CPDW18 PXRD BASICS – SAMPLE PREPARATION

Powder XRD Sample Preparation

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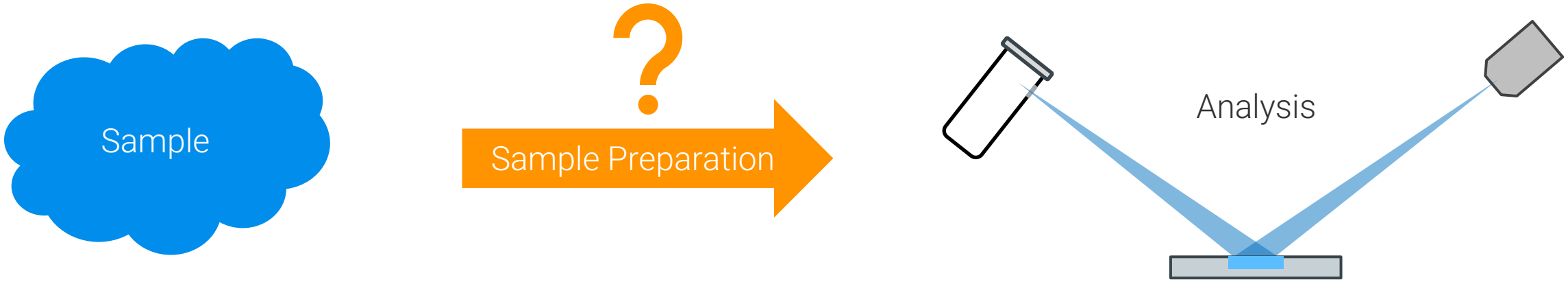
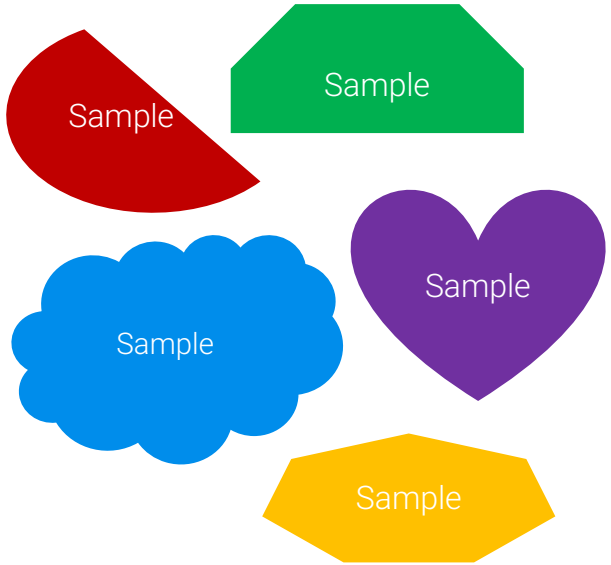
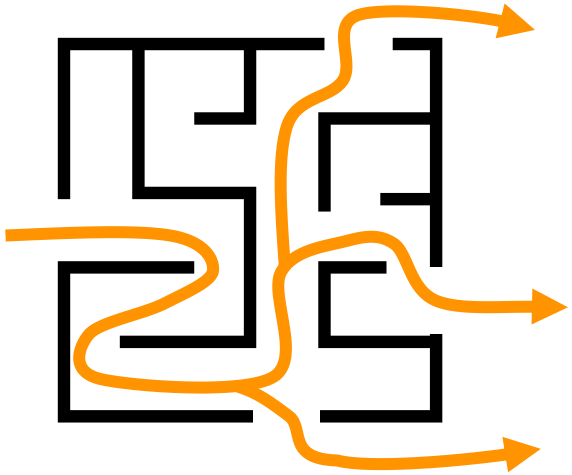
Ideal Sample Prep Scenario



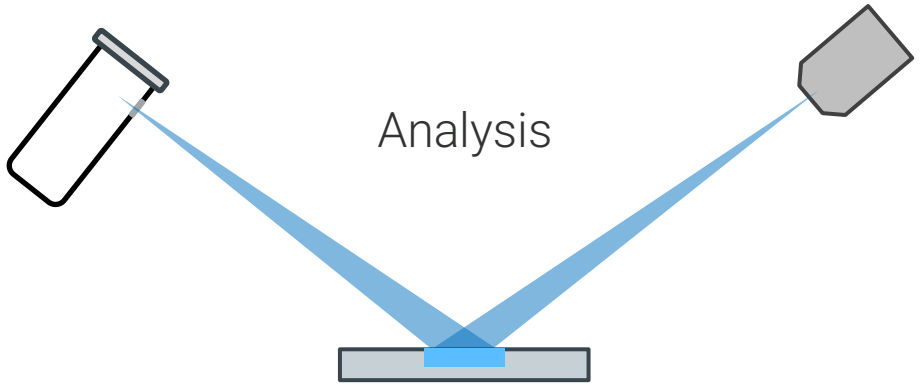
Sample Prep Map

The path you choose will depend on your sample and analytical goal.





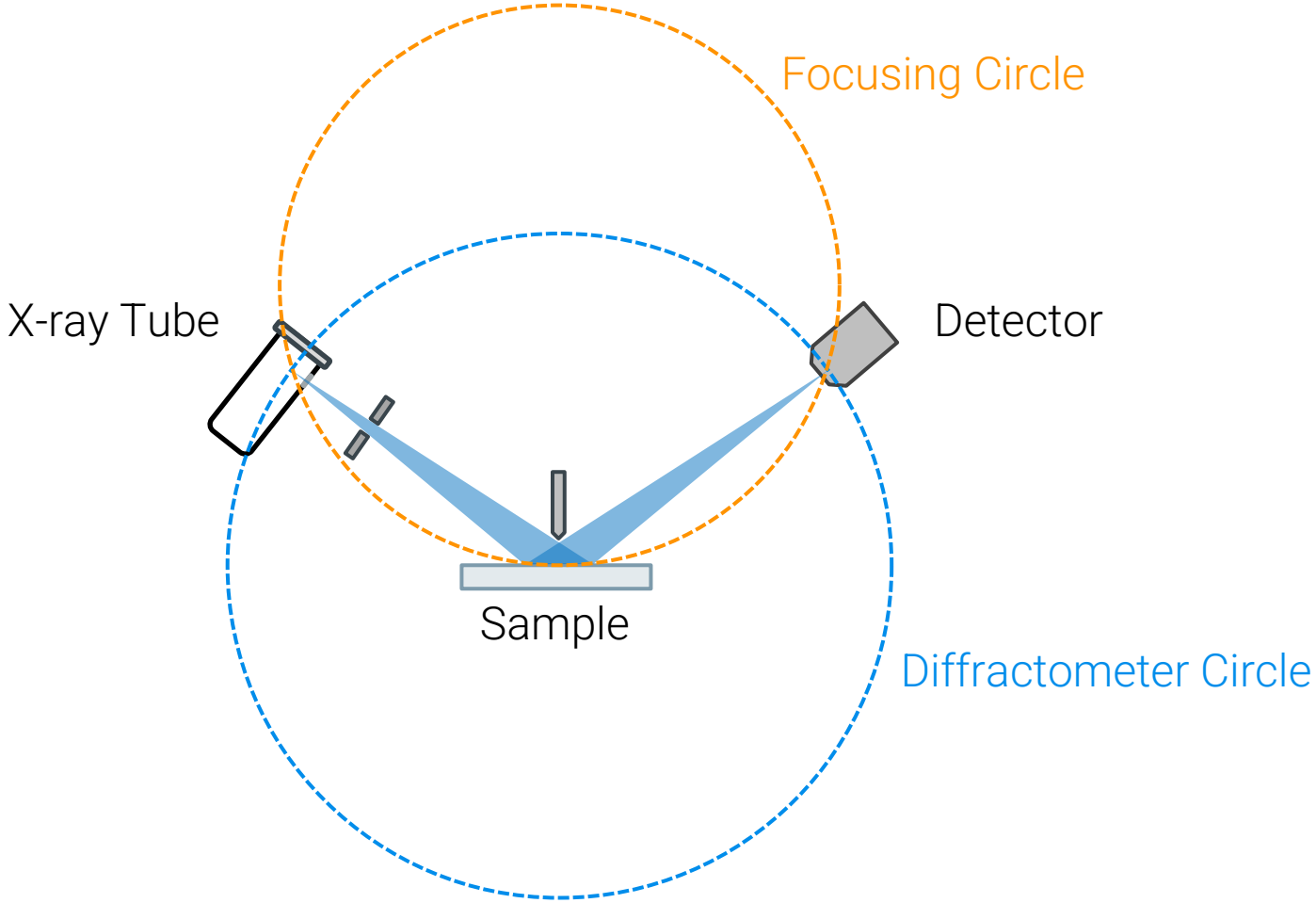
Reduce particle size?
Which holder to use?
How to load the material?



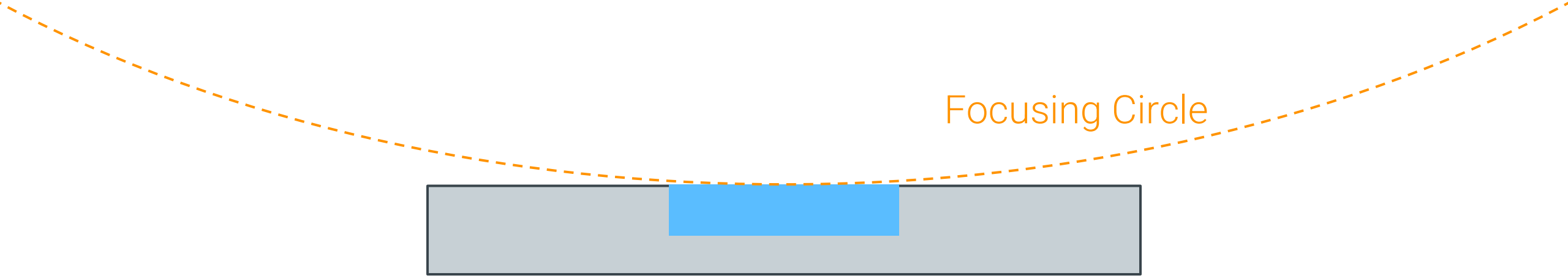
Ideal Sample for Bragg-Brentano Geometry

- **Flat**
  - Sample is level with top surface of holder
  - Affected by sample displacement (sample height)
- **Smooth**
  - Powder is smooth and fine-grained
  - Affected by graininess (rough or coarse powder with large grains)
- **Random**
  - Completely randomize crystallite statistics
  - Affected by preferred orientation (over- or under-represented diffraction planes)

