Powder diffraction specimen preparation

Matteo Leoni, Gilberto Artioli, Norberto Masciocchi
University of Trento
University of Milan
University of Insubria - Como

The quality of collected data cannot be greater than the quality of specimen and specimen preparation!

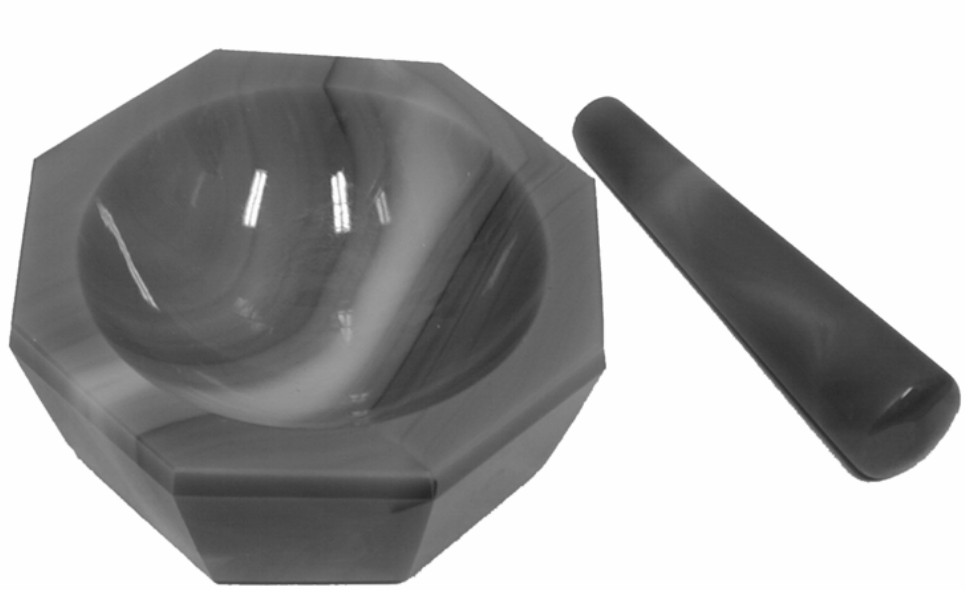
Badly prepared specimen → Limited use of the collected data

Based on the scope of the analysis (phase recognition, indexing, structure solution/refinement, etc.), the care in preparing the specimen can be tuned.

A sample is ideal when its diffraction pattern does not change (it is therefore reproducible) by varying the preparation technique

Most materials analysed by XRD are in a non-ideal state of “aggregation” (rocks, metal pieces, tablets, etc.) and must be ground to obtain a fine powder.

- Mortar and pestle
  - Glass for soft materials
  - Agate for hard materials
  - BN for abrasives
- Ball mill
  - Spheres chosen as above



Based on the material, milling can last from seconds to minutes

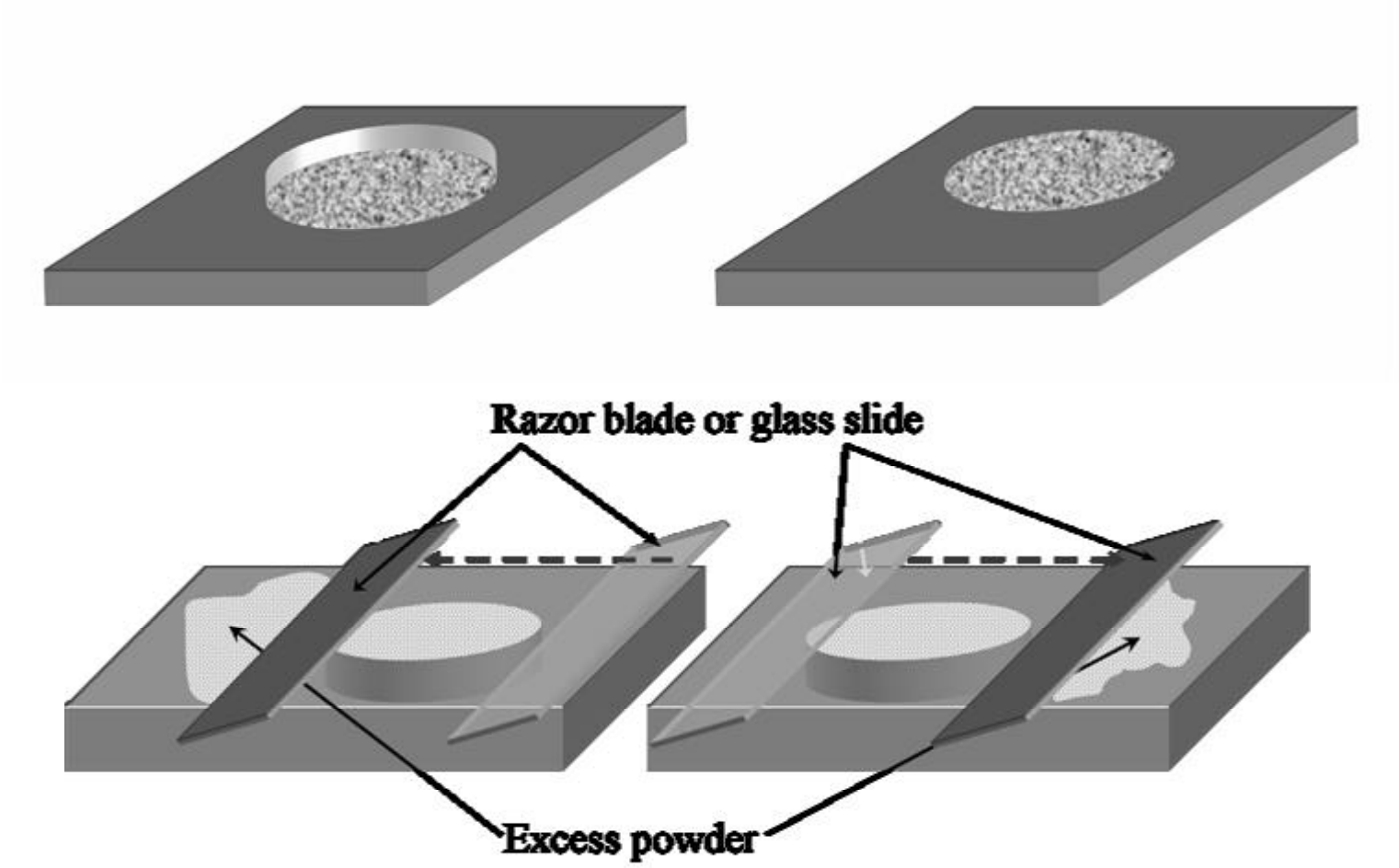
Attention! Prolonged milling can produce a powder with very high specific surface area (surface effects), agglomeration, loss of crystallinity or chemical reactions (phase transition, desolvation, polimerization).

