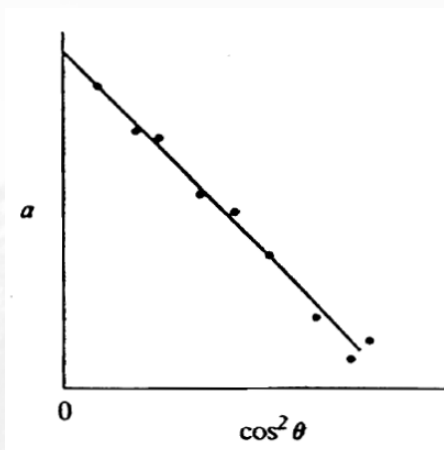


Error

Accuracy & Precision

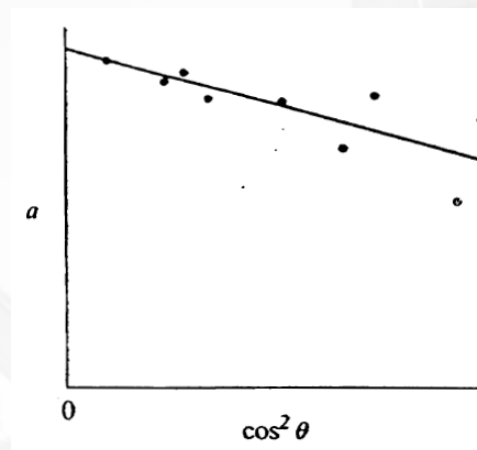
A lot of contents are from the presentation of Dr. Arnt Kern of Bruker.

Systematic error vs. random error



systematic error

random error



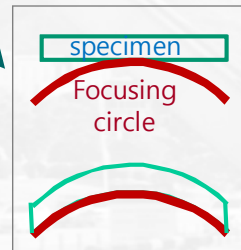
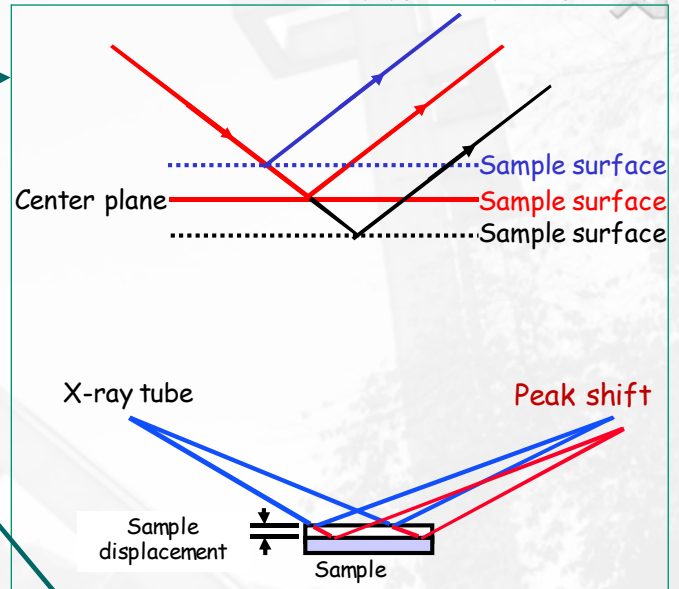
systematic error

random error

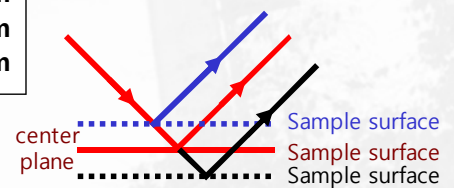
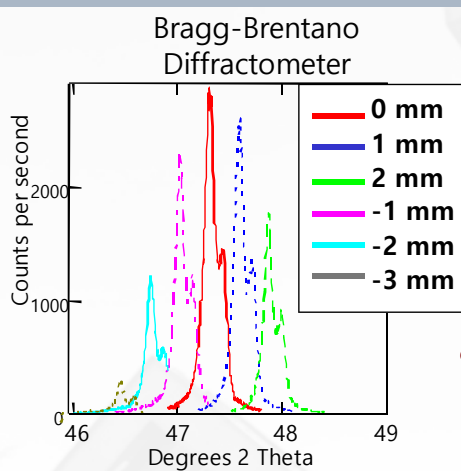
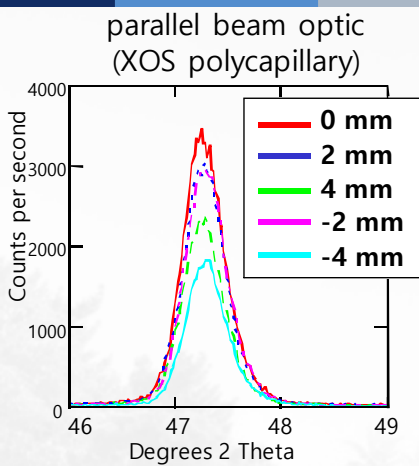
Errors > sources of 2θ position errors in XRPD

- Specimen displacement
- Specimen transparency
- Flat specimen error
- Instrumental misalignment
- Mis-setting of the $2:1$ position
- Error in zero 2θ position
- Axial X-ray beam divergence
- Peak distortion due to $K\alpha_1$ and $K\alpha_2$ wavelength
- Incorrect application of data smoothing

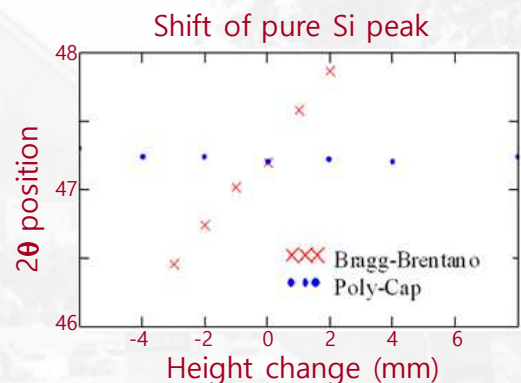
Chap 3 of Bish & Post



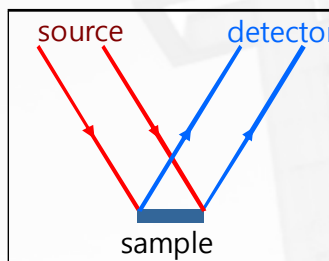
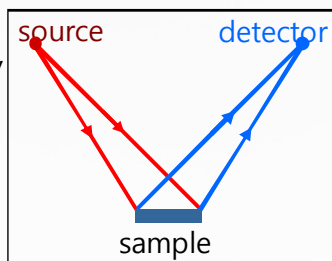
Sample displacement error > peak position of Si (220) (SRM640c)



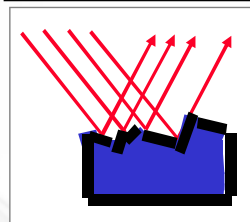
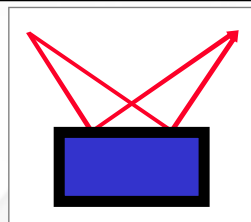
- Parallel beam
 - ✓ can remove sample-dependent errors.
 - ✓ Analysis of non-ideal samples such as tablets, fibers, and railroad car wheels
 - ✓ Precise peak position measurement – no specimen displacement error
 - ✓ Can use Goebel mirror or polycapillary bundles.



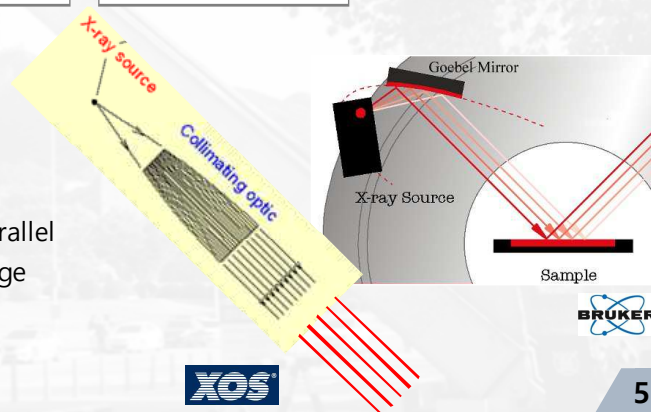
Bragg-Brentano geometry (parafocusing geometry)



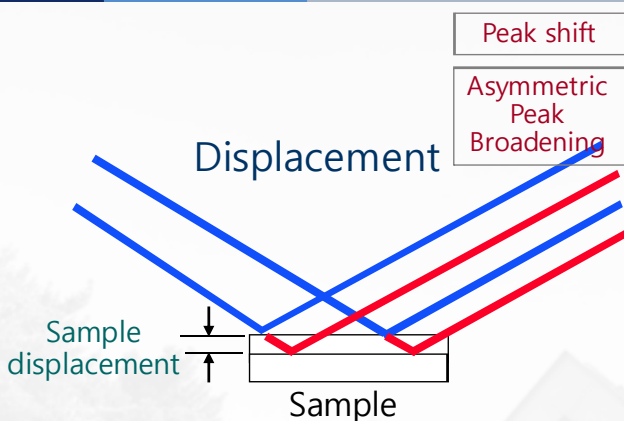
Parallel beam geometry



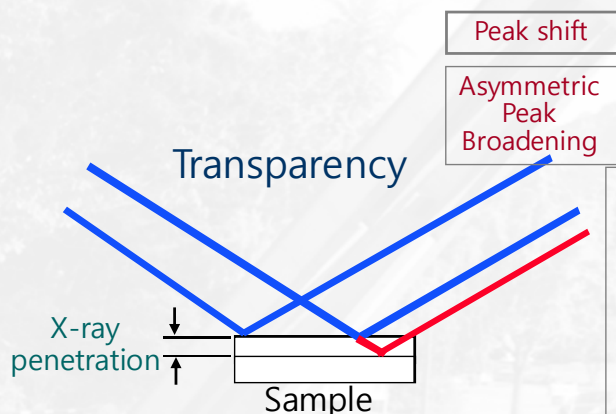
For sample displacement error in parafocusing vs. parallel geometry, see page 160 Krawitz, page 366 Cullity, page 194 Jenkins & Snyder.