Bragg-Brentano Parafocusing Geometry



Sample Displacement



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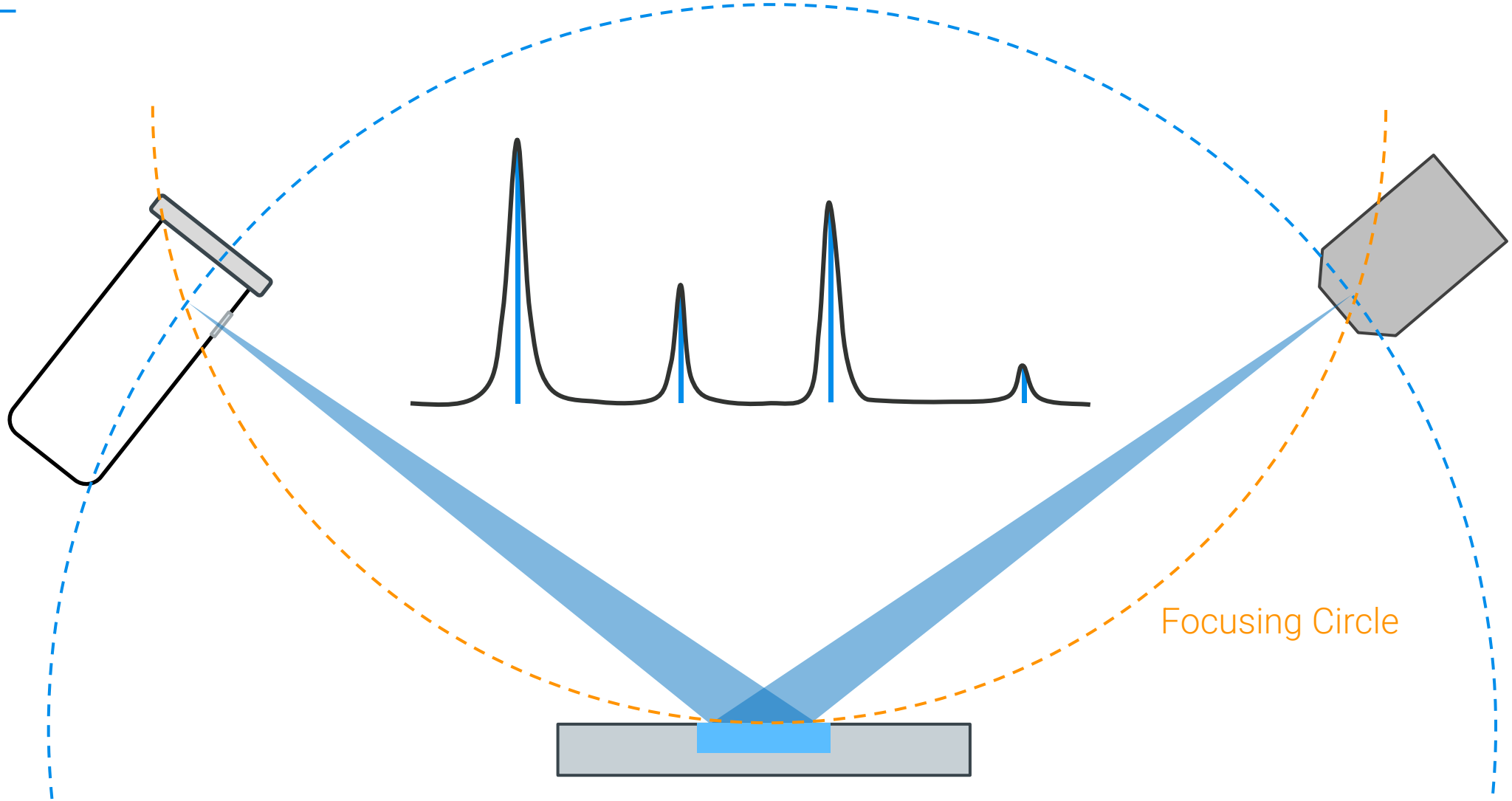
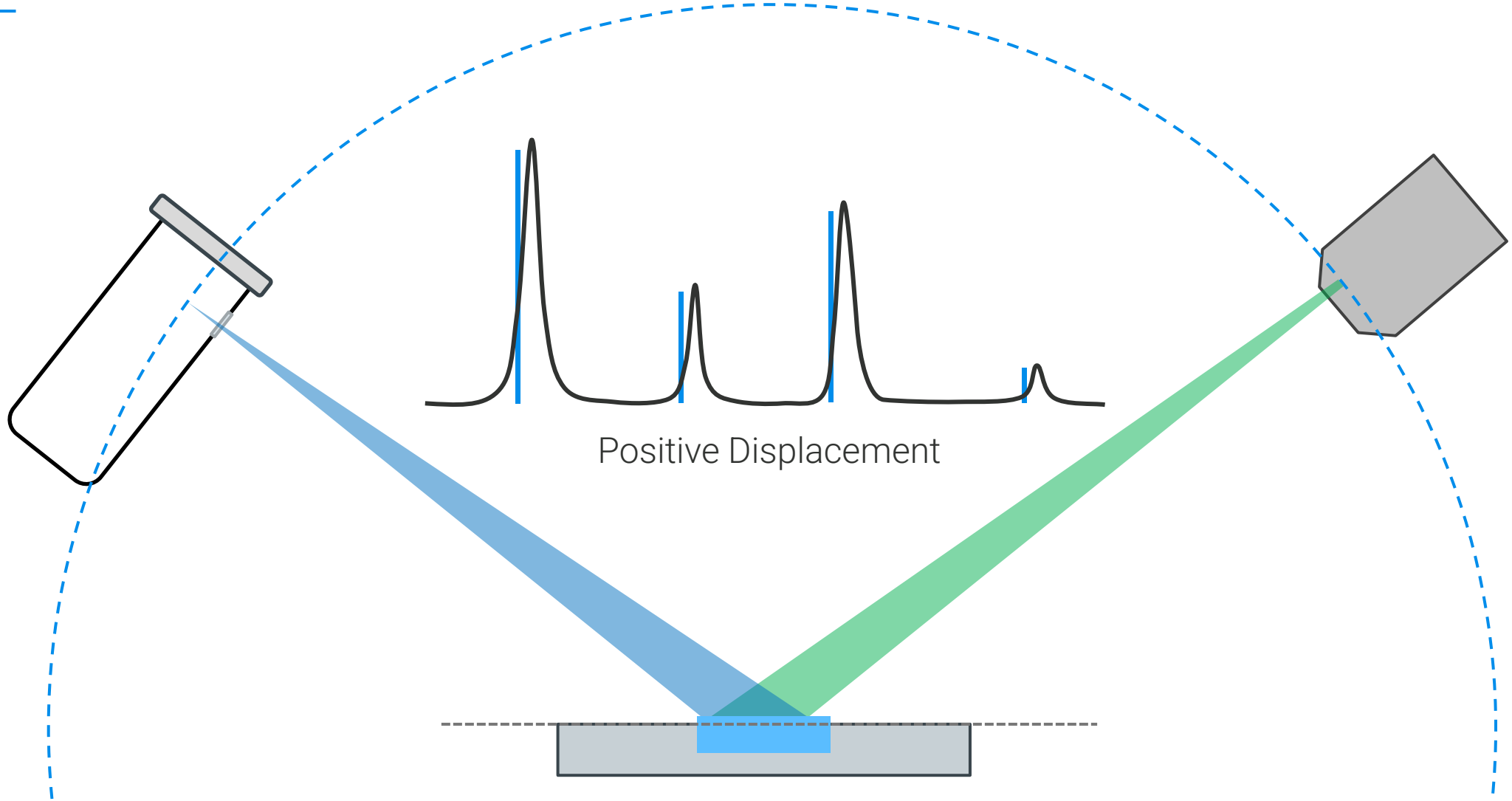
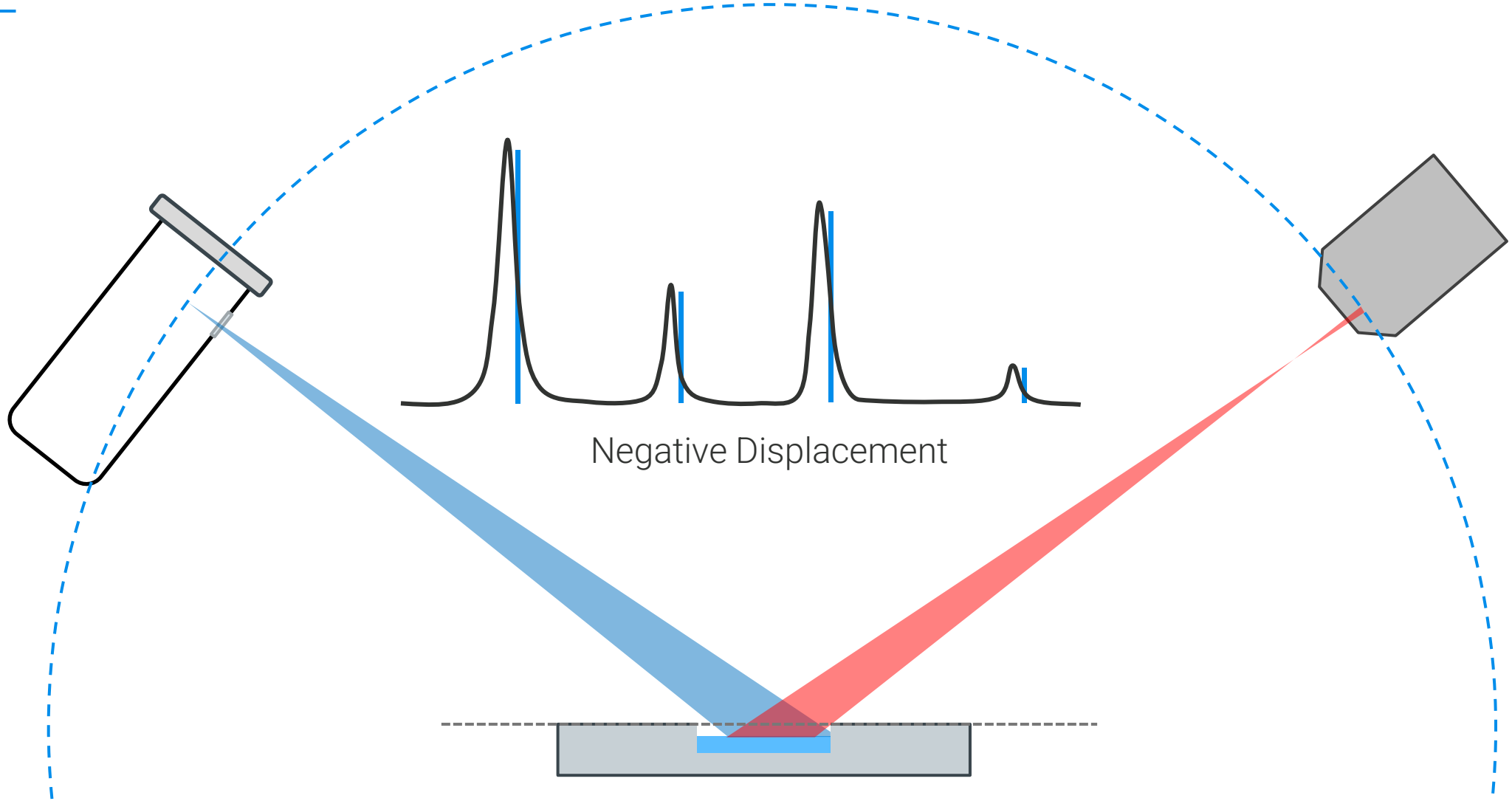


