{\sin \theta}{\lambda} \right)}{\sin^2 \left( 2 \pi D \frac{\sin \theta}{\lambda} \right)}$$

where:

- D = separation of lines (*e.g.*,  $d_{001}$ )
- N = the total number coherent scattering domains) Note: as N gets smaller, so does the breadth of line.
- N x D is crystallite size
- If N = 1 then  $\Phi = 1$  at all angles. Bragg reflection cannot occur from a single scattering center.
- If N = 100, then  $\Phi$  at the ideal Bragg angle is large. At the same time  $\Phi$  is small away from the Bragg angle. In other words the peaks are very intense and narrow.

This relationship is shown graphically in the figure below.



Excessive grinding of a sample, during preparation can induce defects in the crystal structure and reduce coherent scattering intensity.

## 2. Preferred orientation

The XRD powder method relies on principle that all possible crystallographic orientations are presented to the beam. This concept is known a random orientation. If there is a bias of orientations of one or more crystallographic plane, then this is known a preferred orientation. Preferred orientation is likely the most common cause of intensity variations in XRD powder experiments.

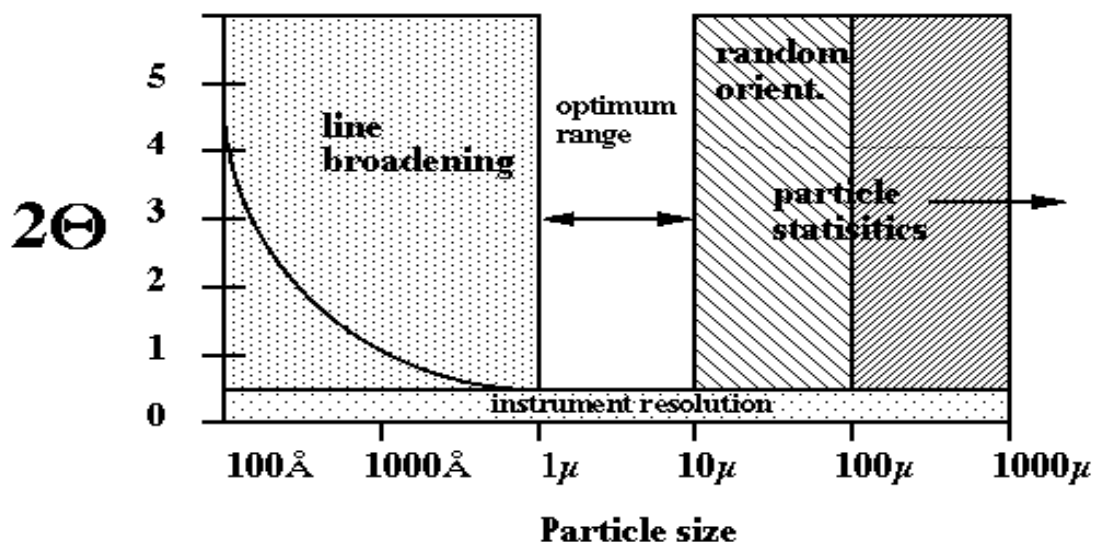
Particles with perfect cleavage or acicular shapes, such as clay minerals, are the most prone to preferred orientation. Intensity variations up to 100% are possible. Here are some tips to minimize the effects of preferred orientation.

a. Be consistent with sample mounting and packing methods. Sprinkling and backpacking may reduce preferred orientation. Apply a constant pressure (e.g. 200 psi for 20 s).

b. Reduce the particle size of the material to about 5 to 10  $\mu\text{m}$ . This also minimized primary and secondary extinction effects. Using a wet grinding method reduces defects.

c. Mix the sample with 20% internal standard. Pick an internal standard that has equant particles and that does not interfere with the peaks of interest.

d. Slurry mounting with acetone can minimized preferred orientation. Water is a polar compound, where as acetone is less polar and it evaporates quickly. If particles are kept away from each other while drying, then van der waal forces will not let them to attract to each other and self align. The pitfall of slurry mounting is that the sample may be too thin (see below).



### 3. Powder thickness and transparency

The thickness of the powder should be great enough to prevent the beam from passing through to the substrate below. The generally accepted reduction of the beam intensity is about 1/1000th of the initial beam intensity. This condition is termed "infinite thickness".

Examples of powder thickness ( $\mu\text{m}$ ) required for attenuation of a  $\text{CuK}\alpha$  beam to 0.01 and 0.001 times incident intensity as a function of  $2\theta$ .