Errors > displacement error & transparency error

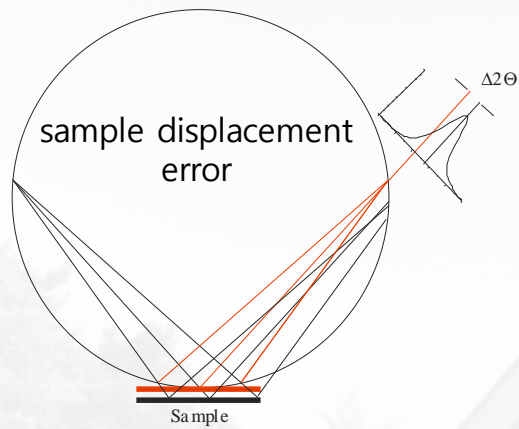


- Specimen not positioned right or the instrument not calibrated correctly
- ✓ This can be avoided with careful specimen preparation and consistent instrument alignment.



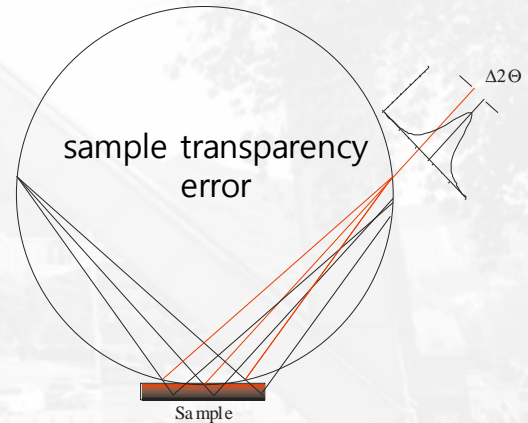
- Inherent error associated with depth of beam penetration into specimen
- Varies for materials.
- ✓ Always displaces peaks to lower 2θ .

Errors > sample displacement error, sample transparency error

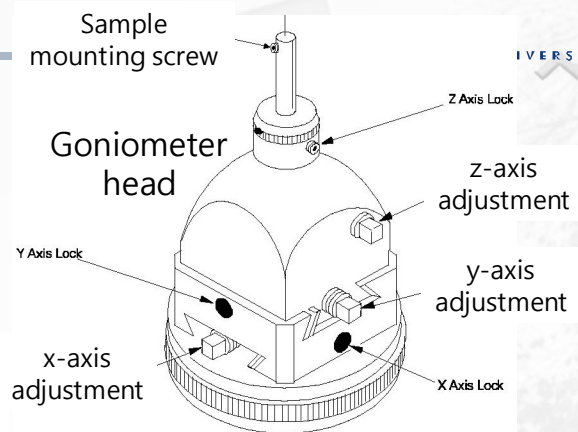


- The sample must be tangent to the focusing circle.
- Any deviations lead to **peak shifts and asymmetric broadening**.
- Typically the largest error found in Bragg-Brentano geometry

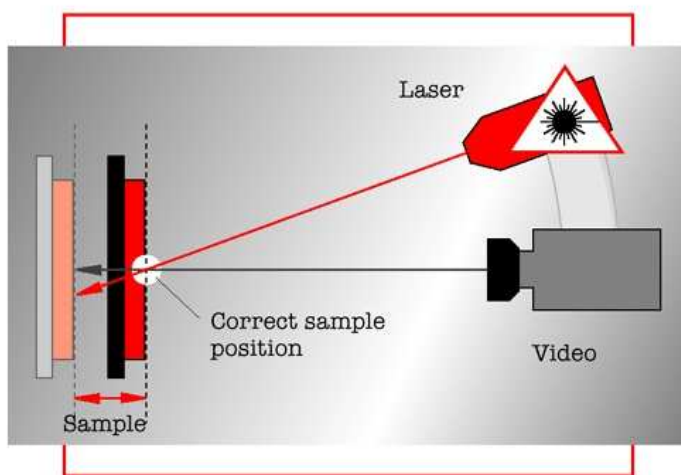
- In low absorbing samples, the average diffracting surface lies below the physical sample surface leading to **peak shifts and asymmetric broadening**.
- The sample transparency error is equivalent to the sample displacement error.



Errors > sample displacement error

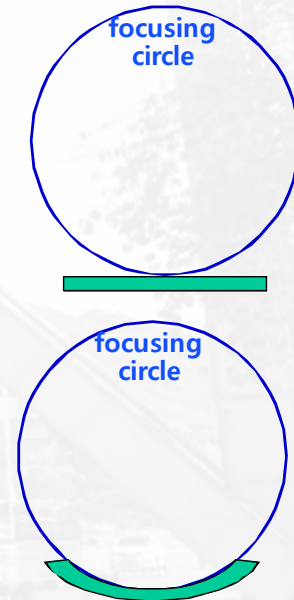
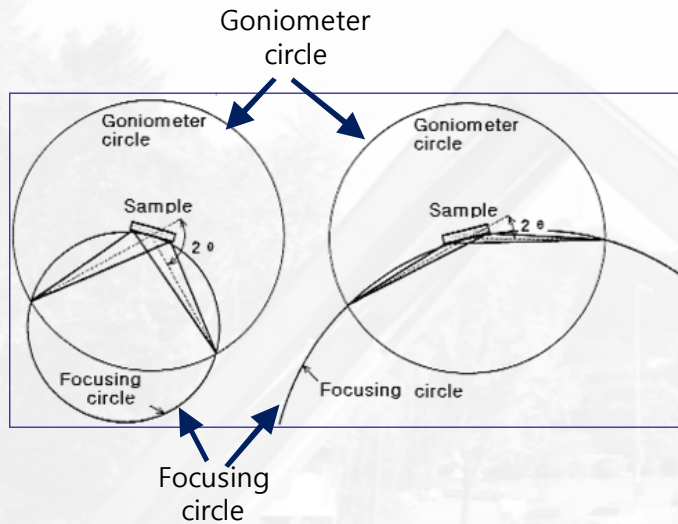


Sample positioning using laser

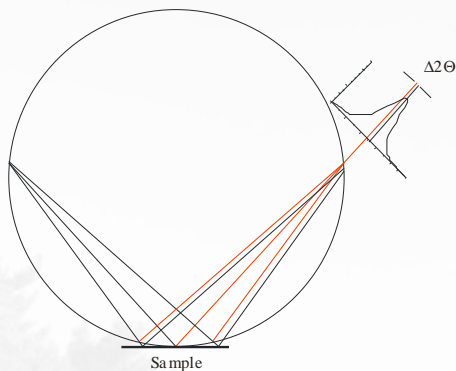


Errors > flat specimen error

- Perfect focusing need specimen curved to fit the focusing circle.
- Flat specimen → peak broadening, shift in peak position – these effects can be lessened by decreasing divergence of incident beam at the expense of decreased intensity.

