chem 5390

# Advanced X-ray Analysis

## LECTURE 10

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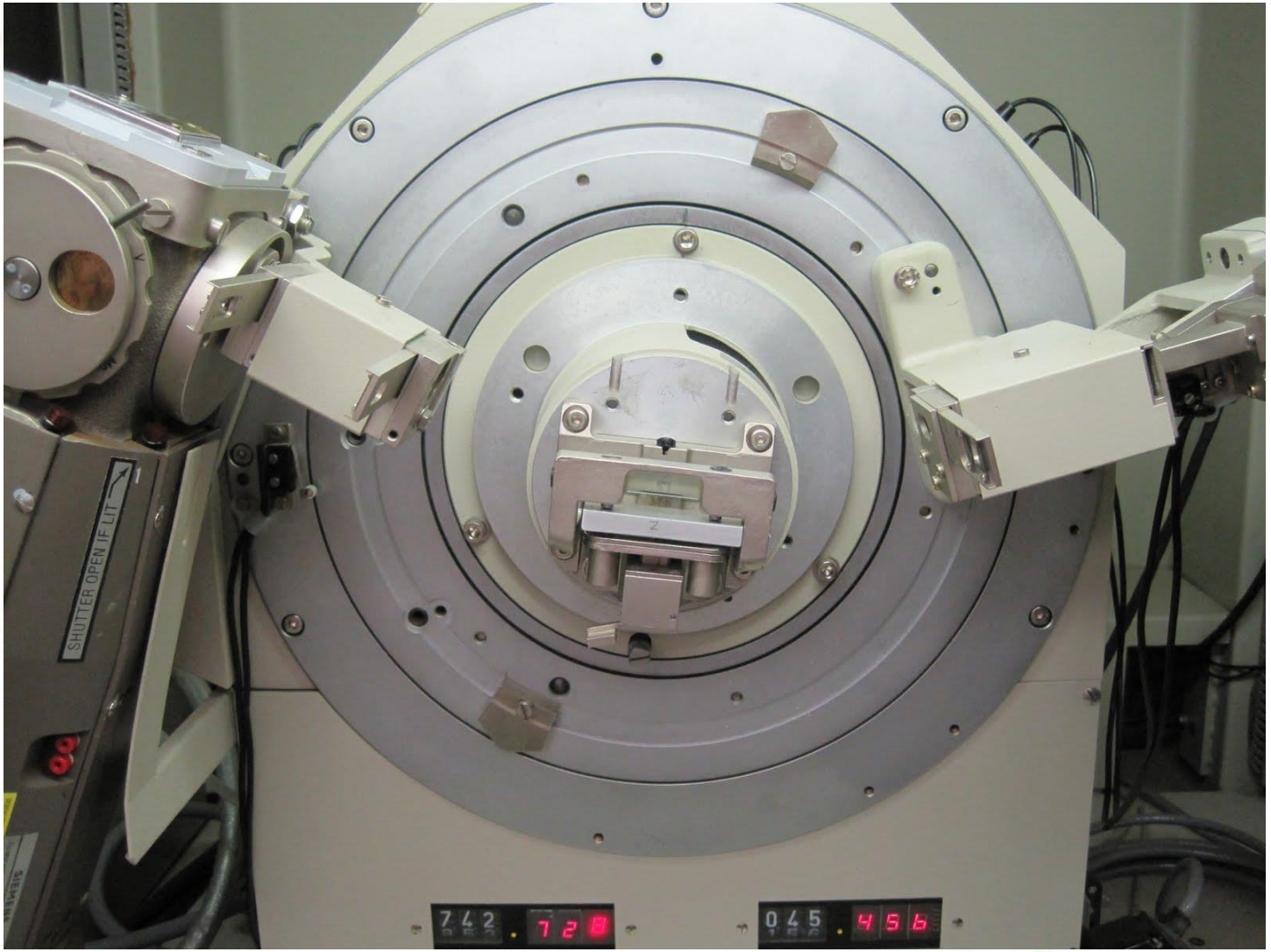
**University of North Texas**
**Department of Chemistry**