- Mill a polymer in LN2 (to make it fragile)
- Heat up the material (10-30 min) @ 1/3 Tm (in K) to anneal defects
- Use a milling agent to keep particles separated
- Sieve between 25 and 75 μm, possibly under pressure or in (liquid) flux

Attention! Avoid contamination of the powder by the mill and be careful with ductile materials

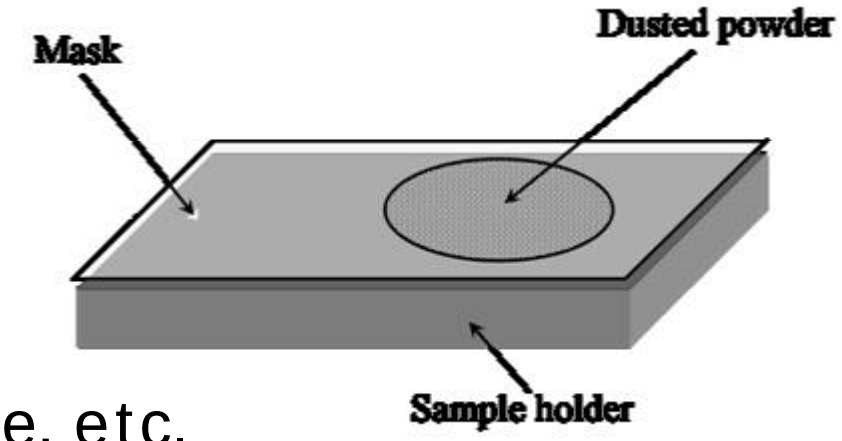
Preparation methods (Bragg-Brentano geometry)

- Plastics, aluminum or glass holder
  - Powder filling a cavity (front loading)



Attention! Preferred orientation can appear if grain shape is not isotropic

Other preparation methods (Bragg-Brentano geometry)



- Dry dusting
- Dusting in oil, grease, silicone, etc.
- Back filling / Side Loading
- Mixing with inerts (e.g. cabosil®)
- Volatile suspendents (acetone, ethanol, etc.)
- High-biling-point liquids (amile acetate, + 5% collodion)
- Spray drying (sperical particles)
- Thin film over miscut monocrystal (e.g. Si wafer) e.g. for transparent materials, small amounts

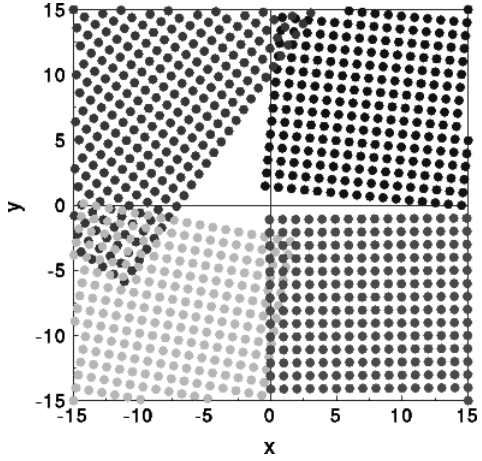
Other preparation methods (transmission geometry)

- Dusting on transparent films

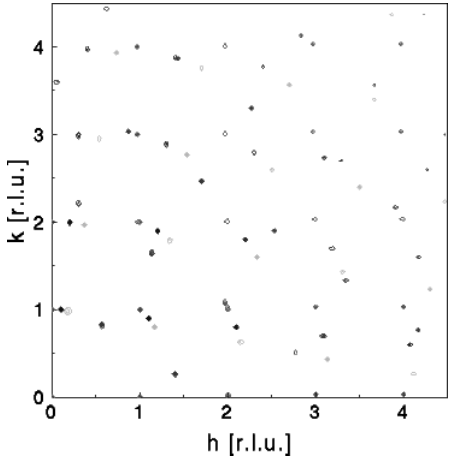
Other preparation methods (Debye-Scherrer geometry)

- Capillary immersed in a liquid (organic solvent, oil, etc.) and then in the powder
- Some as above, but with pre-mixing of liquid and powder
- Capillary filled by gravity in an ultrasonic bath
- Sealed capillary (with or without mother liquor) for unstable specimens