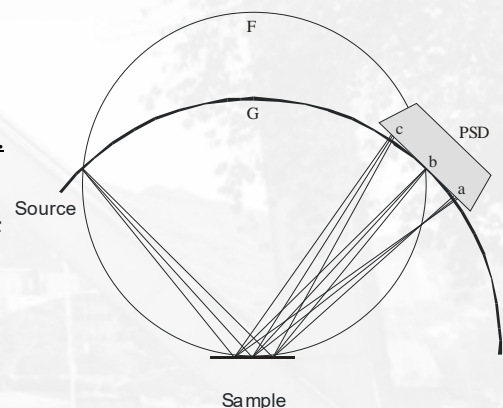


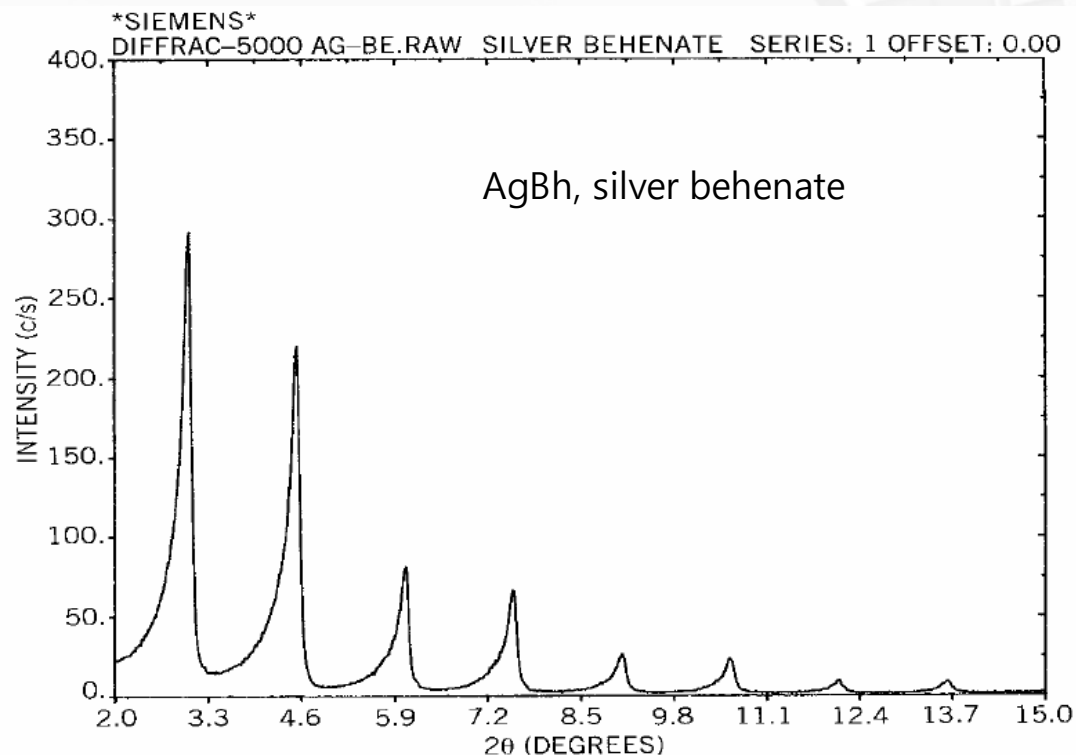
Errors > flat specimen error, flat detector error



- Sample is tangent to the variable focusing circle → **peak shifts & asymmetric broadening**.
- ➔ Small divergence slits help on the expense of intensity.

- 1D detector is tangent to the goniometer circle. → **peak shifts & asymmetric broadening**
- ➔ Small detector window helps on the expense of intensity.
- 1D detectors have severe deficiencies at low angles $2\theta (< 10^\circ 2\theta)$.





Functional forms of 2θ position errors

axial divergence error

$$\Delta 2\theta = -h^2(K_1 \cot 2\theta + K_2 \operatorname{cosec} 2\theta)/3R^2$$

h = axial width; R = goniometer radius

K₁, K₂ = functions of collimators

flat specimen error

$$\Delta 2\theta = -\frac{\alpha^2 \cot \theta}{343.8} \quad \alpha = \text{angular aperture of divergence slit}$$

specimen displacement error

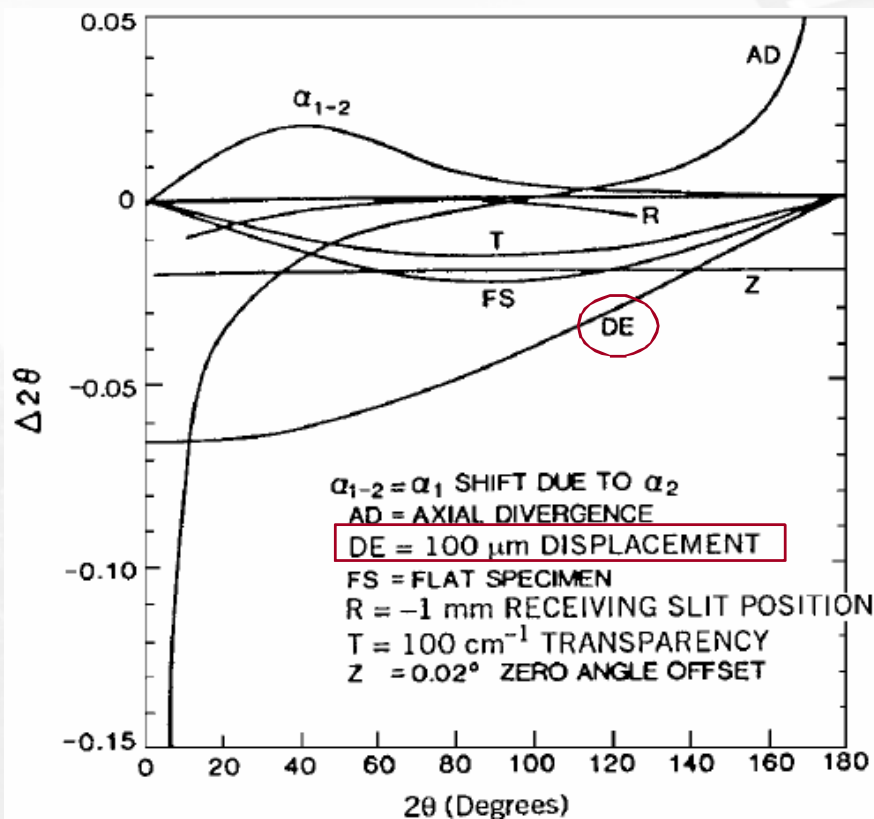
$$\Delta 2\theta = -\frac{2s \cos \theta}{R} \text{ (in radians)}$$

s = specimen displacement

$$\Delta 2\theta = -\frac{114.59s \cos \theta}{R} \text{ (in degrees)}$$

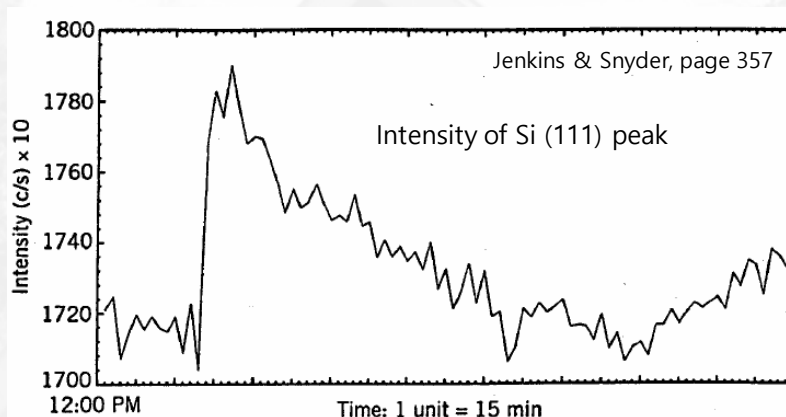
specimen transparency error

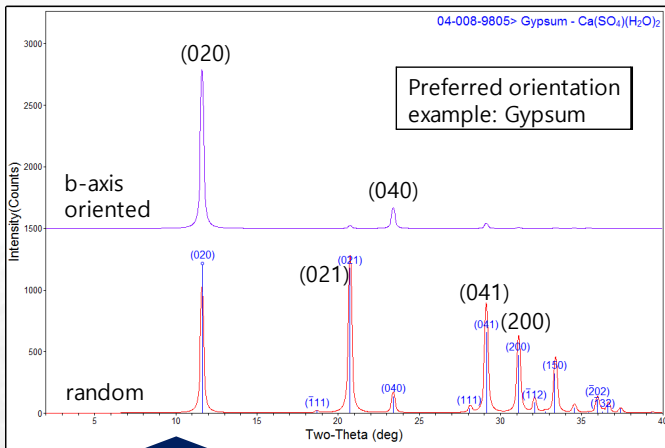
$$\Delta 2\theta = \frac{\sin 2\theta}{2\mu R}$$



Errors > principal errors in Intensity measurement

- Inherent
 - ✓ Primary extinction
 - ✓ Crystallinity
- Instrumental
 - ✓ Generator stability
- Specimen dependent
 - ✓ Microabsorption
 - ✓ **Preferred orientation (texture)**
 - Is the powder sample randomly oriented?
 - ✓ **Crystallite statistics**
 - Are there enough diffracting crystallites?





Low sampling statistics manifests itself in a diffraction pattern as:

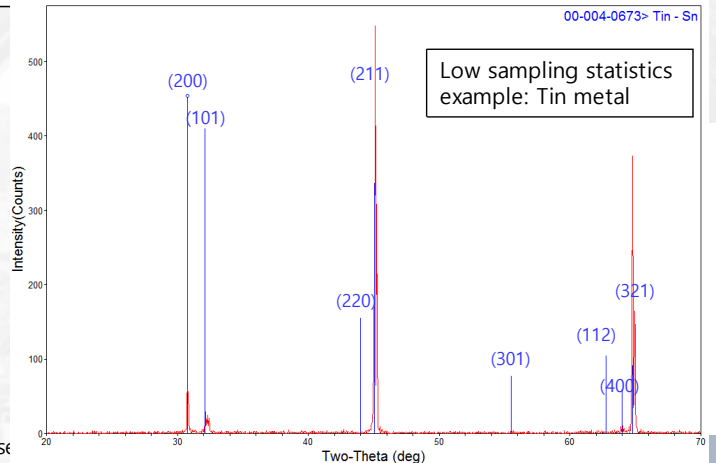
- 1) Array of peaks displaying very inconsistent relative intensities
- 2) no predictable family of planes
- 3) strong peaks of atypical orientations, e.g. the Sn (321) in the pattern below

Preferred orientation manifests itself as strong intensity for:

- 1) a specific family of planes
- 2) at the expense of other planes
- 3) in a predictable fashion

From presentation of Dr. Mark Rodriguez @ DXC 2017 "What usually causes trouble?"