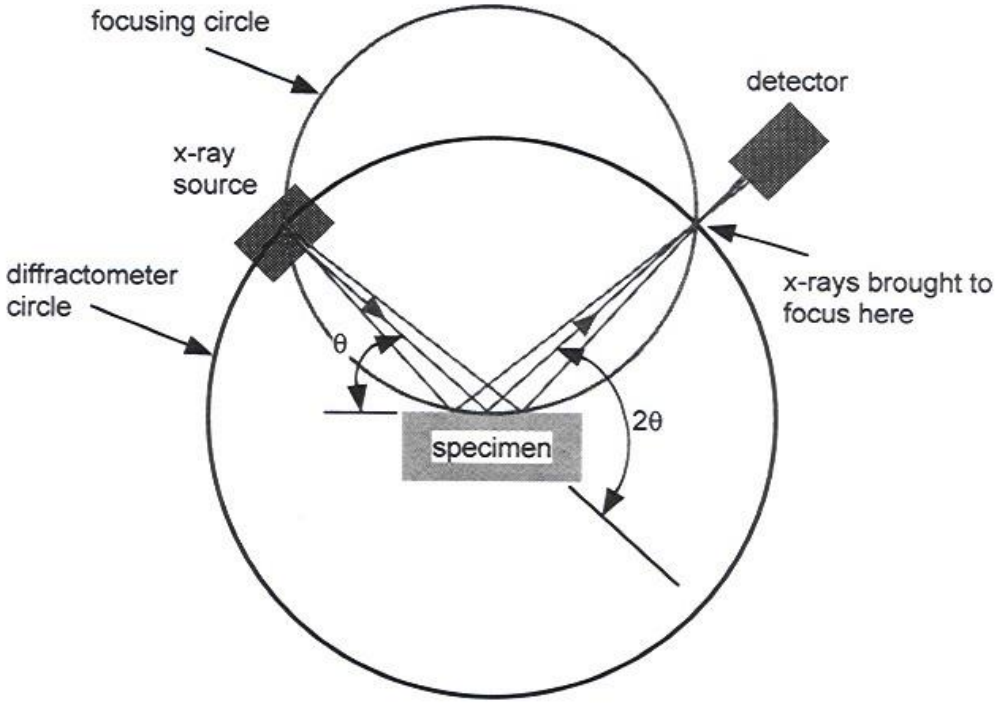
# Instrumentation




chem 5390
Advanced X-ray Analysis

# Instrumentation

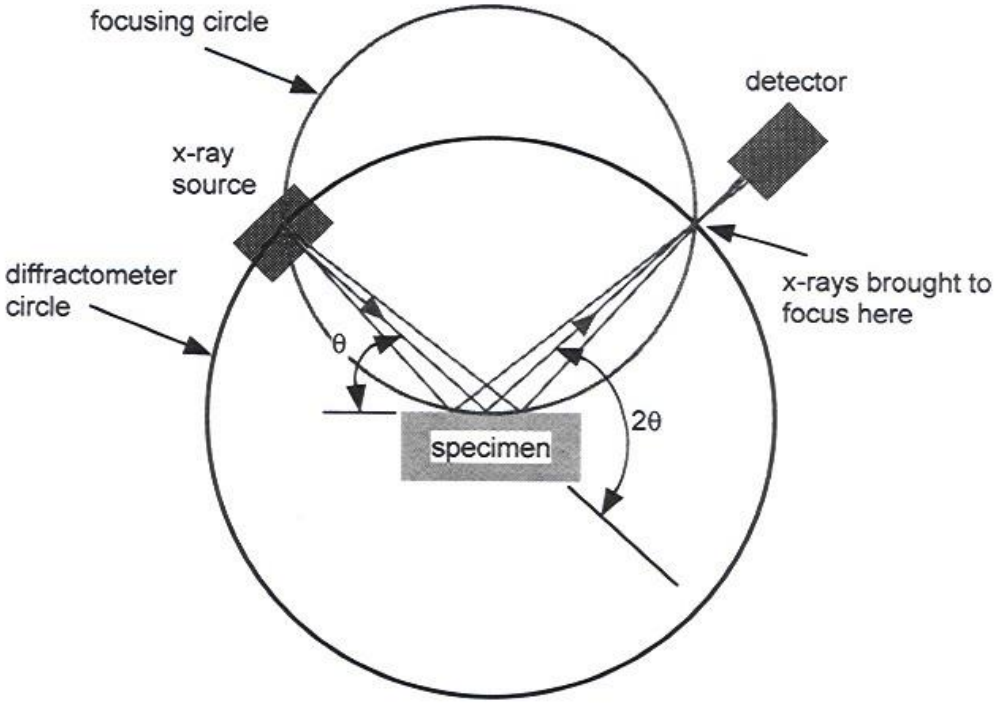
## E. Goniometer




**Goniometer circle - centered at the sample, with the x-ray source and detector on the circumference of the circle.**

# Instrumentation

## E. Goniometer

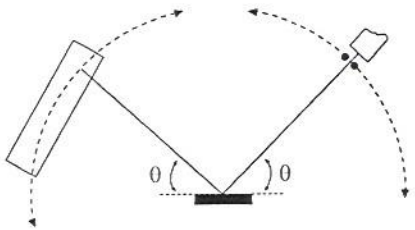



**Focusing circle – the source, sample, and receiving slits all lie on the circumference. It has a radius of rf, which varies with diffraction angle.**

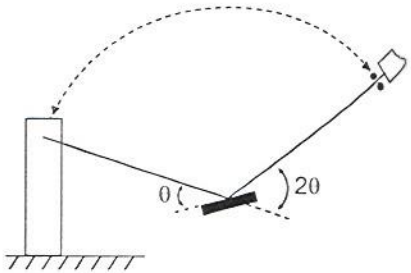
# Instrumentation

## E. Goniometer

(*a*) Vertical θ:θ

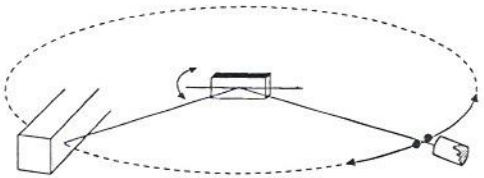



(*b*) Vertical θ:2θ




**There are several common arrangements for the goniometer.**

(*c*) Horizontal θ:2θ

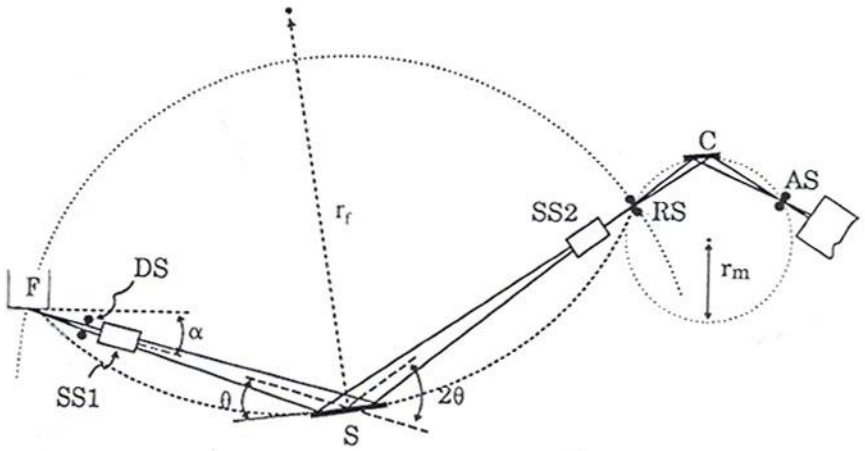


# Instrumentation

## E. Goniometer

**The θ:2θ vertical arrangement is the most common, easy to do powders.**

**The common θ – 2θ geometry is also known as the Bragg-Brentano arrangement.**




Goniometer Circle Radius

R = F → S = S → RS

# Instrumentation

## E. Goniometer

**The horizontal θ:2θ arrangement is common when there are many attachments on the detector arm, but harder to do powders.**

# Instrumentation

## E. Goniometer

**θ – 2θ geometry – most common (the x-ray source is fixed)**

**The θ:2θ system is mechanically simple.**

**For θ:2θ scans, the goniometer rotates the sample about the same axis as the detector, but at half the rotational speed, in a θ:2θ motion.**

**The surface of the sample remains tangential to the focusing circle, rf.**

# Instrumentation

## E. Goniometer

**θ – θ geometry – x-ray source and detector move in opposite direction above the center of the specimen, scan is omega (ω) scan, provides a measure of strain.**

**The θ:θ system is useful for temperature experiments.**

# Instrumentation

## E. Goniometer

**All of the arrangements can rotate or rock the sample for texture analysis.**

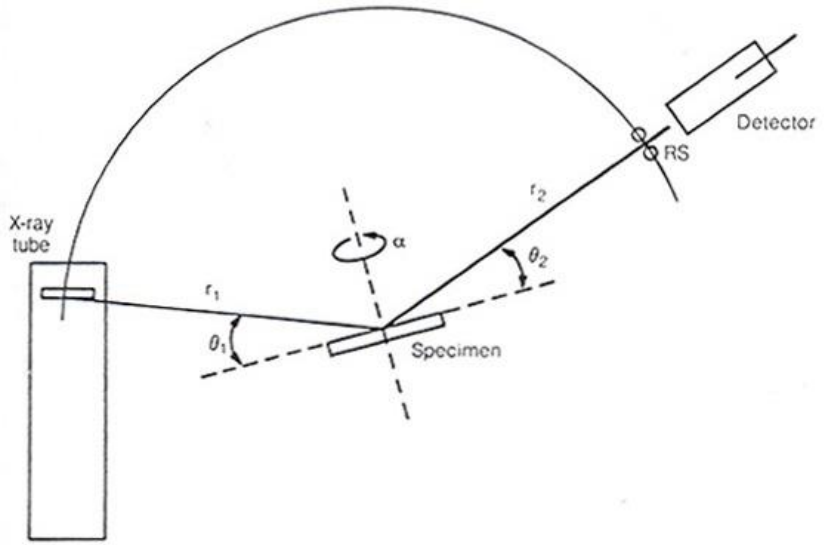
**The Seeman-Bohlin arrangement is common for camera work. r2 is measured from the sample to the film, this is variable, so the film slides on a runner for various focal points.**