Attenuation factor		0.01				0.001			
Porosity		solid	0.9	0.8	0.7	solid	0.9	0.8	0.7
Gibbsite $\mu=56.8 \text{ cm}^{-1}$ $\mu=24.2 \text{ cm}^2\text{g}^{-1}$	4°	14.1	15.7	17.7	20.2	21.2	23.6	26.5	30.3
	20°	70.4	78.2	88.0	100.5	105.6	117.3	131.9	150.8
	40°	138.6	154.0	173.3	198.0	207.9	231.0	259.9	297.0
	80°	261.0	289.0	326.0	372.0	391.0	434.0	488.0	559.0
Quartz $\mu=96.5 \text{ cm}^{-1}$ $\mu=36.4 \text{ cm}^2\text{g}^{-1}$	4°	8.3	9.3	10.4	11.9	12.5	13.9	15.6	17.8
	20°	41.4	46.0	51.8	59.2	62.2	69.1	77.7	88.8
	40°	81.6	90.7	102.0	116.6	122.4	136.0	153.0	174.9
	80°	153.4	170.5	191.8	219.2	230.1	255.7	287.6	328.7
Hematite $\mu=1124.4 \text{ cm}^{-1}$ $\mu=216.2 \text{ cm}^2\text{g}^{-1}$	4°	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.5
	20°	3.6	4.0	4.34	5.1	5.3	5.9	6.7	7.6
	40°	7.0	7.8	8.8	10.0	10.5	11.7	13.1	15.0
	80°	13.2	14.6	16.5	18.8	19.7	21.9	24.7	28.2

Factors that influence the transparency of a specimen include:

1. The mass absorption coefficient of the sample. The previous table gives requisite powder thickness for various materials with small, medium and large mass absorption coefficients and with different porosity.
2. Thickness of the sample. Sometimes you just don't have enough material to pack your holder. Using a "zero-background" plate minimizes scatter from the substrate. A common zero-background plate is a quartz crystal cut and polished 6° of the *c*-axis.
3. Porosity of the sample. This is minimized by good sample packing. If the sample is porous and thin, then the higher order (angle) reflections will be compromised.

## Data Processing and Interpretation

### **K<sub>α2</sub> stripping.**

At low angles of  $2\Theta$  K<sub>α1</sub> and K<sub>α2</sub> peaks are closely overlapped. There are computer programs that will mathematically remove the K<sub>α2</sub> peak component. They use relationships between K<sub>α1</sub> and K<sub>α2</sub> radiation (1.54059Å and 1.5440Å, respectively) via Bragg's law and the assumption that the K<sub>α1</sub> peak intensity is one-half of the K<sub>α2</sub> peak. The net intensity of stripped data is therefore one-third the observed intensity.

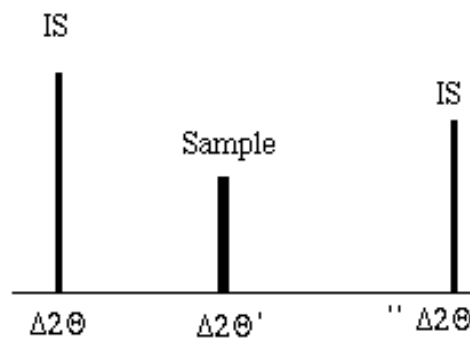
## Peak finding.

There various degrees of sophistication for determining peak properties. In increasing order of complexity they are as follows:

1. Graphically picking peak intensity and positions with a cursor
2. Second-derivative peak finding routine
3. Profile fitting
4. Rietveld refinement

## Calibration/correction.

NIST SRM640b Silicon metal, SRM675 synthetic fluoro-phlogopite.



$\Delta 2\Theta$  = practical d-value - observed d-value

Correction to the sample peak position is by simple linear interpolation.

$$2\Theta'_c = 2\Theta'_o + * (\Delta 2\Theta''_{po} - \Delta 2\Theta_{po})$$

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## Qualitative analysis - phase identification

- **Assertion** - If you can enumerate the steps used to solve a problem, then a computer can do it for you.
- **Conversely** - No computer can solve a problem for which and algorithm cannot be written.
- **Corollary** - Don't expect a computer algorithm to produce results based information you do not supply to it!



What do you do once you have the d's and I's ?

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## Search/match procedures

Introduction to the Joint Committee Powder Diffraction Standards data base.

Now called the International Centre for Diffraction Data - Powder Diffraction Files (PDF)

As of 2000 there are 49 sets of inorganic and organic data files.

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## Preconceived notions and the alphabetical listing

Each phase in the data base is listed by chemical name and permutations of the name:

Chemical Name: /mineral chemical formula Strongest 2nd 3rd PDF #

iron carbonate:/ Siderite  $\text{FeCO}_3$  2.80x 1.734 1.743 29-696

carbonate iron:/ Siderite  $\text{FeCO}_3$  2.80x 1.734 1.743 29-696

What if the sample is a mixture?

Example: Beach sand, you think it is quartz.