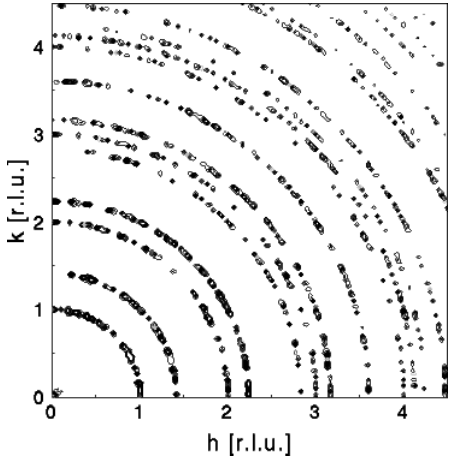
Preferred orientation effects



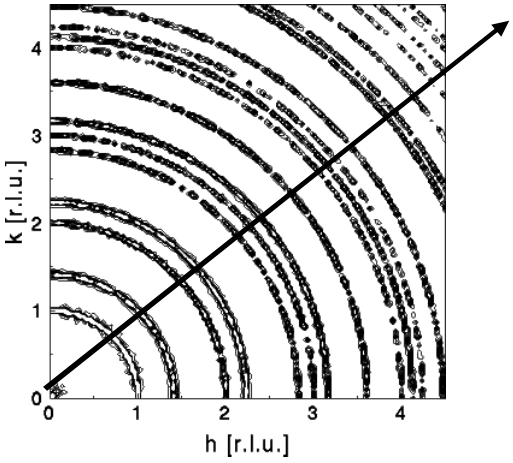
4 crystals (real space)



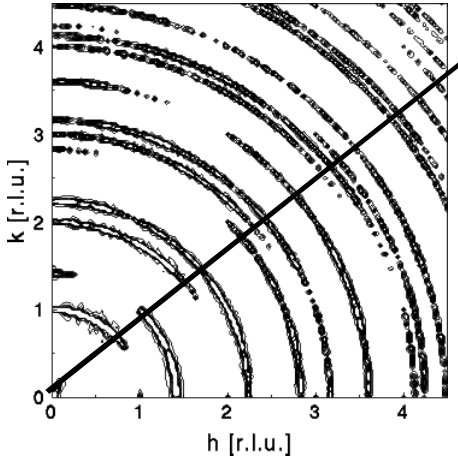
4 reciprocal lattices

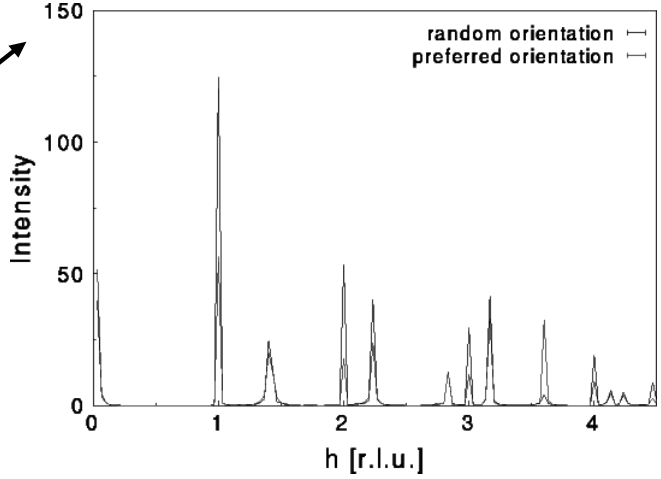


40 reciprocal lattices



200 reciprocal lattices
without preferred orientations





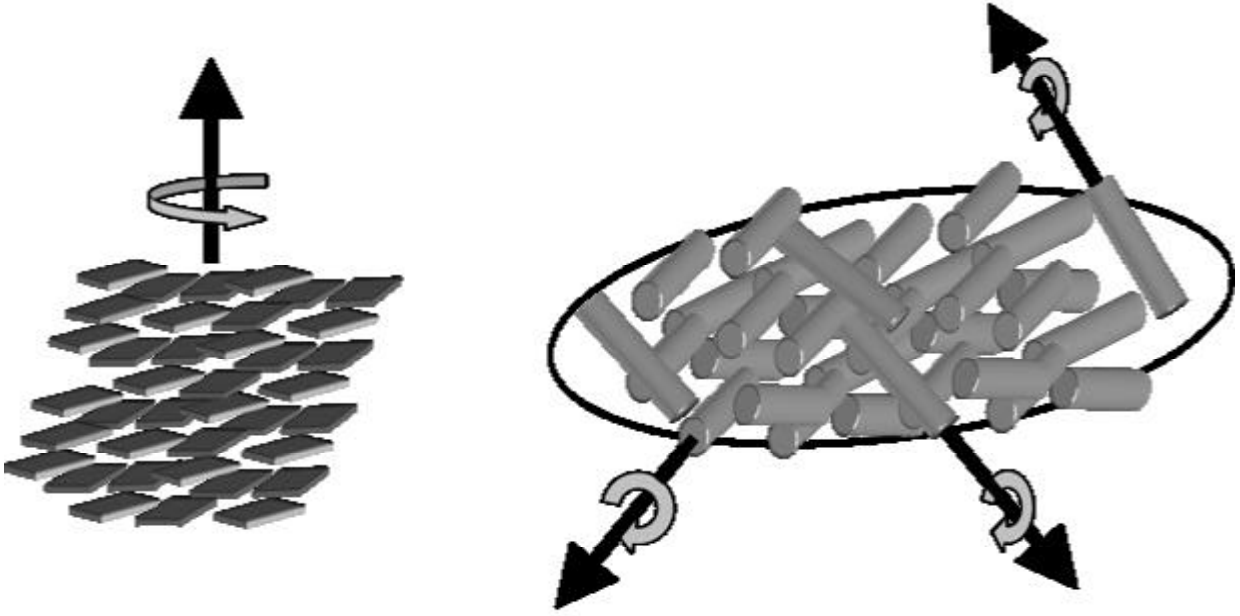
XRPD pattern (1D)
with preferred orientation