# Instrumentation

## E. Goniometer

### 1. Bragg-Brentano

**Majority of commercial instruments employ the Bragg-Brentano geometry in the horizontal or vertical position.**

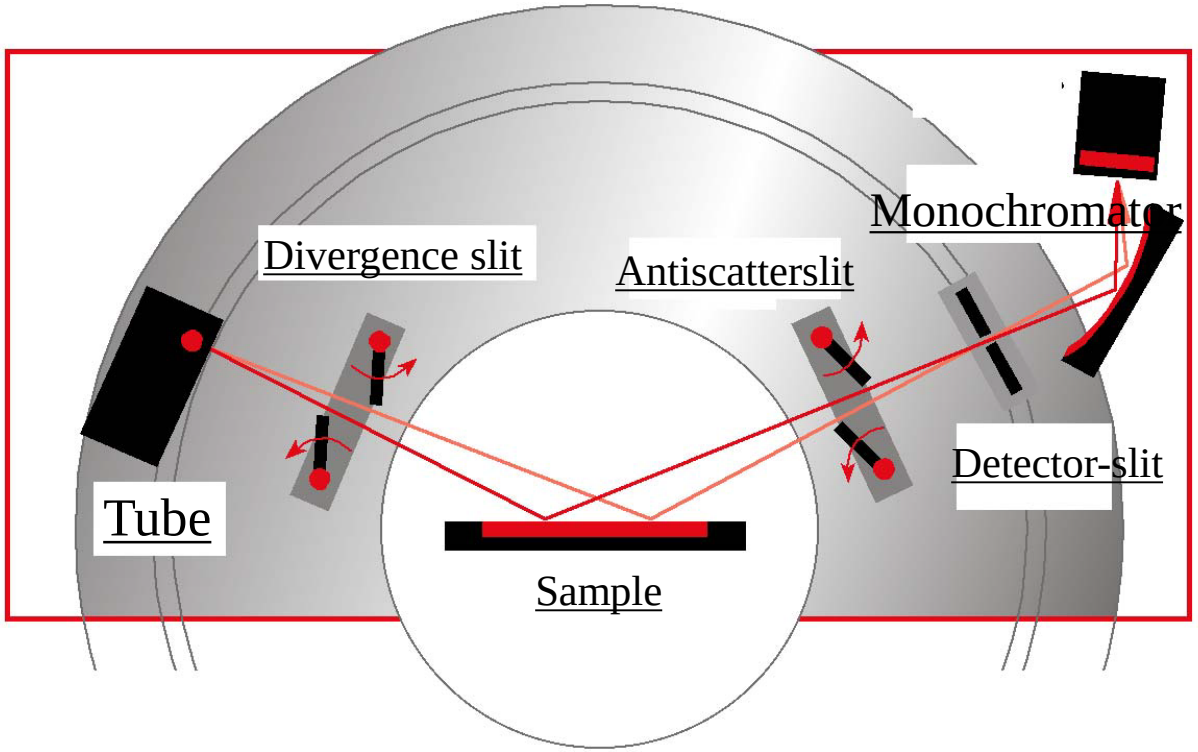


# Instrumentation

## E. Goniometer

### 1. Bragg-Brentano

**In the Bragg-Brentano geometry, the diffraction vector is always normal to the surface of the sample. The diffraction vector is the vector that bisects the angle between the incident and scattered beam.**