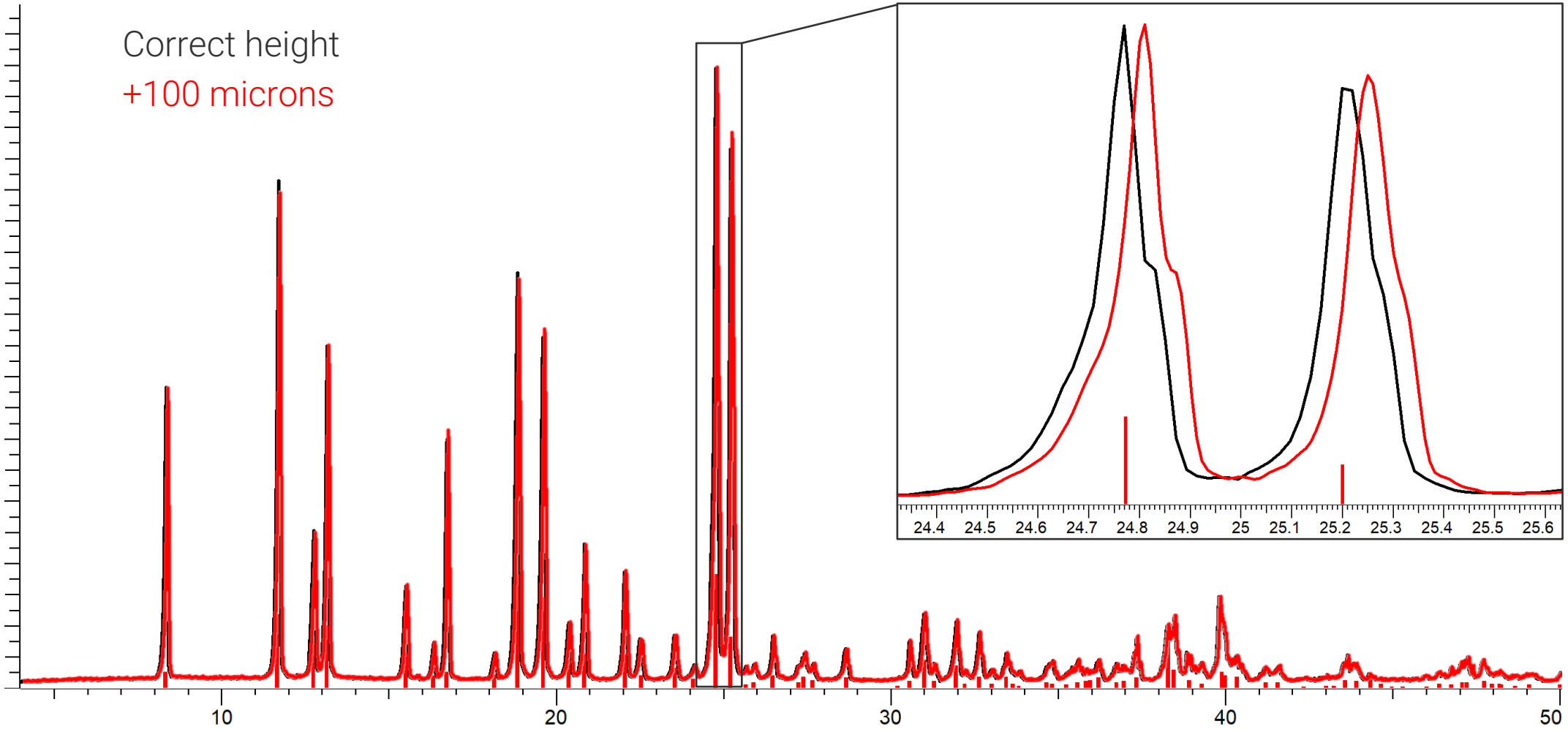
Sample Displacement



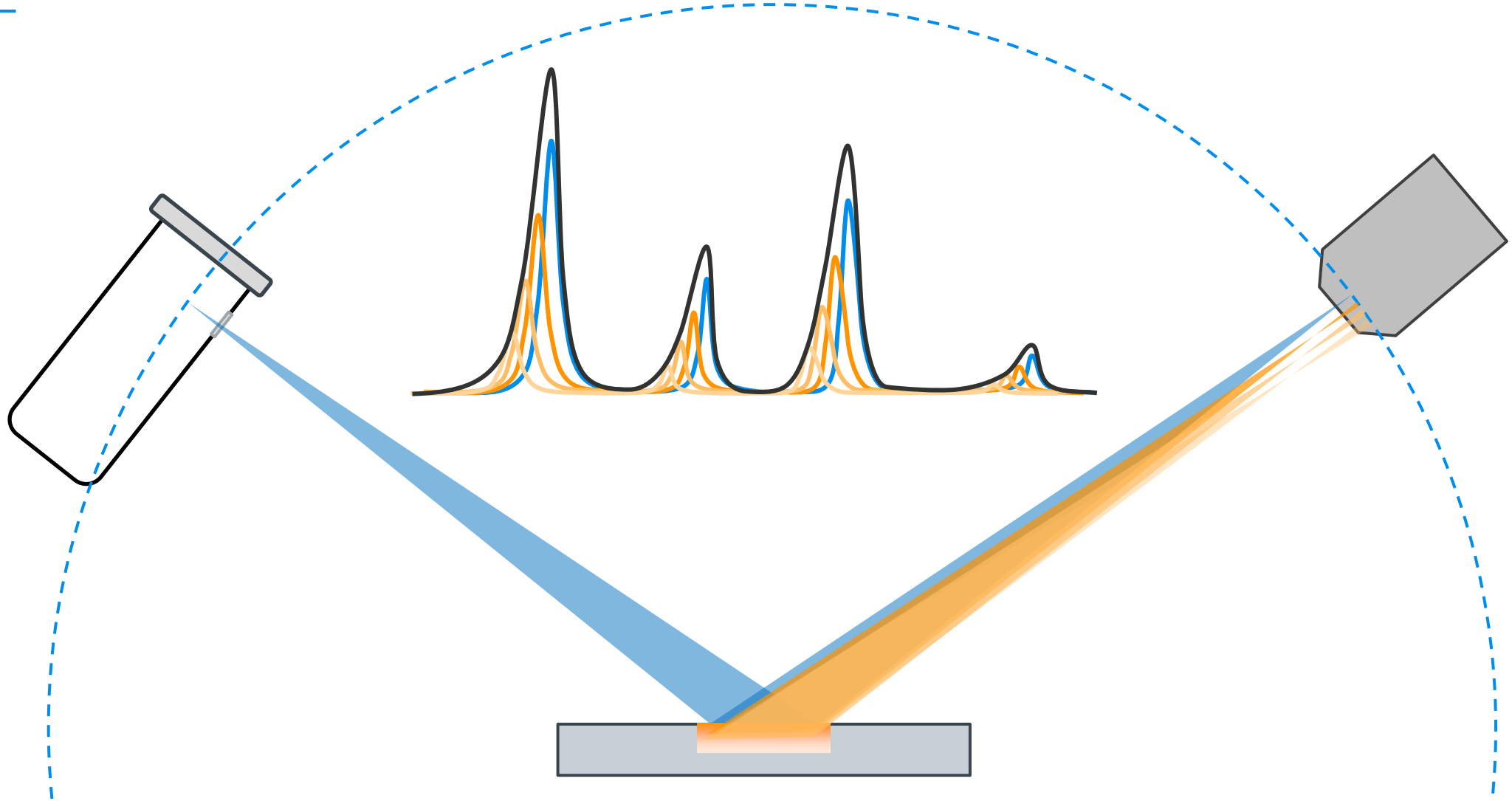
Sample Displacement



Sample Displacement (Sucrose)



Sample Transparency (Light Elements)



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  - Completely randomize crystallite statistics
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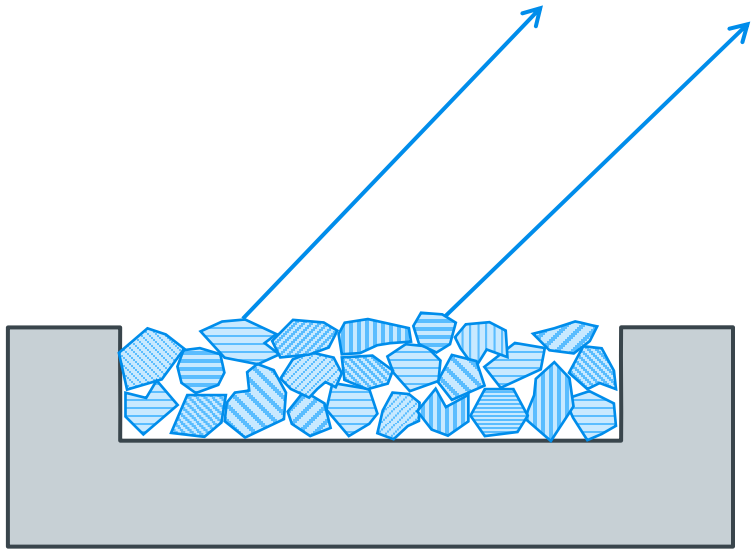
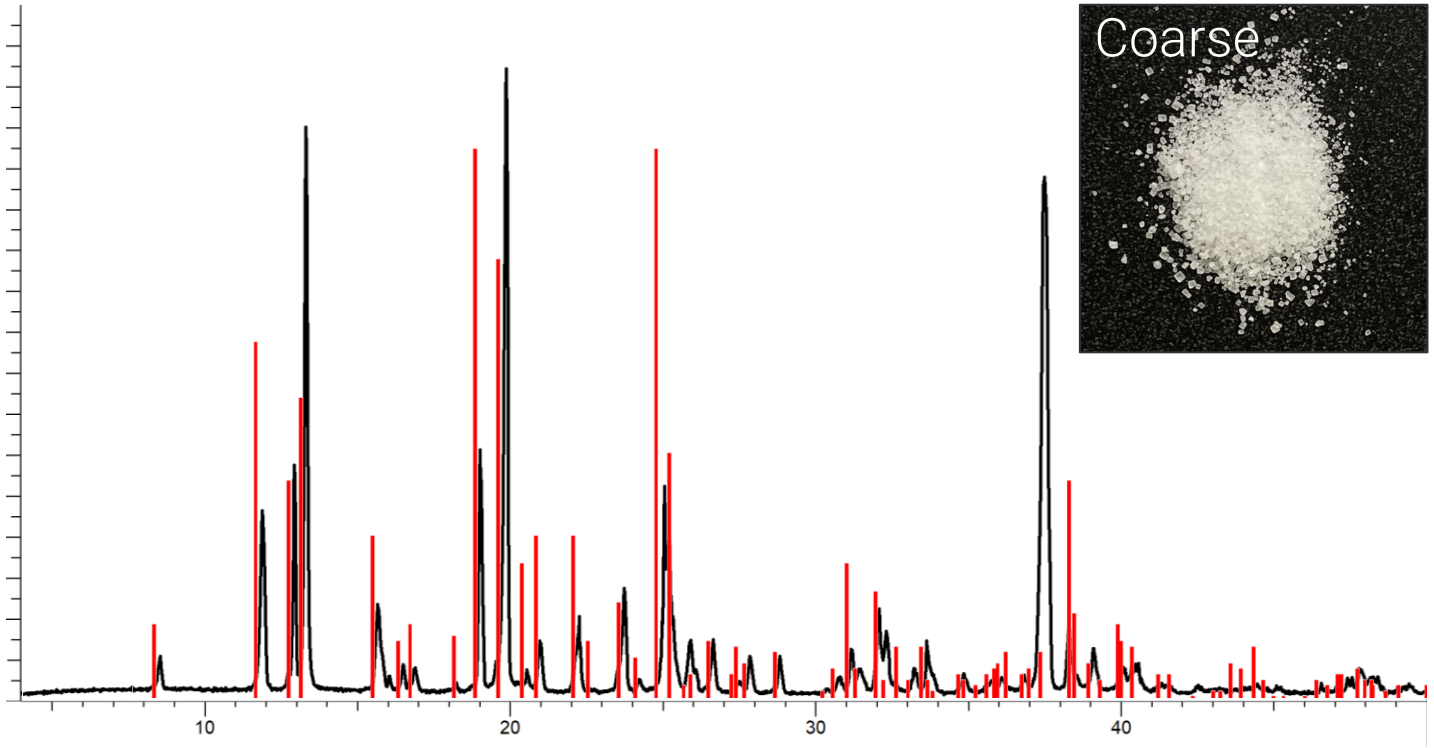
Coarse or Grainy Powders

