RMS

Testing · Research · Consulting

BGMN/Profex User Meeting 2019

# Good Diffraction Data

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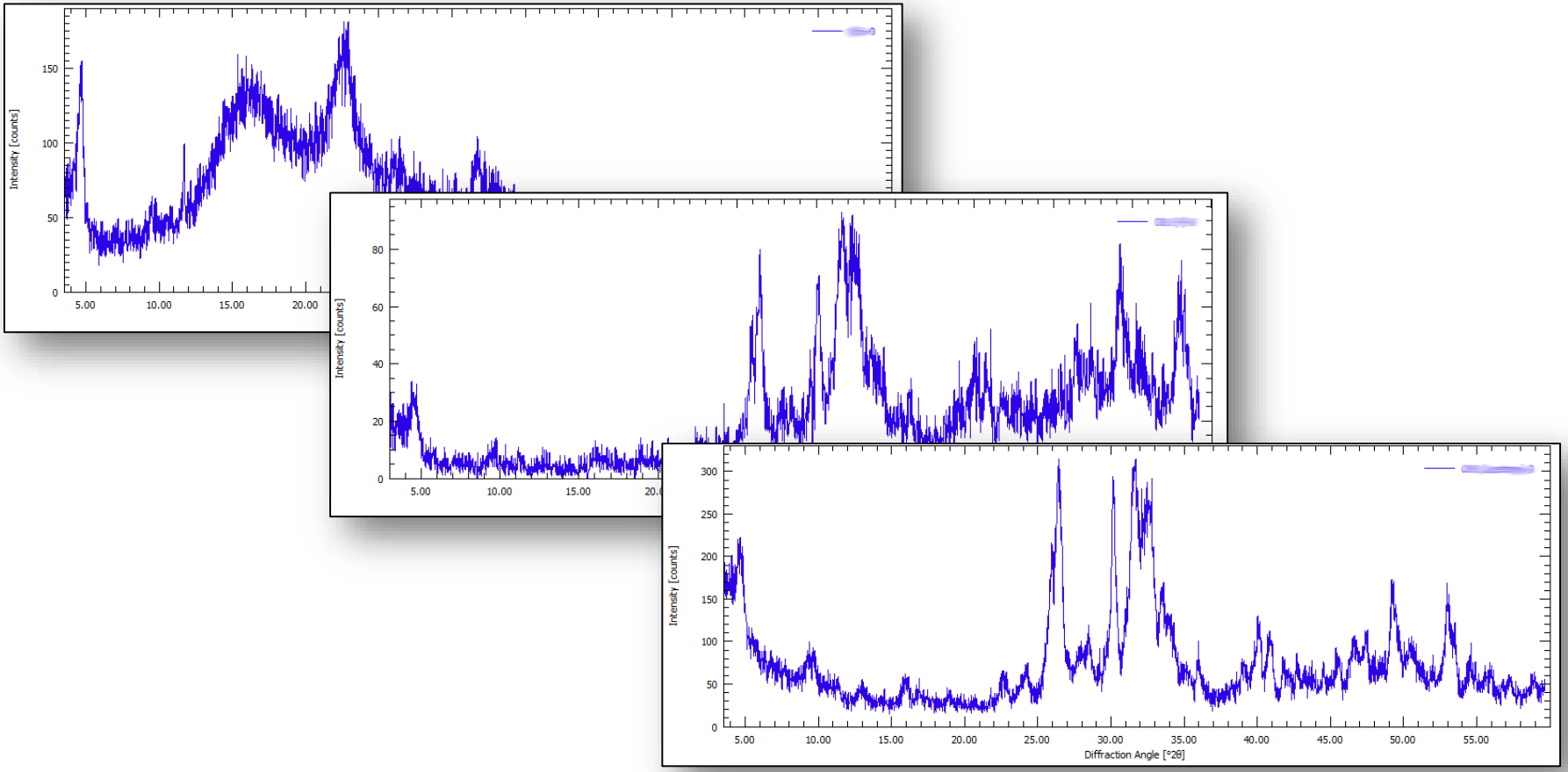
# Good Diffraction Data



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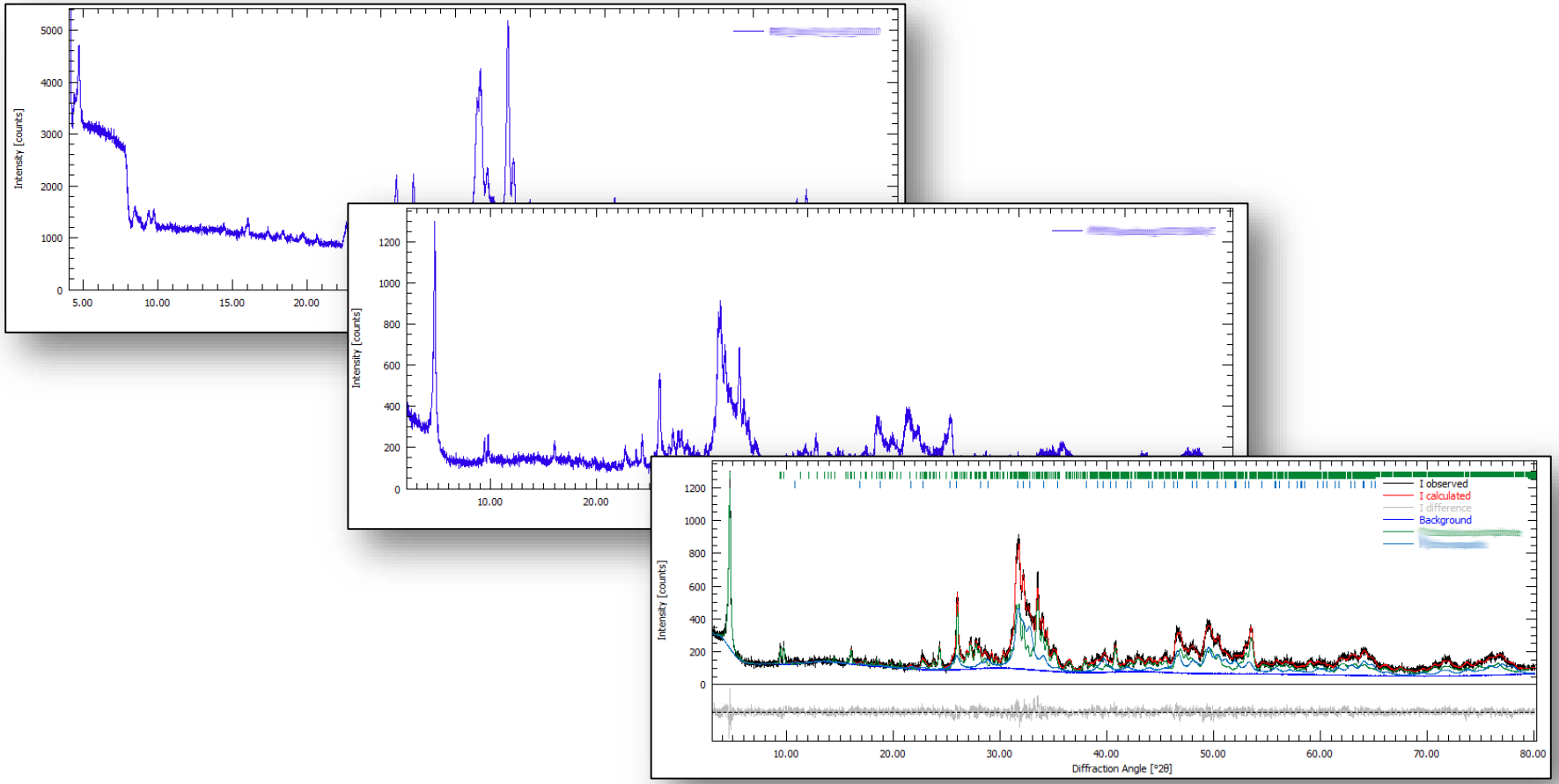
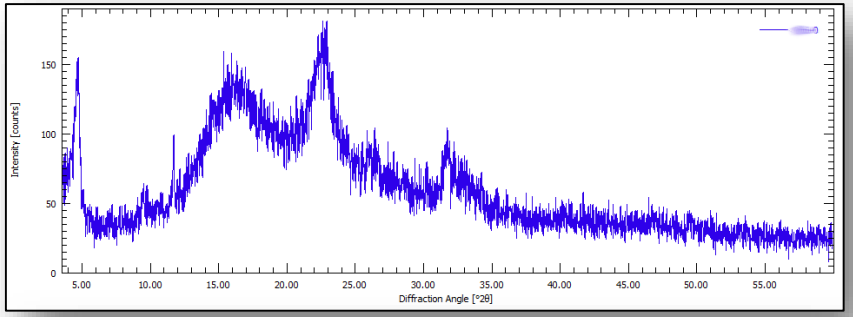
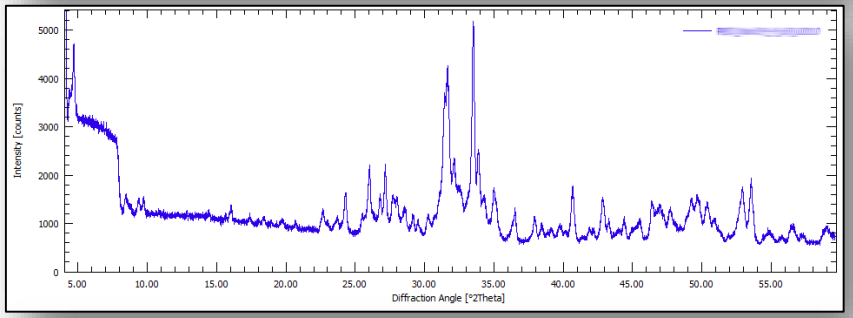
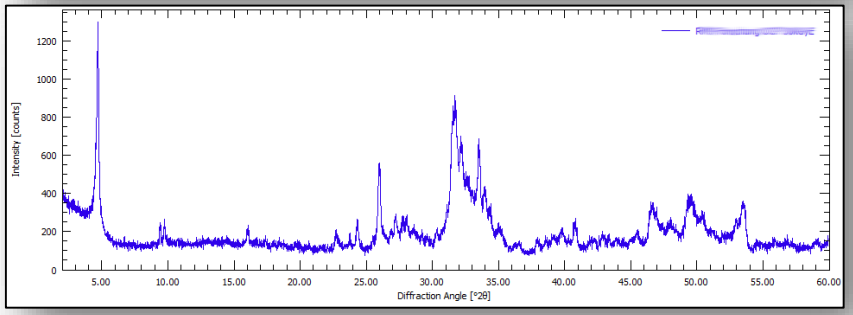


# Good Diffraction Data



# Good Diffraction Data

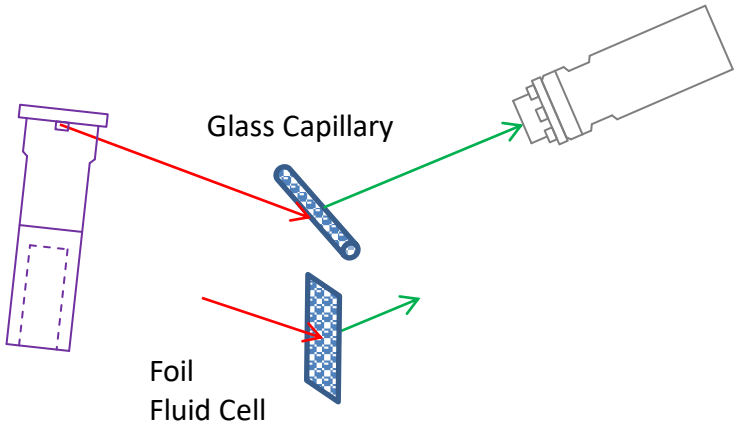
- Complex phase composition
  - Large number of phases
  - Low-symmetry phases
  - Low crystallinity / glass / organic content
- Fluorescence
- Sample preparation
  - Graininess
  - Texture
  - Height displacements
- Instrument setup
  - S/N ratio
  - Background
  - Angular resolution (peak width / asymmetry)

Inherent to the sample

Can (should) be minimized

# Digital Diffractometers

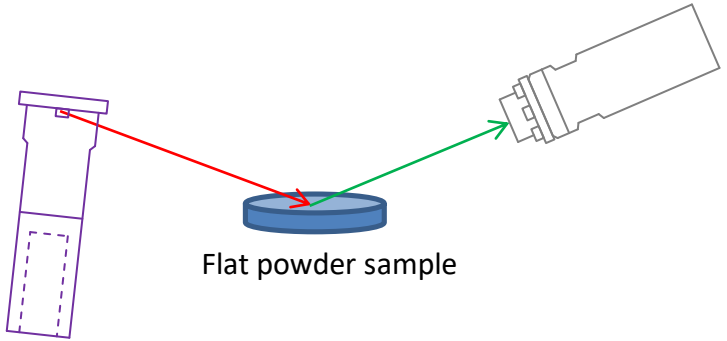
## Transmission Geometry
## Debye-Scherrer Geometry




Capillaries are ideal for:
- Light atoms (Polymers, Pharmaceuticals)
- Small amounts
- Hazardous materials
- Air-sensitive materials

Use characteristic radiation with **low** absorption coefficient

## Reflective Geometry
## Bragg-Brentano Geometry

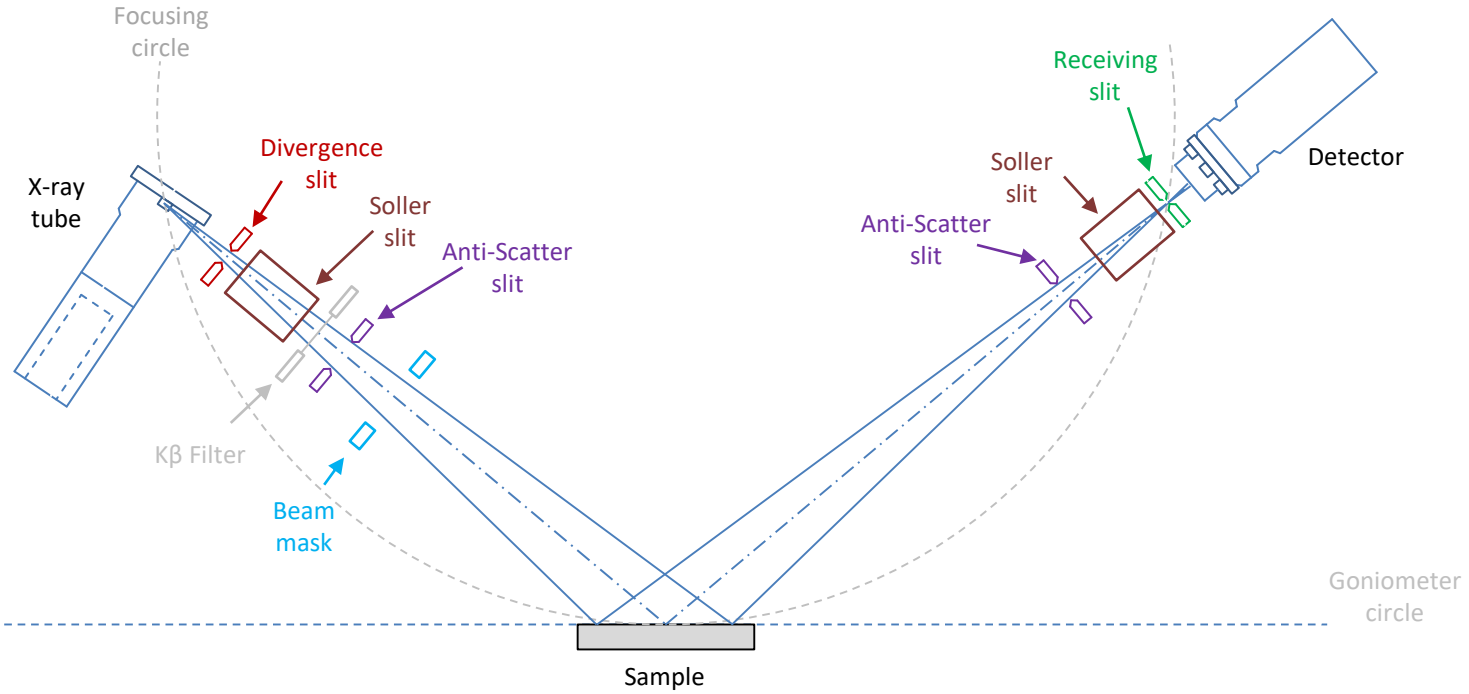



Reflective Geometry is ideal for:
- Absorbing materials (Ceramics, Metals)
- Thin films
- Texture analysis