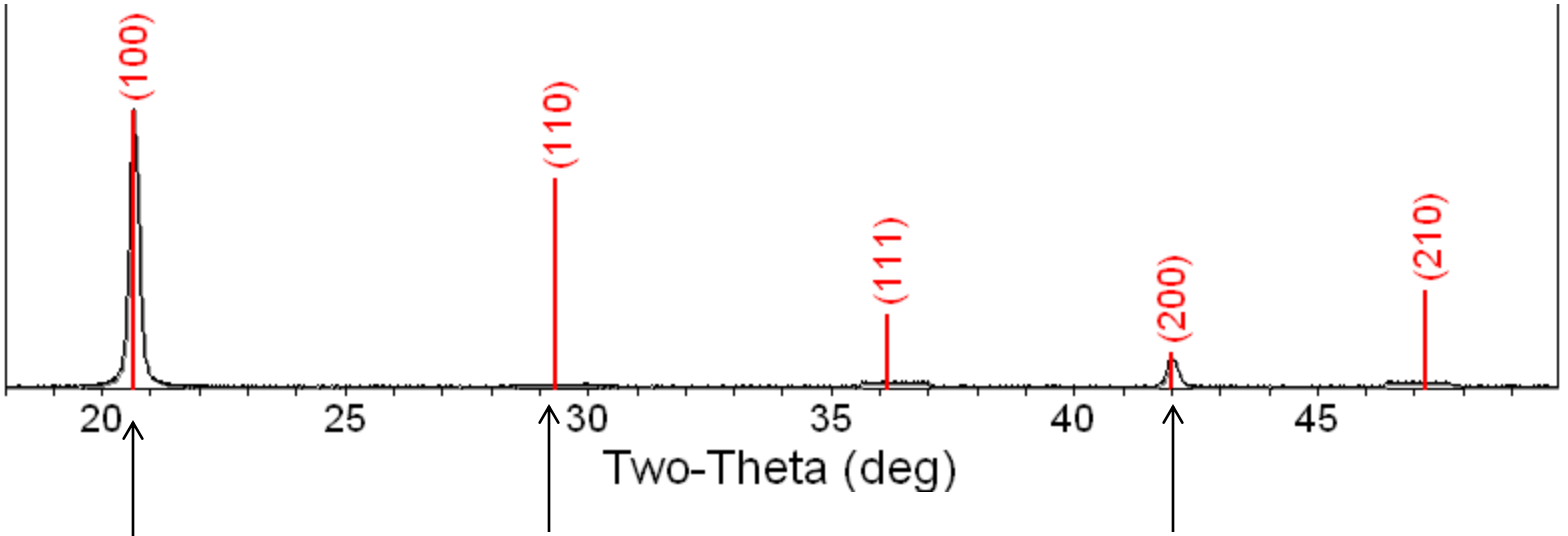


# Instrumentation

## E. Goniometer

### 1. Bragg-Brentano

**A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.**




**At 20.6° 2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.**

**The (110) planes would diffract at 29.3° 2θ; however, they are not properly aligned to produce a diffraction peak.**

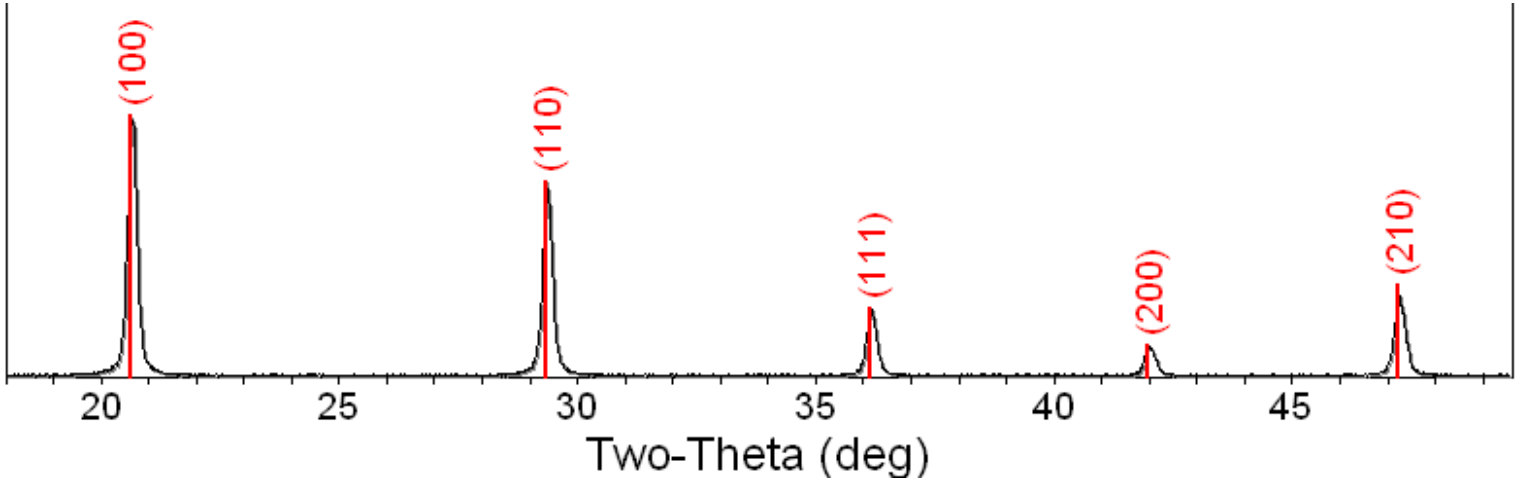
**The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d200 is ½ d100, they appear at 42 °2θ.**

# Instrumentation

## E. Goniometer

### 1. Bragg-Brentano

**A polycrystalline sample should contain thousands of crystallites. Therefore, all possible diffraction peaks should be observed.**



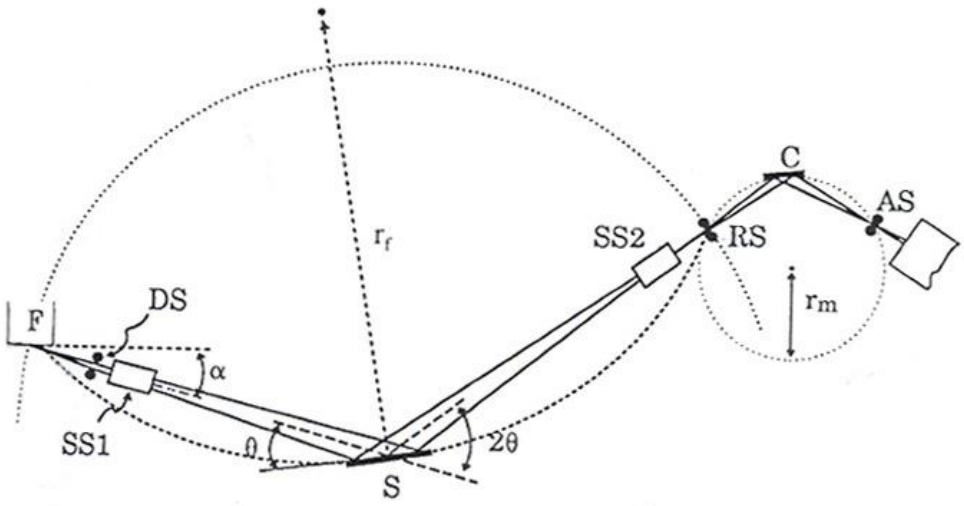

**For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).**
**Basic assumptions that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.**

# Instrumentation

## E. Goniometer

### 1. Bragg-Brentano

**The incident x-ray beam comes from a line of focus (F) through the divergent slits (DS) and soller slits (SS1) to strike the sample at an angle θ.**




Goniometer Circle Radius

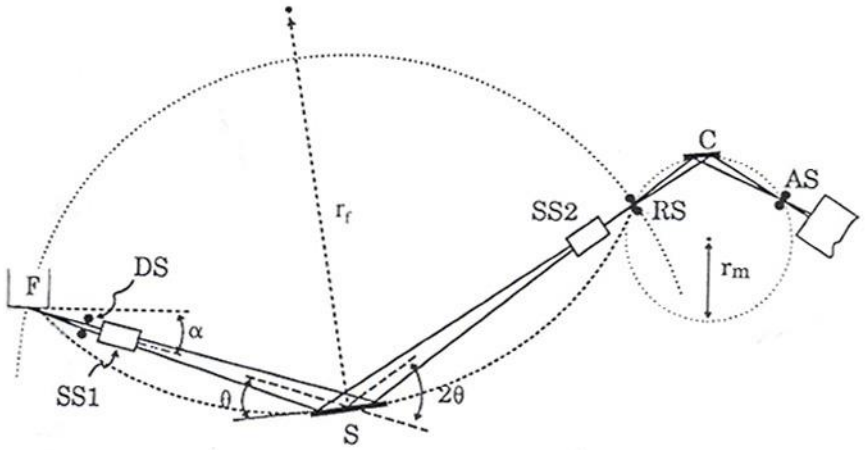
R = F → S = S → RS

# Instrumentation

## E. Goniometer

### 1. Bragg-Brentano

**The diffracted beam leaves the sample at an angle of 2θ to the incident beam (this is θ to the sample), passes through soller slits (SS2) and receiving slits (RS) to the detector.**




Goniometer Circle Radius

R = F → S = S → RS

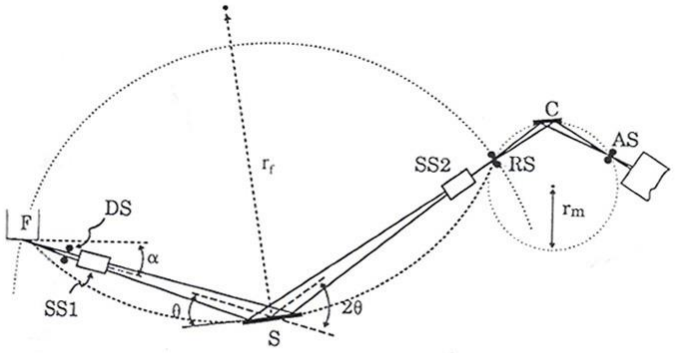
# Instrumentation

## E. Goniometer

### 1. Bragg-Brentano

**Notice the beam is in focus at F and RS.**

**For this condition to occur the axes of the line focus of the x-ray tube and of the receiving slit are at equal distance from the axis of the goniometer (defines the goniometer circle). The radius of the goniometer (R) is fixed.**




