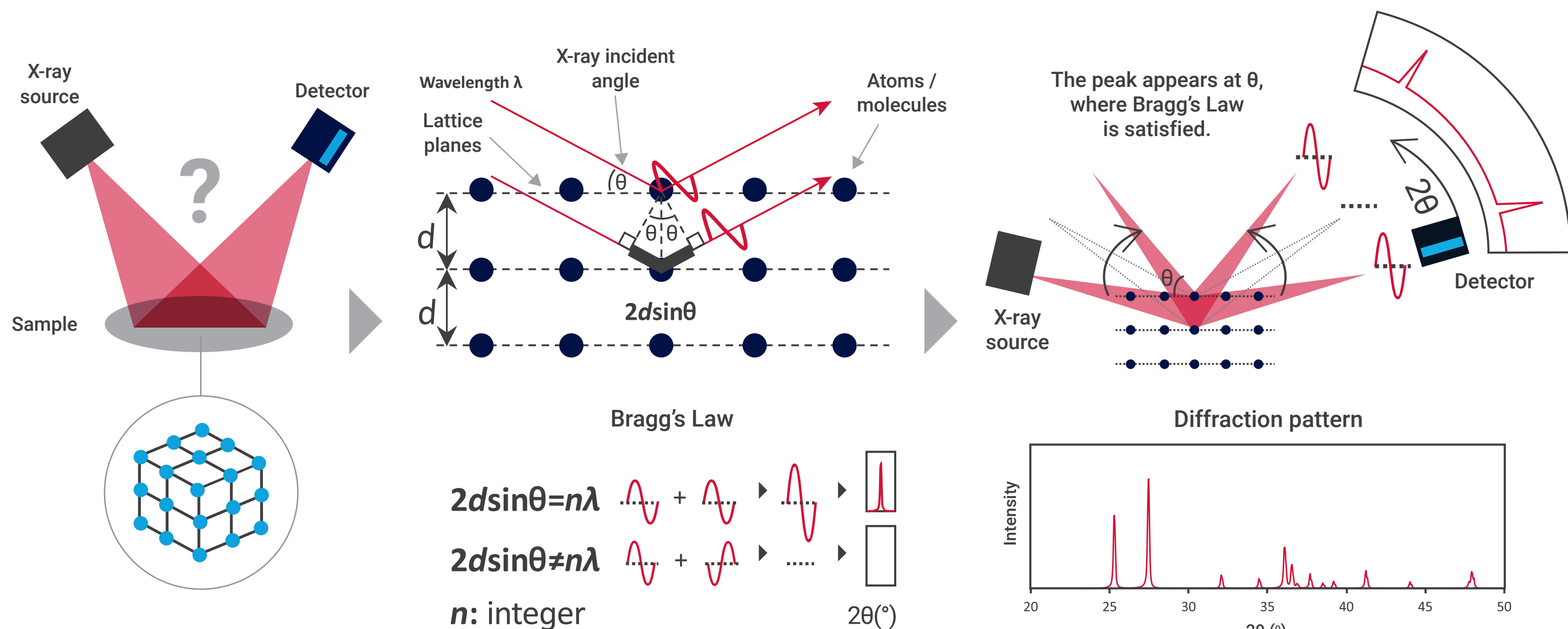




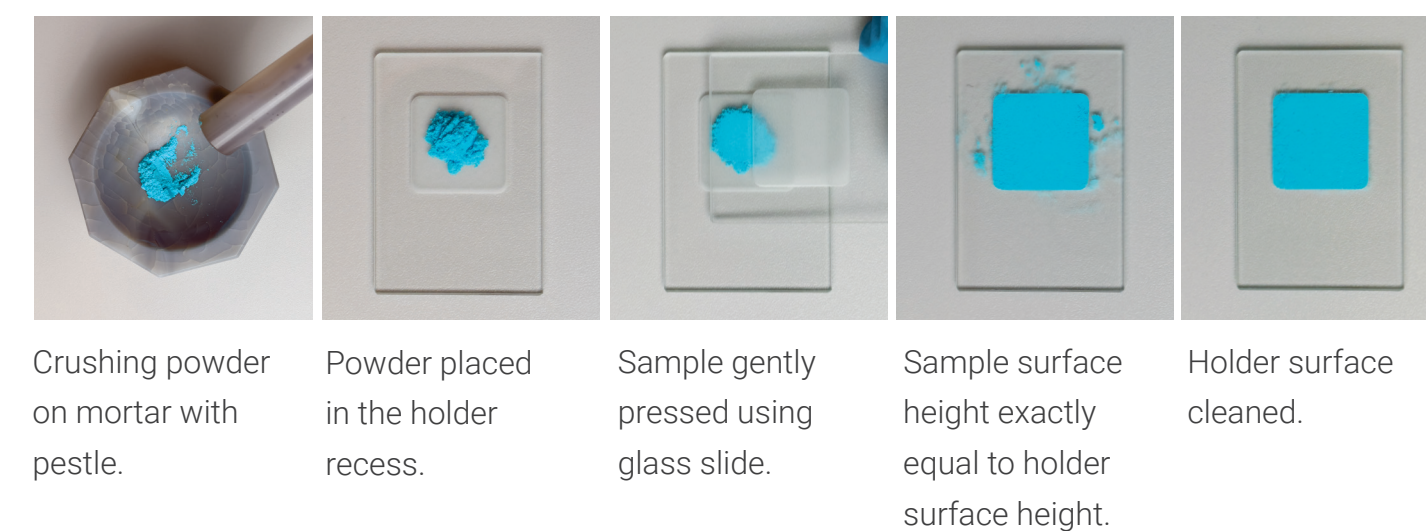
How does XRD work?