Use characteristic radiation with **high** absorption coefficient

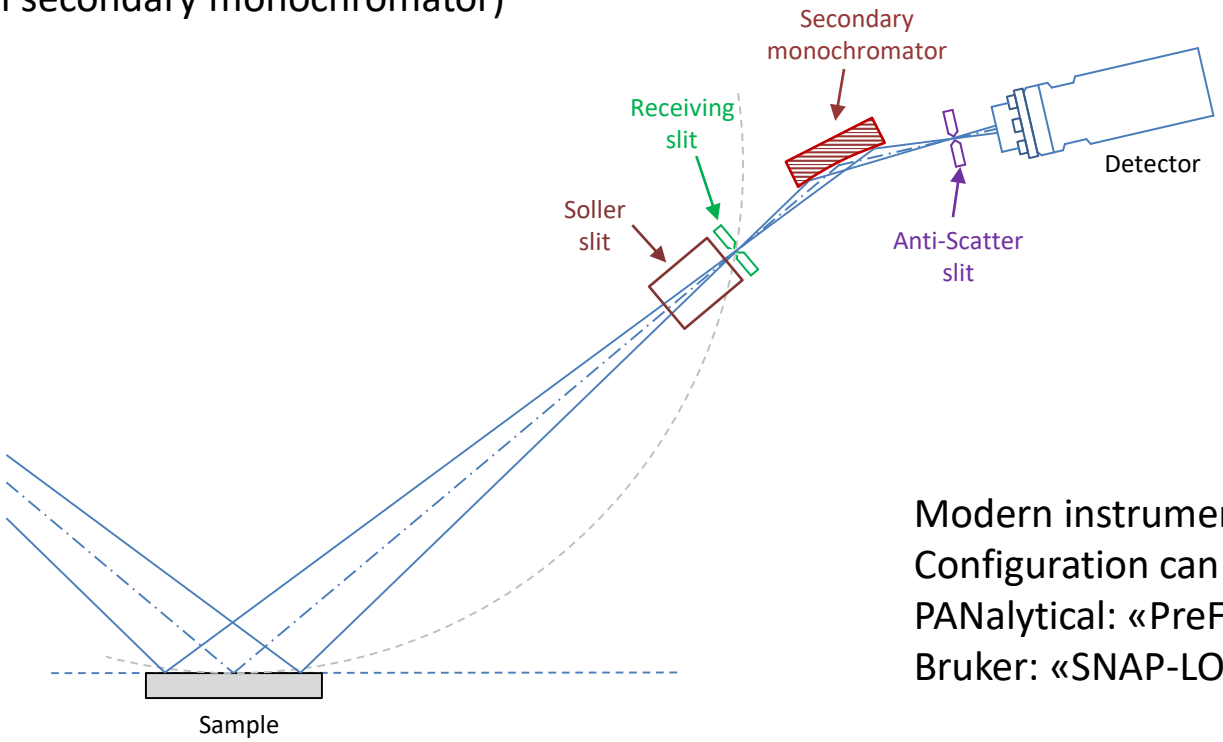
# Bragg-Brentano Parafocusing Diffractometer

## Typical Configuration (with Kβ filter)



# Bragg-Brentano Parafocusing Diffractometer

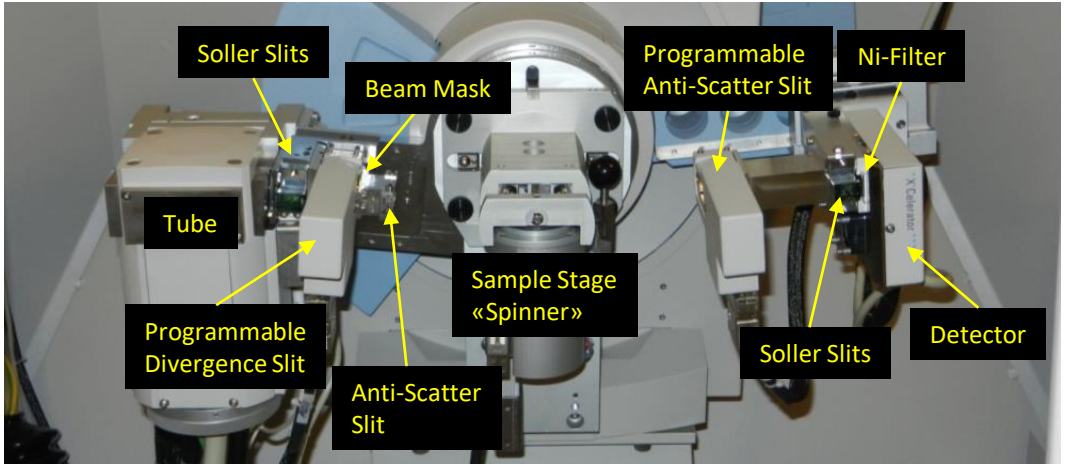
Typical Configuration
(with secondary monochromator)



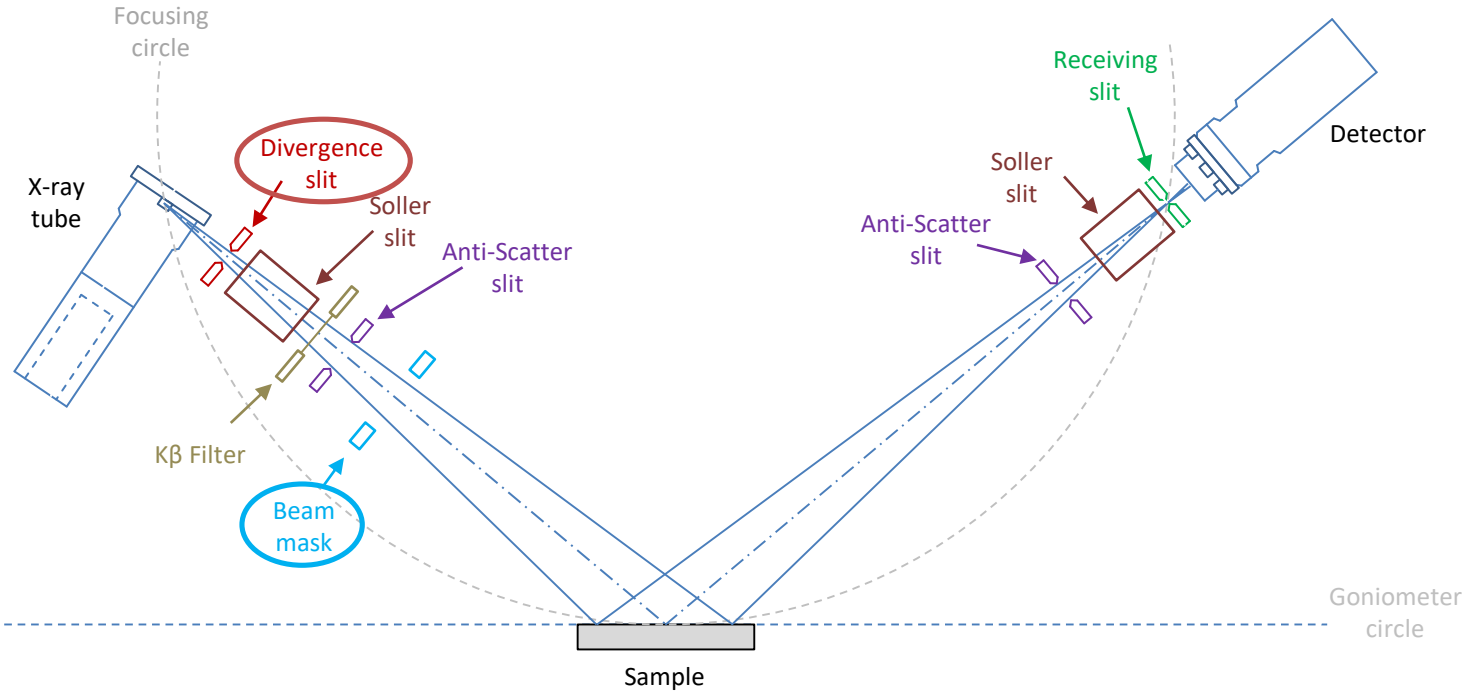

Modern instruments are modular.
Configuration can be changed easily.
PANalytical: «PreFIX»
Bruker: «SNAP-LOCK»

# Instrument Configuration

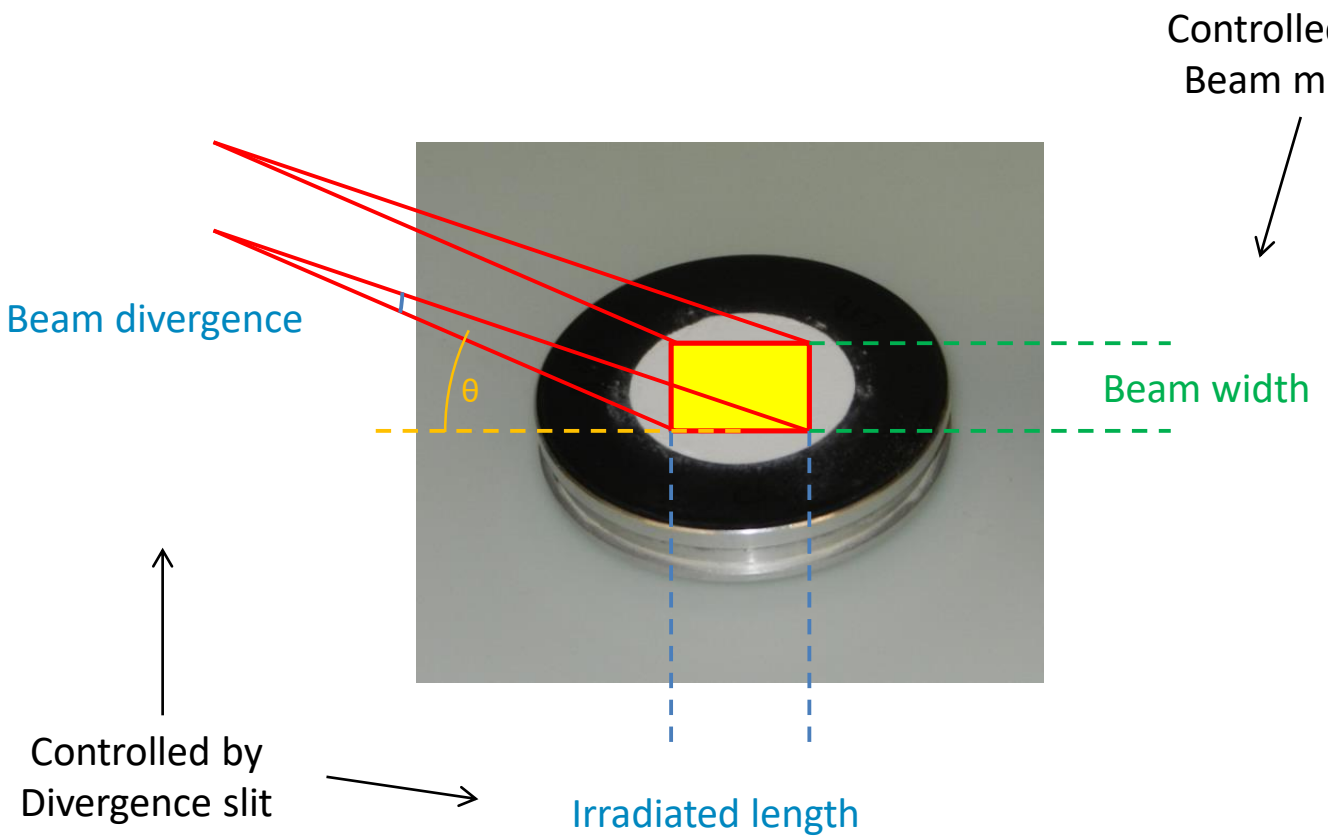
- Many optical elements = many options to optimize data quality
- How to find the best configuration?



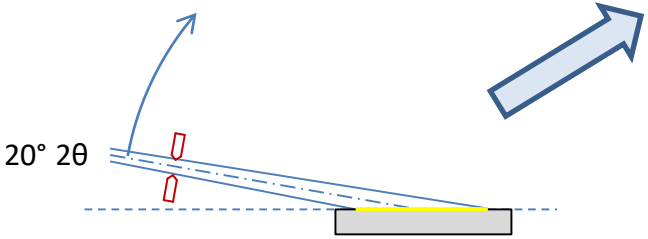

# Divergence Slit and Beam Mask



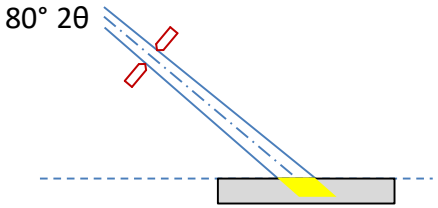
# Optimum Settings: Divergence Slit & Beam Mask



# Optimum Settings: Divergence Slit

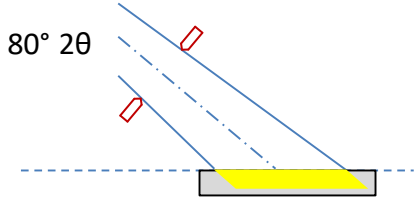



Fix divergence slit:



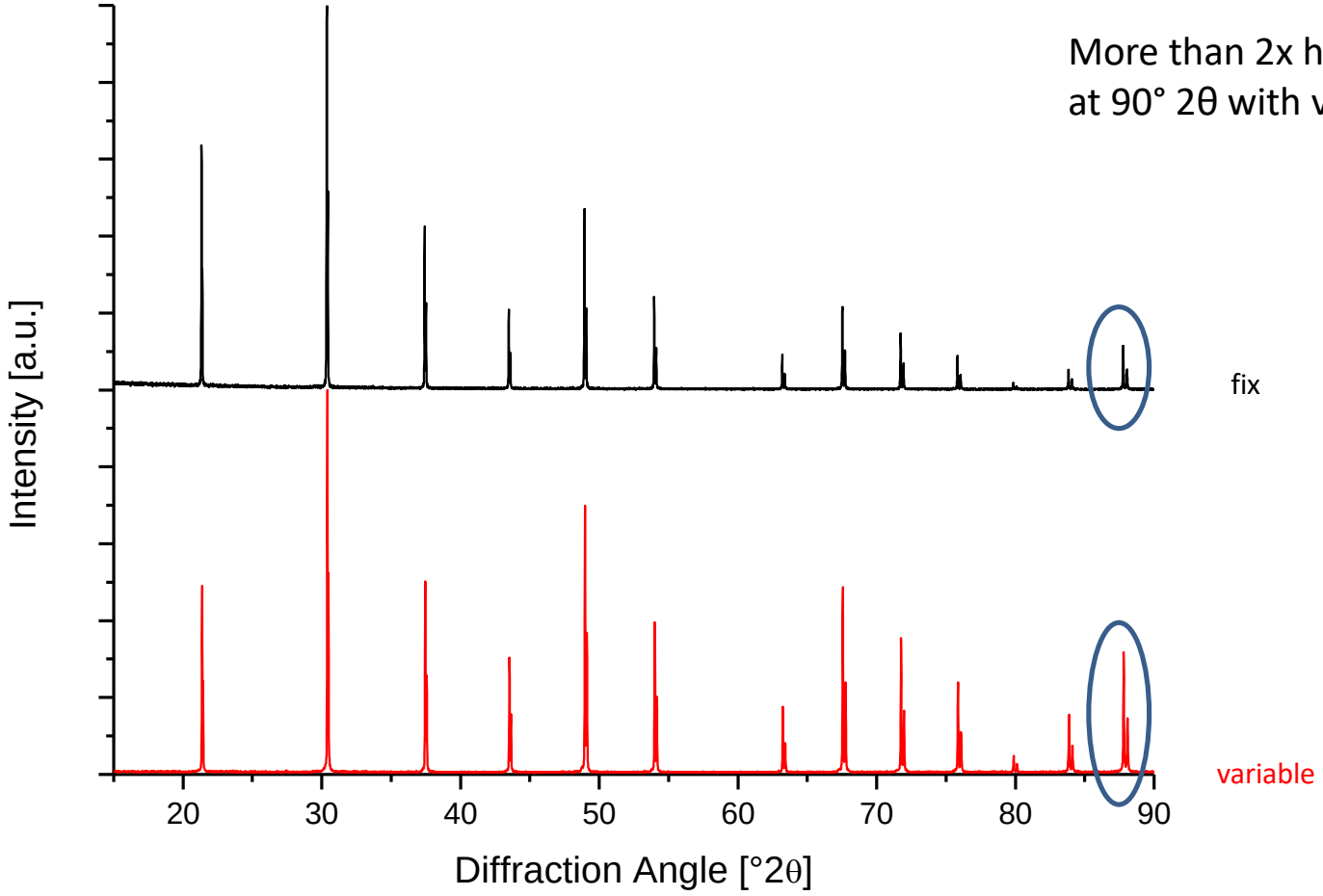

- Constant intensity
+ No mechanical parts

Variable / Automatic divergence slit:



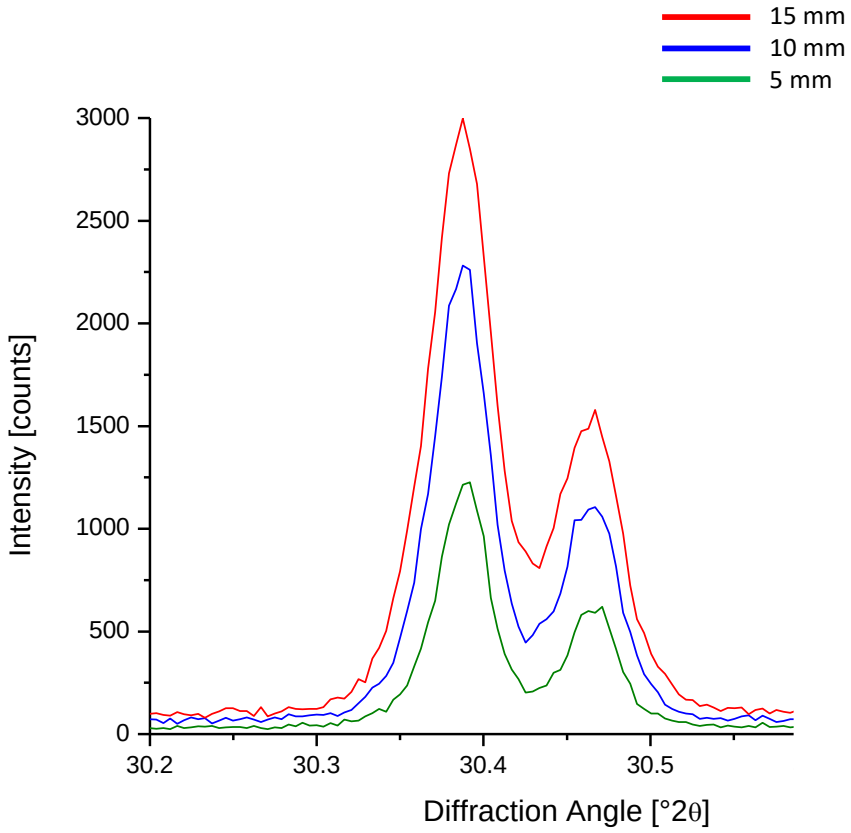

+ Gain of intensity at high 2θ
- Backlash in slit mechanics

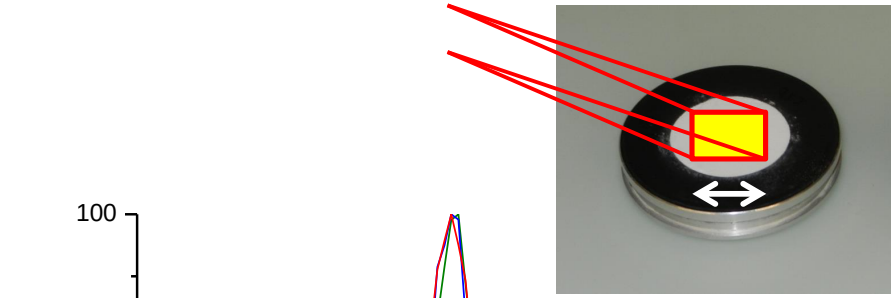
# Fixed vs. Variable Divergence Slit

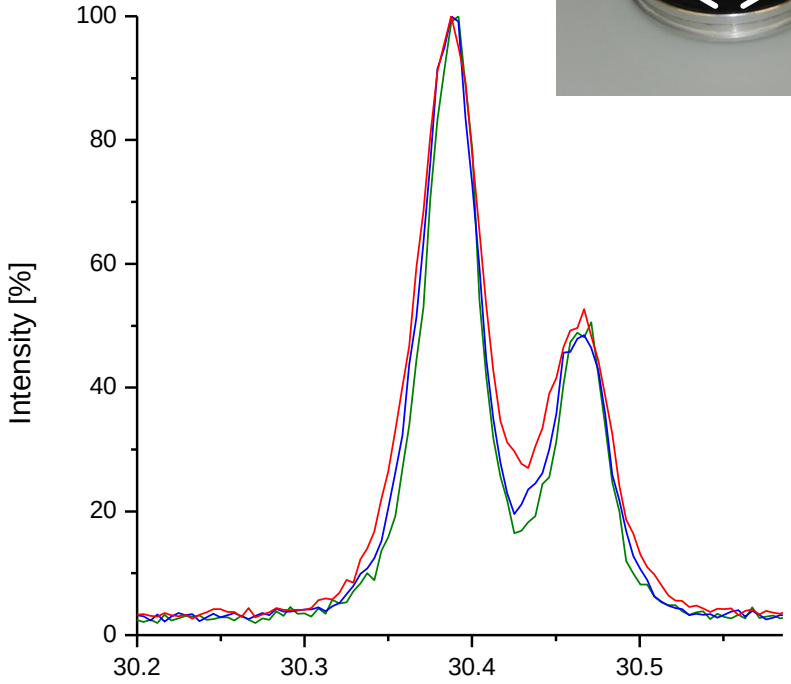



More than 2x higher intensity
at 90° 2θ with variable DS

# Divergence Slit: Irradiated Length

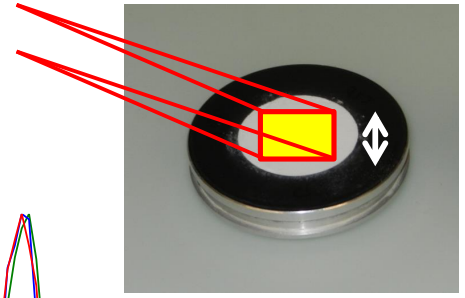


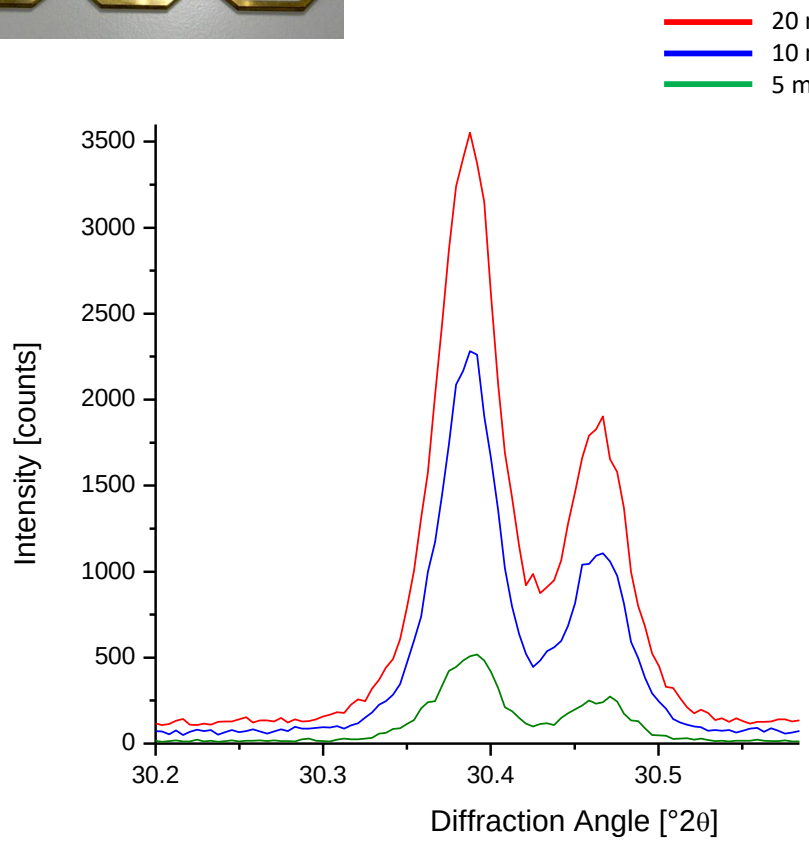



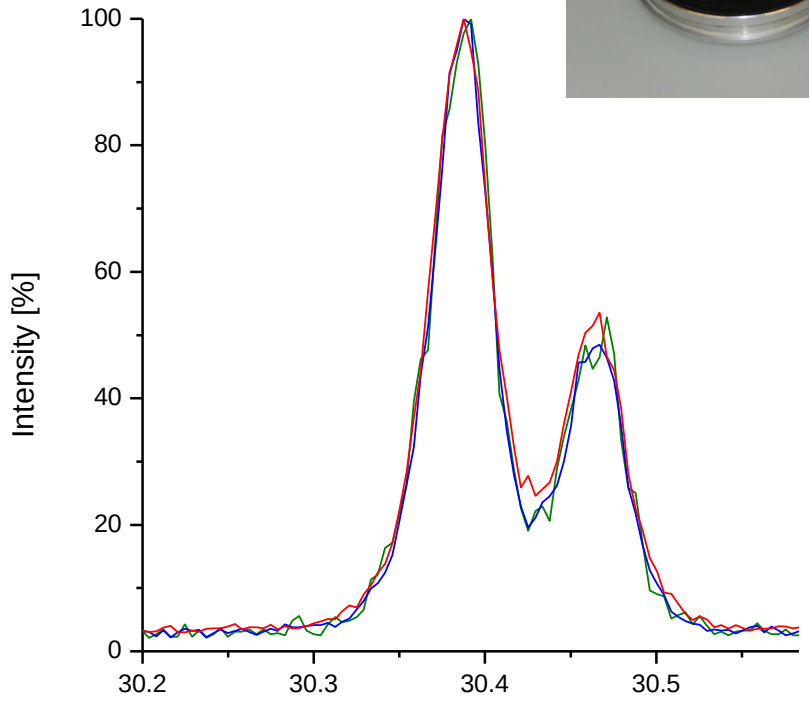



Soller Slits: 0.02 rad, Beam Mask: 10mm

# Beam Mask



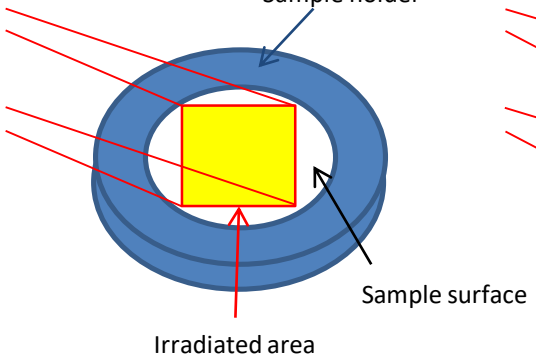


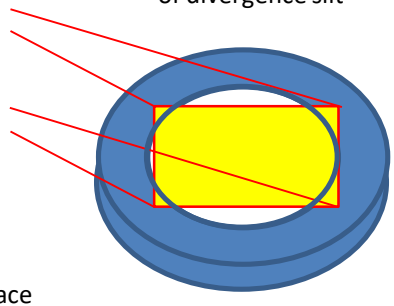

Soller Slits: 0.02 rad, Irradiated Length: 10mm

# Optimum Settings: Divergence Slit & Beam Mask

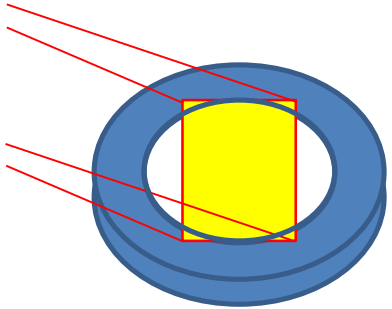
Correct!




Wrong!




Wrong!



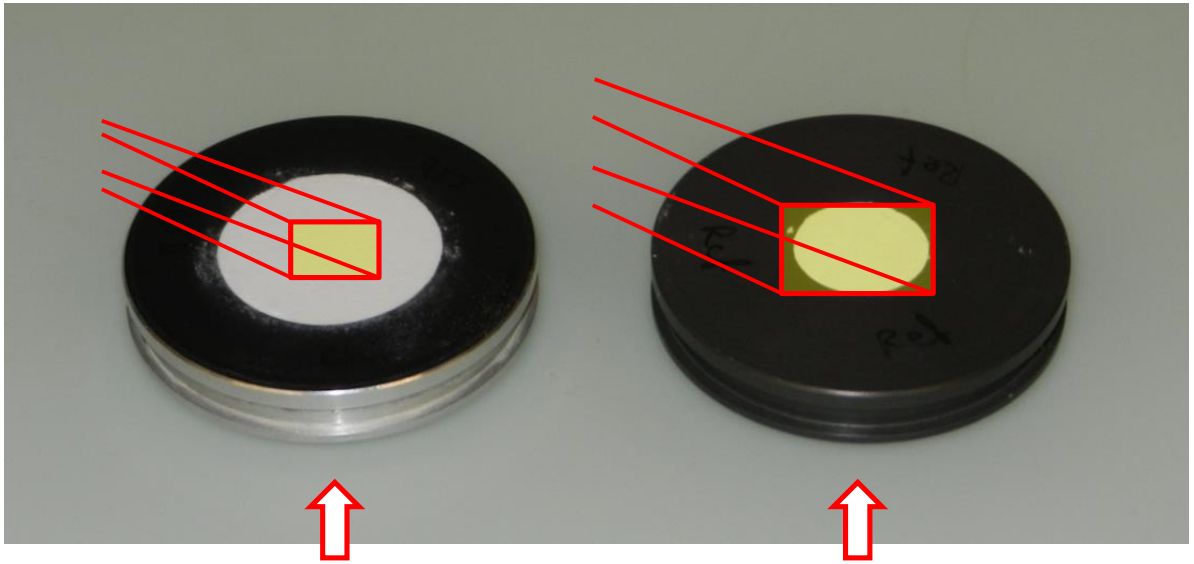

For **phase quantifications**:
- Variable divergence slit
- Adjust «irradiated length» and beam mask for maximum illumination
- Avoid beam spill-over!

For **structure refinements**:
- Fix divergence slit
- Adjust «slit size» and beam mask for maximum illumination **at lowest 2θ**
- Avoid beam spill-over!