Goniometer Circle Radius

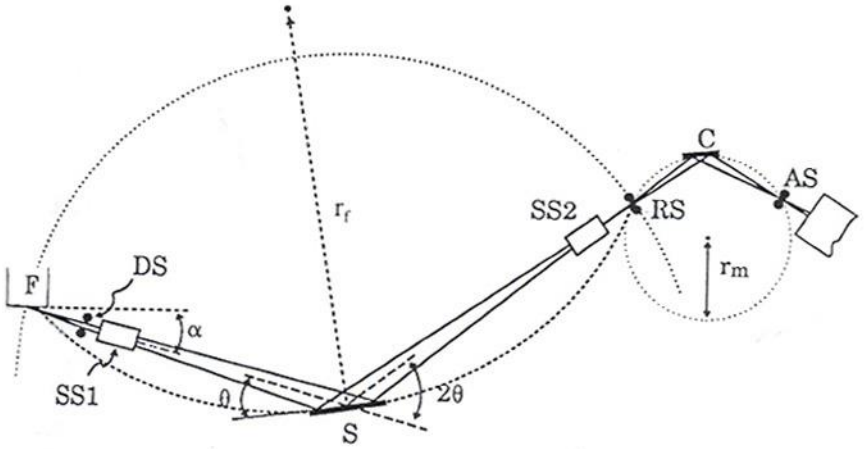
R = F → S = S → RS

# Instrumentation

## E. Goniometer

### 1. Bragg-Brentano

**Another focus occurs between the receiving slit (RS) and the detector slit (DS) which lie on the circumference of the focusing circle of the monochromator.**




Goniometer Circle Radius

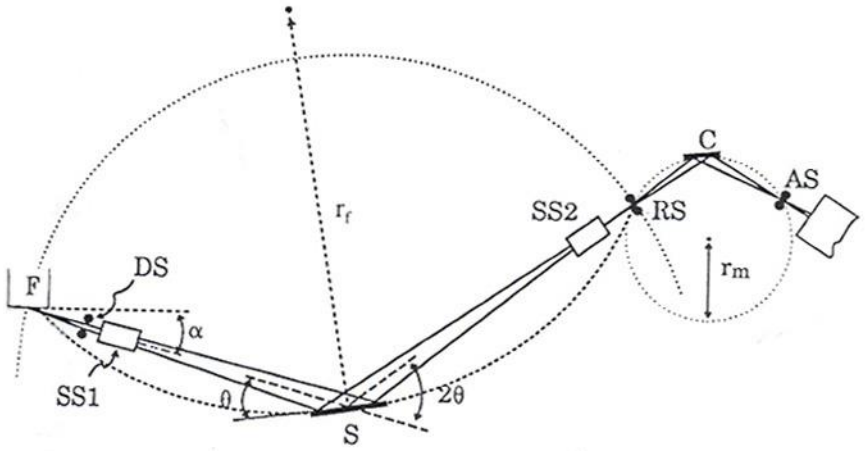
$R = F \rightarrow S = S \rightarrow RS$

# Instrumentation

## E. Goniometer

### 1. Bragg-Brentano

**Three circles are generated by the Bragg-Brentano arrangement - the monochromator circle, goniometer circle and the focusing circle.**




Goniometer Circle Radius

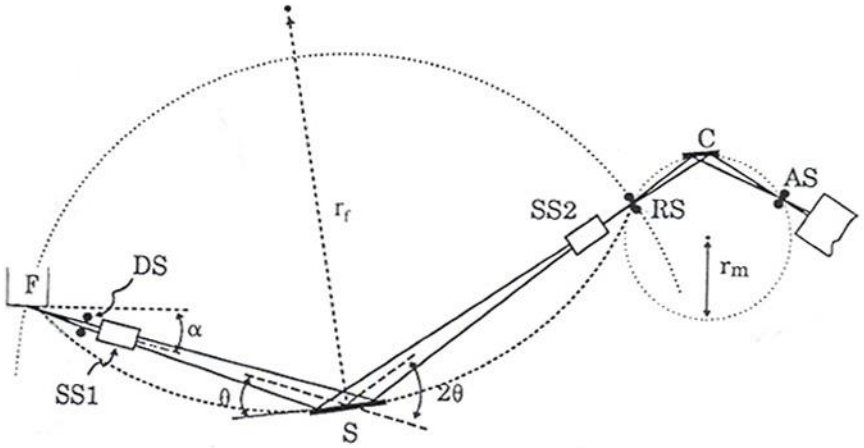
$R = F \rightarrow S = S \rightarrow RS$

# Instrumentation

## E. Goniometer

### 1. Bragg-Brentano

**Focusing circle - the source (F), sample (S) and receiving slits (RS) all lie on the circumference of this circle, which has a radius of rf. The radius of the focusing circle varies with angle.**




Goniometer Circle Radius

$R = F \rightarrow S = S \rightarrow RS$

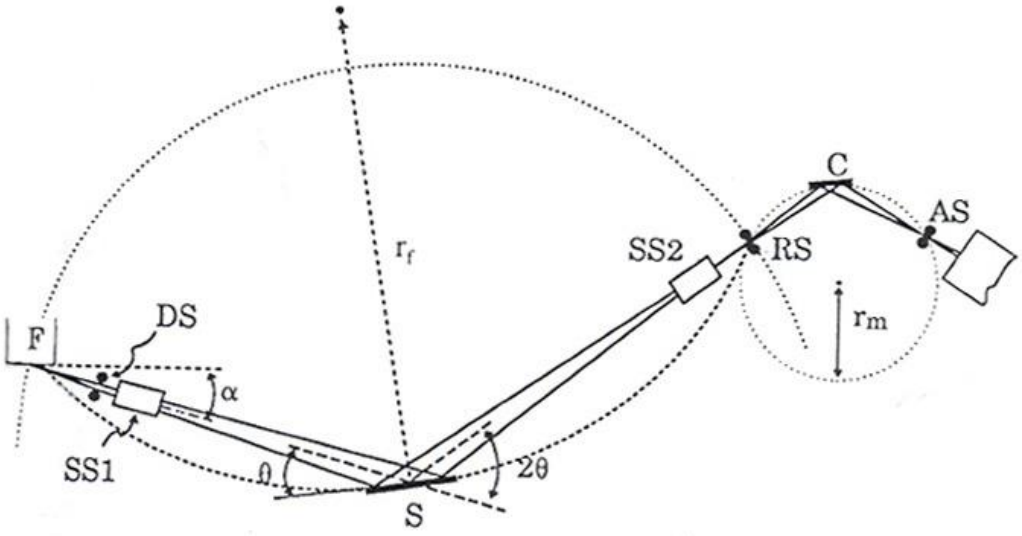
# Instrumentation

## E. Goniometer

### 1. Bragg-Brentano

**The relationship between these two circles is simple:**

**$r_f = R/2\sin\theta$ (R – radius of goniometer)**




Goniometer Circle Radius

R = F → S = S → RS

# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

**When the goniometer is properly aligned, there still may be some errors in measurement, these include:**

**axial divergence error**

**flat specimen error**

**transparency error**

**sample displacement error**

# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### a. Axial Divergence Error

**Occurs when the x-ray beam diverges out of plane of the focusing circle causing an asymmetric broadening in the diffraction profile especially at low angles.**

**Can be controlled by soller slits.**

# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### a. Axial Divergence Error

**Axial divergence of the beam begins as soon as the beam leaves the x-ray tube.**

**Divergent slits help reduce the spread, but does not adequately limit divergence of the beam in the plane of the sample.**

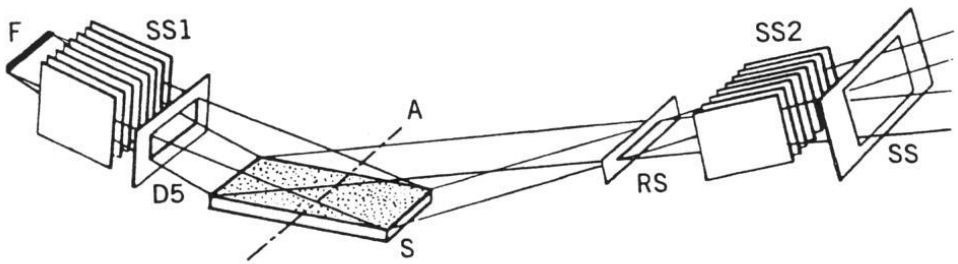



Figure 7-10

# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### a. Axial Divergence Error

This axial divergence is controlled by soller slits.