Preferred orientation effects

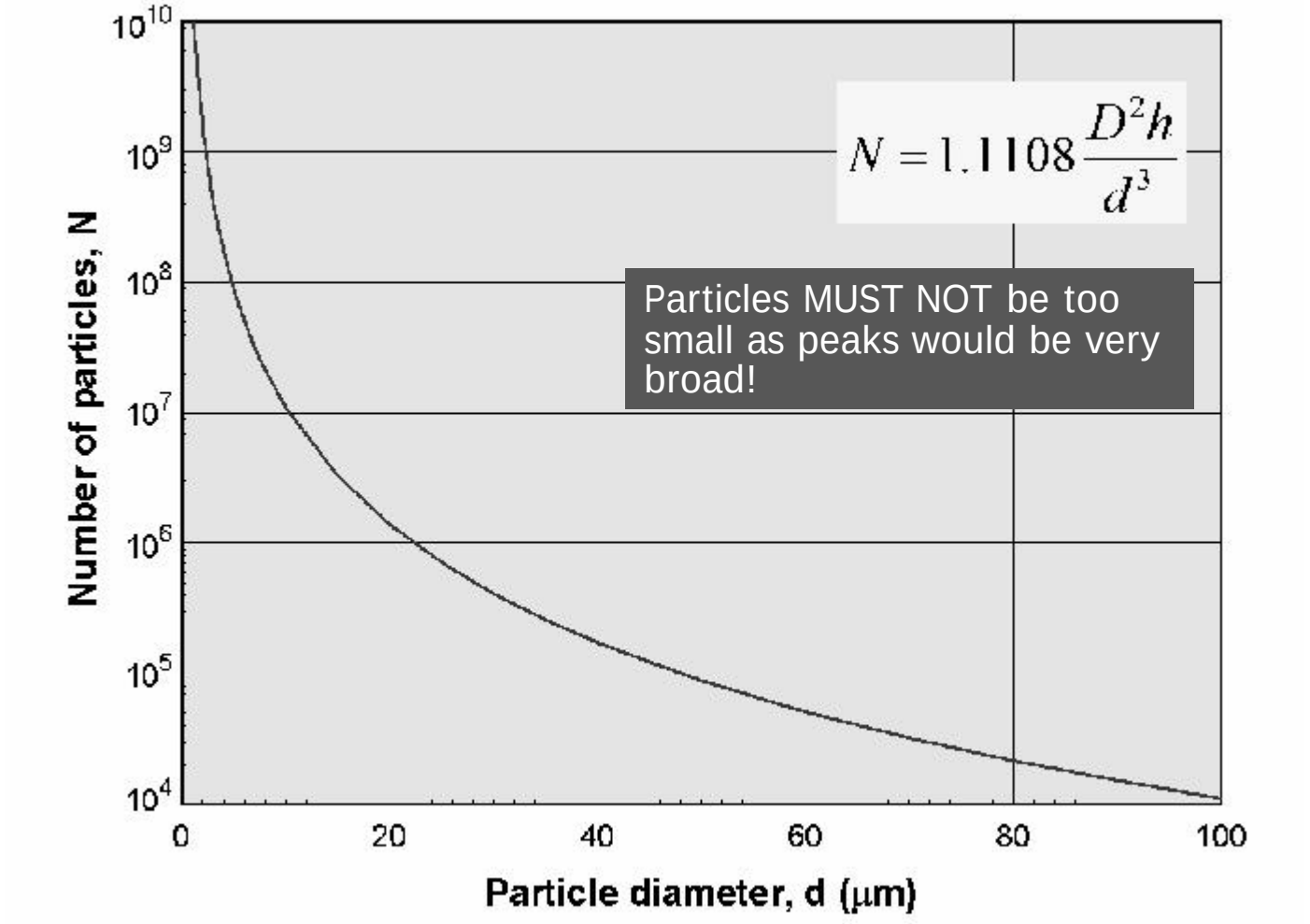
If it cannot be eliminated, preferred orientation must be reduced and possibly interpreted in terms of preferred cleavage planes and crystalline structure:

Layered structures (normal to c) lead to estremely intense 00l peaks (XRPD pattern is 'monodimensional')

Chain structures/polymers (along c) can lead to estremely low 00l peaks (XRPD pattern is 'bidimensional')