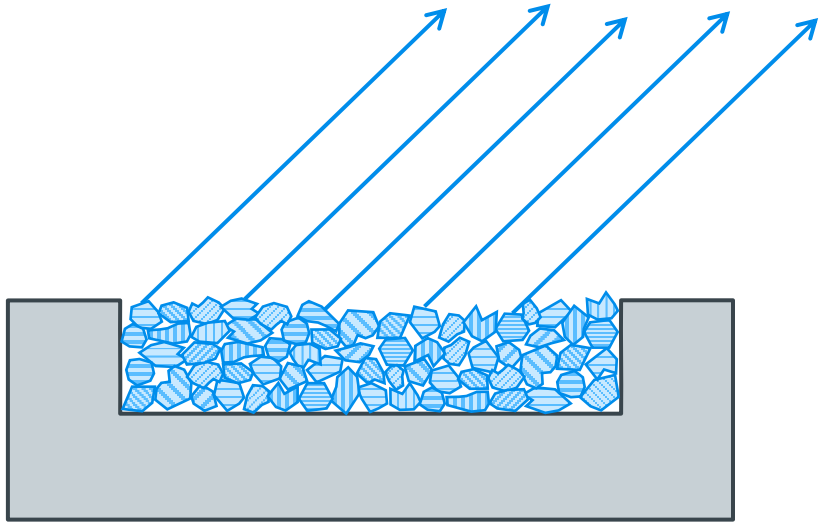
Coarse or Grainy Powders

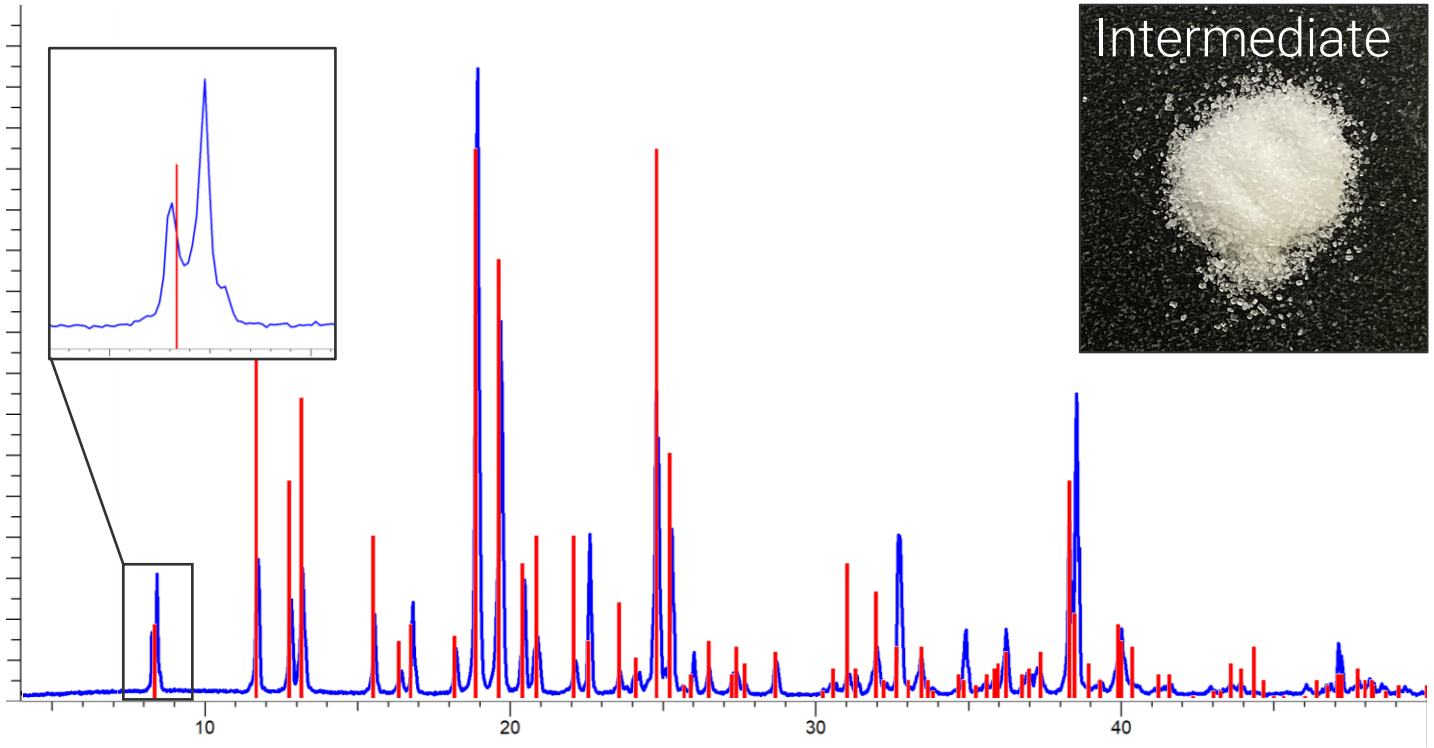




Samples with large grains have a limited number of crystals
in the correct orientation for diffraction to occur (wrong intensities)

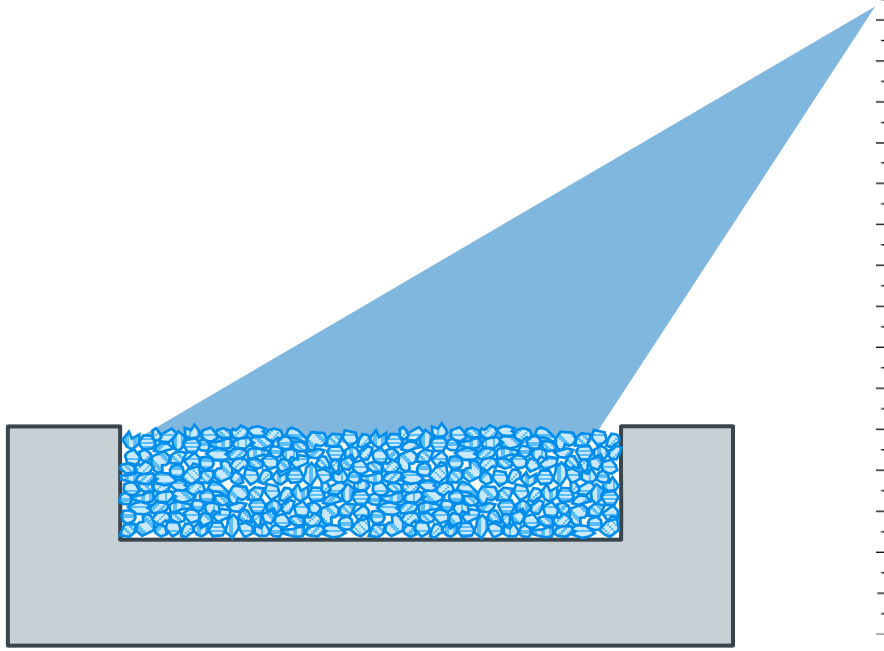
Coarse or Grainy Powders

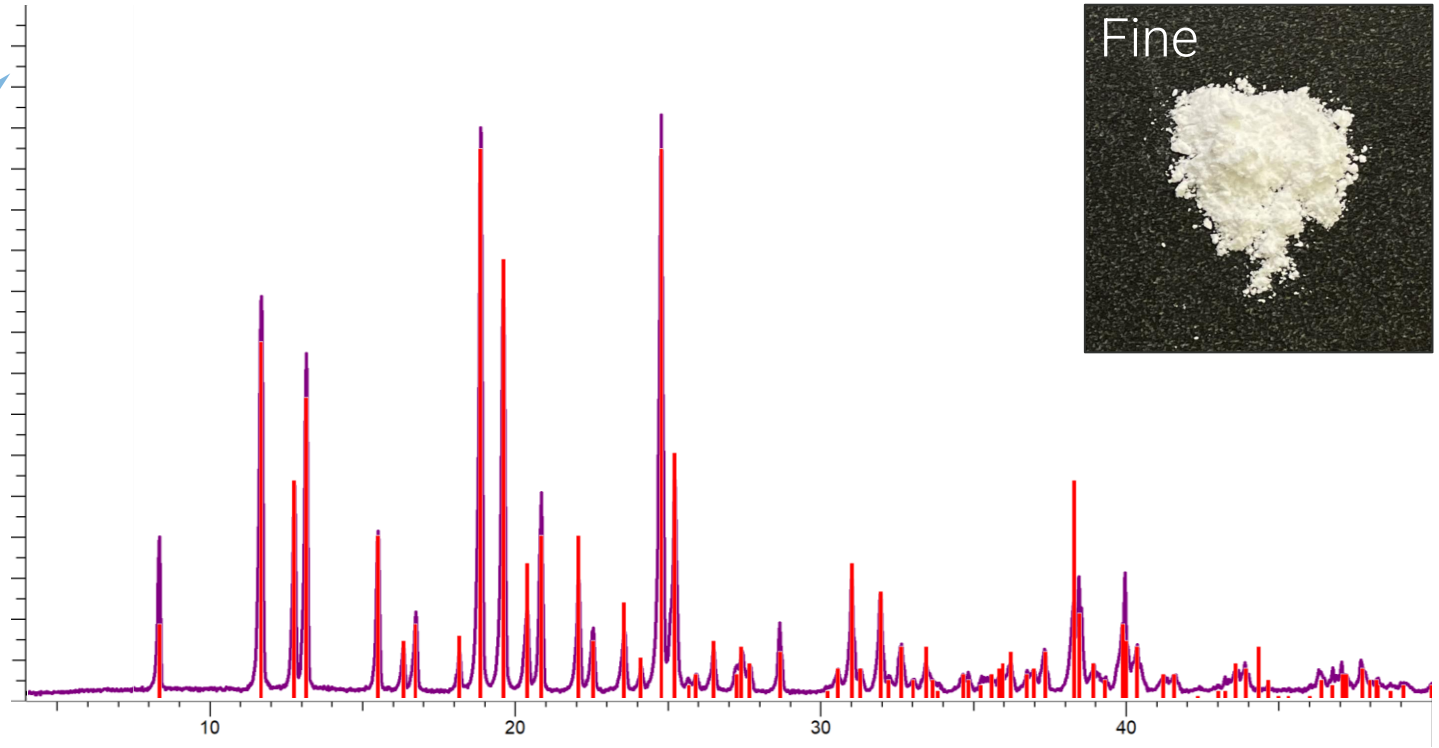




Grainy samples are difficult to pack evenly, leading to surface roughness and multiple sample heights (peak shifting or doubling)