# Optimum Settings: Divergence Slit & Beam Mask

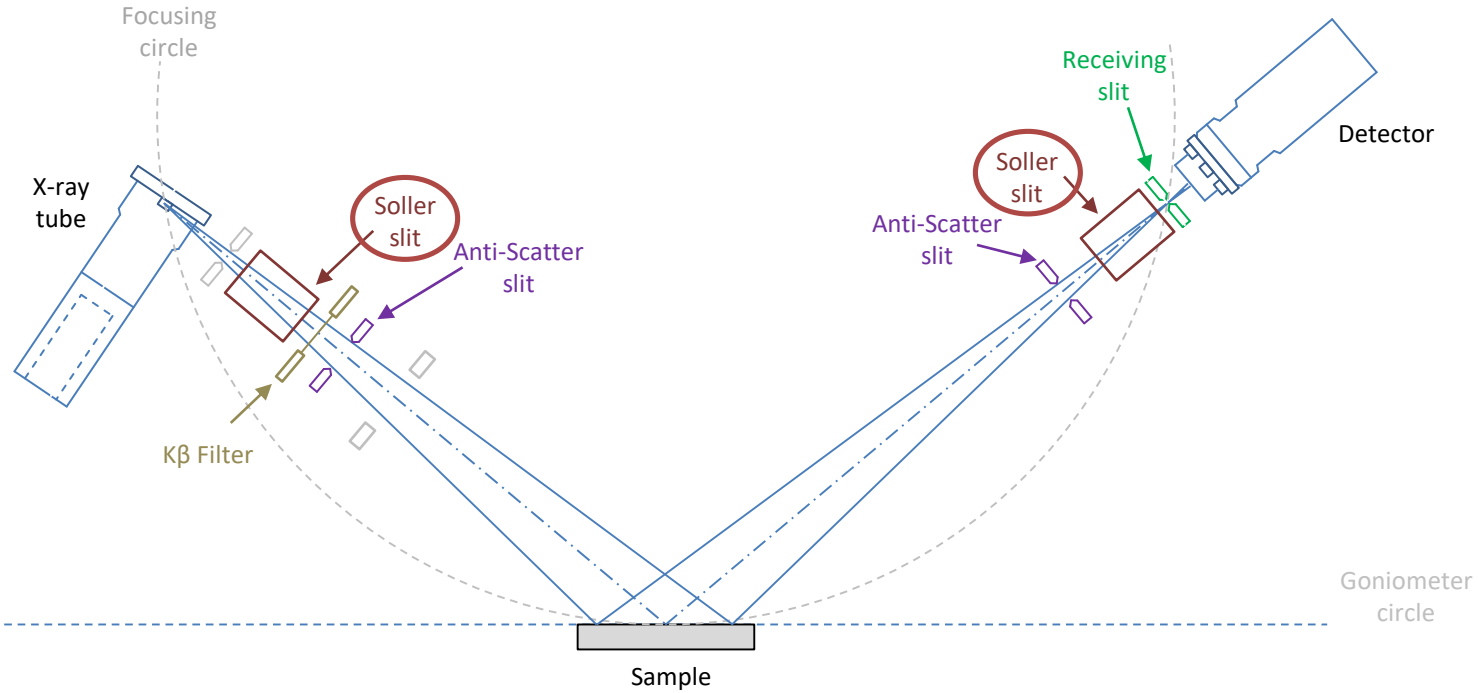
Using sample holders of various sizes?

⇒ Match your Divergence Slit and Beam Mask!

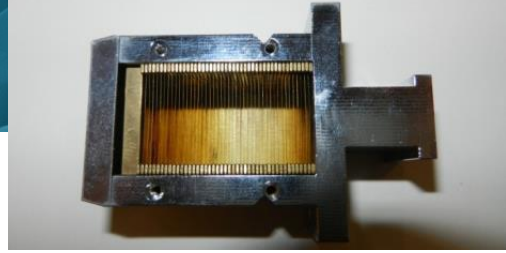


Or else: Waste of intensity or Beam spill-over

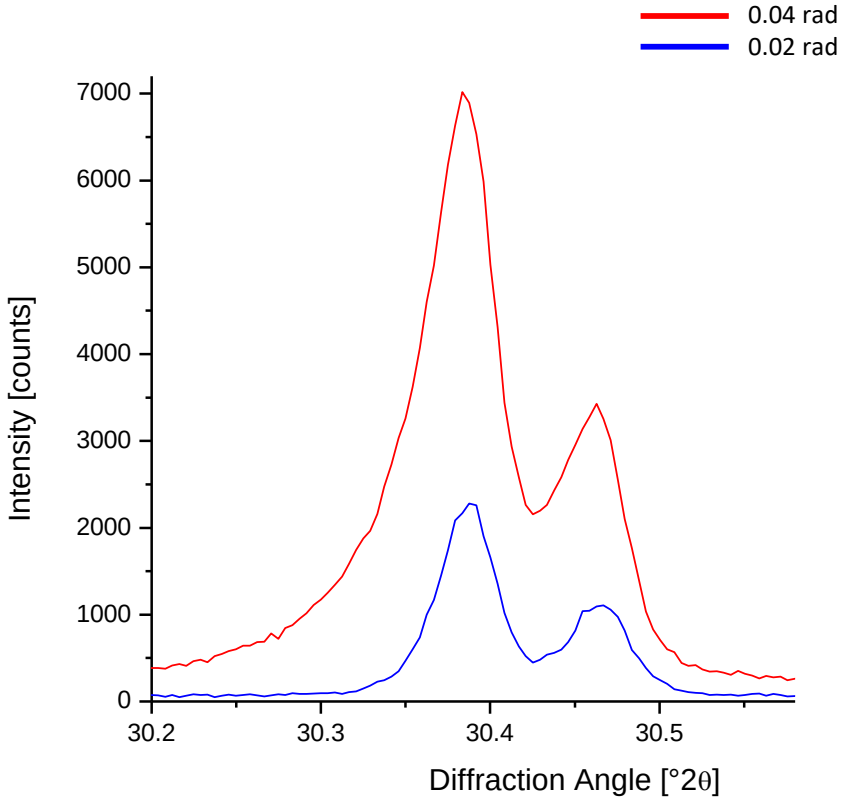
# Soller Slits / Collimators

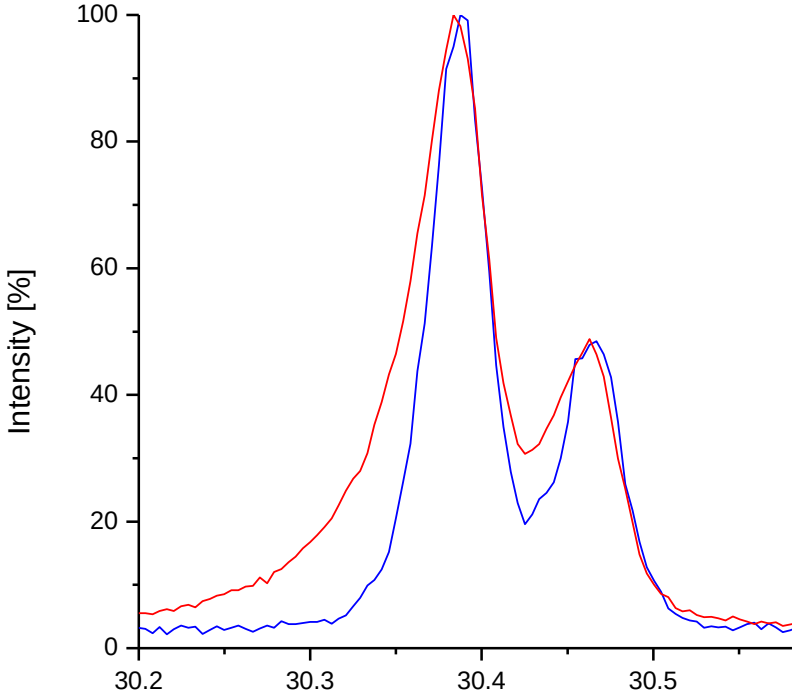


# Soller Slits / Collimators



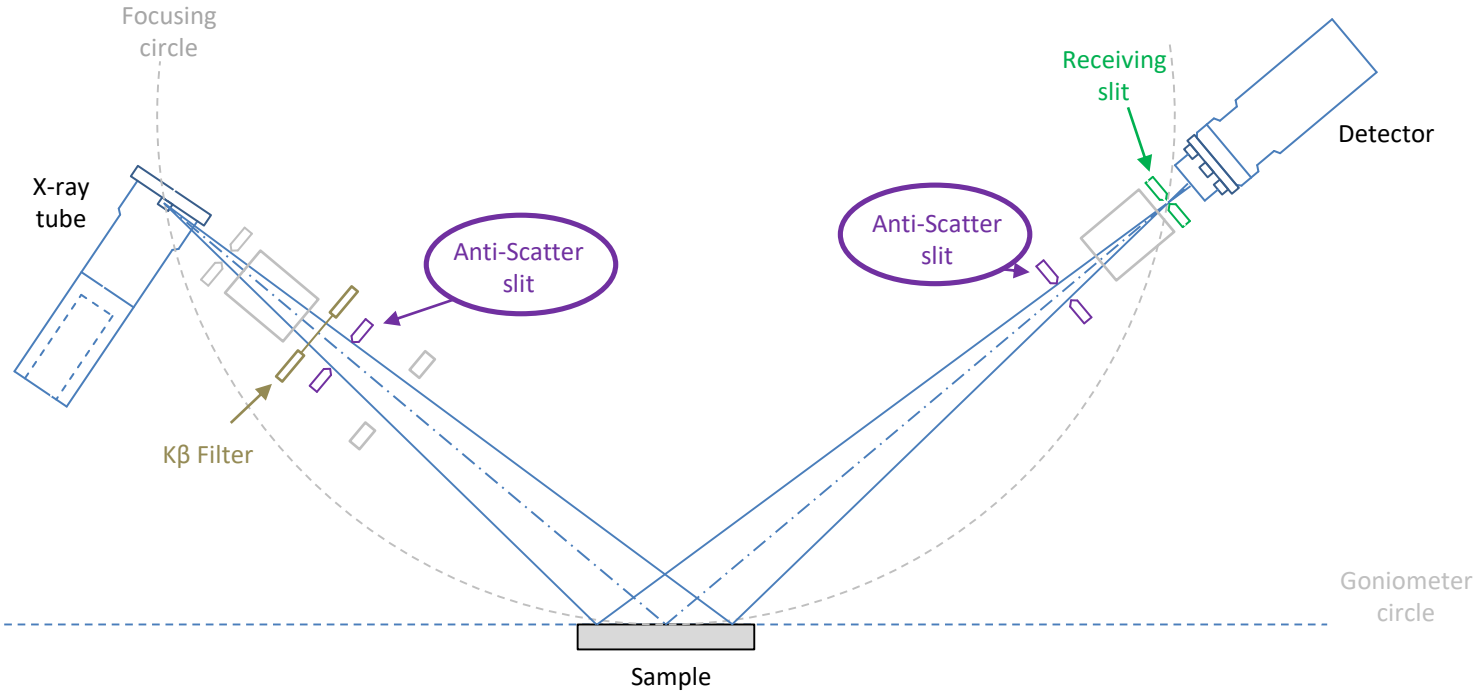
Asymmetry more pronounced at low 2θ, less at high 2θ



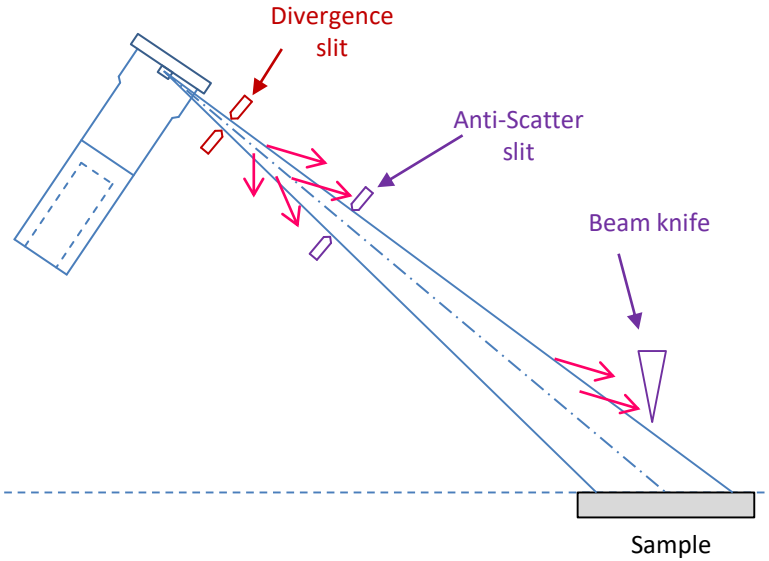




In primary & secondary beam, Beam Mask: 10mm, Irradiated Length: 10mm

# Anti-Scatter Slits



# Anti-Scatter Slits and Beam Knifes




Removes radiation scattered at air molecules

=

Lower background signal

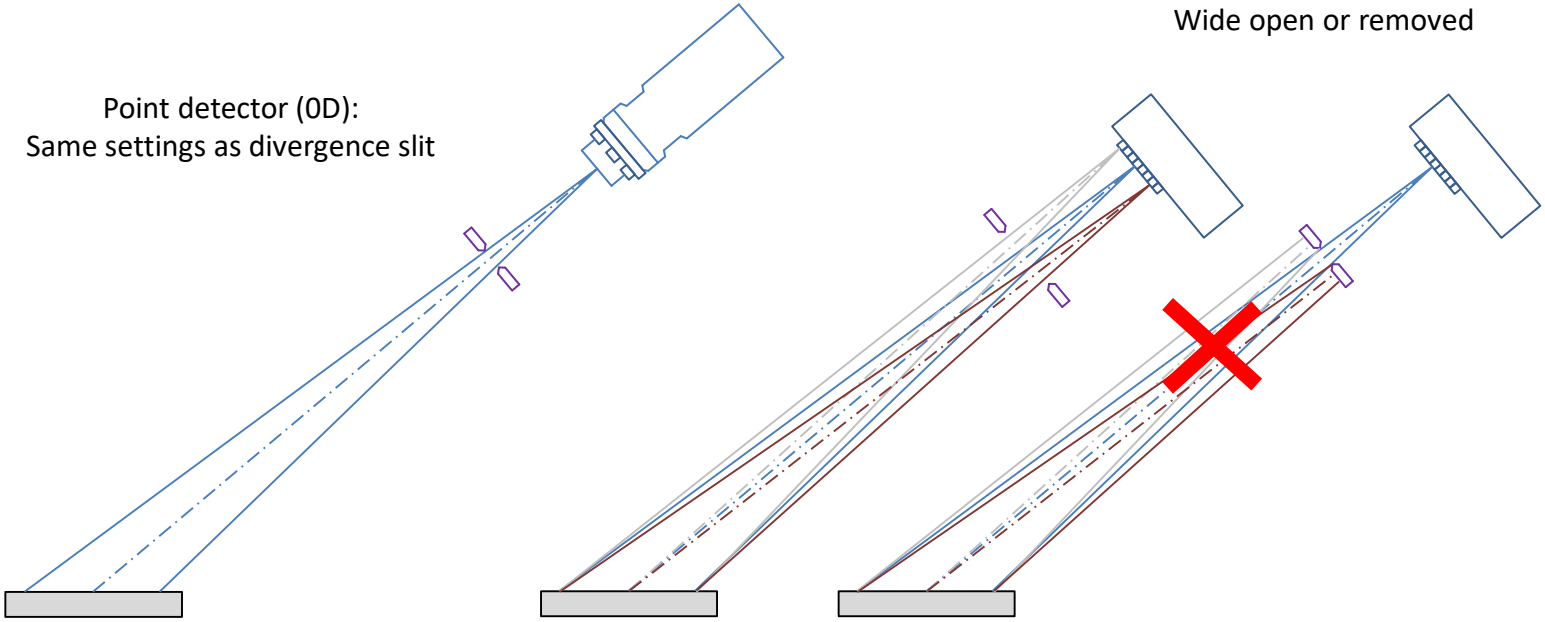
In primary beam:
Same settings as divergence slit