CHAN PARK, MSE, SNU Spring-2022 Crystal Structure Analyse



Sampling statistics ???

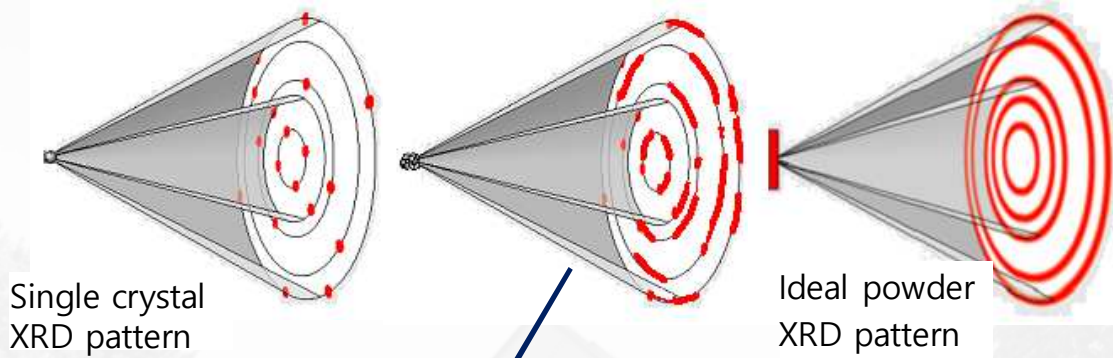
- How many crystallites am I truly sampling ?
- Answer: Not that many.
- Imagine you are looking at newly-fallen snow.
- Out of the billions of snow flakes, just a few perfectly-positioned flakes can reflect the sunlight to your eyes.



www.shutterstock.com • 1239064870

www.shutterstock.com/image-photo/winter-background-sparkling-snow-bokehwinter-landscape-1239064870

From presentation of Dr. Mark Rodriguez @ DXC 2017 "What usually causes trouble?"



Polycrystalline samples with poor grain sampling statistics

- large grain size
- thin film
- inhomogeneous structure
- small amount of sample
- micro area

From presentation of Dr. Mark Rodriguez @ DXC 2017 "What usually causes trouble?"

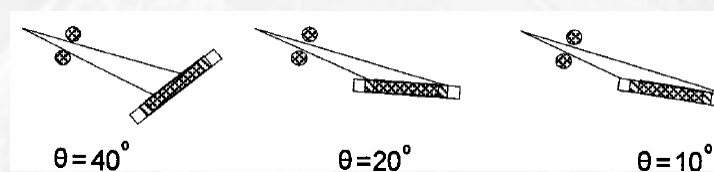
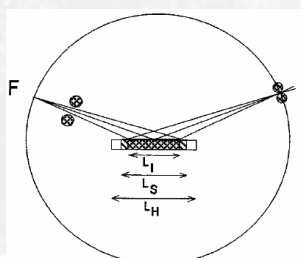
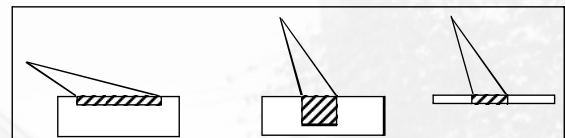
Ideal XRD specimen, sample preparation

➤ Ideal specimen for X-ray powder diffraction

- ✓ Completely homogeneous
- ✓ Constant particle size between 1 and 10 μm
- ✓ No preferred orientation or strain

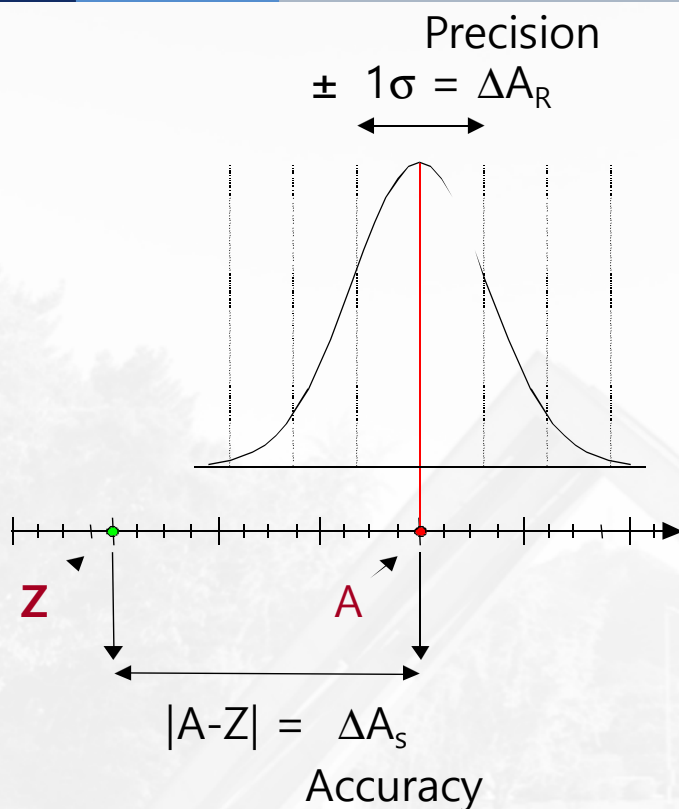
➤ Sample preparation

- ✓ Random orientation of the particles
- ✓ Smooth flat surface
- ✓ Sample oscillation/spinning
- ✓ Irradiation area vs. irradiated volume (flux input)



Accuracy & Precision

Accuracy & Precision



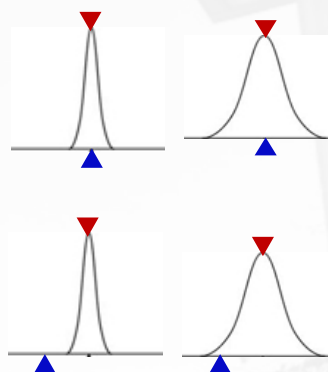
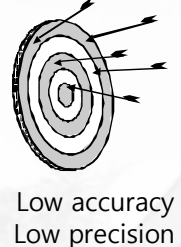
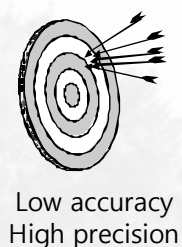
Z : "Certified" = "true" value

A : Measurement result

ΔA_S : Accuracy

ΔA_R : Precision

= standard deviation



Measured mean
Real value

Precision - reproducibility
Accuracy - approach to the "true" value

- **Precision** ; the degree to which further measurements show the same or similar results
- **Accuracy** ; the degree of conformity of a measured quantity to its true value

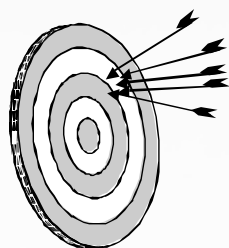
celebrating200years.noaa.gov/magazine/tct/accuracy_vs_precision_220.jpg

CHAN PARK, MSE, SNU Spring-2022 Crystal Structure Analyses

Arnt Kern of



Low accuracy
High precision



You can shoot extremely precise...
... and never hit the target !

- ✓ Accuracy and precision are frequently confused.
- ✓ A good reproducibility, expressed by a small *standard deviation*, often leads to the erroneous assumption, that good data/results have been obtained.
- ✓ The *standard deviation* is a measure for statistical (random) errors, but the systematic error remains completely unknown!

CHAN PARK, MSE, SNU Spring-2022 Crystal Structure Analyses

Arnt Kern of



- Any diffraction experiment can be divided into 5 parts.



- Without a close consideration of each part, which must be repeated for each different experiment, one will most unlikely to obtain an optimum analytical outcome.

1/5 > Early decisions

- What is the aim of the experiment?
- What accuracy and precision is necessary?
- What are the sample properties?
- What instrument and measurement parameters to use?
- What evaluation methods and models to use?

By answering all these questions before executing any experiment, one can save a whole lot of time as well as protect himself against erroneous results and frustration!

- What is the form of the sample?
- How much sample is there?
- What instruments are available?
- What instrument setup are available?
 - ✓ Primary optics?
 - ✓ Sample holders?
 - ✓ Detectors?
- What intensity / resolution is required?
- ...

Methodical limits

- Peak overlap
- Speed of analysis

Measurement errors

- Alignment errors
- Others...