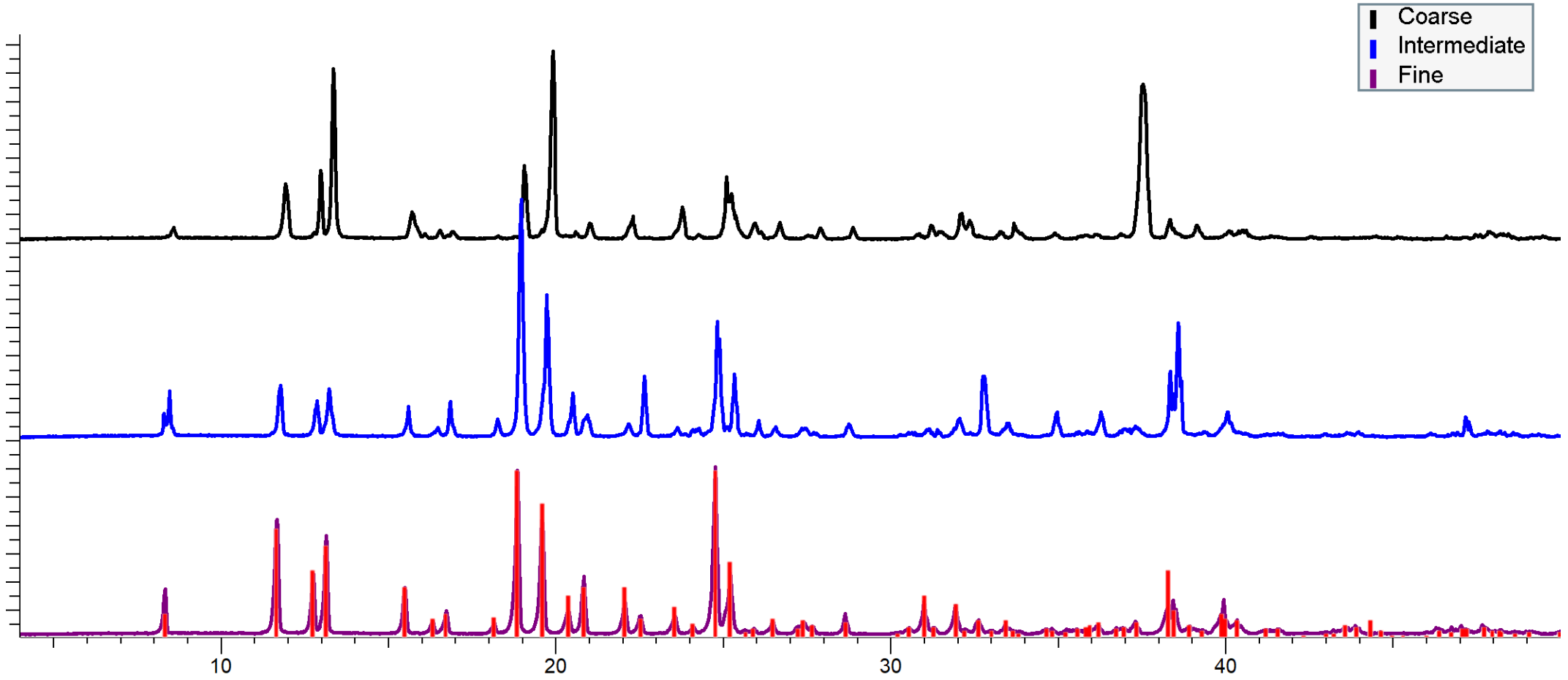
Coarse or Grainy Powders



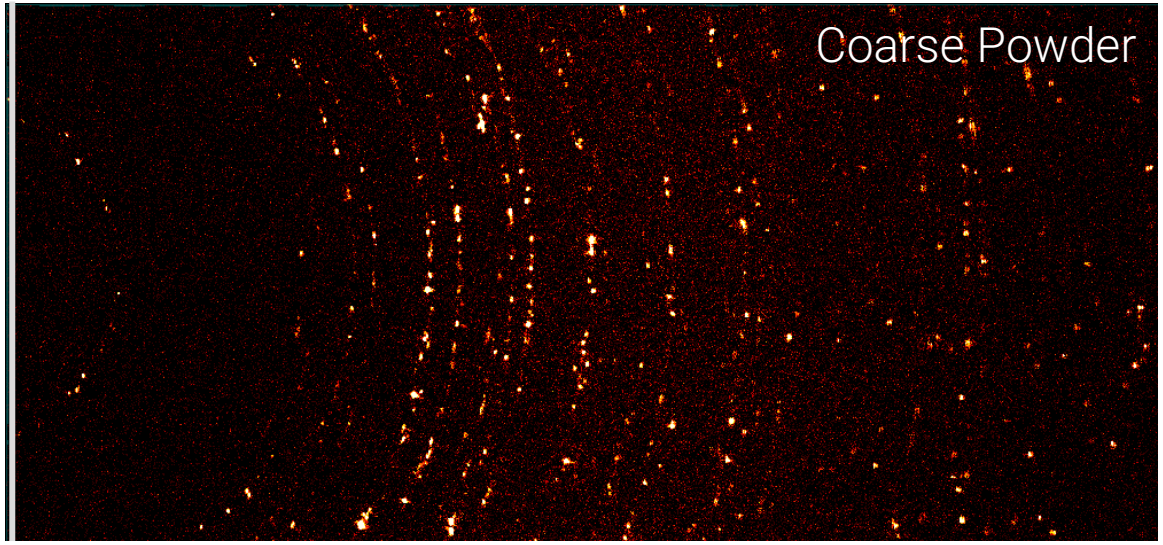


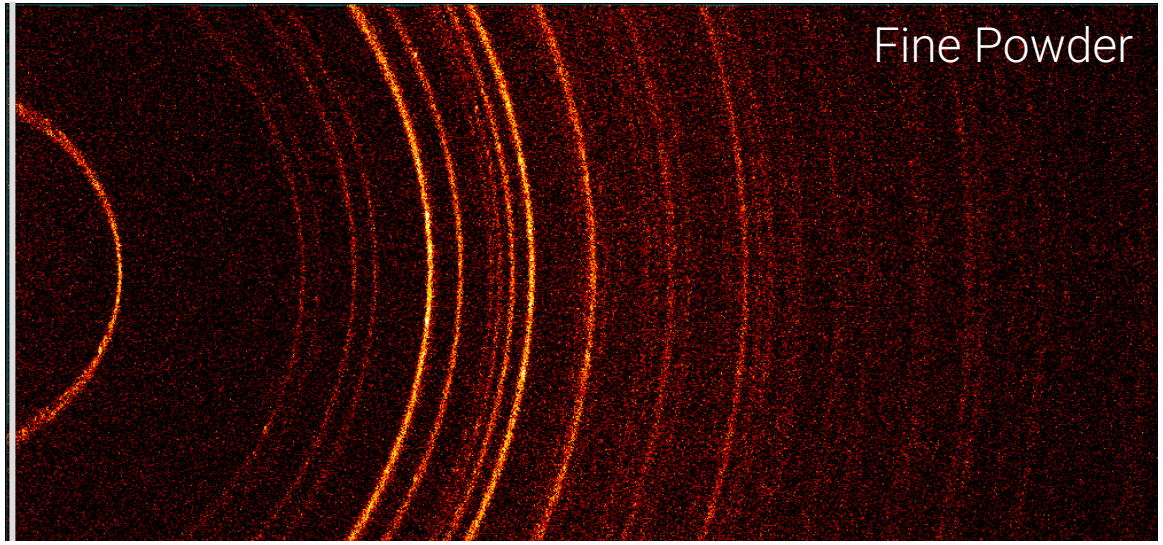
Fine powders are easier to prepare as a smooth surface and have large enough statistics to observe each crystal orientation