Bragg's Law: constructive interference occurs when the path difference between X-rays reflected from successive planes equals an integer multiple of the wavelength. Lattice spacing d is determined from the diffraction angle θ .

Sample preparation

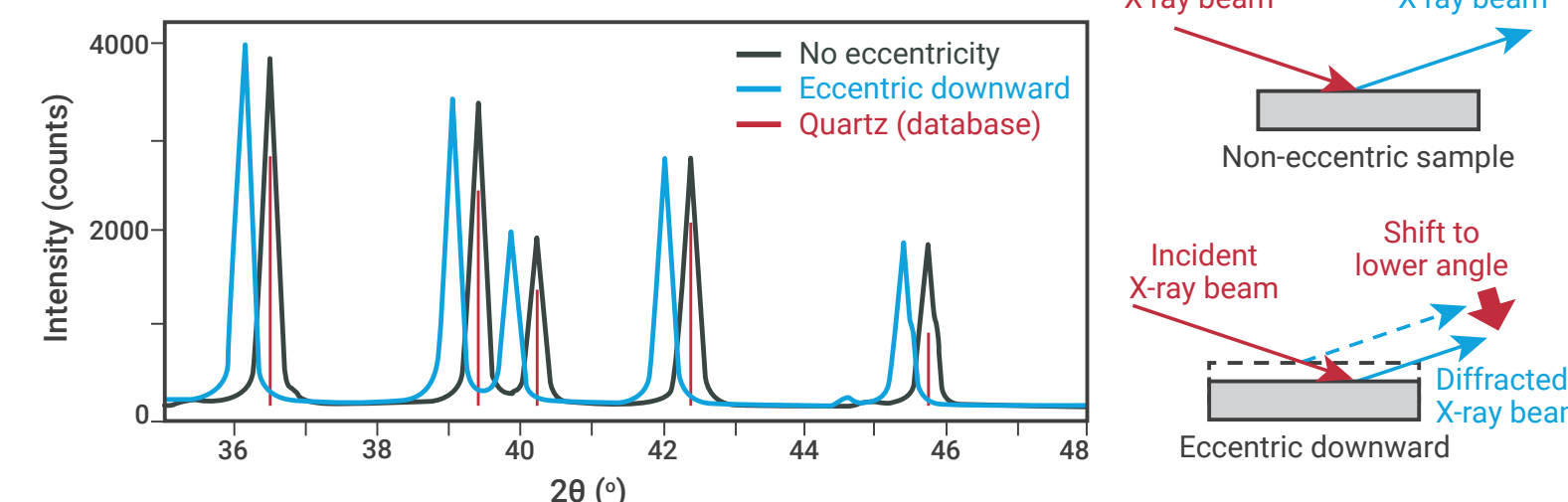
- Powder sample with optimum grain size: 1-10 μm
- Flat surface
- Height of the sample exactly the same as the holder surface