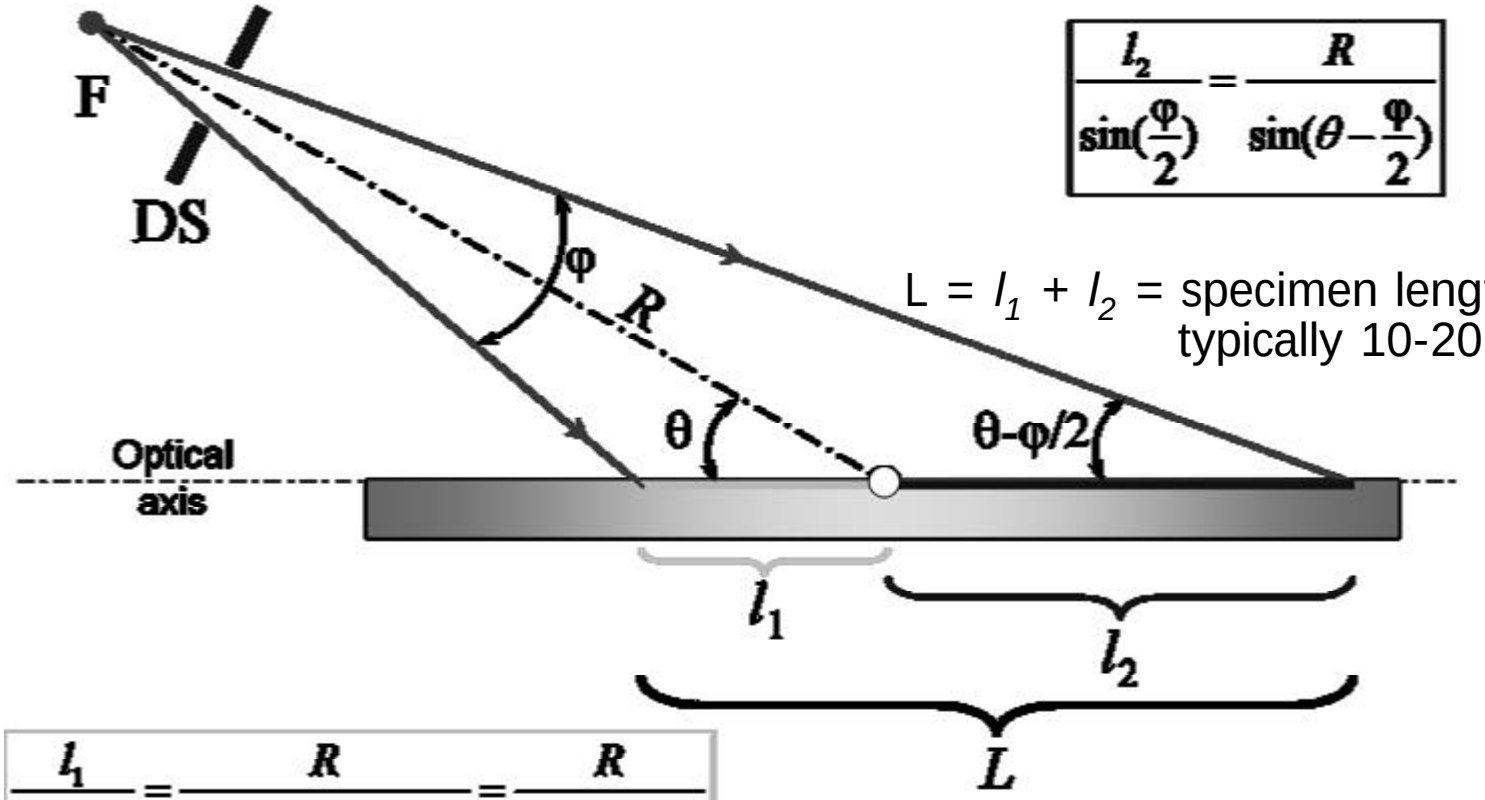


Statistical homogeneity of the specimen



Cylindrical specimen D = Diameter = 10 mm; h = height = 0.1 mm; spherical particles Ø = d

Effect of specimen size (width)



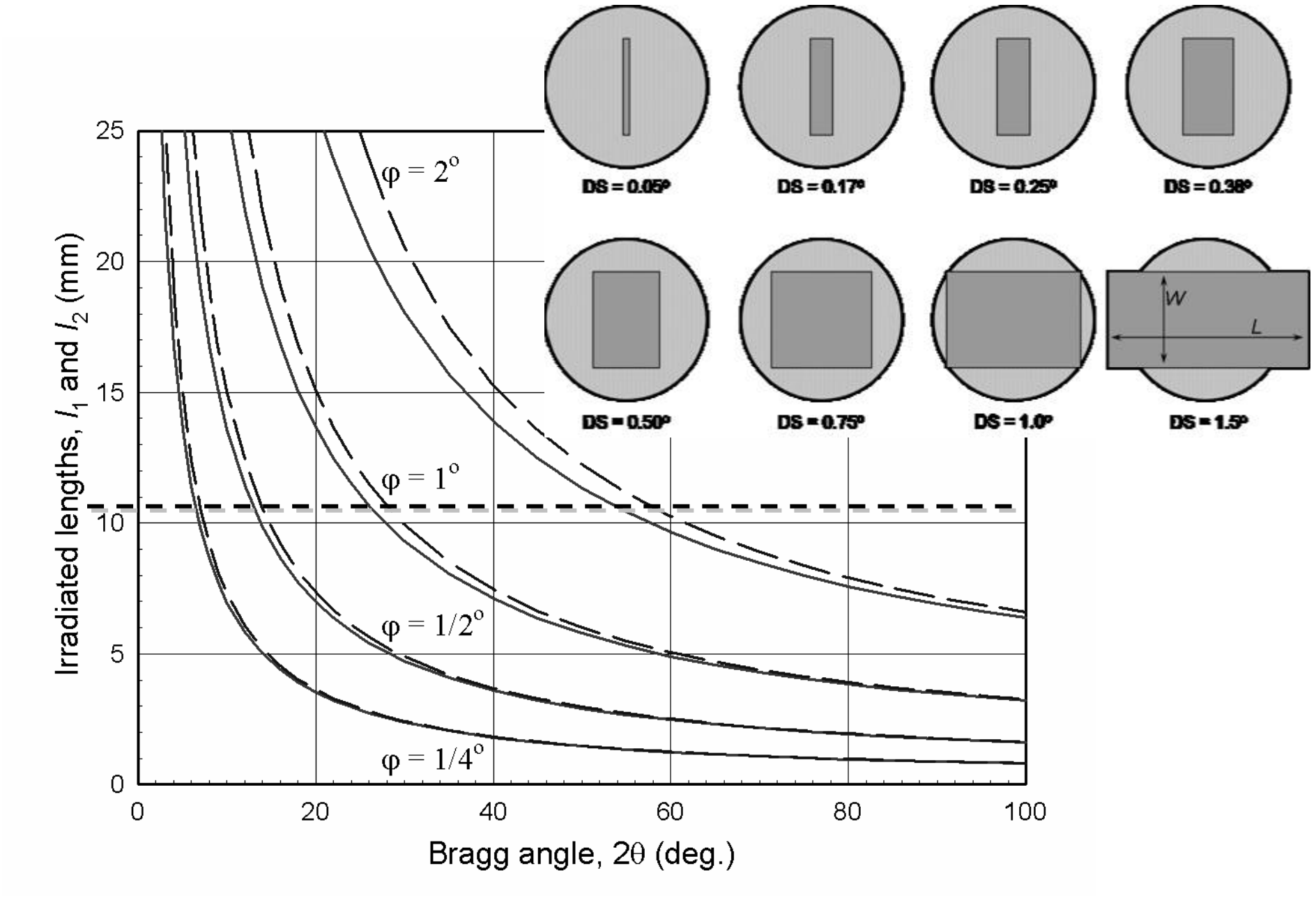
$$\frac{l_2}{\sin(\frac{\varphi}{2})} = \frac{R}{\sin(\theta - \frac{\varphi}{2})}$$