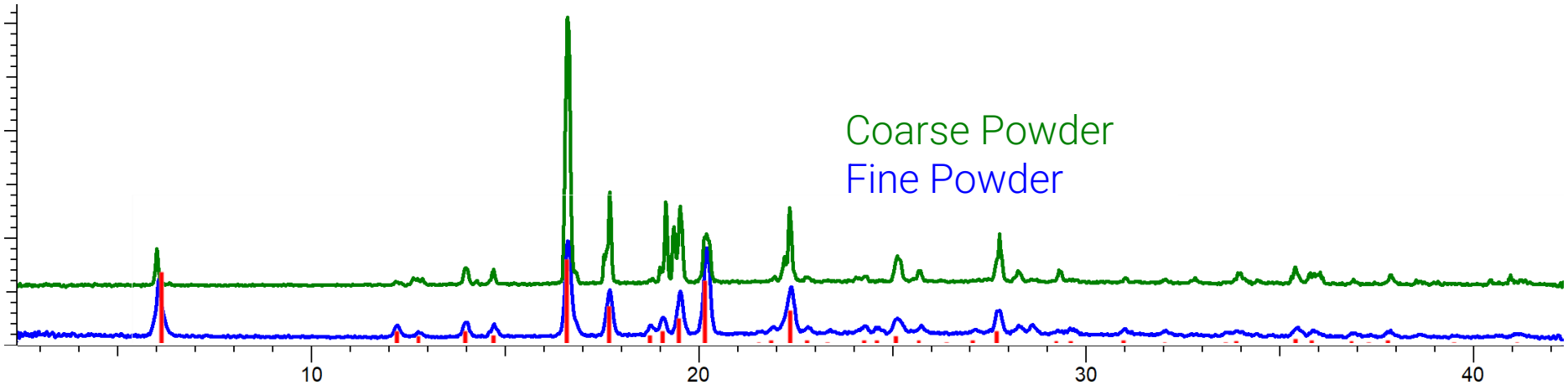
Coarse or Grainy Powders



Coarse or Grainy Powders

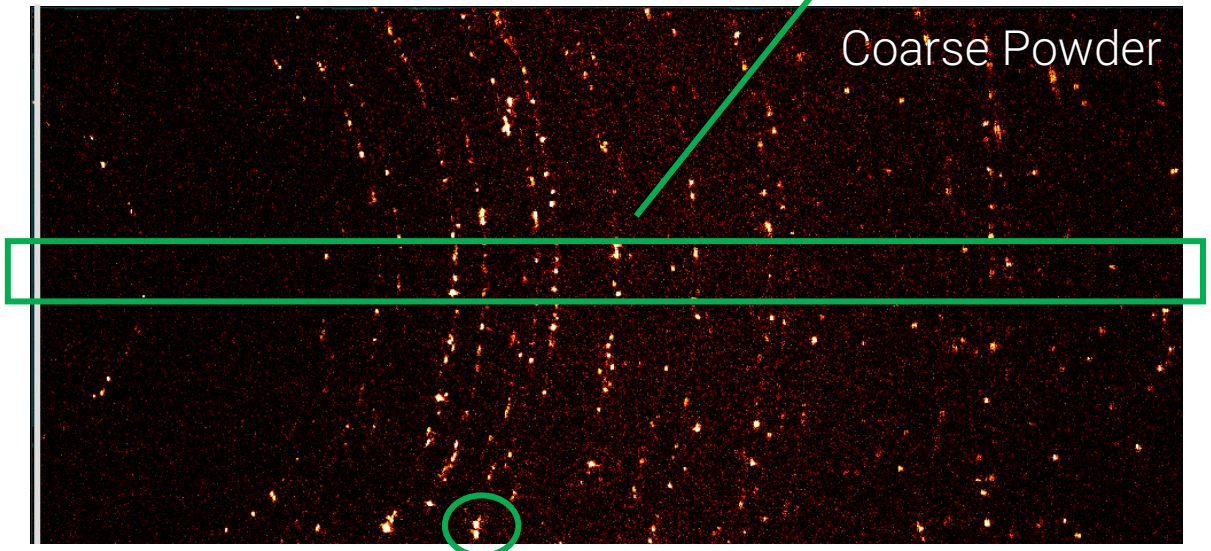


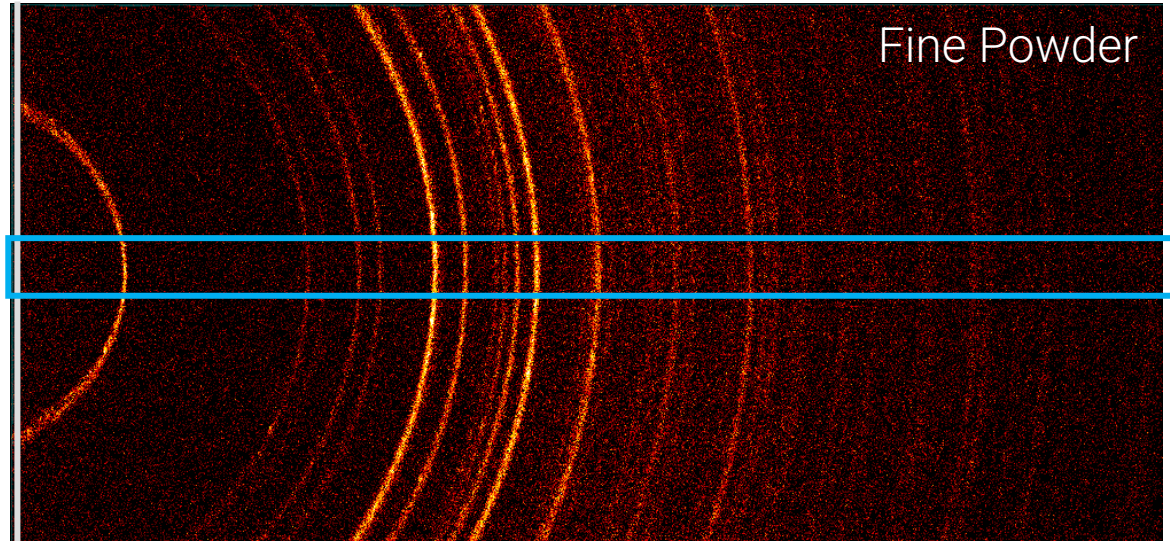




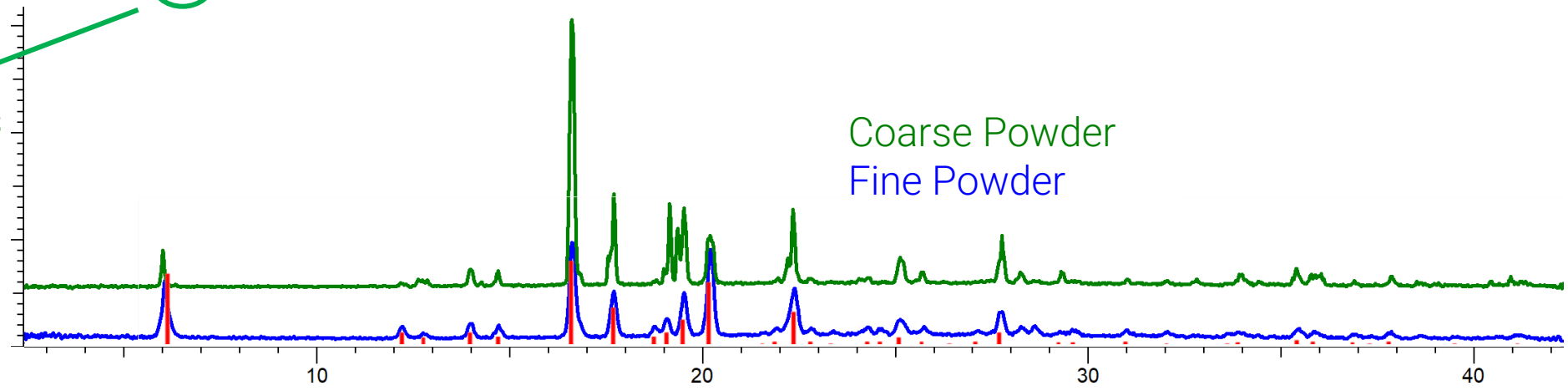
Coarse or Grainy Powders

1D detectors do not integrate over the entire area; some reflections are under/over-represented





Multiple spots on same Debye ring result in the split peak

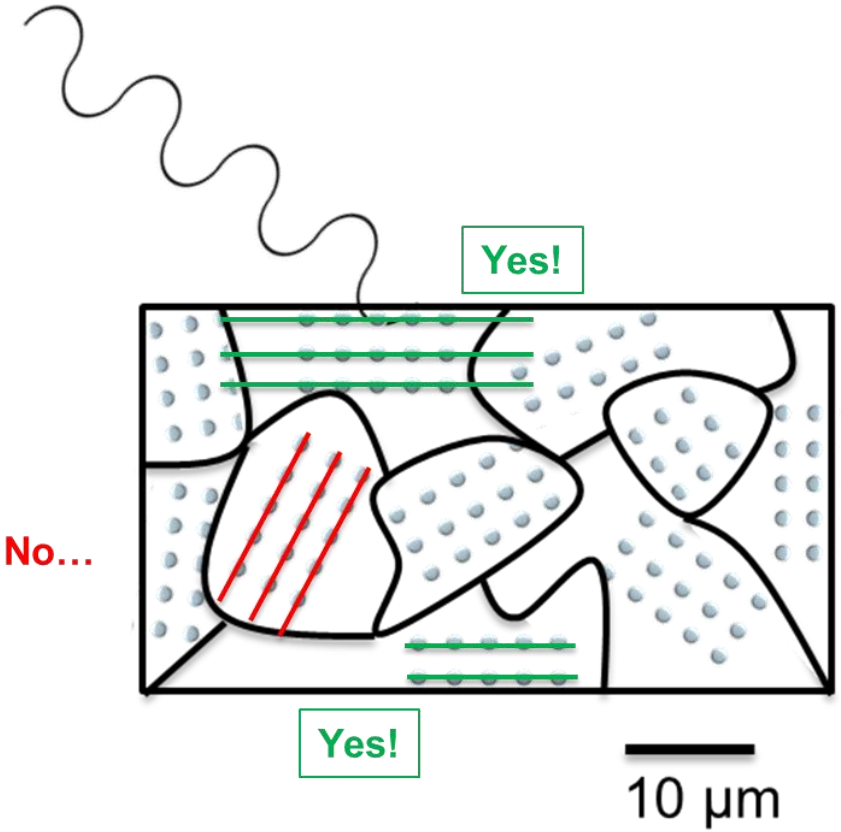


Coarse or Grainy Powders

- Accurate, reproducible diffraction intensities require small crystallite sizes
- Number of diffracting crystallites is directly related to size

Diameter	40 micron	10 micron	1 micron
Crystallites / 20 mm^3	597 000	38 000 000	3 820 000 000
Number Diffracting	12	760	38 000

Aim for a smooth powder
Crush (don't grind) organic samples
Rotate or spin to increase particle statistics



Smith, D.K. "Evaluation of the Detectability and Quantification of Respirable Crystalline Silica by X-ray Powder Diffraction Methods" *1992*

Reducing Particle Size

Mortar and Pestle

Micronising Mill

Ball Mill

Ring and Puck Mill

CryoMill

Wig-L-Bug

Impact Mortar

- Consider how the grinding process will affect your material
- Remember to use grinding media of appropriate hardness to avoid contamination

*This is not an exhaustive list of particle size reduction techniques. Images used are not endorsements for specific products.

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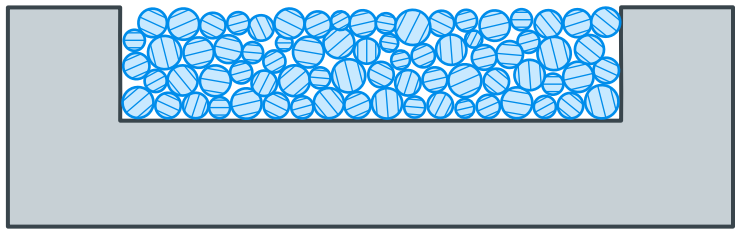
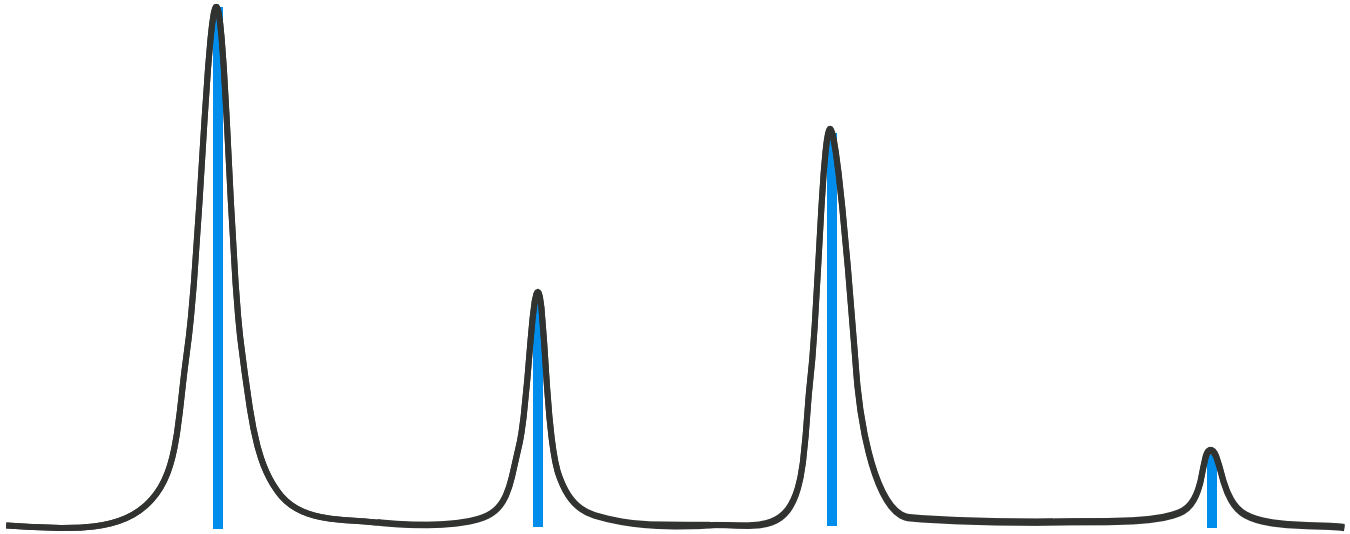
- Random
  - Completely randomize crystallite statistics
  - Affected by preferred orientation (over- or under-represented diffraction planes)