Sample holders

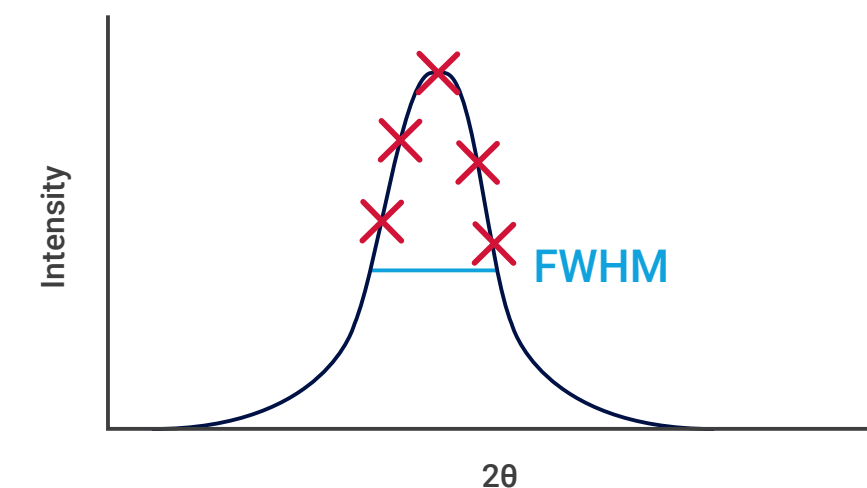
- Inorganic samples: Aluminum, glass holders 2 mm or 0.5 mm depth
- Organic samples: Aluminum holders (0.5 mm or 0.2 mm groove), zero-background holders
- Amorphous samples: Zero-background sample holders
- Air-sensitive sample: Air-tight sample holders

Eccentric sample



Counting statistics

- 3000 cts (phase ID) for highest peak
- 10000 cts (Rietveld Analysis) for highest peak
- Step size: 5-10 data points above FWHM
- Speed 5-10°/min



Quantitative analysis with Rietveld method

- Phase ID (search/match routine, cif file import etc.)
- Order of refinement: Scale factor, background and profile for main phase and then minor phase(s)
- Unit cell parameters for main phase, then minor phase(s)
- Preferred orientation if applicable

The goal is to minimize the residual:

$$S = \sum \omega_i (y_i^{obs} - y_i^{calc})^2$$

$$\omega_i = \frac{1}{y_i^{obs}}$$

Calculated Intensity:

The calculated intensity at each point is a sum over all Bragg reflections:

$$y_i^{calc} = \sum_k L_k |F_k|^2 \phi(2\theta_i - 2\theta_k) P_k A_k + y_i^{bkg}$$

Quality of the fit:

R_{wp} = Weighted profile R-value R_e = Expected R-value S = Goodness of fit

$$R_{wp} = \sqrt{\frac{\sum \omega_i (y_i^{obs} - y_i^{calc})^2}{\sum \omega_i (y_i^{obs})^2}}$$

$$R_e = \sqrt{\frac{N-P}{\sum \omega_i (y_i^{obs})^2}}$$

$$S = \frac{R_{wp}}{R_e}$$

- Residual plot should be flat (small deviation between calculated and measured profiles)
- Results should make physical and chemical sense, e.g. lattice parameters should not be too large or too small
- Set limits or use stiffness factors if required

Comprehensive analysis:

$$\text{Crystallinity Doc} = \frac{\text{Scattering intensity of the crystalline phase}}{\text{Total scattering intensity (crystalline+amorphous)}} \times 100 (\%)$$

Crystallite size applicable: 10-1000 Å (1-100 nm)

$$\text{Crystallite size } D_{hkl} = \frac{k\lambda}{\beta \cos \theta} \quad \beta_c = \sqrt{B^2 + b^2}$$

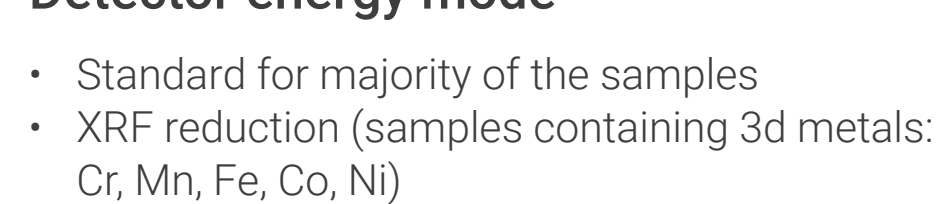
Formulas:

$$\text{Standard deviation } \sigma = \sqrt{I_{counts}}$$

$$\text{Relative Standard deviation (\%)} = \frac{\sigma}{I_{counts}} \times 100 = \frac{1}{\sqrt{I_{counts}}} \times 100$$

$$\text{SN ratio } SN = \frac{1-B_1}{\sqrt{B_1}} \quad \text{Limit of Detection } LOD = B_1 + 3.3\sqrt{B_1} \quad \text{Limit of Quantification } LOQ = B_1 + 10\sqrt{B_1}$$