# Anti-Scatter Slits

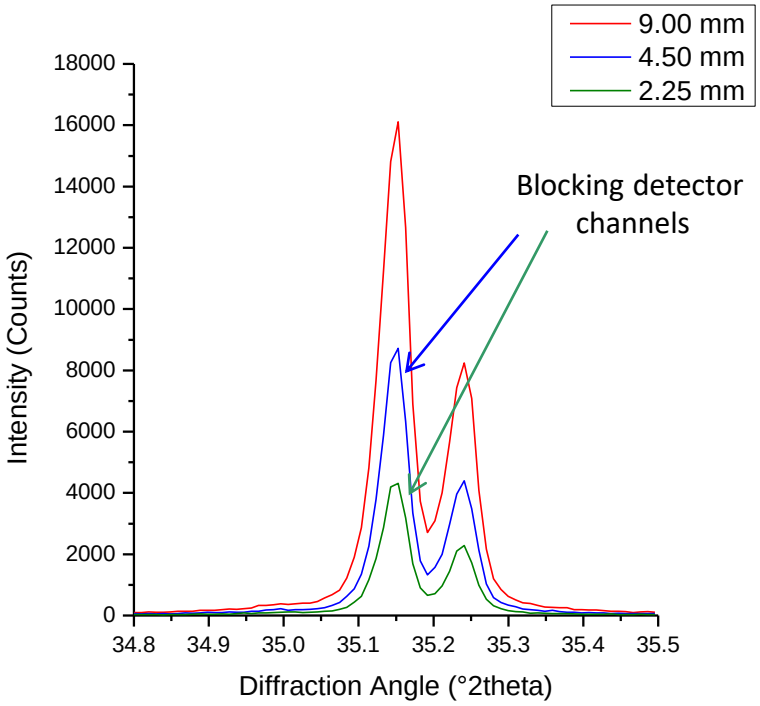
## Secondary beam

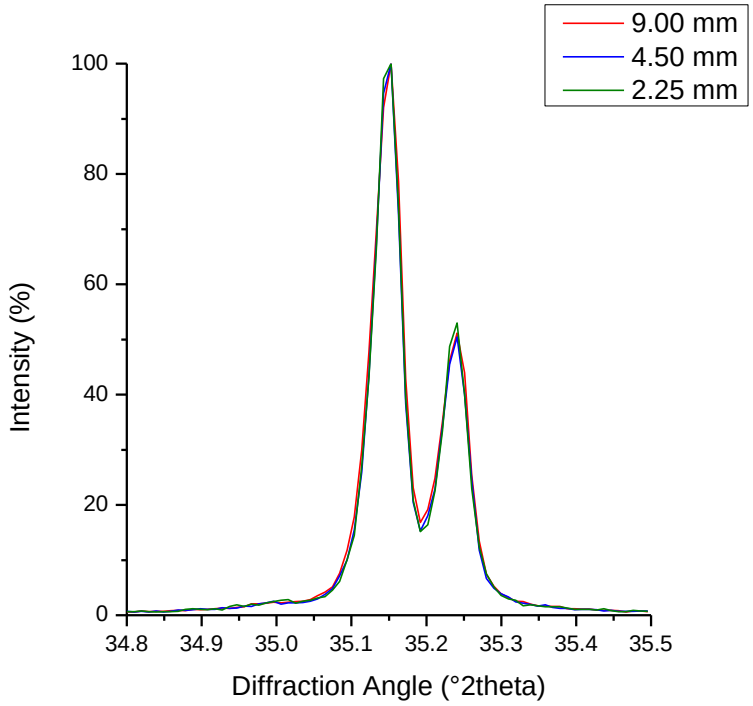
Point detector (0D):
Same settings as divergence slit