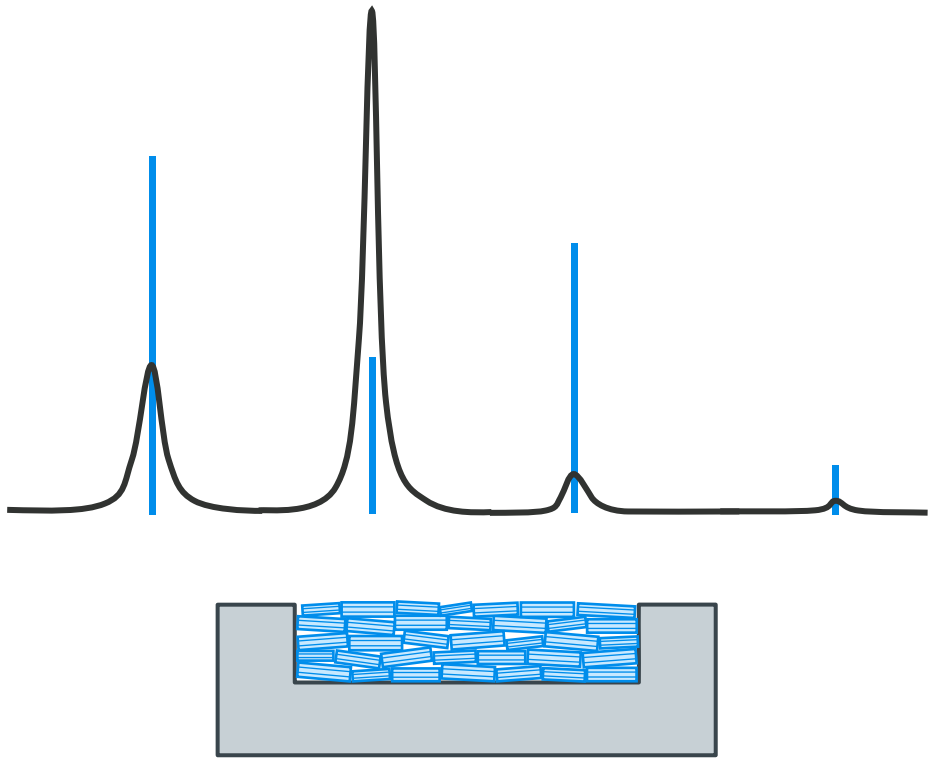
Preferred or Non-Random Orientation



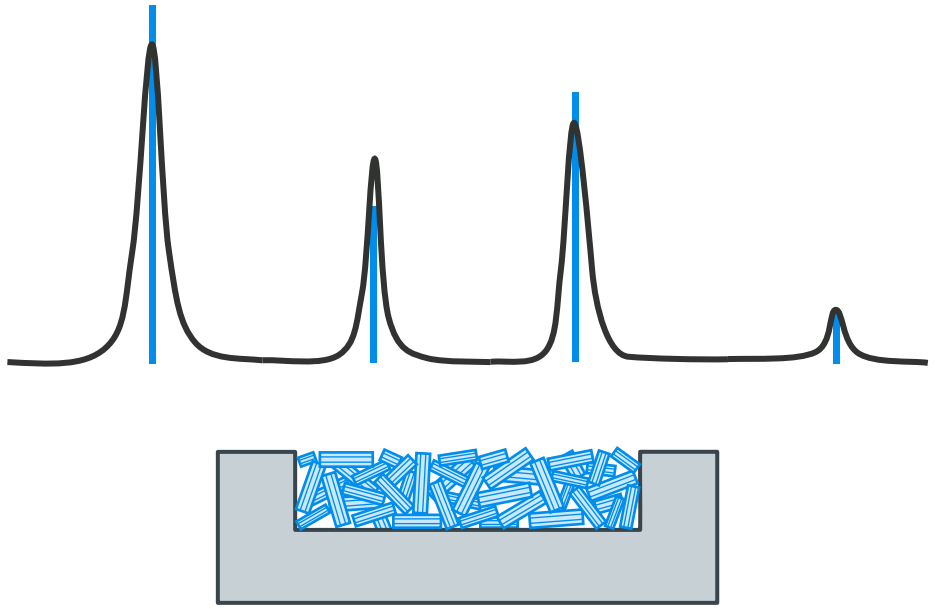


An ideal powder has particle shapes
that are conducive to random orientations

Preferred or Non-Random Orientation

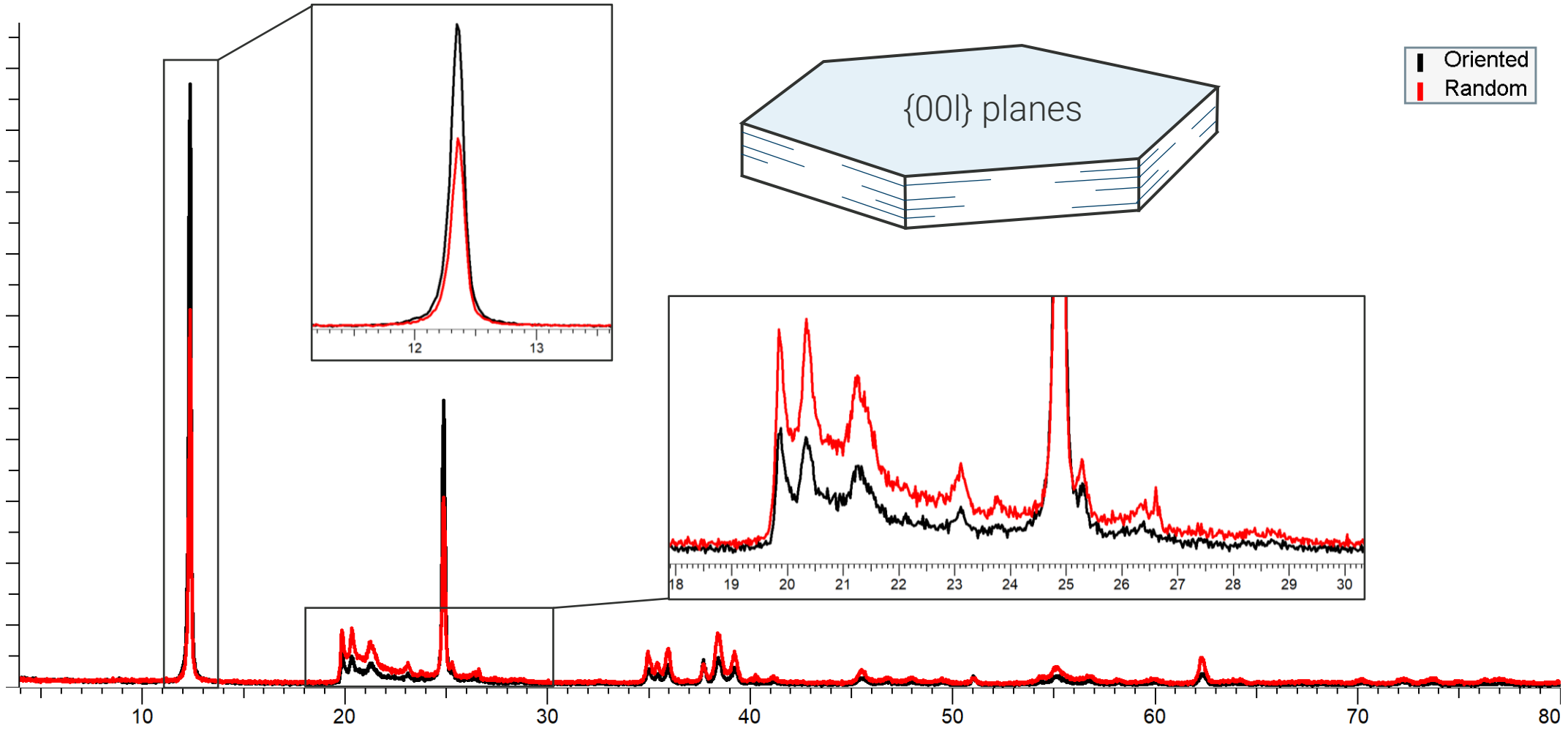


If a material has particles that are shaped like plates or needles, certain crystal orientations can be overrepresented (incorrect intensities)