Fluorescence suppression by detector

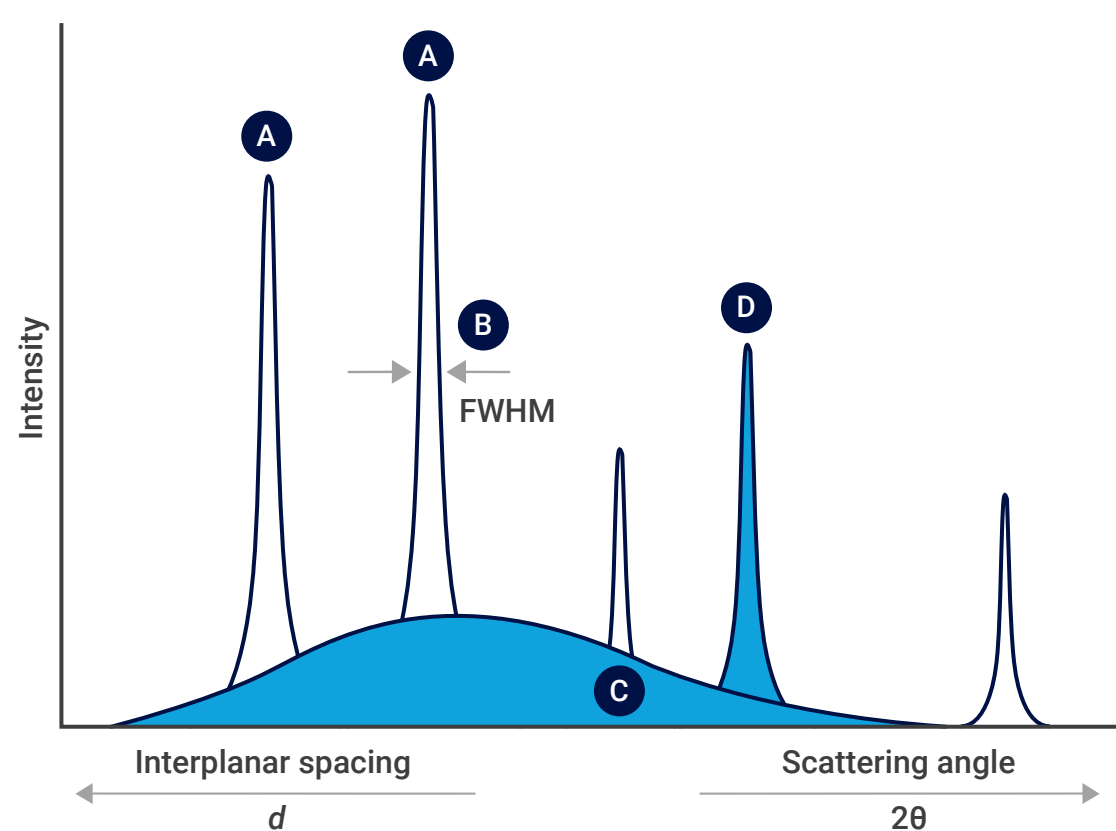


- Standard for majority of the samples
- XRF reduction (samples containing 3d metals: e.g. Cr, Mn, Fe, Co, Ni)
- Phases with lowest figure of merit (FOM) preferable