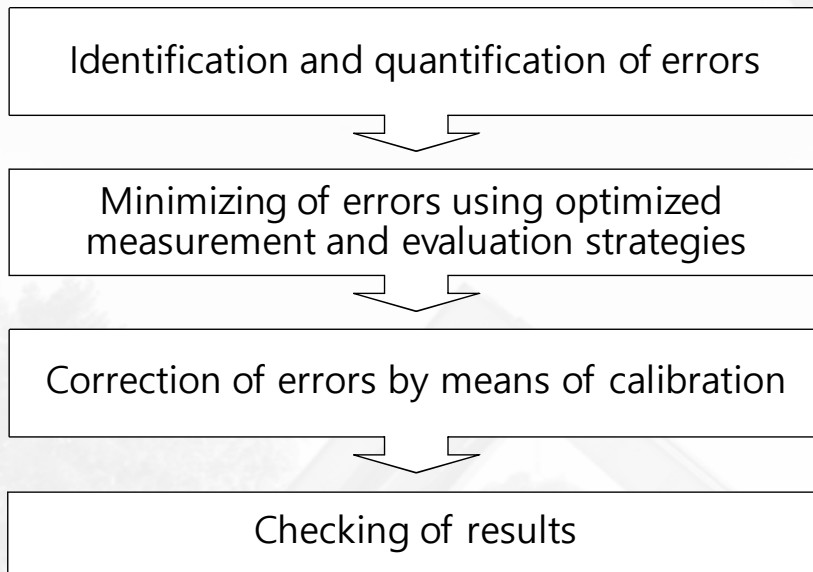
Accuracy
and precision
of results

Calibration errors

- Use of standards
- Quality of calibration

Evaluation errors

- Software errors
- User errors
- Quality of methods



2/5 > Sample > general considerations

- One of the most important steps before data collection is the minimization of systematic sample related effects!
- Avoid persisting with poor data - if possible.
 - Re-prepare or remake the sample.
 - Find a better sample.
 - Change instrument or instrument setup.
 - Improve instrument & measurement parameters.
- Typical sample related problems
 - ✓ Not enough scattering particles (spottiness)
 - ✓ Sample not representative for the bulk
 - Bad sampling / particle heterogeneity / phase separation
 - ✓ Preferred orientation, Extinction, Microabsorption (multiphase samples)

"Sample problems" can also provide important information:

preferred orientation	→	degree of orientation
peak broadening	→	crystallite size and strain

2/5 > Sample > number of crystallites needed

- Peak intensities for structure refinement required to be accurate to $\pm 2\%$
- Accurate, reproducible diffraction intensities require small crystallite size.

Typical intensity reproducibility for Quartz (113) reflection with Cu-Kalpha is

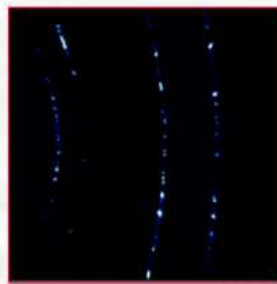
15-20 μm	5-50 μm	5-15 μm	<5 μm
18.2%	10.1%	2.1%	1.2%

- The number of crystallites diffracting is related to size (diameter).

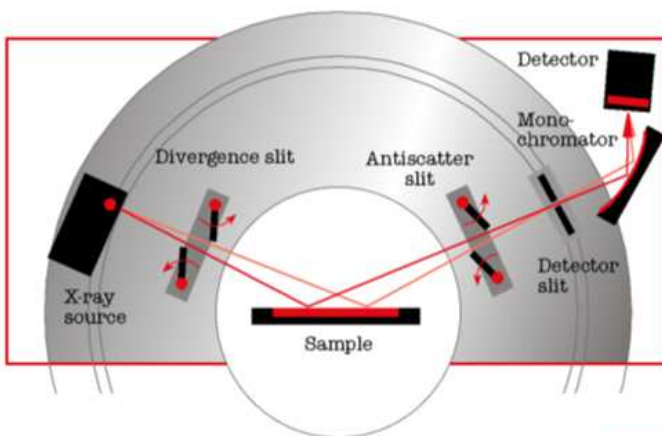
μm	40 μm	10 μm	1 μm
crystallites / 20mm^3	597,000	38,000,000	3,820,000,000
number diffracting	12	760	38,000

Smith, 1992

Particle size or "Spottiness" effect



3/5 > Instrument



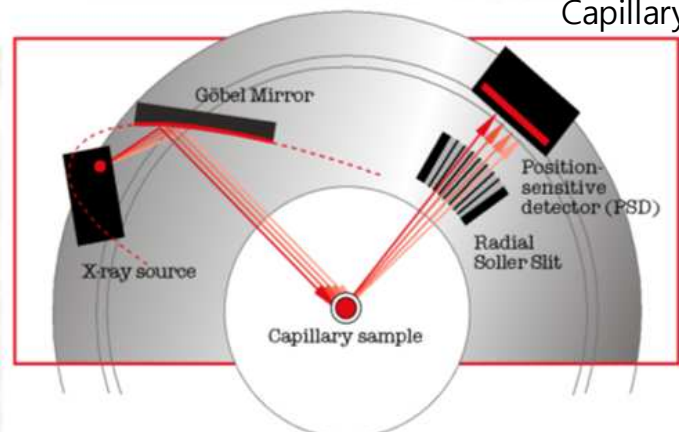
Bragg-Brentano

- sample displacement error
- sample transparency error
- flat specimen error
- flat detector error

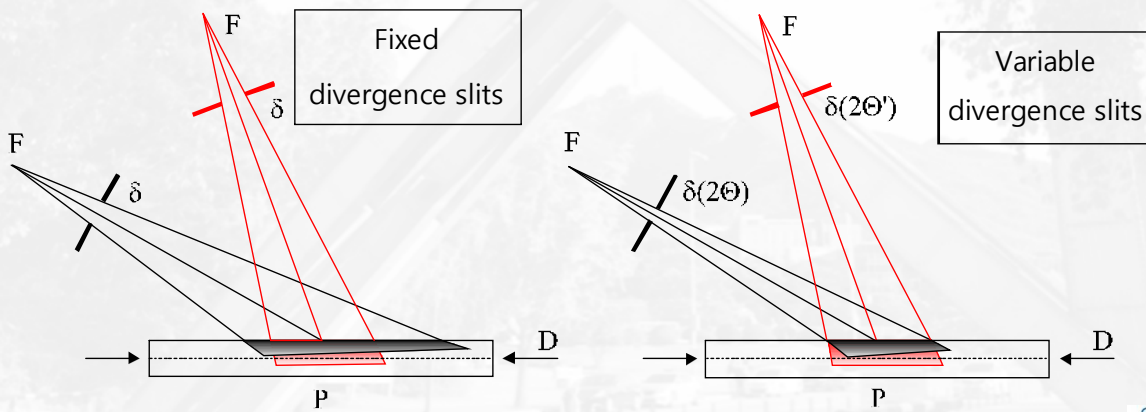


Capillary tube
quartz, glass, alumina
0.01mm thick, 80mm long, 0.1~5mm OD

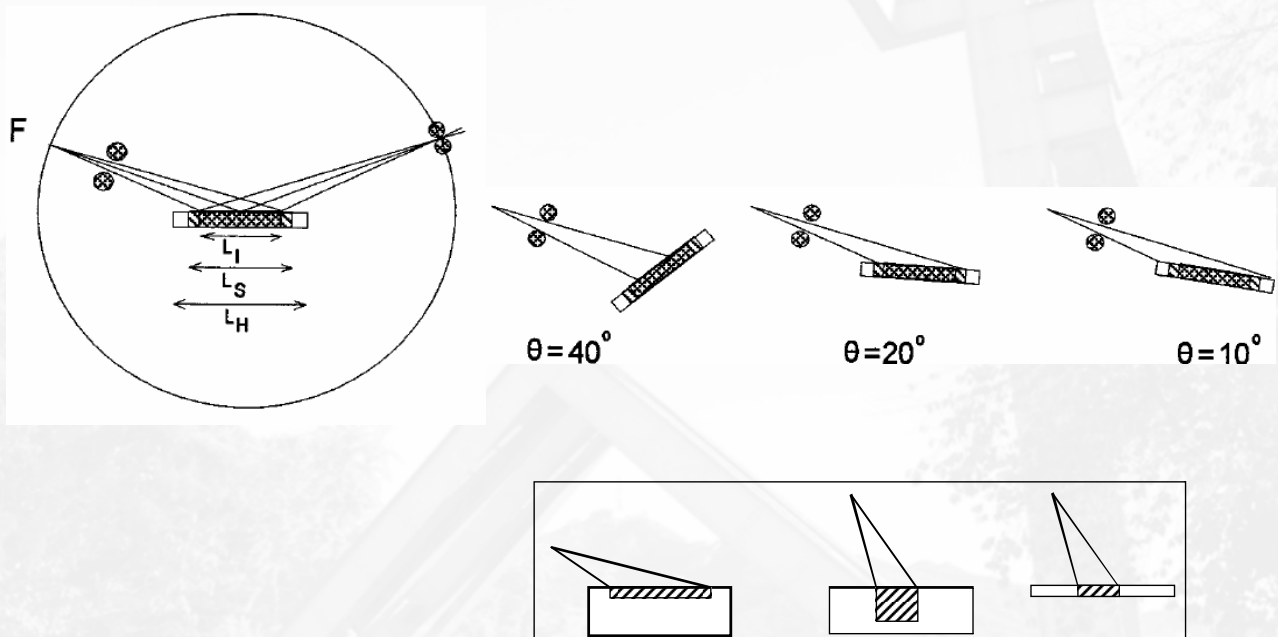
Debye-Scherrer Capillary



- Bragg-Brentano
 - ✓ Absorption is independent of 2θ : constant diffraction volume.
 - ✓ Transparency effect may cause problems.
 - High absorption: Use reflection geometry.
 - Low absorption: Use transmission geometry.
- Debye-Scherrer
 - ✓ Absorption is 2θ -dependent: variable diffraction volume.
 - ✓ An intensity correction ($\mu_{\text{eff}}R$) is crucial, if accurate intensities are needed.