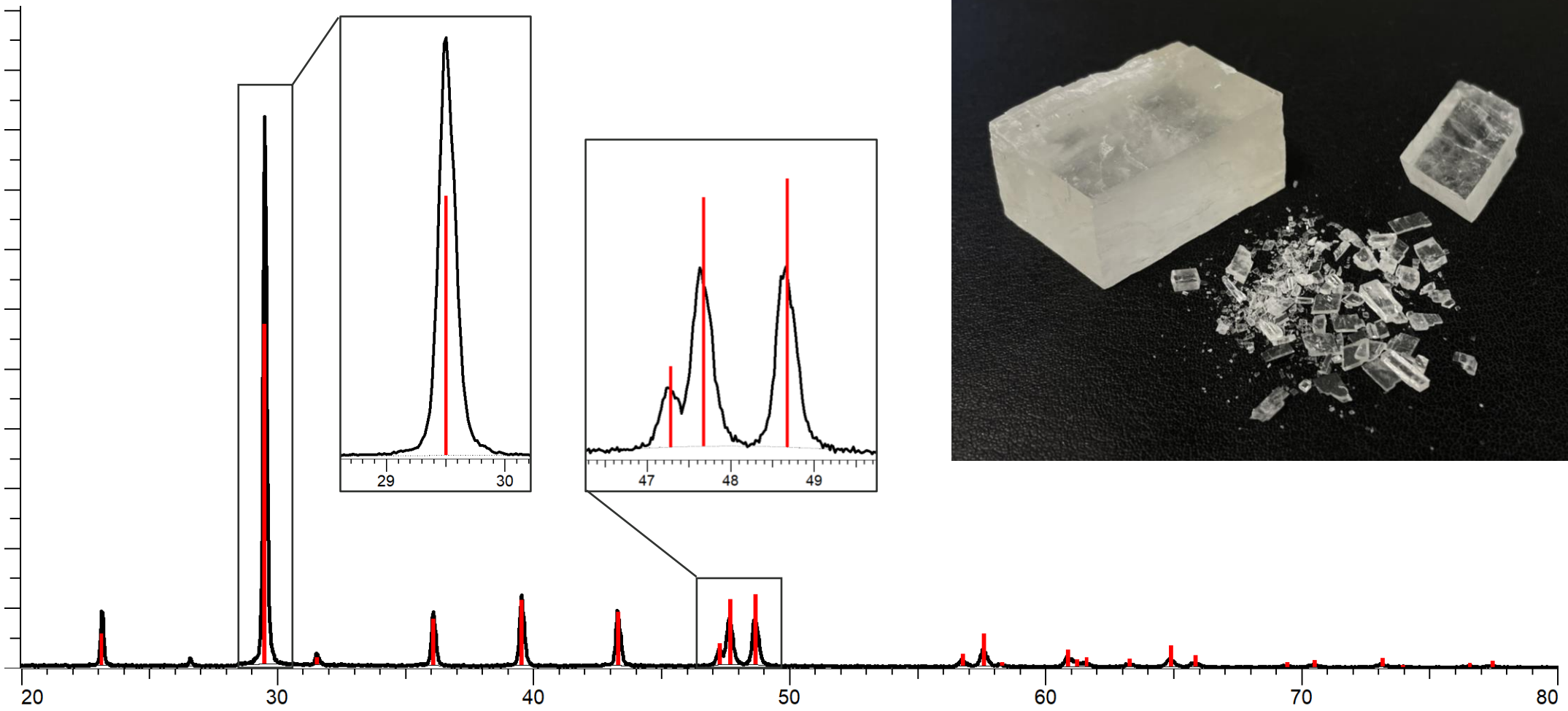


If a material tends to orient, try to increase randomization during sample preparation (gentle packing, back- or side-loading)

Preferred or Non-Random Orientation (Kaolinite)



Preferred or Non-Random Orientation (Calcite)



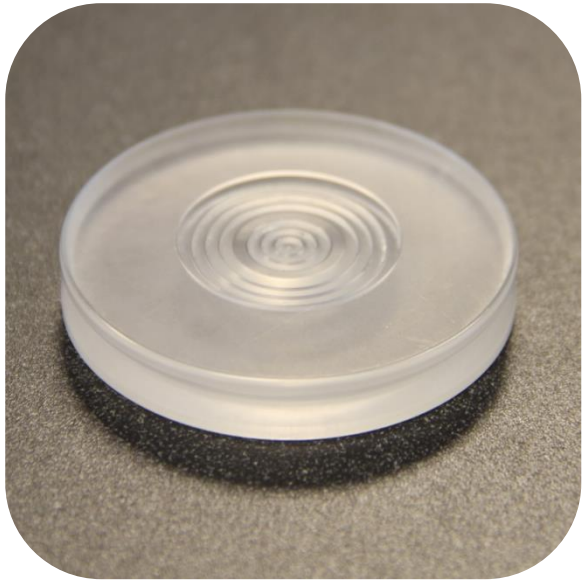
Concept Summary

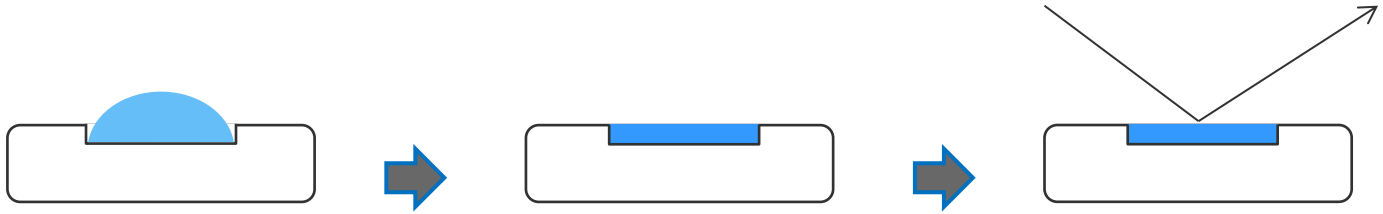
- The ideal powder diffraction specimen is flat, smooth, and random
  - Sample displacement affects observed peak positions
  - Graininess affects peak intensities and shapes
  - Preferred orientation affects relative peak intensities

- Accurate, high-quality diffraction data is achieved through careful sample preparation

- Phase identification, phase quantification, and structural refinement are all improved with better quality data

Frontload Holder (Cavity Holder)





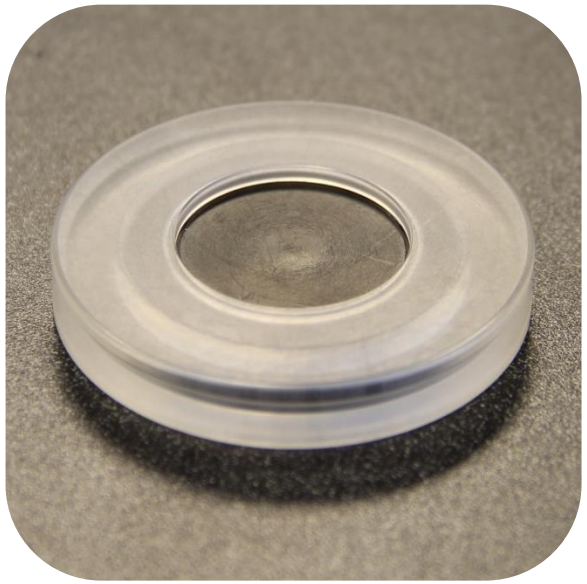
Advantages:

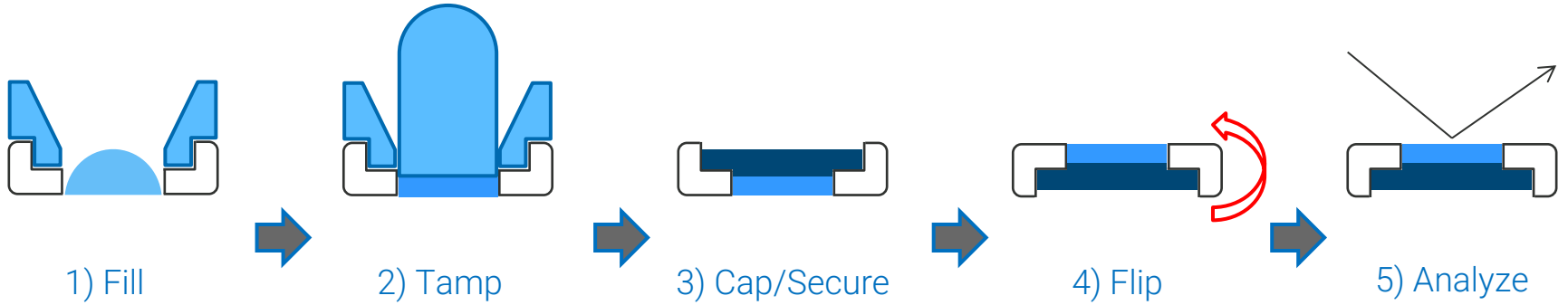
- Larger sample volume offers more homogeneous sampling from bulk materials
- Better overall particle statistics
- Cavity holders may be available in variable depths for variable sample amounts (i.e. 6 mm, 1 mm, 0.5 mm)

Disadvantages:

- For organic materials/light elements, may encounter peak broadening due to sample transparency
- Smoothing of the sample may encourage preferred orientation (if applicable)

Backload Holder





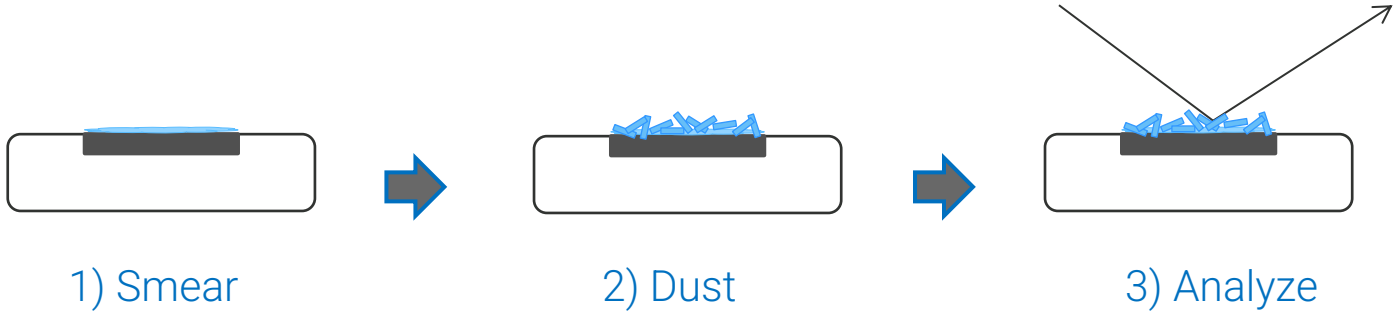
Advantages:

- The backloading insert may allow for variable sample amounts
- For samples that are difficult to smooth, may offer a technique to ensure a flat sample preparation
- May help with minimizing preferred orientation effects

Disadvantages:

- Loading too much material into the holder may cause the pellet to pop out of the holder when loaded into the instrument (fix by re-preparing with a lesser amount)

Low Background Holder



Advantages:

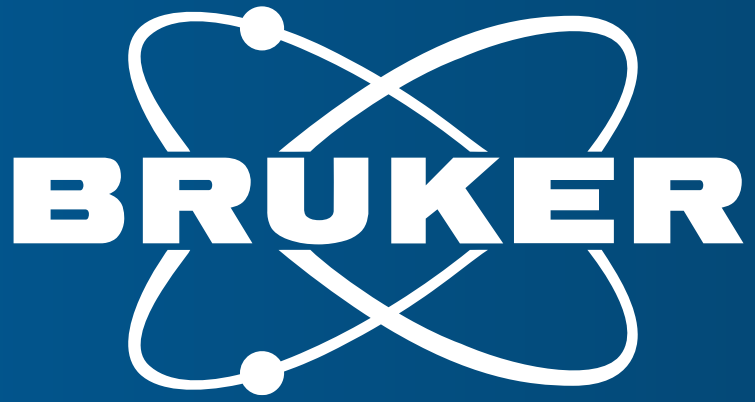
- Ideal if only small amounts of materials are available
- A thin, flat sample preparation is achievable

Disadvantages:

- Smaller sample volumes limit homogeneous sampling and/or particle statistics
- Longer counting times may be needed to improve sample statistics
- May not be ideal for quantitative work

Practical Approach

Do we need the ideal sample to accomplish our analytical goals?



Innovation with Integrity