Linear / area detector (1D / 2D):
Wide open or removed



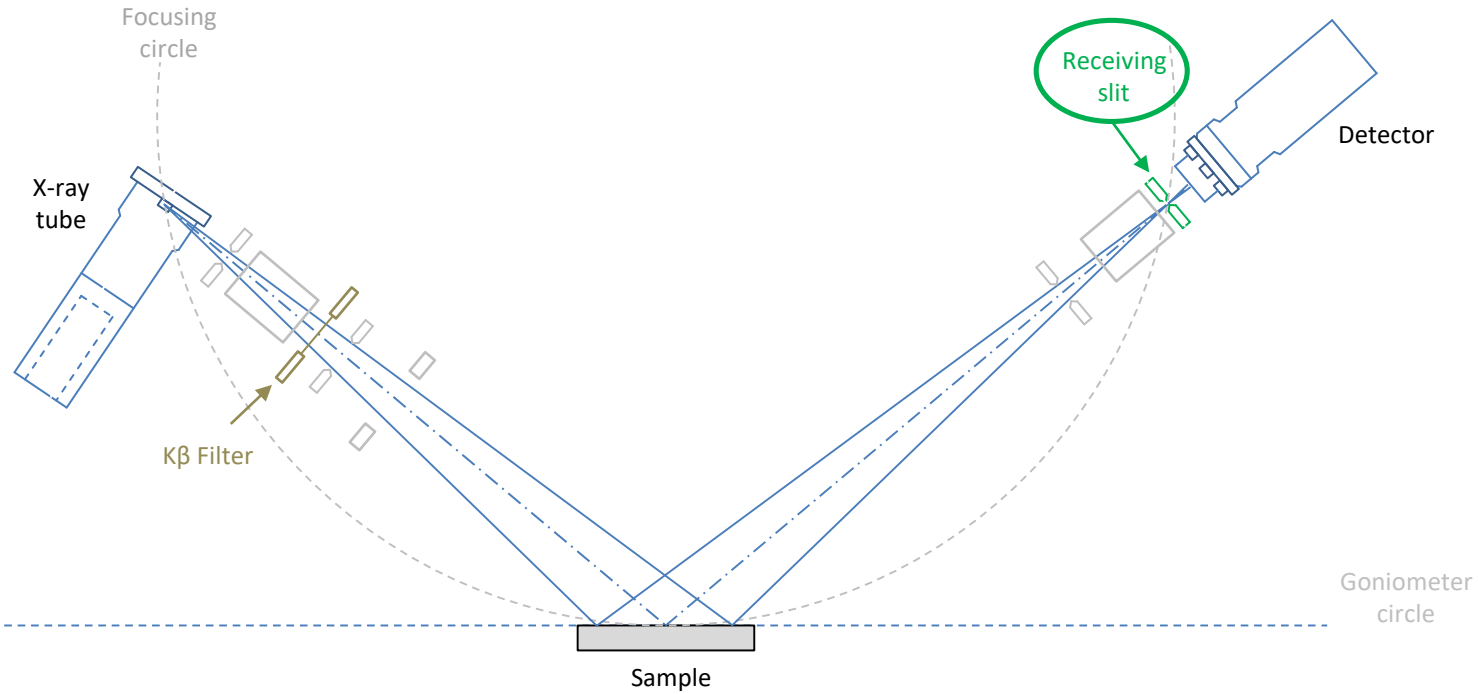
# Anti-Scatter Slits



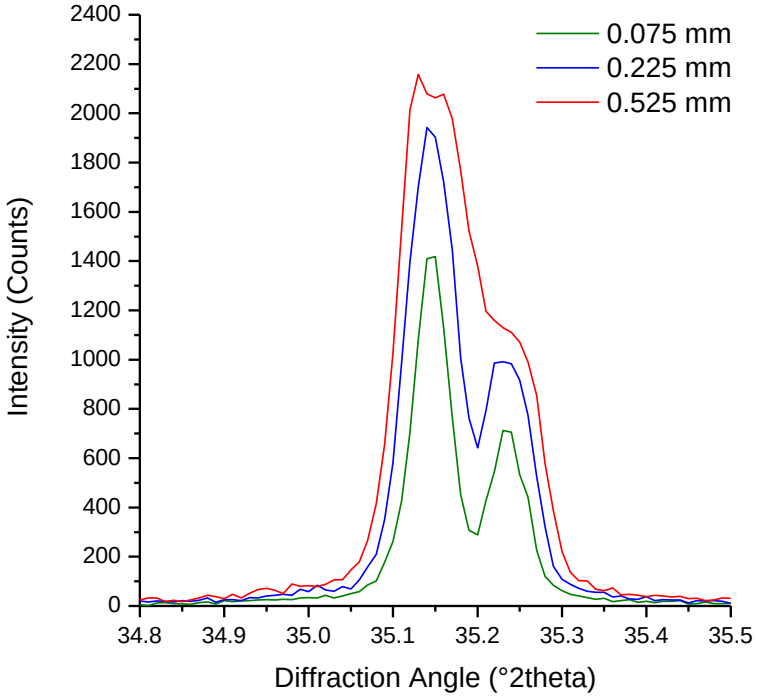



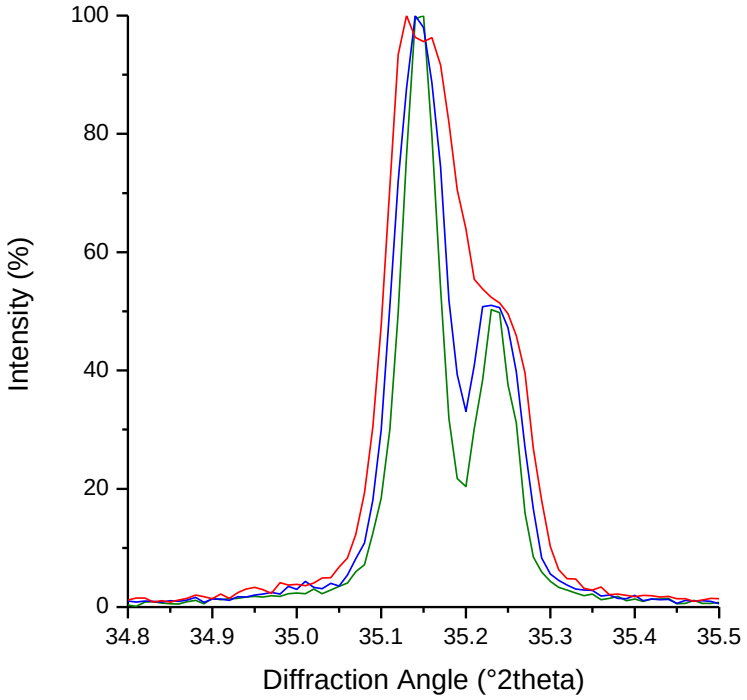

Soller Slits: 2.5 deg, Irradiated Length: 15mm, LynxEye XE in 1D mode

# Receiving Slit



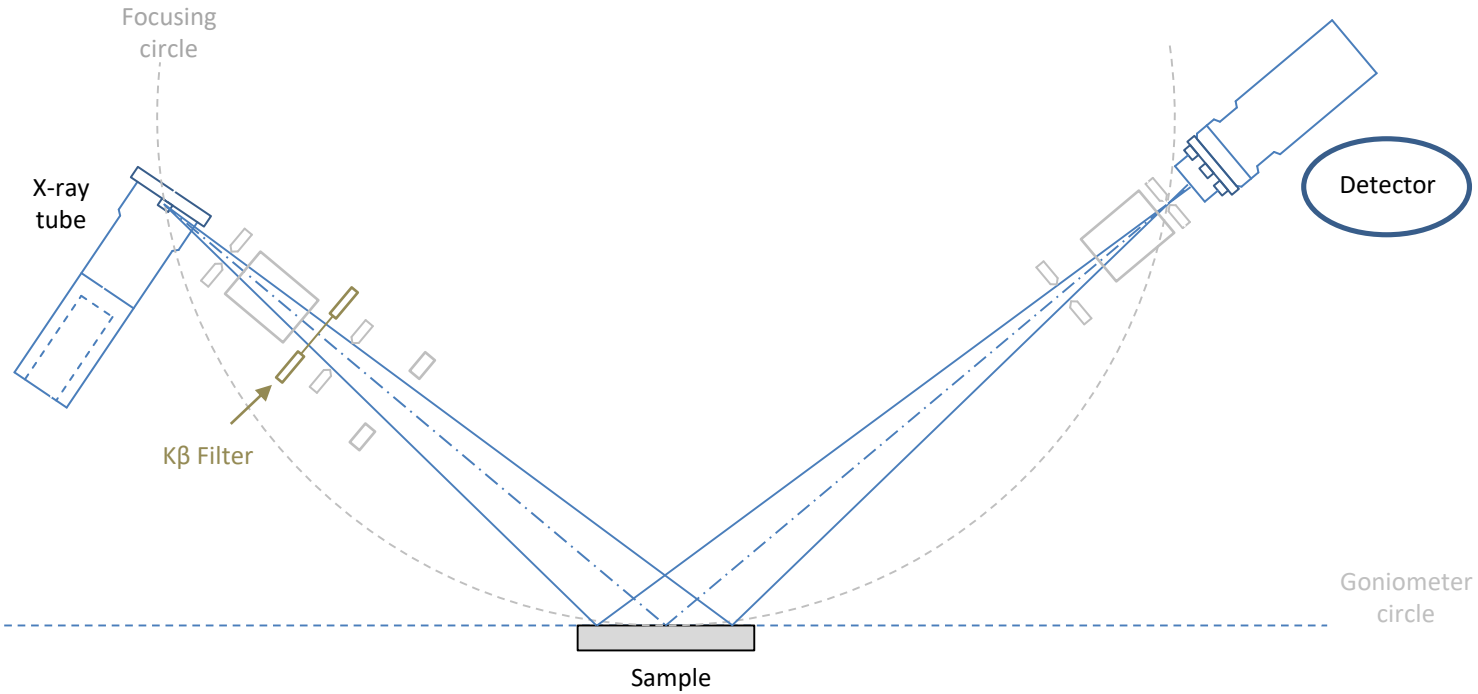
# Receiving Slit



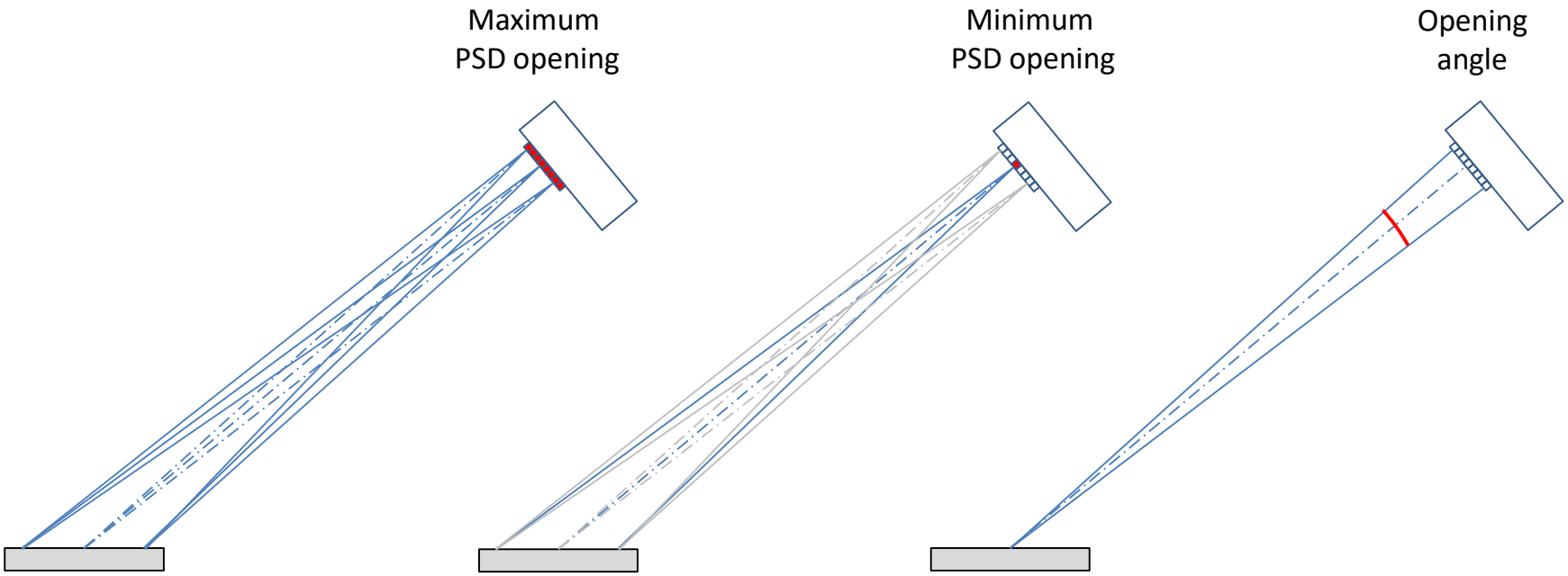

Soller Slits: 2.5 deg, Irradiated Length: 15mm, LynxEye XE in 0D mode

# Detector Opening (PSD Opening)

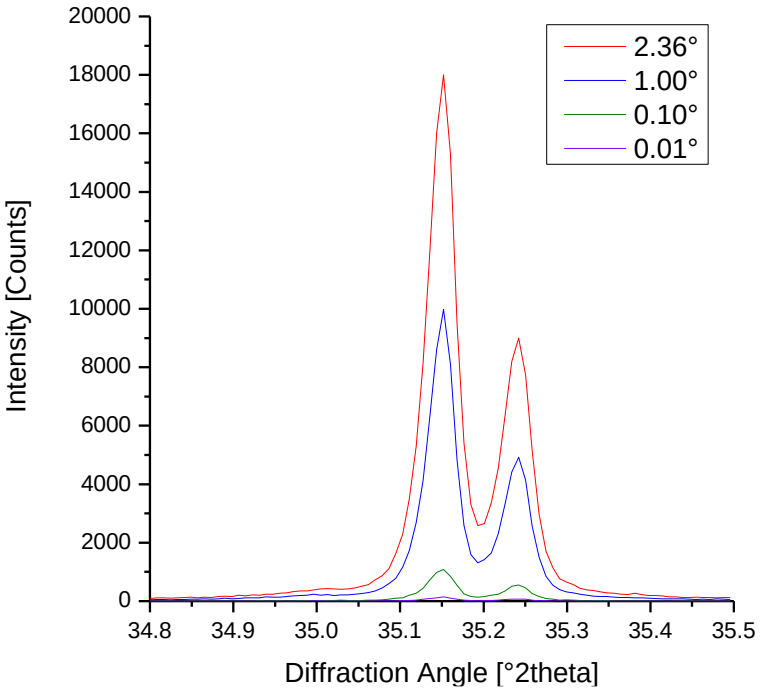


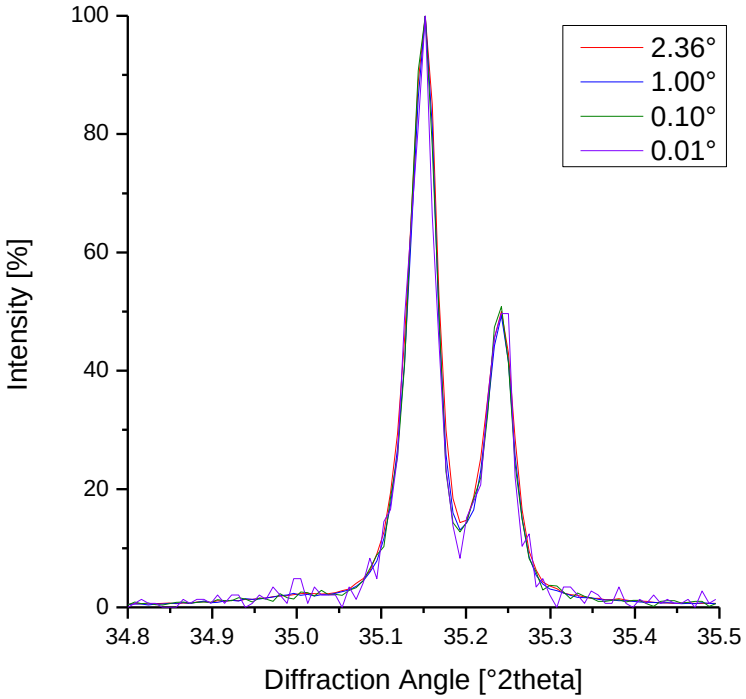
# Detector Opening (PSD Opening)

Position-sensitive detectors (1D, 2D)



# Detector Opening (PSD Opening)

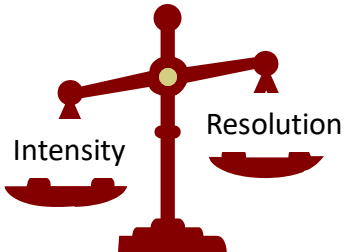


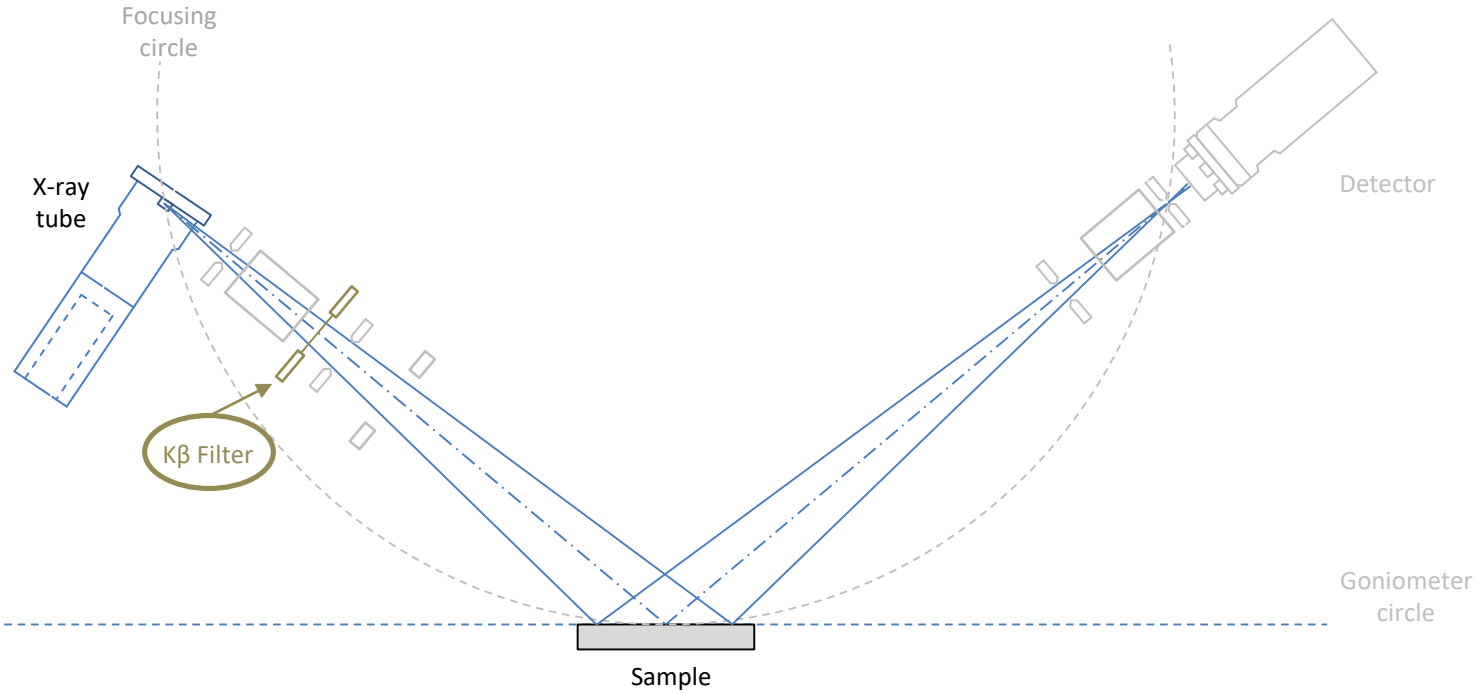

Soller Slits: 2.5 deg, Irradiated Length: 15mm, LynxEye XE in 1D mode

# Summary: Optical Elements

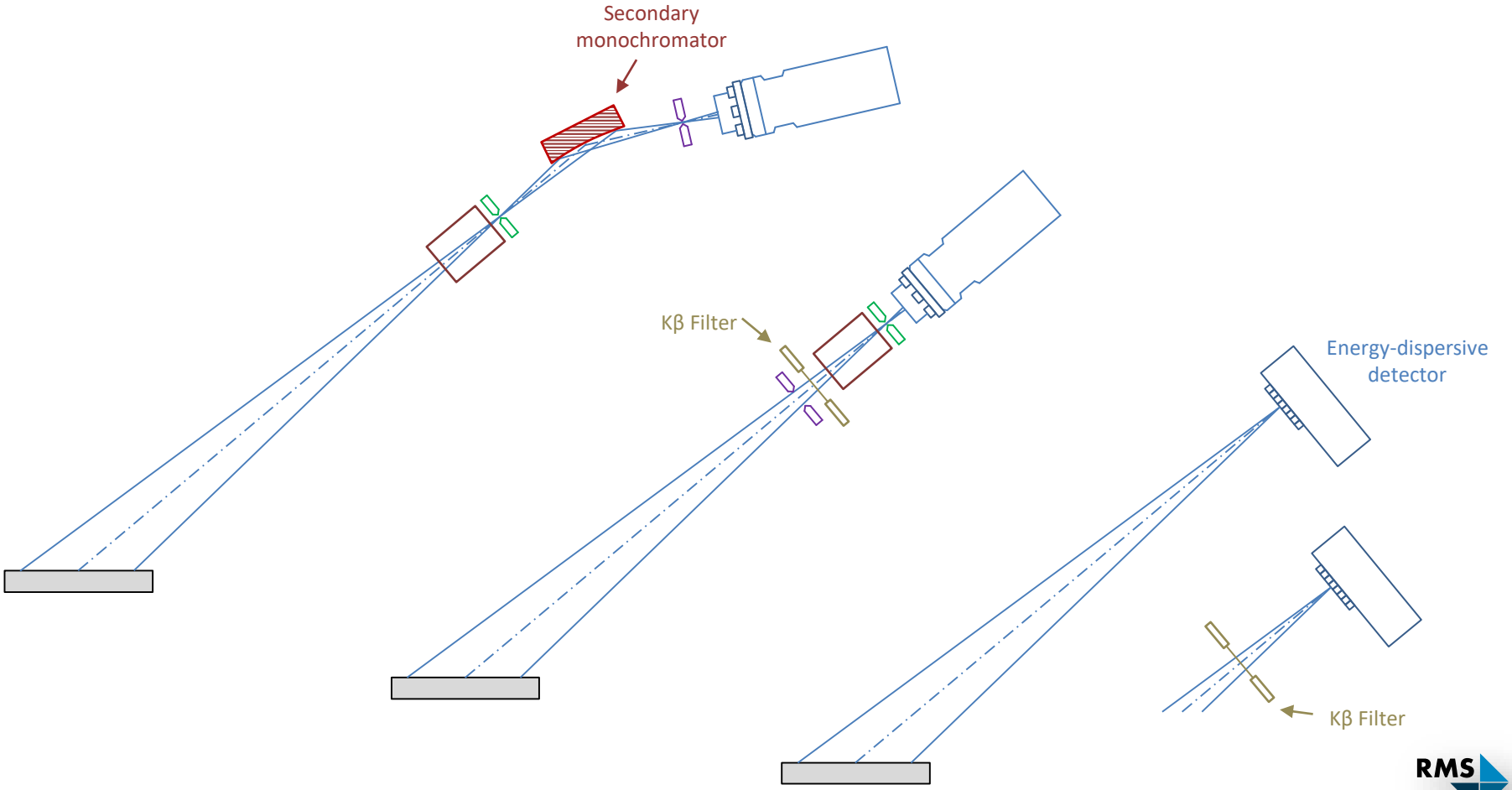
| Optical Element | Effect | (Too) Small | (Too) Large |
|---|---|---|---|
| Divergence Slit | Adjusts beam length on the sample | Loss of intensity | Beam spills over sample |
| Beam Mask | Adjusts beam width on the sample | Loss of intensity | Beam spills over sample |
| Soller Slit | Reduces peak asymmetry | Loss of intensity, Better resolution | More asymmetry, Less resolution |
| Anti-Scatter Slit | Reduces background signal | Loss of intensity | High background |
| Receiving Slit | Adjusts peak width / resolution | Loss of intensity Better resolution | Loss of resolution Higher intensity |
| PSD Opening | Adjusts the number of active detector channels | Loss of intensity | - |



# Filters and Monochromators

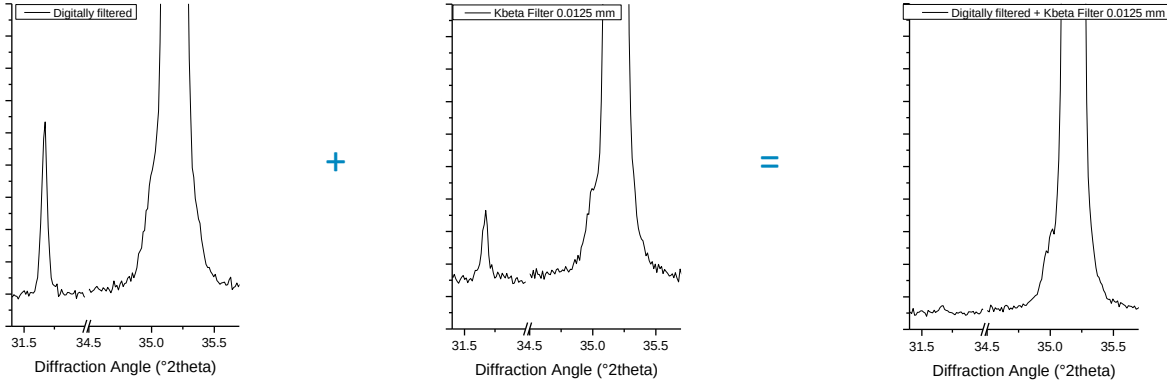


# Filters and Monochromators



# Summary: Filters and Monochromators

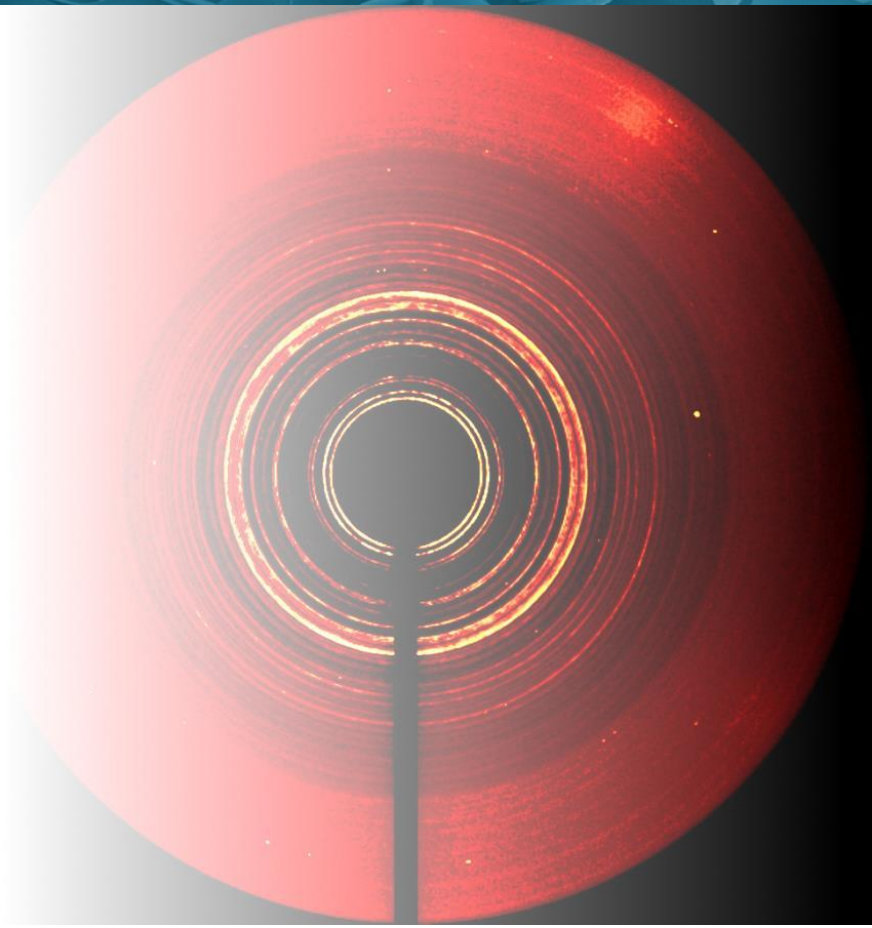
| Optical Element | Filter effect | Effect on Kα Intensity | Comment |
|---|---|---|---|
| Primary beam monochromator | Eliminates Kβ | Strong loss | Works with 1D / 2D detectors |
| Secondary beam monochromator | Eliminates Kβ peaks<br>Eliminates Fluorescence | Strong loss | 0D detectors only |
| Kβ Filter | Reduces Kβ peaks | Moderate loss | Can be combined |
| Energy dispersive Detector | Reduces Kβ peaks<br>Eliminates Fluorescence | Little loss | |