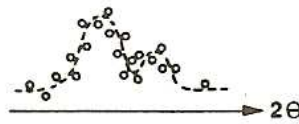


Effect of 2θ on beam footprint



XRD peak intensities from powder/bulk sample is different from those from thin film sample.

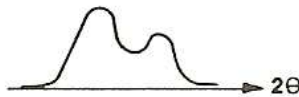
1 Data Collection



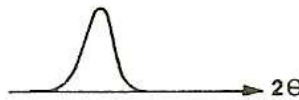
2 Smoothing



3 Background Subtraction



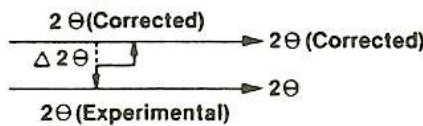
4 α₂ Stripping



5 Peak Location



6 2θ Calibration



7 Calibration and Reporting of d

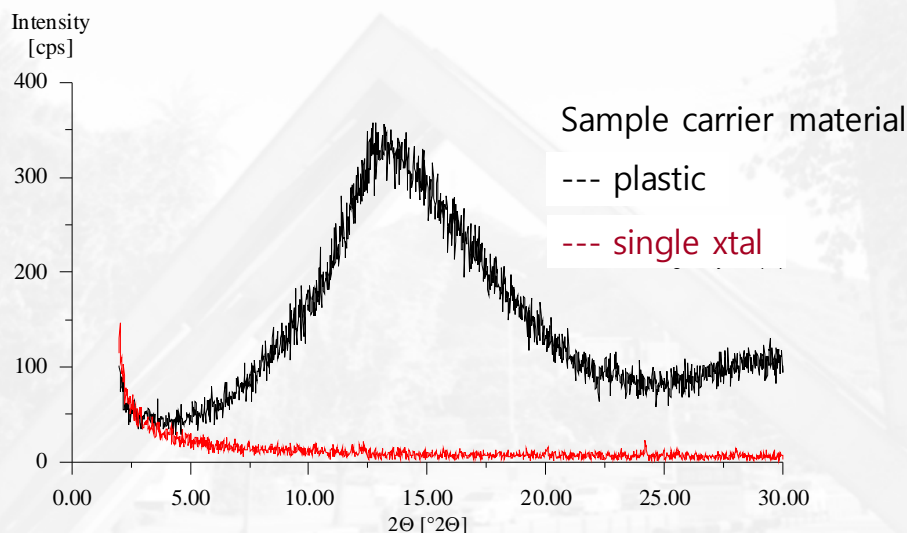
$$d \text{ (Calculated)} = \frac{\lambda}{2} \frac{1}{\sin(\theta \text{ Corrected})} \quad d \text{ (Reported)} = \boxed{015710421}$$

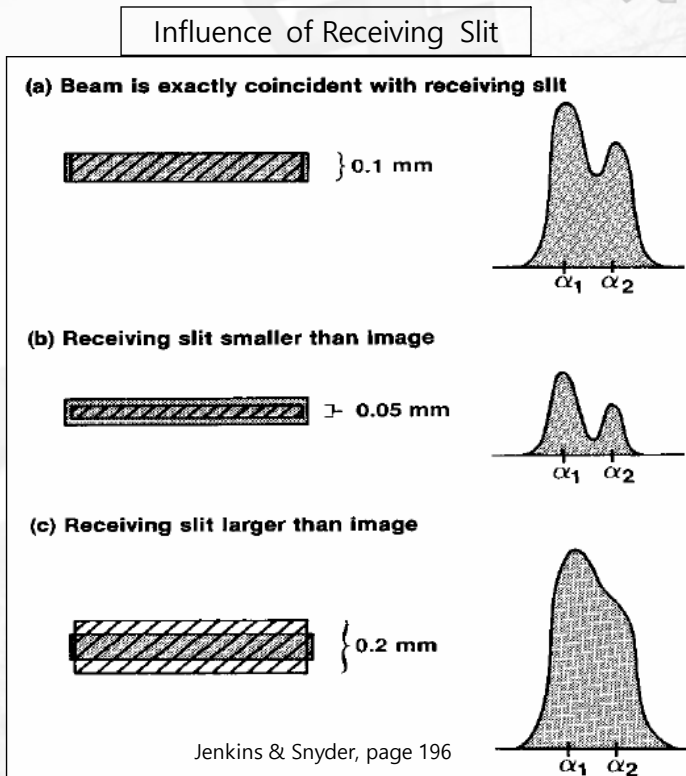
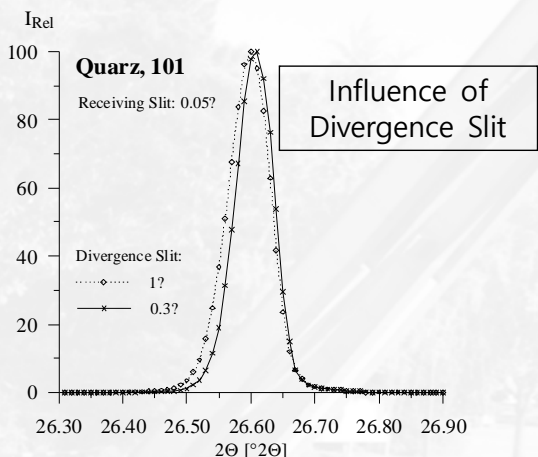
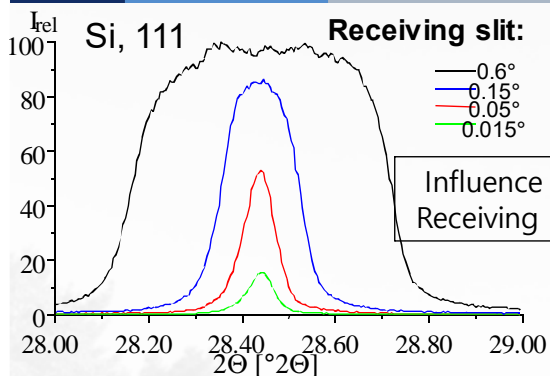
4/5 > Data Collection

A very crucial step in each experiment is the choice of optimum instrument and measurement parameters.

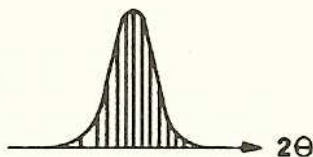
Important examples are:

- Sample carrier material
- Detector slit
- Divergence and anti-scatter slits
- Soller slit(s)



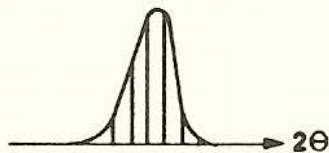


**1 Peak width narrow
Step size small**



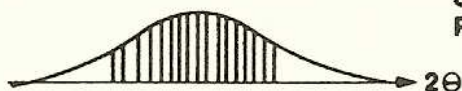
**Smoothing helps
Peak definition good**

**2 Peak width narrow
Step size large**



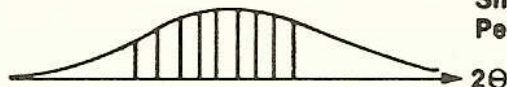
**Smoothing suppresses
Peak definition poor**