L = l_1 + l_2 = specimen length, typically 10-20 mm

$$\frac{l_1}{\sin(\frac{\varphi}{2})} = \frac{R}{\sin(180 - \theta - \frac{\varphi}{2})} = \frac{R}{\sin(\theta + \frac{\varphi}{2})}$$

ϕ = primary beam divergence (typically 0.25 – 1.0°);
R = goniometer radius (typically 170-290 mm);
θ = Bragg angle (typically 2θ > 5°)

If 2q < lower limit, i.e. 2 ArcSin[2 R/L Sin(f/2)] (approximate)



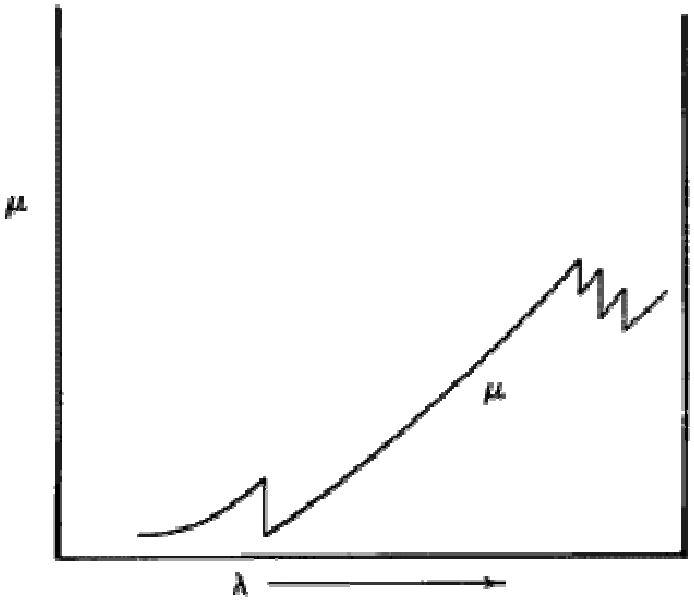
Effect of specimen size (thickness)

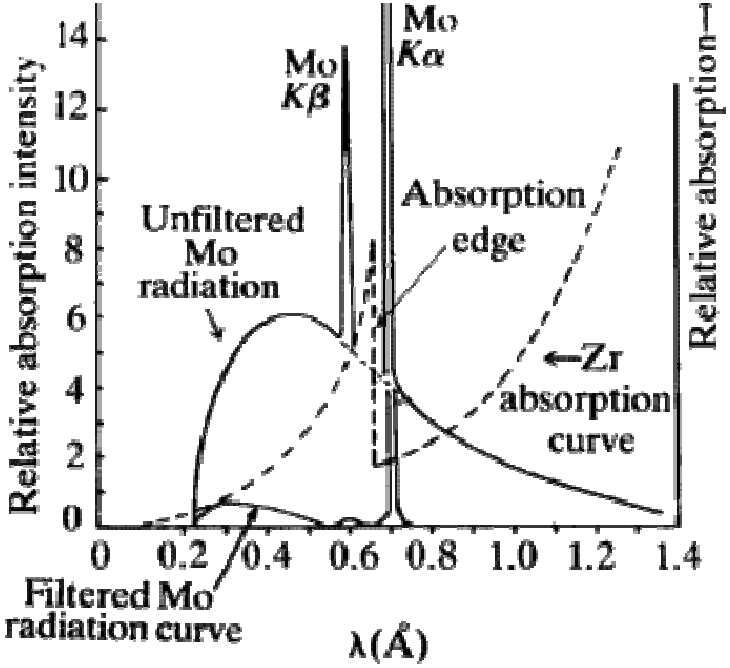
Remember “Lambert-Beer” absorption effect

$I/Io = \exp(-\mu t)$, with $t = t(\theta)$ based on the geometry

For a Bragg-Brentano instrument:

$I/Io = \exp(-2\mu t/\sin\theta)$





Attention! 99.9% radiation absorbed for $t_{min} \approx 3.45/\mu$

if $\mu = 0.1 – 10\ mm^{-1}$, $t_{min} \approx 34 – 0.34$ mm

Effect of specimen displacement from goniometer axis

$\Delta 2\theta = 2S/R \cos\theta$

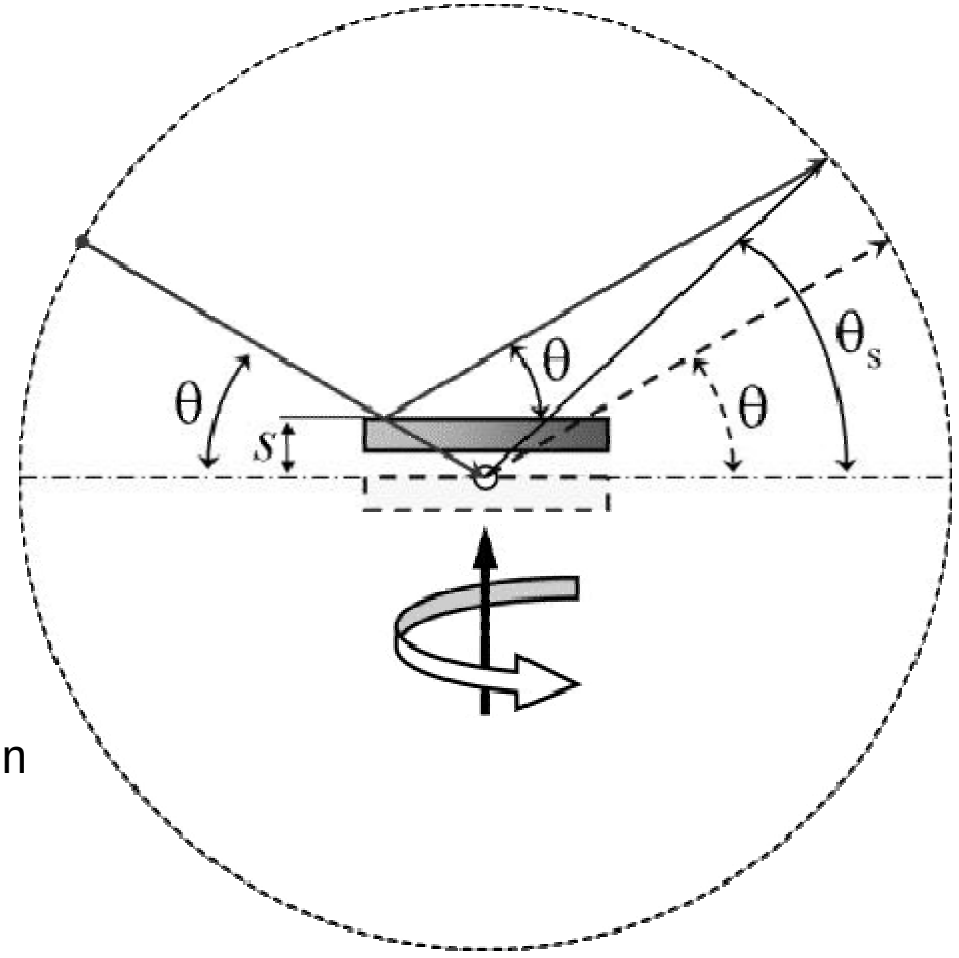
If R = 175 mm and $2\theta < 20°$

S = 10 μm $\Delta 2\theta = 0.006°$

S = 50 μm $\Delta 2\theta = 0.032°$

S = 100 μm $\Delta 2\theta = 0.065°$

S = 200 μm $\Delta 2\theta = 0.130°$

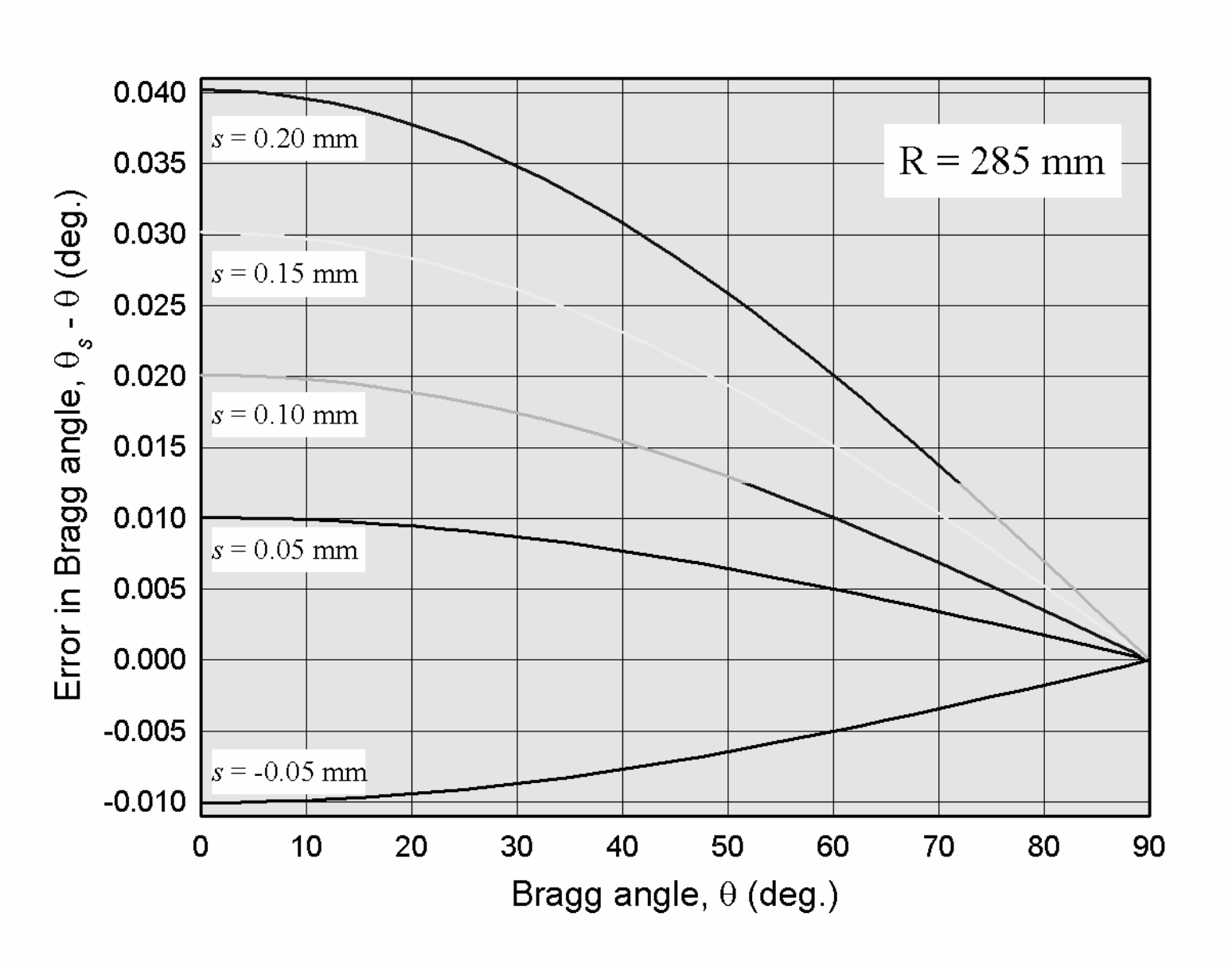


For **Search-Match**, data with precision less than 0.10° usually suffice

For **Indexing** a pattern of an unknown phase, **precision and accuracy** better than 0.02° are wanted