Soller slits are made of thin Mo foils of fixed length and spacing.

Each slice of the x-ray beam emerging between adjacent plates has its own cone of diffraction.

This causes a variation in the intensity across the receiving slit.

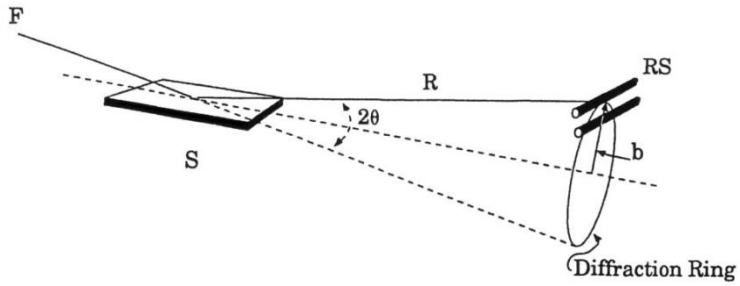



Figure 7-12

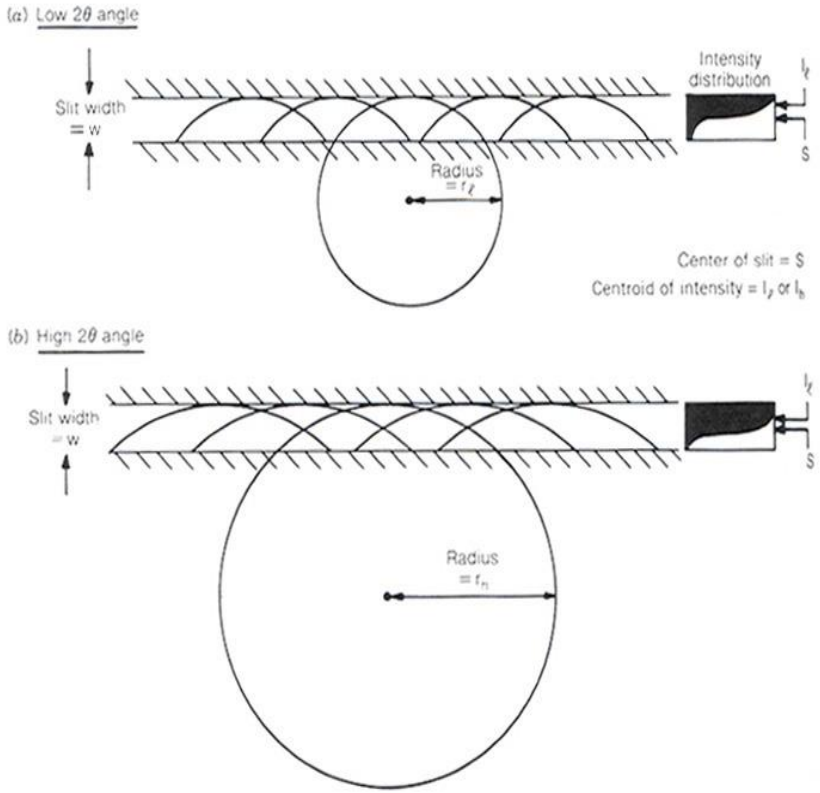
# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### a. Axial Divergence Error

**This causes a variation in the intensity across the receiving slit.**



# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### a. Axial Divergence Error

The effect of this axial divergence causes:

-the low angle side of the diffraction profile to rise more slowly than the high angle side.

-creates peak shift: negative below 90° and positive above 90° 2theta.

-reduced by Soller slits and/or capillary lenses

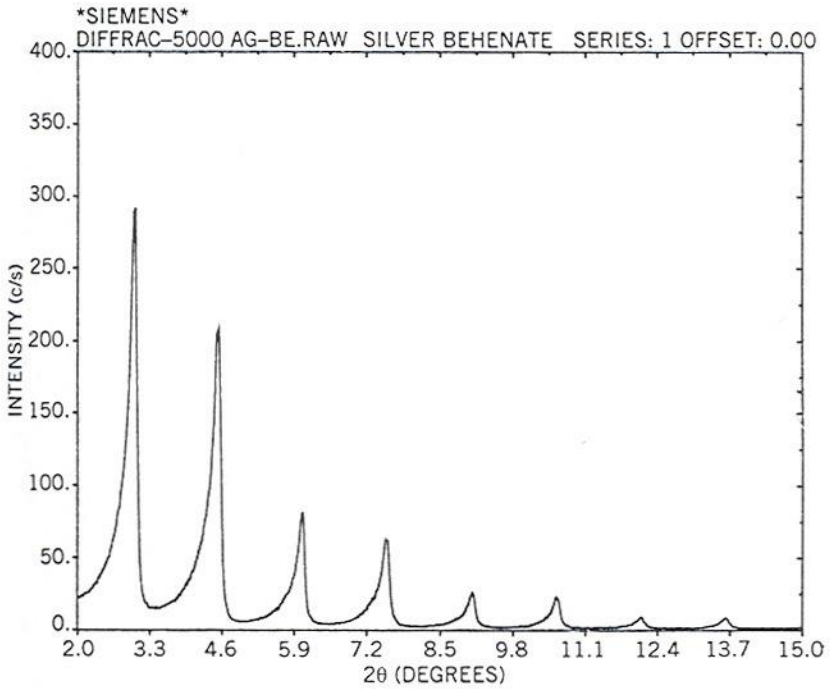
# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### a. Axial Divergence Error

**The peak asymmetry becomes more pronounced at low angles.**



# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### b. Flat sample error

**The surface of the sample is flat, while the focusing circle is curved, this causes an asymmetric broadening in the diffraction peak.**