**3 Peak width broad
Step size small**



**Smoothing hinders
Peak definition poor**

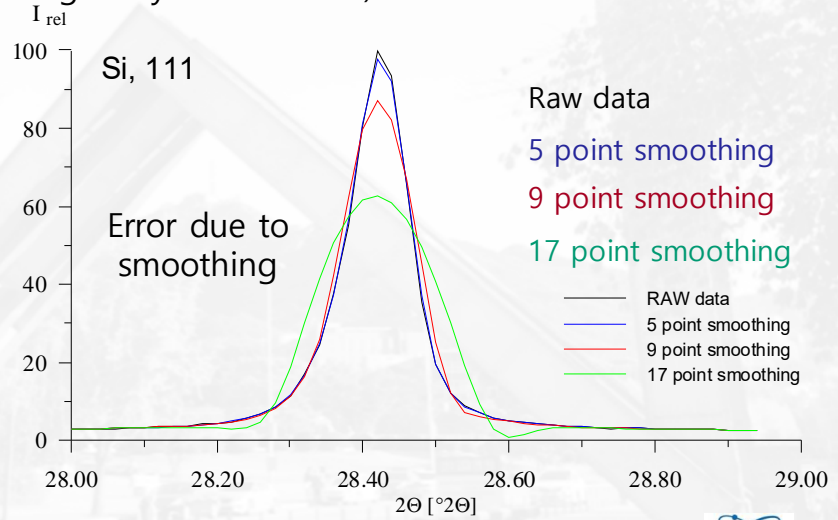
**4 Peak width broad
Step size large**



**Smoothing helps
Peak definition fair**

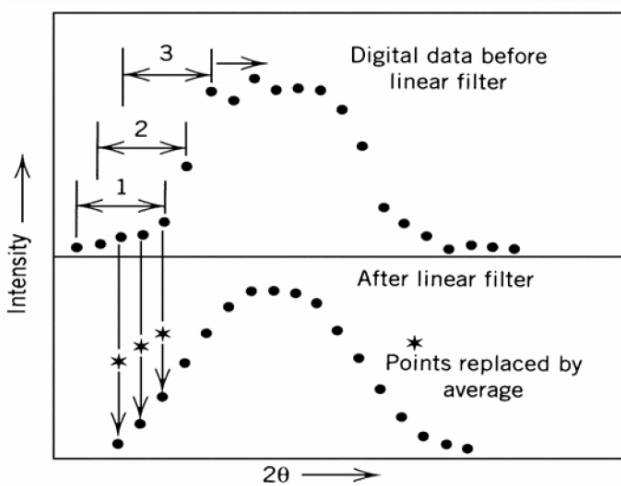
5/5 > Evaluation > most important errors

- Software errors
- User errors
 - ✓ Smoothing, background subtraction
- Quality of methods
 - ✓ 2theta Determination
 - ✓ Profile fitting (when using analytical function)

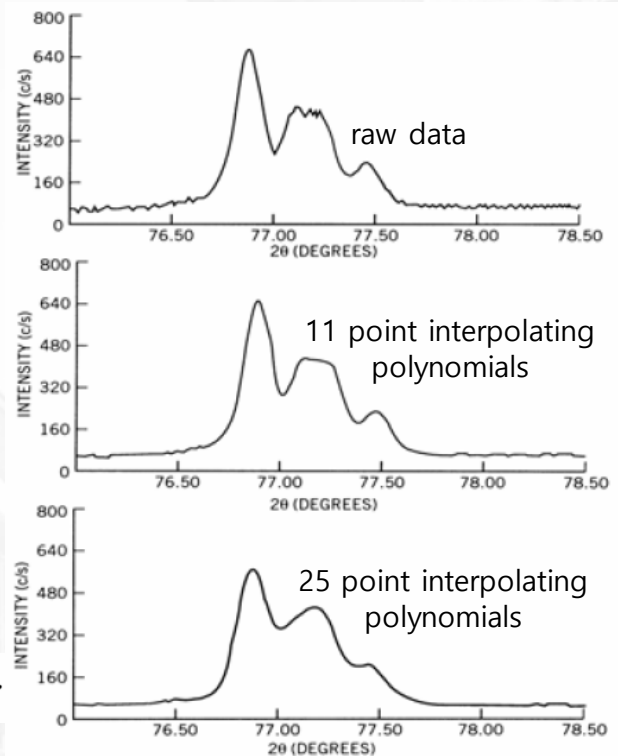


5/5 > Evaluation > Effect of Data smoothing

Data smoothing with a polynomial digital filter

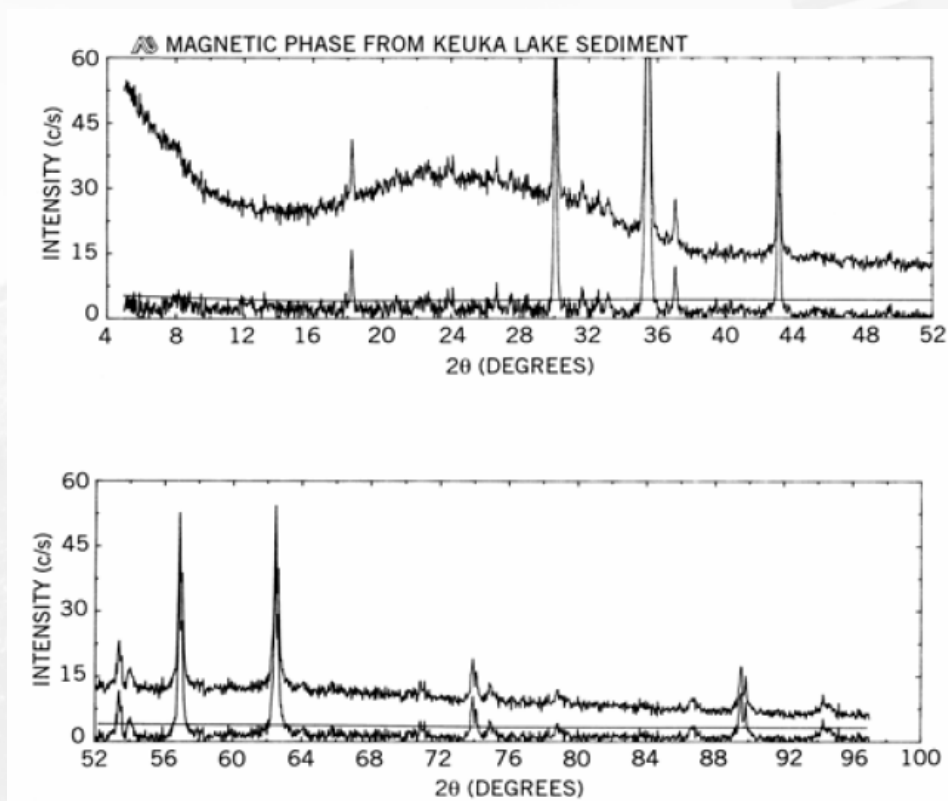


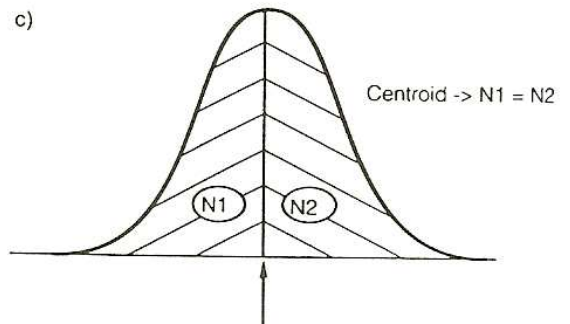
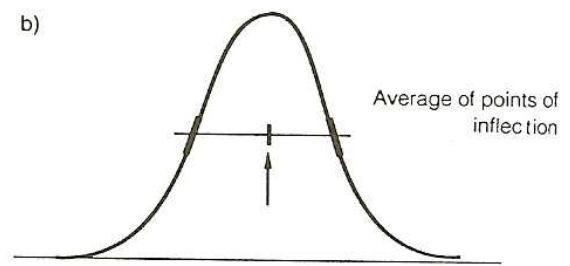
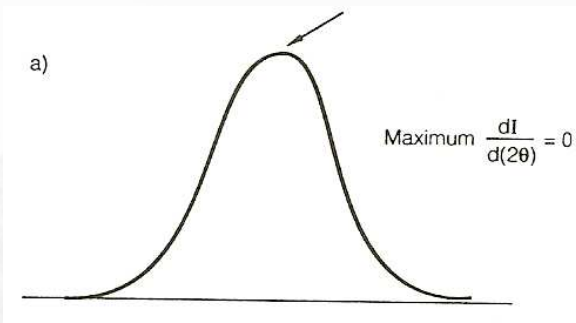
$$2\theta_{\text{calc}} = a + b(2\theta_{\text{obs}}) + c(2\theta_{\text{obs}})^2 + d(2\theta_{\text{obs}})^3 + \dots$$



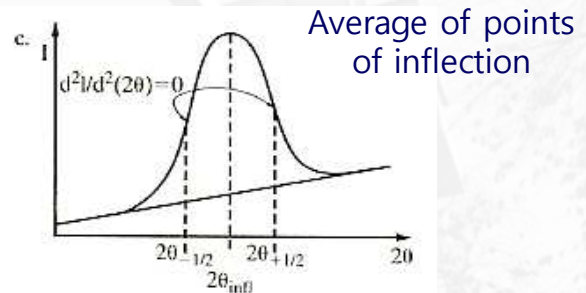
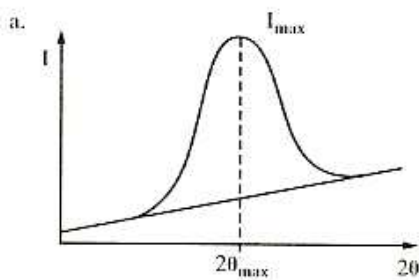
- Scatter from sample holder
 - ✓ Generally seen at low 2θ values where too wide a divergence slit is chosen.
- Fluorescence from specimen
 - ✓ Controllable to a certain extent by using diffracted beam monochromator or by pulse height selection.
- Presence of significant amounts of amorphous material in specimen
- Scatter from specimen mount substrate
 - ✓ Seen in "thin" specimens but controllable by use of ZBHs.
- Air scatter
 - ✓ Has the greatest effect at low 2θ values.