# Sample Preparation

Potential Problems:

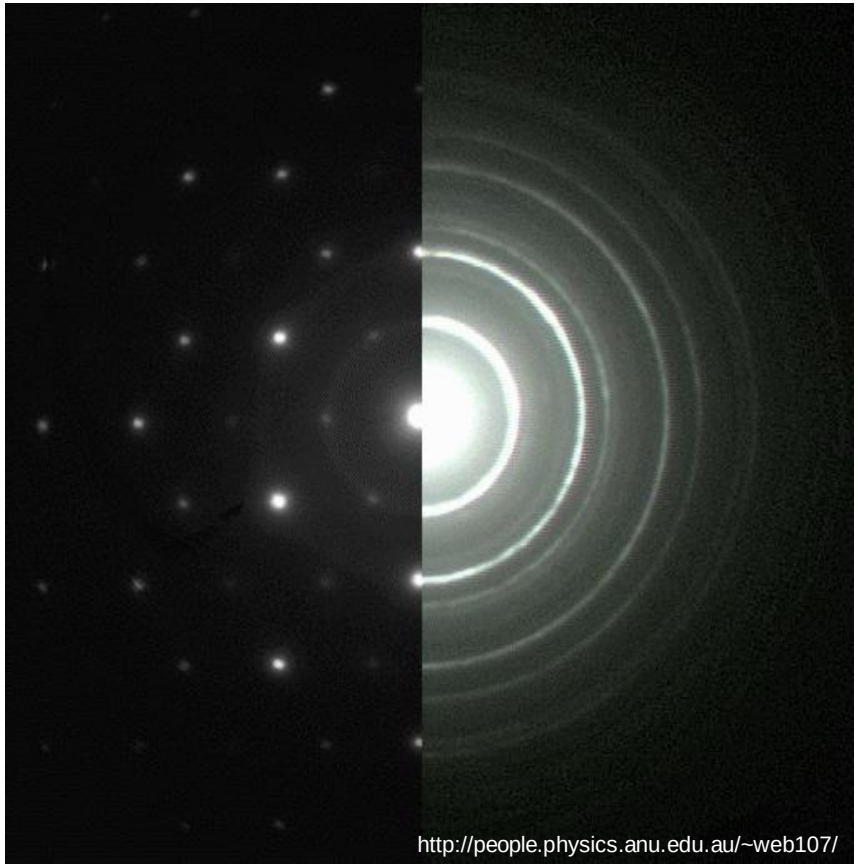
- Graininess
- Micro-absorption
- Texture
- Crystallite size
- Sample height displacement
- Surface roughness
- Sample transparency



# Graininess

Single crystals generate spotty diffracted rays.

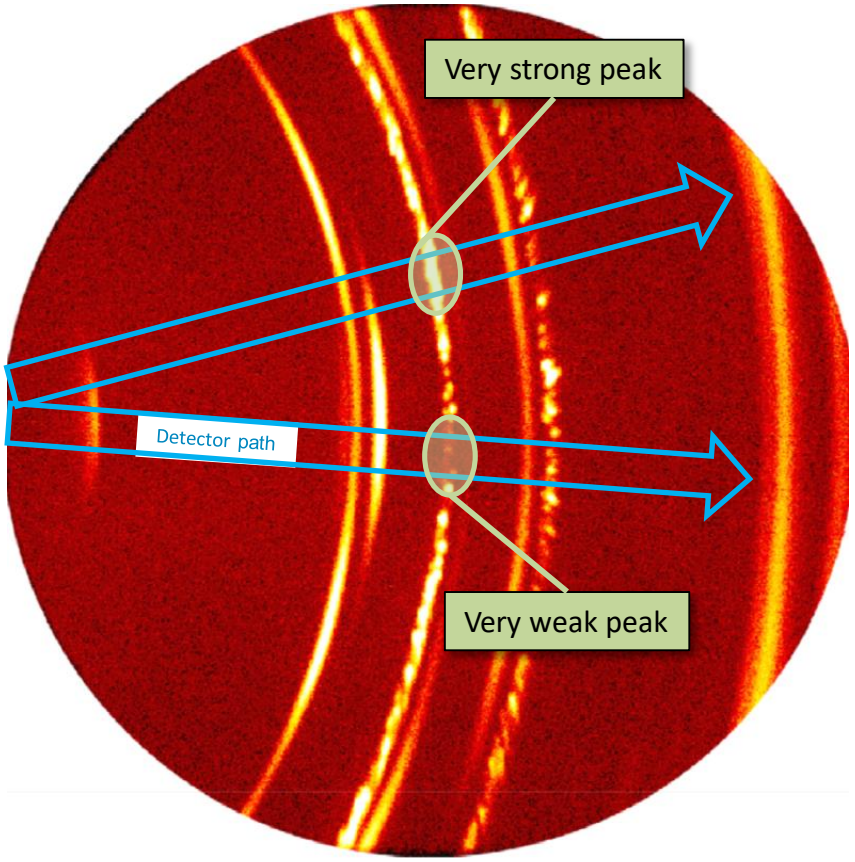
Fine powders generate smooth diffraction rings.



# Graininess

Spotty diffraction rings

The same sample, at
the same 2θ position,
but different intensities!




Grainy samples:
- non-reproducible intensities
- «phantom» peaks
- «missing» peaks

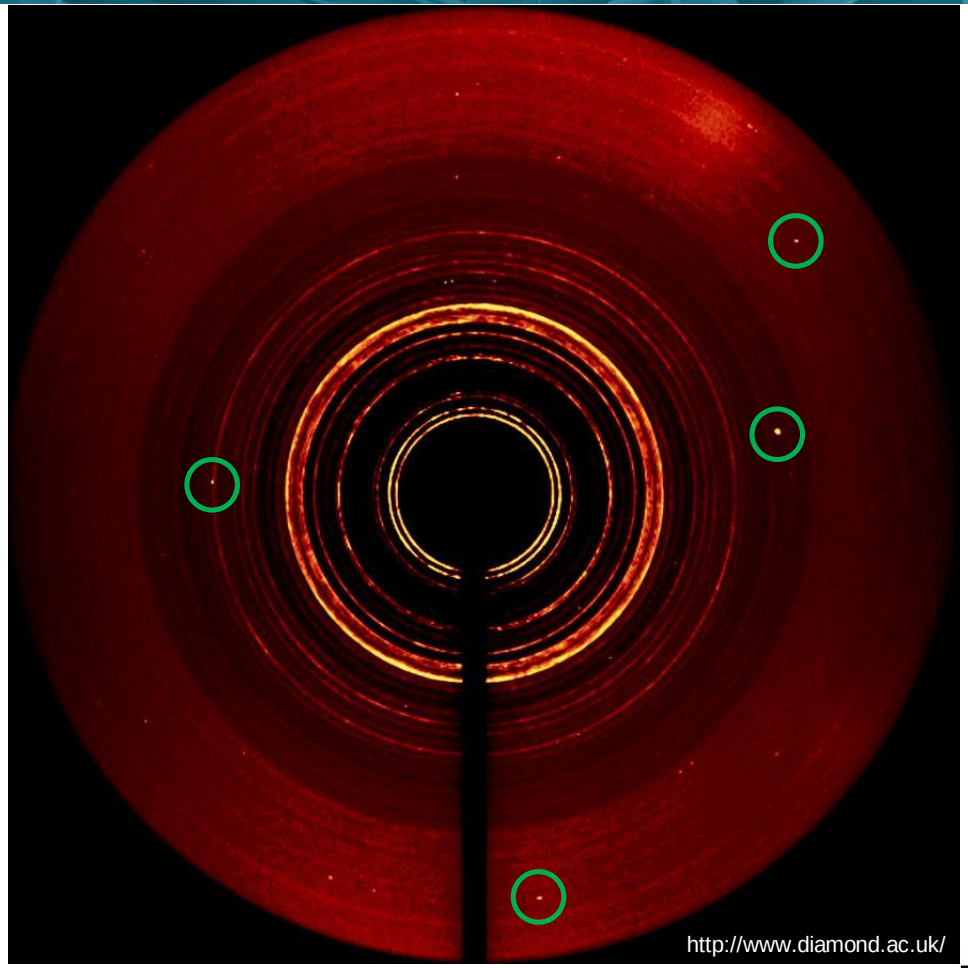
Bruker AXS

RMS

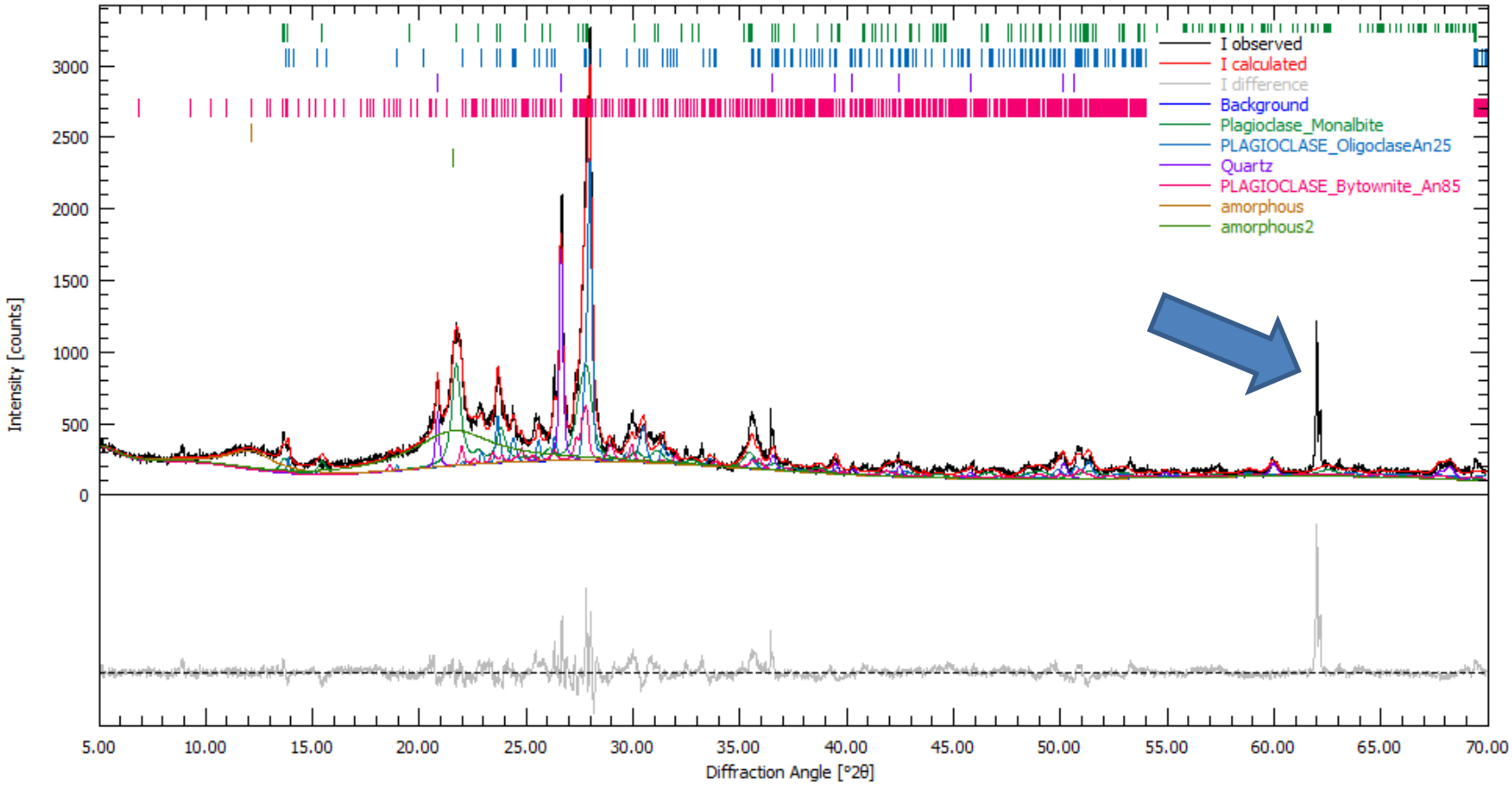
# Graininess: Rocks in Dust

«Rocks in Dust»:
A few large crystals in a fine matrix

Usually invisible, but if scanned: Strong peaks out of nowhere!



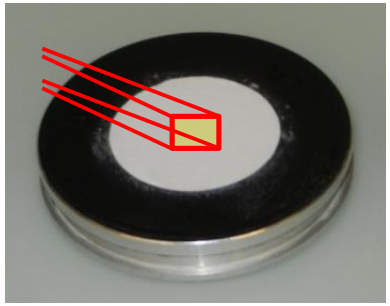
# Graininess: Rocks in Dust



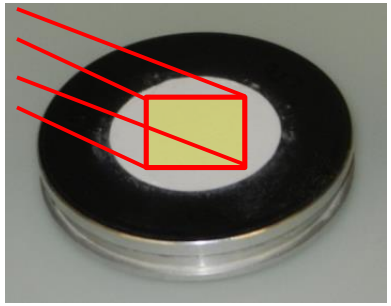
# Graininess

Reducing graininess:

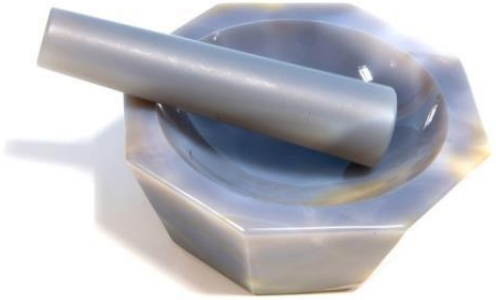
- Grinding / milling
- Adjust divergence slit and beam mask for largest possible irradiated area
  (= more particles contribute to diffraction pattern)
- Use spinning sample stage
  (= better randomisation)
- Counting time per step ≥ 1 revolution of samples stage spinner