**The edges of the sample lie on a different focusing circle, giving a negative systematic error in the maximum of 2θ.**

**This also causes asymmetric broadening of the peak profile on the low 2θ side.**

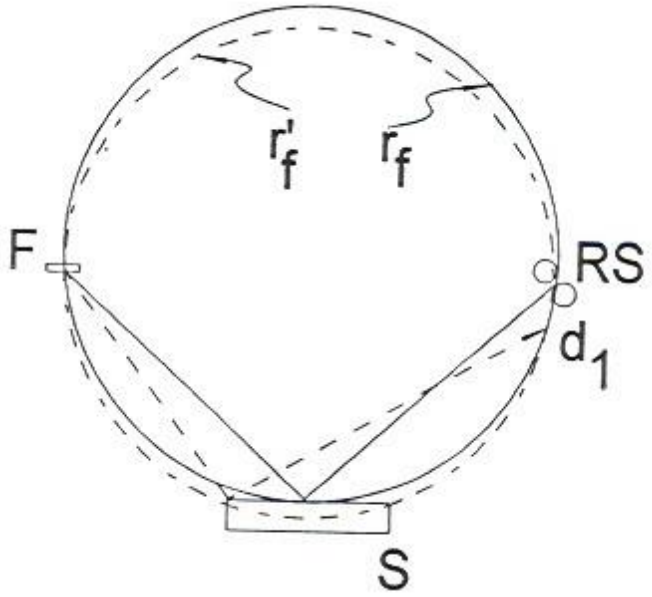
# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### b. Flat sample error

**Flat sample error increases with increasing 2θ, since the radius of the focusing circle decreases with increasing Bragg angle.**



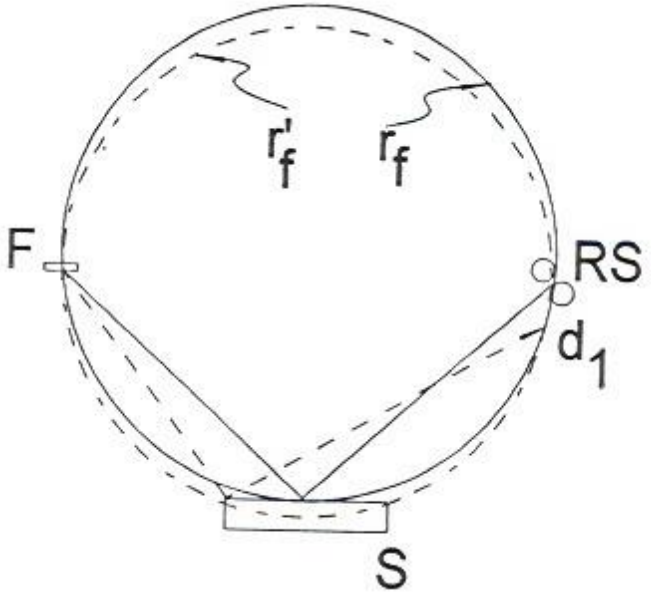
# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

**b. Flat sample error**

**Divergent slit opening can be decreased to expose less of the sample, however this also decreases the intensity.**



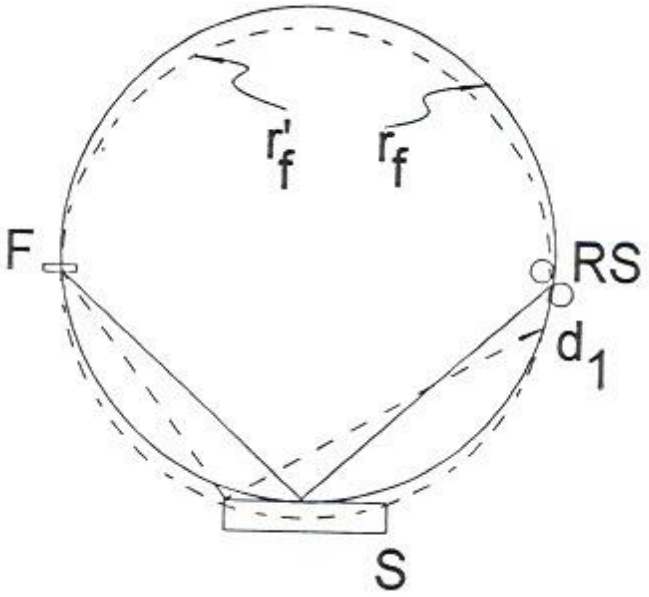
# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### b. Flat sample error

**Reduced by using smaller divergence slits, which produce a shorter beam. For this reason, if you need to increase intensity it is better to make the beam wider rather than longer.**



# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### c. Transparency Error

Occurs because the incident x-ray beam penetrates a measurable depth into the sample, part of the diffraction beam is then below the focusing circle.

Transparency error increases with decreasing absorption of x-rays by the sample, i.e. organic materials have a large transparency error.

Depth of penetration depends on:

- the mass absorption coefficient of your sample
- the incident angle of the X-ray beam

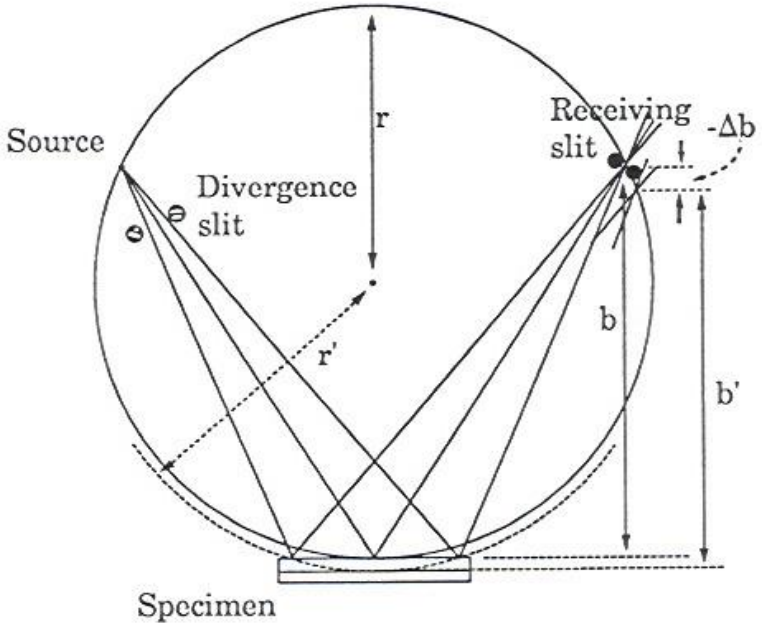
# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### c. Transparency Error

**This error leads to angular errors as much as 0.1 of a degree with asymmetric peak profiles.**



# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### c. Transparency Error

Shown here are three materials, a high-absorbing material ($MoO_3$), medium absorbing material ($CaCO_3$) and low absorbing material (aspirin).

$\mu/\rho$ is the mass attenuation coefficient.