Phase ID

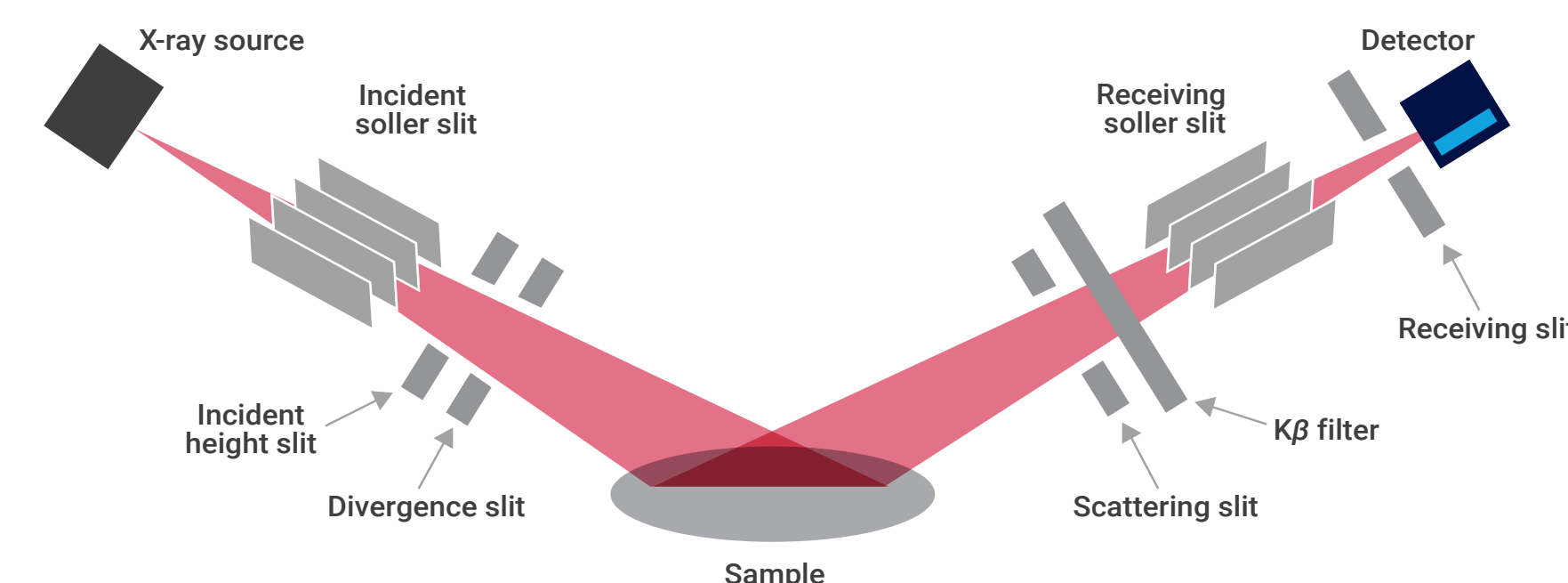
- Peak search and profile fitting
- Search/match routine using database or cif files
- Phases with lowest figure of merit (FOM) preferable

What can we learn from a diffractogram?

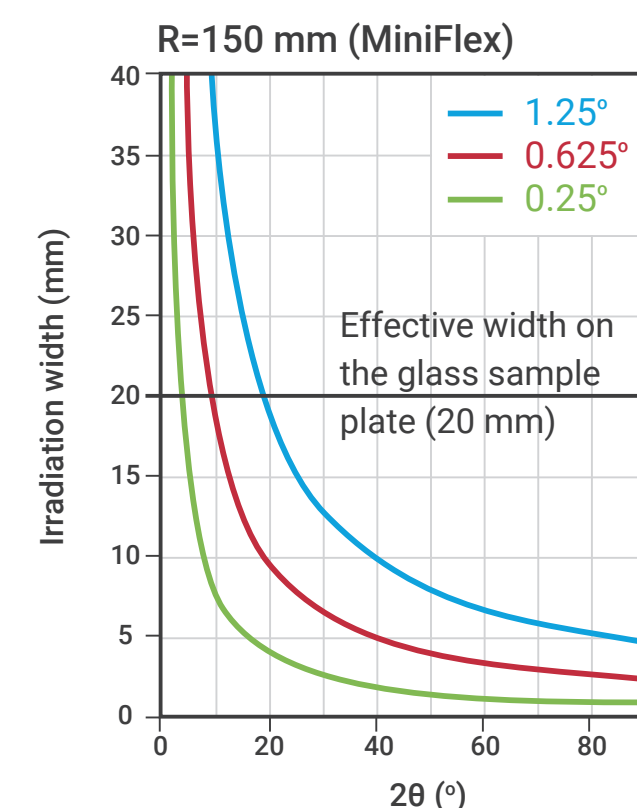


- A** Peak positions: d-values { Phase ID Lattice parameter, d-shift { Residual stress Solid solution
 - B** FWHM (Full width at half maximum): Sample quality, Crystallite size and lattice strain
 - C** Integrated intensity of amorphous } Crystallinity
 - D** Integrated intensity of crystalline phase(s) } Quantitative analysis
- Intensity ratios: Preferred orientation

MiniFlex hardware setup



Incident slit and irradiation area



IHS size	Irradiated width Soller slit 2.5°
10 mm	12 mm
5 mm	7 mm
2 mm	4 mm

$$\text{Irradiation width } 2A = \left[\frac{1}{\sin(\theta + \frac{\beta}{2})} + \frac{1}{\sin(\theta - \frac{\beta}{2})} \right] \times R \sin(\theta + \frac{\beta}{2})$$

θ : Incident angle (diffraction angle $2\theta \div 2$) (°)

β : Incident slit divergence angle (°)

R : Goniometer radius (mm)

Measurement start angle (2θ) $<10^\circ$ $>10^\circ$
Divergence slit 0.625° 1.25°