Ideally, the specimen must be tangent to the focussing circle

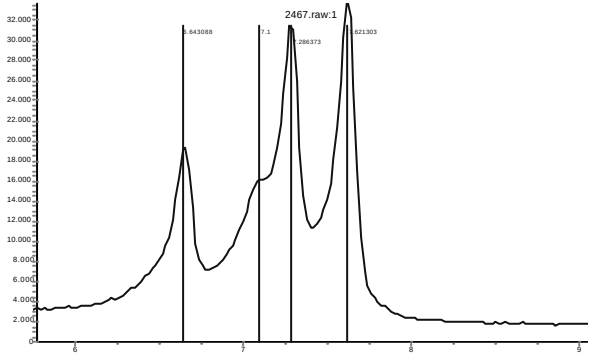
Effect of specimen displacement from goniometer axis



Is the 0.02° accuracy requirement really necessary?

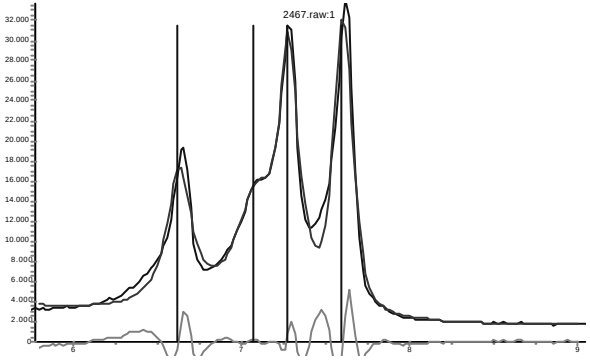
Depends on the technique used for the determination of the peak position. Fitting using physical models for the instrumental effects gives the highest accuracy

Peak Search



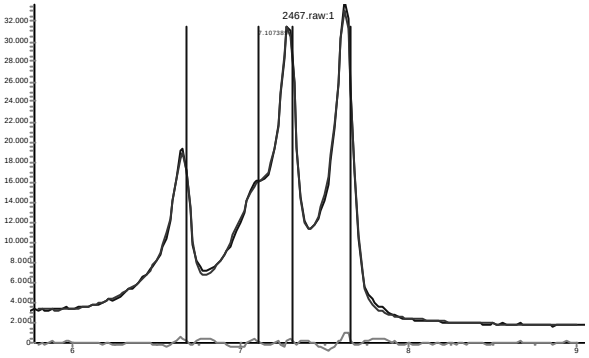
6.643 (0.041)
7.100 (0.010)
7.286 (0.027)
7.621 (0.030)

Profile Fitting pV



6.626 (0.058)
7.078 (0.032)
7.278 (0.035)
7.602 (0.049)

Profile Fitting FPA



6.684
7.110
7.313
7.651

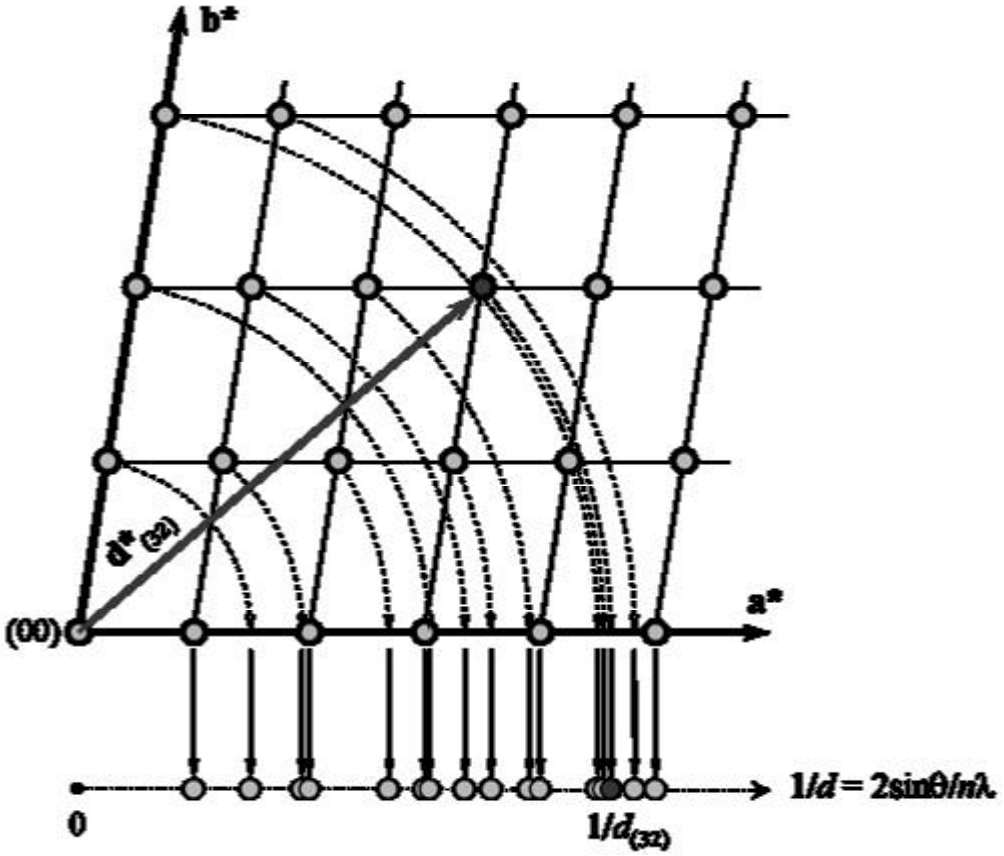
Is the 0.02° accuracy requirement really necessary?

Geometric relationship between

3D reciprocal lattice [vector $d^*(hkl)$]

1D projection $|d^*| = 2\sin\theta/\lambda$

3D



1D

Points are separated

Superposition is present