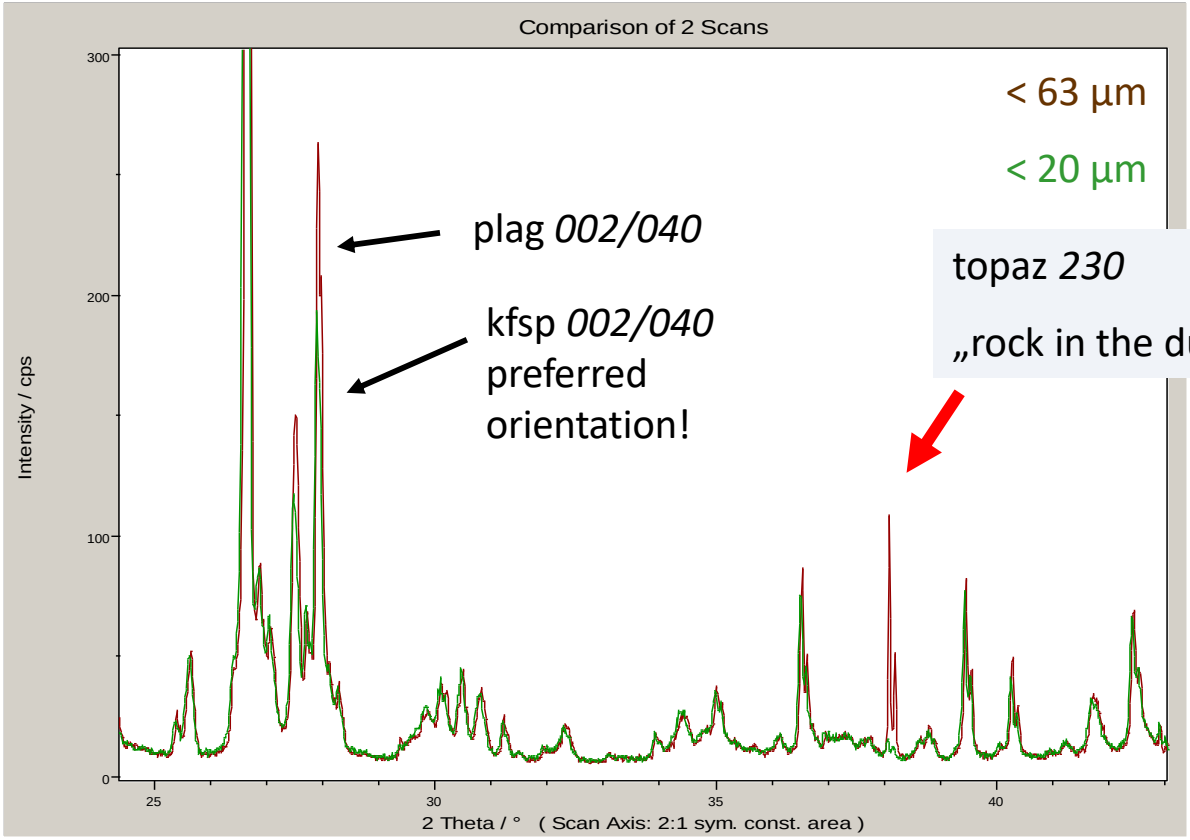
Few diffracting crystallites



Many diffracting crystallites



# Graininess: Rocks in Dust

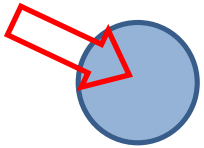



topaz bearing granite, samples ball-milled < 63 µm and hand-ground < 20 µm

Courtesy of R. Kleeberg

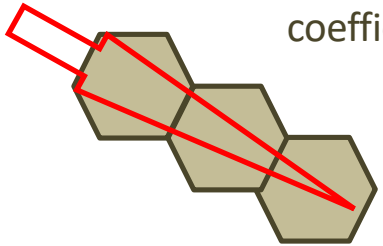
# Micro-absorption

X-rays

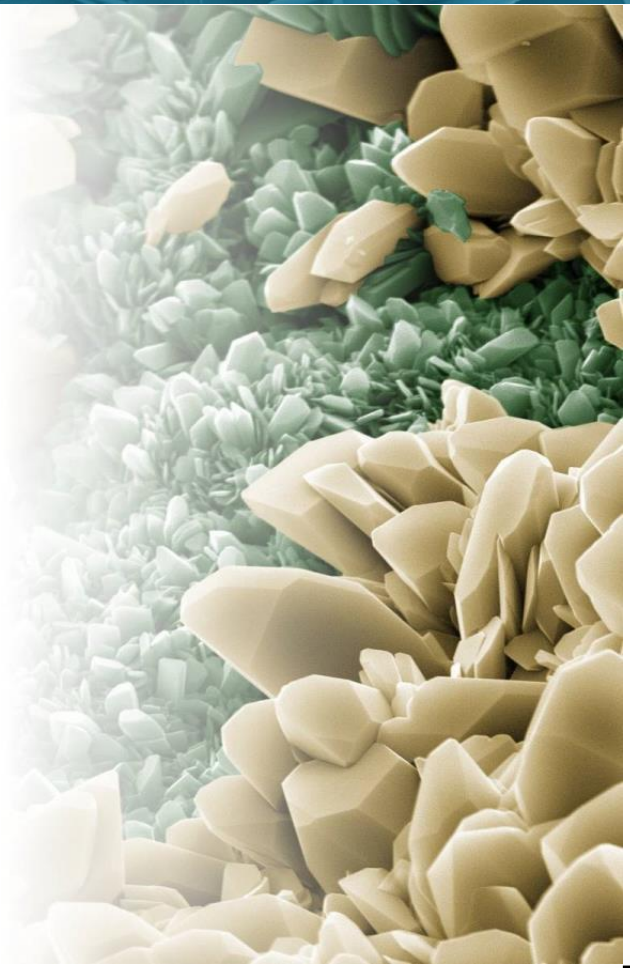


Phase 1: High absorption coefficient for X-radiation

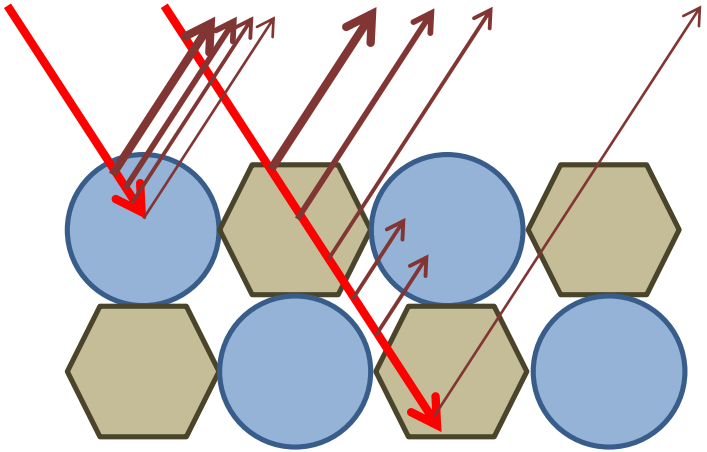
X-rays



Phase 2: Low absorption coefficient for X-radiation

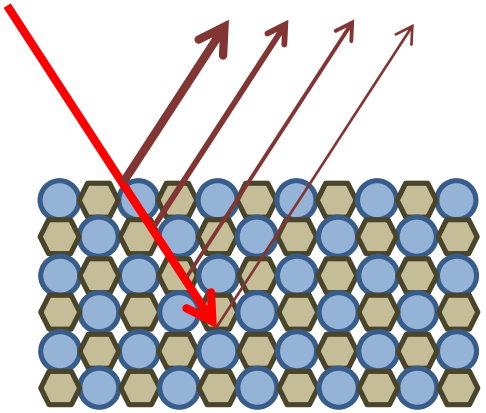


# Micro-absorption



Strong attenuation by phase 1
**Large particles absorb significant part of the radiation.**
→ Small volume of interaction

Weak attenuation by phase 2
→ Large volume of interaction



Small particles absorb insignificant part of the radiation.
→ Volumes of interaction with phases 1 & 2 are representative for phase composition

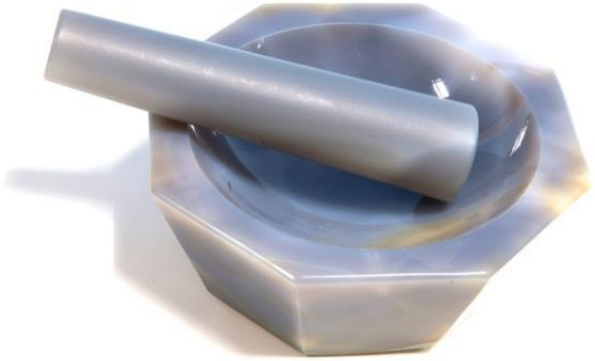
# Micro-absorption

Micro-absorption occurs in samples with…

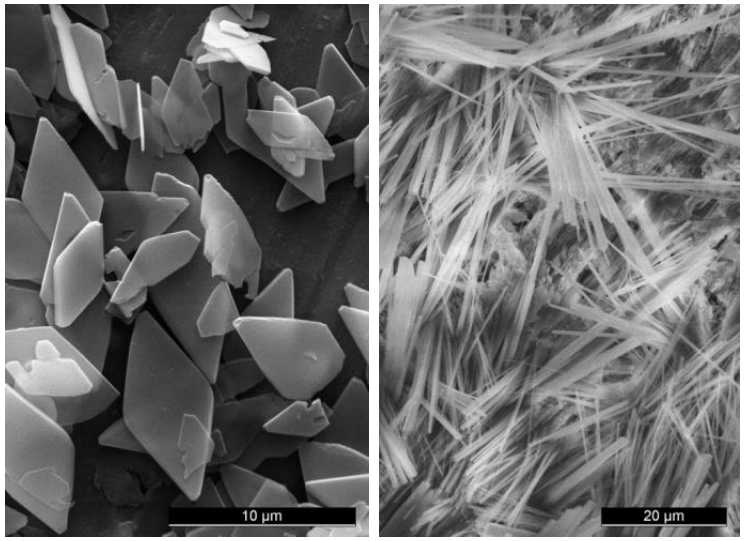
- … large **particles (not crystallites!)**
- … phases with large contrast in absorption coefficients

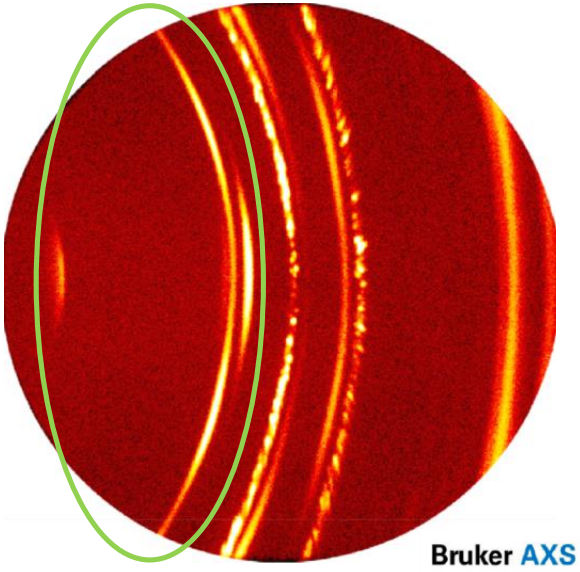
Reducing micro-absorption:

- Grinding / milling to reduce particle size

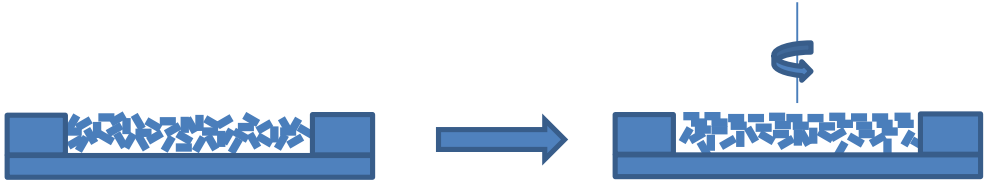


# Texture, Preferred Orientation




Platelets, Needles, Fibers, Whiskers



Random orientation

Preferred orientation

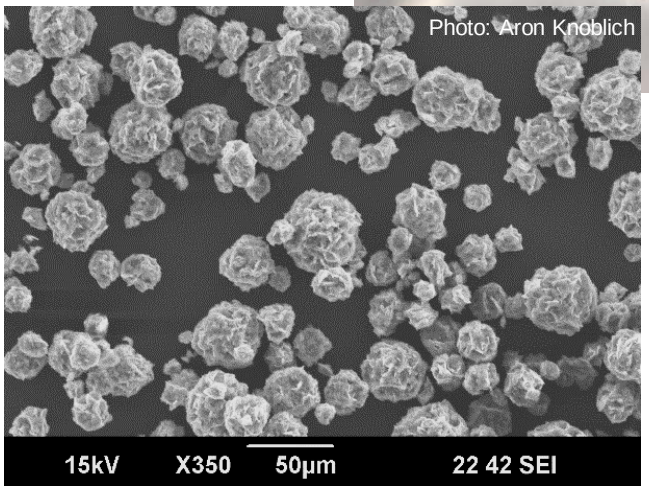
SEM Images: L. Galea, RMS Foundation

# Texture, Preferred Orientation

Try to avoid orientation at the surface of the sample:

- Press powder without «rubbing» the surface
- Use back- or side-loading sample holder
- Disorder surface with textured stamp

- Various creative solutions can be found on the internet (involving Vaseline, hair spray, spray pistols, …)


PO can be corrected mathematically,
but phase quantification will be biased.

# Summary: The Perfect Sample

The perfect sample for Bragg-Brentano diffractometers:

- Crystallites and particles of 1-5 µm size
- Perfectly random orientation
- Perfectly flat surface
- Surface precisely centered in the goniometer
- Not transparent (absorb all primary radiation)

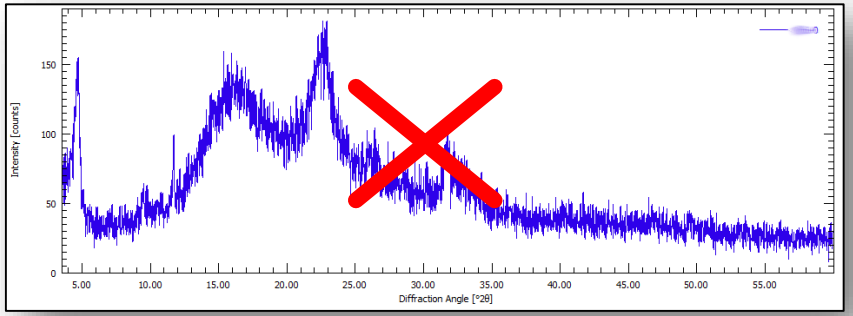

Industry standard for automated XRD sample milling:
McCrone Micronizing Mill (now distributed by Retsch)

# General Rules for Quantitative Phase Analysis

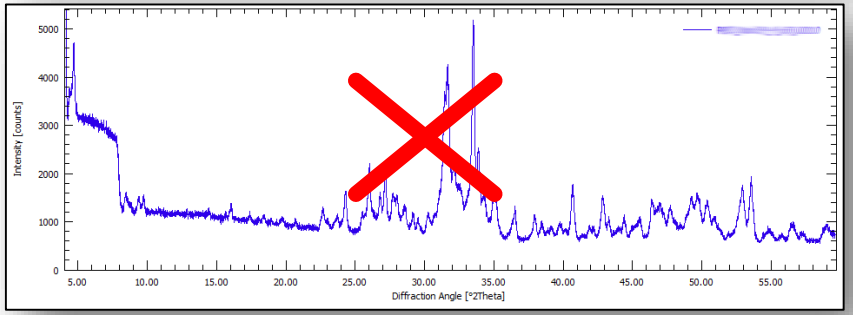
- Instrumental background should be low and linear, no “bumps” or even edges
- Force the peak/background ratio as high as you can
- Peak/noise ratio on maximum as well, but a noise better than the quality of profile description doesn’t make sense
- Irradiate maximum of sample surface (improve grain statistics and intensity)
- Register as much diffracted intensity as you can get without significant loss of resolution
- Parallel beam techniques and high-resolution configuration are bad choices for QPA purpose
- Don’t measure/evaluate angular ranges containing no or potentially biased phase Intensity information (very low angles, high angles)
- Choose step width of approximately 1/5 of FWHM of the sharpest peak

Courtesy of R. Kleeberg

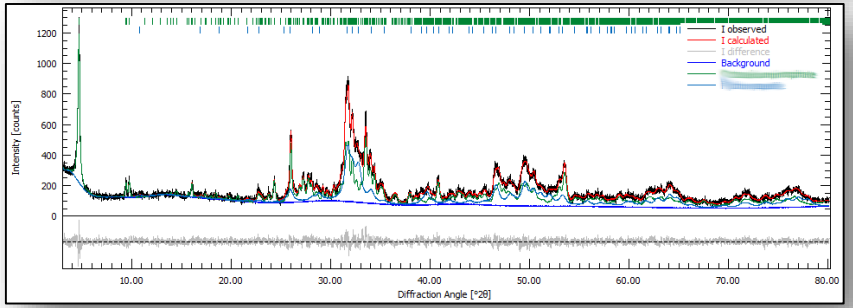
# Good Diffraction Data




Good sample preparation…




…and good instrument settings…




…are crucial for successful Rietveld refinements