5/5 > Evaluation > Background subtraction

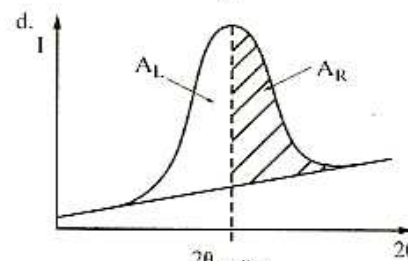
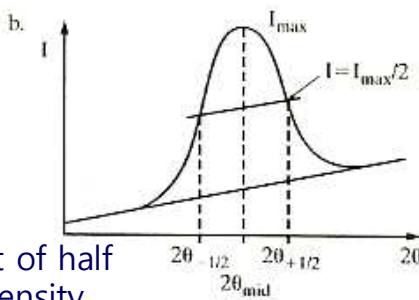




peak maximum



Mid-point of half max intensity



Peak median
Peak centroid

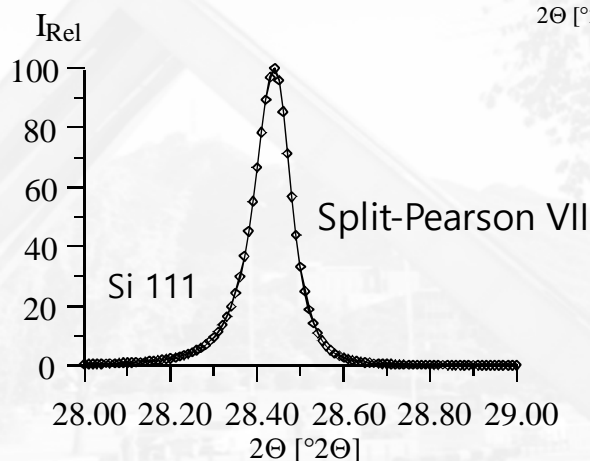
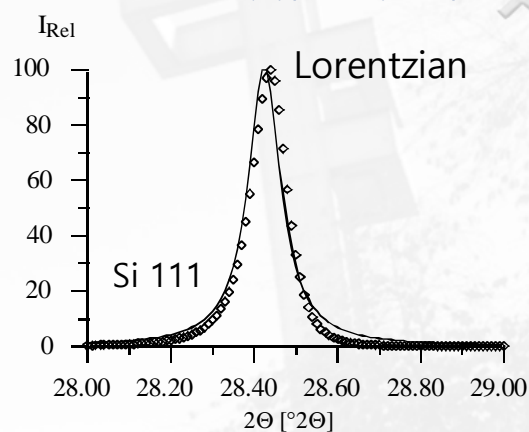
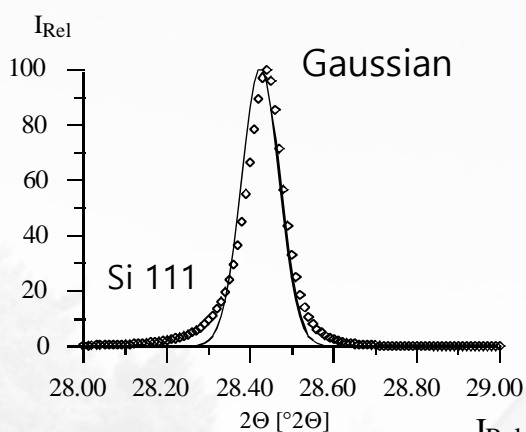
$$2\theta_{max} = d[I_{top}(2\theta) - I_{back}(2\theta)]/d(2\theta)$$

$$2\theta_{mid} = 1/2[2\theta_{-1/2} + 2\theta_{+1/2}]$$

$$2\theta_{inf} = 1/2[2\theta'_{-1/2} + 2\theta'_{+1/2}]$$

$$\langle 2\theta \rangle = \frac{\int 2\theta \cdot I(2\theta) \cdot d(2\theta)}{\int I(2\theta) \cdot d(2\theta)}$$

Peak profile fitting



Standard Reference Materials (SRMs)

- Powder Line Position + Line Shape Std for Powder Dif

✓ **Silicon (SRM 640f); \$745/7.5g**

- Line position - Fluorophlogopite mica (SRM 675); \$809/7.5g

- Line profile - **LaB₆ (SRM 660c); \$907/6g**

← No broadening from size & strain

- Intensity

✓ ZnO, TiO₂ (rutile), Cr₂O₃, CeO₂ (SRM 674b); out of stock

- Quantitative phase analysis

✓ Al₂O₃ (SRM 676a); out of stock, Silicon Nitride (SRM 656); \$580/ 20g

- Instrument Response Std

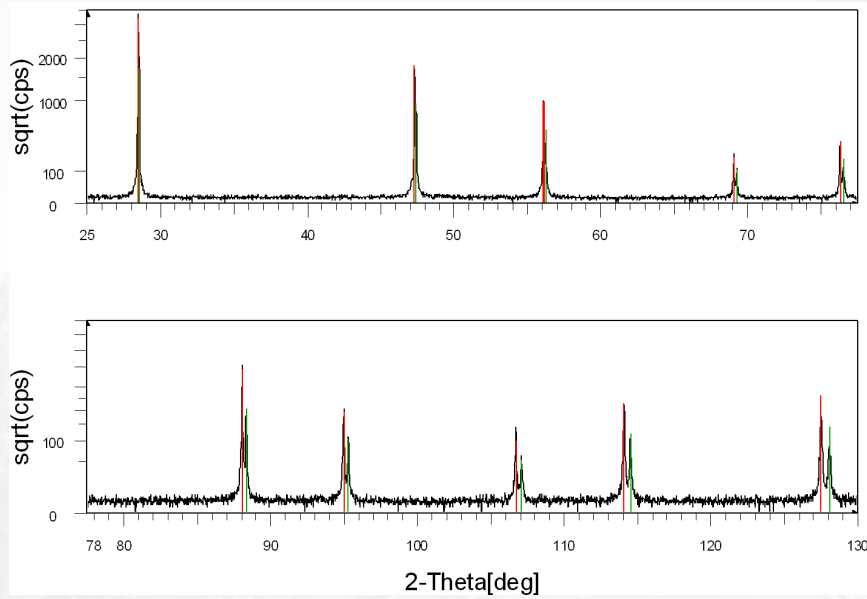
✓ Alumina plate (SRM 1976c); \$721/1 disc

Gold
\$58.66 / gram
(2021-06-17)
goldprice.org

Prices; 2021-06-17

www.nist.gov/srm/index.cfm

Accuracy check with silicon SRM 640C



- 0.5° slits, 2.5° Soller slits, 0.2mm receiving slit, diffracted beam monochromator, and scintillation counter, 0.02°/ step and 2 sec/step: peak positions and intensities match with PDF pattern 27-1402 better than 0.01°, Cu-Kα_{1,2}

PDF card ← ICDD

Joint committee for powder diffraction standards
International Center for Diffraction Data

PDF # 440347, Wavelength = 1.54056 (Å)

44-0347 Quality: " Ca Sr2 Pb0.5 Cu2 Ti0.5 Ox
 Calcium Copper Lead Strontium Thallium Oxide
 Ref: Park, C., Snyder, R., Powder Diffraction, 8, 249 (1993)

CAS Number:
 Molecular Weight: 0.00
 Volume[CD]: 175.41
 Dx: Dm:

Sys: Tetragonal
 Lattice: Primitive
 S.G.: P4/mmm [123]
 Cell Parameters:
 a 3.801 b c 12.135
 x β y

SS/FOM: F30=56(.0141, 38)

I/Icor: 2.36
 Rad: CuKα1
 Lambda: 1.54056
 Filter:
 d-sp: diffractometer

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
7.269	10	0	0	1	37.903	10	1	0	4	61.090	4	0	0	8
14.574	5	0	0	2	44.245	5	1	0	5	61.976	10	2	0	5
21.953	17	0	0	3	44.738	22	0	0	6	62.601	5	2	1	4
23.376	6	1	0	0	45.010	19	1	1	4	66.264	4	1	0	8
24.506	26	1	0	1	47.796	42	2	0	0	67.199	2	2	1	5
27.659	45	1	0	2	50.616	16	1	1	5	67.561	5	2	0	6
29.429	16	0	0	4	51.095	11	1	0	6	69.913	9	2	2	0
32.278	100	1	0	3	56.128	7	2	1	2	71.328	6	1	1	8
33.301	81	1	1	0	56.952	12	1	1	6	72.579	5	2	1	6
34.149	14	1	1	1	57.129	<1	2	0	4	78.804	8	0	0	10
36.523	3	1	1	2	58.469	15	1	0	7	79.147	9	3	0	3
37.019	23	0	0	5	58.849	30	2	1	3	79.653	9	3	1	0

- Smith & Snyder Figure of Merit
- To quantify better the quality of a given set of d-spacings
- The higher, the better.
- < 20 → poor quality

$$F_N = \frac{1}{|\Delta 2\theta|} \frac{N_{\text{obs}}}{N_{\text{poss}}}$$

F_N = Figure of merit

$\Delta 2\theta$ = The average error in 2θ

N_{obs} = The number of lines observed

N_{poss} = Number of lines possible