Observed Card #4-590 Residual Card #5-628

$d\text{\AA}$  Irel  $d\text{\AA}$  Irel  $\pm\Delta d$   $d\text{\AA}$  Irel  $d\text{\AA}$  Irel  $\pm\Delta d$

4.26 30 4.26 35 0.000

3.345 100 3.343 100 0.002

3.260 5 3.260 5 (11) 3.258 13 0.002

2.822 45 2.822 45 (100) 2.821 100 0.001

2.459 12 2.458 12 0.001

2.283 14 2.282 12 0.001 2.283 2(4)

There are no rules when it comes to identifying an unknown! Don't be too proud to ask the person who gave you the sample some questions about its origin. In the case above, there is a residual. Common sense tells you that shells are often found on the beach, so therefore why not go directly to the card for calcite and eliminate it as a possibility? The residual turns out to be calcite.

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## Hanawalt Search method

Hanawalt "grouping" is based upon the d-spacings of the three most lines in the pattern.

The lines are arranged as follows:

dA dB dC dD dE dF dG dH

where, A, B, C...H are the eight strongest lines in descending order.

If  $> 0.75$  and  $< 0.75$ , then

**dB dA dC dD dE dF dG dH**

If  $> 0.75$  and  $< 0.75$ , then

**dC dA dB dD dE dF dG dH**

If  $> 0.75$ , then

**dD dA dB dC dE dF dG dH**

The entire file is then arranged into groups based upon ranges of  $d(\text{\AA})$ .

999.99 - 10.00

9.99 - 8.00

7.99 - 6.00

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1.39 - 1.00

1. Begin the search by arranging the observed d's from strongest ----> weakest.
2. Select the strongest unused line. (example is quartz - 3.34Å)
3. Proceed to the **main** group. The patterns are arranged into **subgroups** based upon descending d-values of the either the second or third strongest lines.
4. If a match is suspected, then the other eight d-values and intensities area checked to see if they are present in the observed pattern.
5. Note: There are errors ranges associated with each group. Peaks with d-values outside the range of the main group can be found within the group. This allows for errors from sample sensitive and specimen sensitive variations.
6. If a match is likely, proceed to the actual JCPDF card file.
7. Subtract the pattern and look for residual peaks.

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## Fink Search method

Fink "grouping" is based upon the eight strongest lines in the pattern.

Works better than Hanawalt method when.

- large number of equal intensity lines
- significant number of large d-values
- Relies less on intensity match, ∴ better when there is preferred orientation.

There are four entries for each pattern, each starting with one of the four most intense lines.

The remaining seven lines in each entry are arranged in descending order of d-value.

Example: Lines ordered in terms of descending d-values (**bold** four most intense).

**d9** d3 d6 **dx** **d7** d5 **d8** d4

The permutations then become:

**dx** **d7** d5 **d8** d4**d9** d3 d6  
**d7** d5 **d8** d4**d9** d3 d6 **dx**  
**d8** d4**d9** d3 d6 **dx** **d7** d5

Like the Hanawalt system the entire file is then arranged into approximately equal size groups based upon ranges of d(Å).

999.99 - 10.00

9.99 - 8.00

7.99 - 6.00

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1.39 - 1.00

Within each group entries are listed in descending order of the second d-value.

1. Begin the search by arranging the observed d's from largest ----> smallest.
2. Select the unused line with the largest d-spacing (one of the four strongest) (example is quartz 4.27Å)
3. Proceed to the **main** group. The patterns are arranged into **subgroups** based upon descending d-values of the second d-value.
4. If a match is suspected, then the other eight d-values and intensities area checked to see if they are present in the observed pattern.
5. Note: errors ranges associated with each group. Peaks with d-values outside the range of the main group can be found within the group. This allows for errors from sample sensitive and specimen sensitive variations.
6. If a match is likely, proceed to the actual JCPDF card file.
7. Subtract the pattern and look for residual peaks.

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## Criteria for a match.

The tolerance for a possible window in d is related to the following factors:

$$\pm\Delta d\text{\AA} = \text{precision} + \text{accuracy} + \text{chemical purity}$$

Accuracy is achieved by the appropriate calibrations and corrections (*i.e.*, internal standard corrections).

If you expect additional variations due to solid solution substitutions (*i.e.*, a change in  $f_n$  and  $f_x$ ,  $f_y$ ,  $f_z$ )

Error windows for d-values:

		10°2Θ/minute		1°2Θ/minute	
dÅ	°2Θ(CuKα)	±ΔdÅ	±Δ°2Θ	±ΔdÅ	±Δ°2Θ
5.0	17.7	0.030	0.1	0.010	0.04
3.0	29.8	0.010	0.1	0.003	0.04
1.5	61.8	0.003	0.1	0.001	0.04