The numbers under the angles are the "working thickness" of the sample.

| Material | $\mu/\rho$ | $\rho$ | 20° | 40° | 60° |
|---|---|---|---|---|---|
| $MoO_3$ | 92.7 | 4.71 | 1.8 | 2.7 | 3.6 |
| $CaCO_3$ | 39.9 | 2.71 | 7.4 | 11 | 15 |
| Aspirin | 7.0 | 1.40 | 82 | 121 | 161 |

# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### c. Transparency Error

**To decrease this error, use thin slices (films) of material on a zero-background holder.**

# Instrumentation

## E. Goniometer

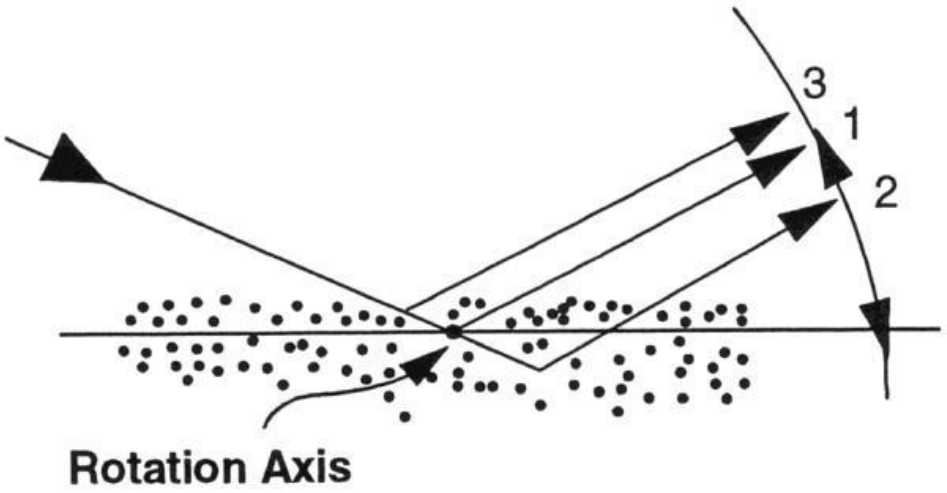
### 3. Systematic Aberrations in Goniometer Geometry

#### d. Sample Displacement Error

Related to the sample transparency error.

Occurs when the surface of the sample is not level with the sample holder.

This is an experimental error due to operator error.



# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### d. Sample Displacement Error

**Causes an asymmetric broadening of the peak profile on the low $2\theta$ side and gives a peak shift in $2\theta$ position of $0.01^{o}$ $2\theta$ for every 15 $\mu$m displacement.**

**This error is larger than all the others, therefore sample preparation is critical.**

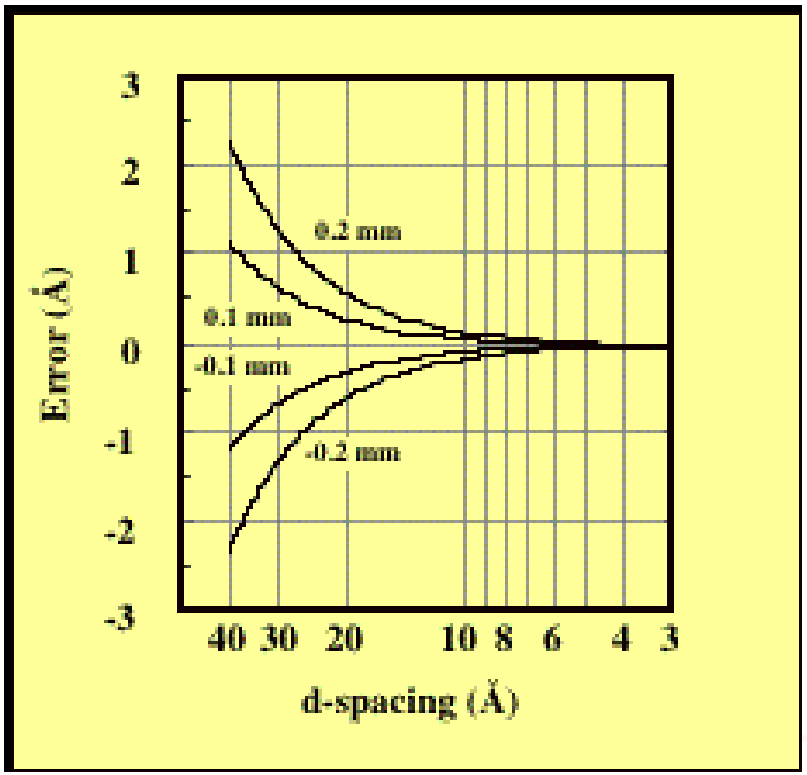
# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### d. Sample Displacement Error

**Displacement error increases rapidly as 2θ falls below 20°**



# Instrumentation

## E. Goniometer

### 3. Systematic Aberrations in Goniometer Geometry

#### d. Sample Displacement Error

**Ways to compensate for sample displacement:**

**-use an internal calibration standard especially for publication quality data**

**-minimize by using a zero background sample holder**

# Instrumentation

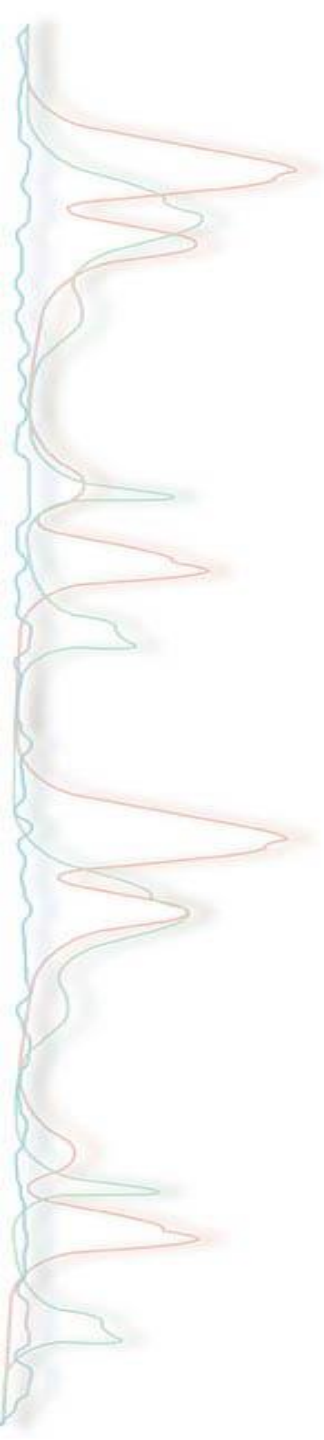
**Read the following articles:**

1. The Synthesis of XRay Spectrometer Line Profiles with Application to Crystallite Size Measurements, by Leroy Alexander, Journal of Applied Physics 25, 155 (1954);
   http://dx.doi.org/10.1063/1.1721595
2. Geometrical Factors Affecting the Contours of XRay Spectrometer Maxima. I. Factors Causing Asymmetry, by Leroy Alexander, Journal of Applied Physics 19, 1068 (1948);
   http://dx.doi.org/10.1063/1.1698013
3. Geometrical Factors Affecting the Contours of XRay Spectrometer Maxima. II. Factors Causing Broadening, by Leroy Alexander, Journal of Applied Physics 21, 126 (1950);
   http://dx.doi.org/10.1063/1.1699611
4. XRay Diffraction from Small Crystallites, by Tiensuu, Ergun, and Leroy Alexander, Journal of Applied Physics 35, 1718 (1964);
   http://dx.doi.org/10.1063/1.1713726
5. Determination of Crystallite Size with the XRay Spectrometer, by Leroy Alexander and Harold P. Klug, Journal of Applied Physics 21, 137 (1950);
   http://dx.doi.org/10.1063/1.1699612

**Reading Assignment:**

**Read Chapter 5, 6, and 7 from:**

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



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Advanced X-ray Analysis