Practical XRD with Confidence

Episode 2 – Quantitative XRD in Practice: From Phase Estimates to Defensible Results

Wednesday, May 20, 2026, at 1 pm CDT

Presenter: Akhilesh Tripathi, PhD

Host: Tom Concolino, PhD

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- *You will be muted during the workshop*
- *You can ask questions using the Q&A tool.*
- *You should hear music if your sound is working*

Presenter:
Akhilesh Tripathi
Applications Scientist

Host:
Tom Concolino
Sales Manager, XRD

You can ask questions during the presentation. Please use the Q&A to ask questions.

Recording will be available tomorrow.

Rigaku

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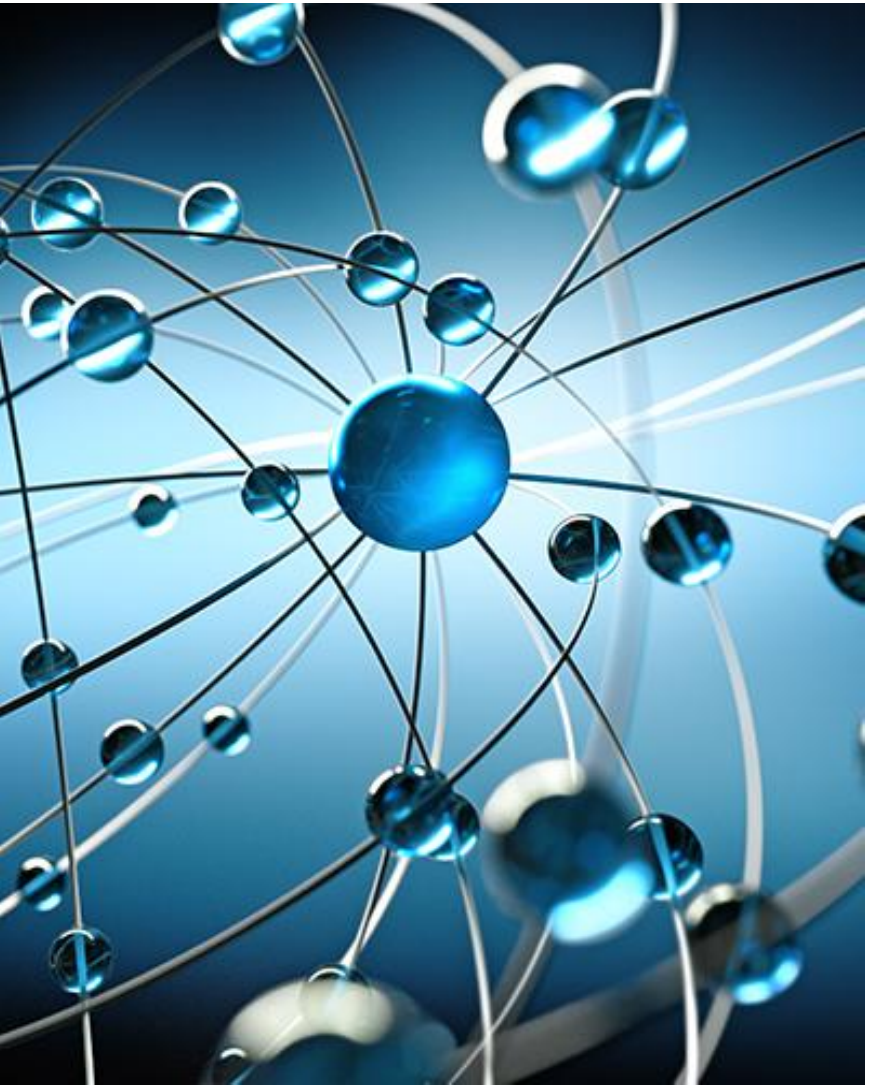
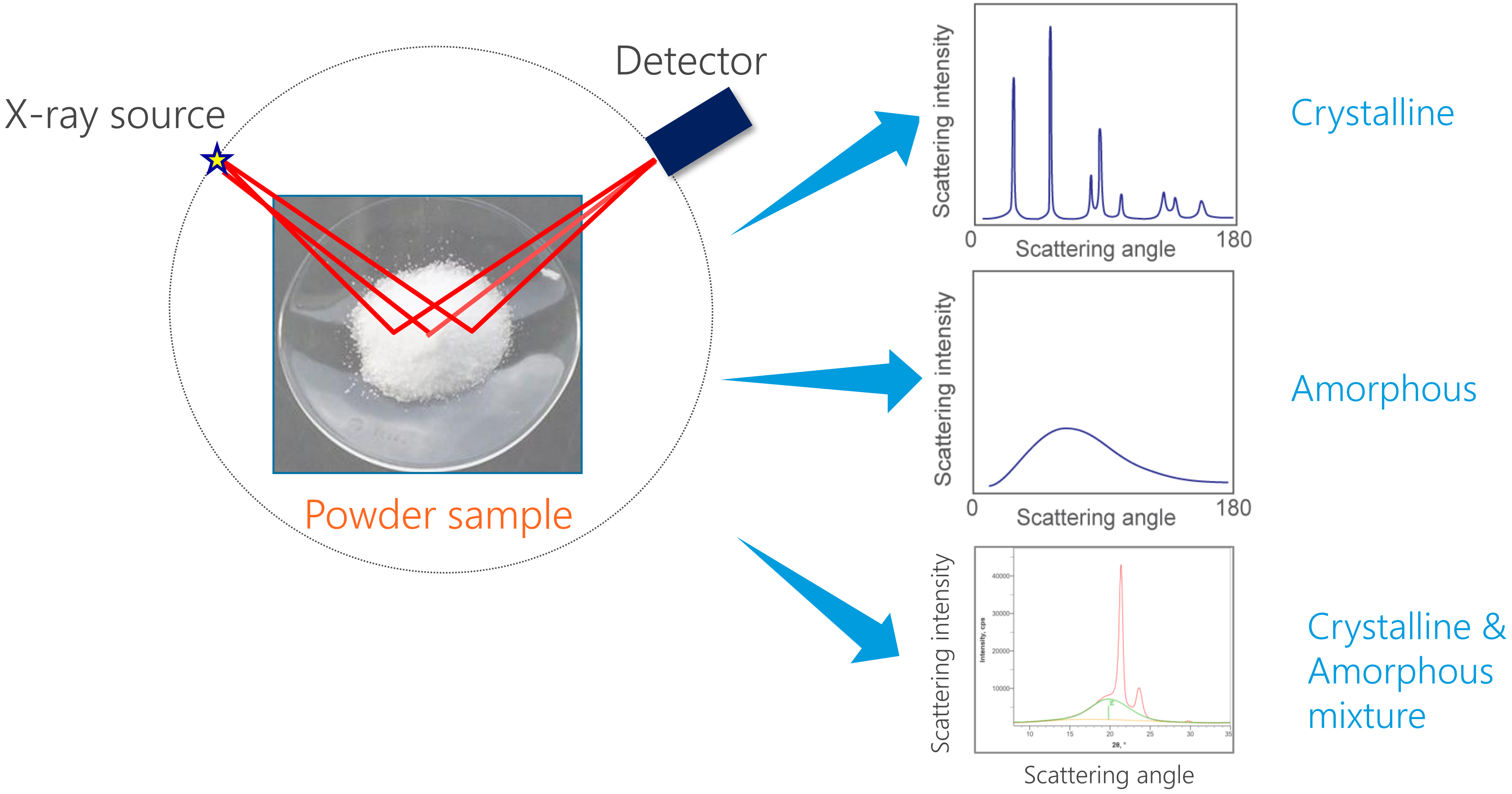


What I will cover today:

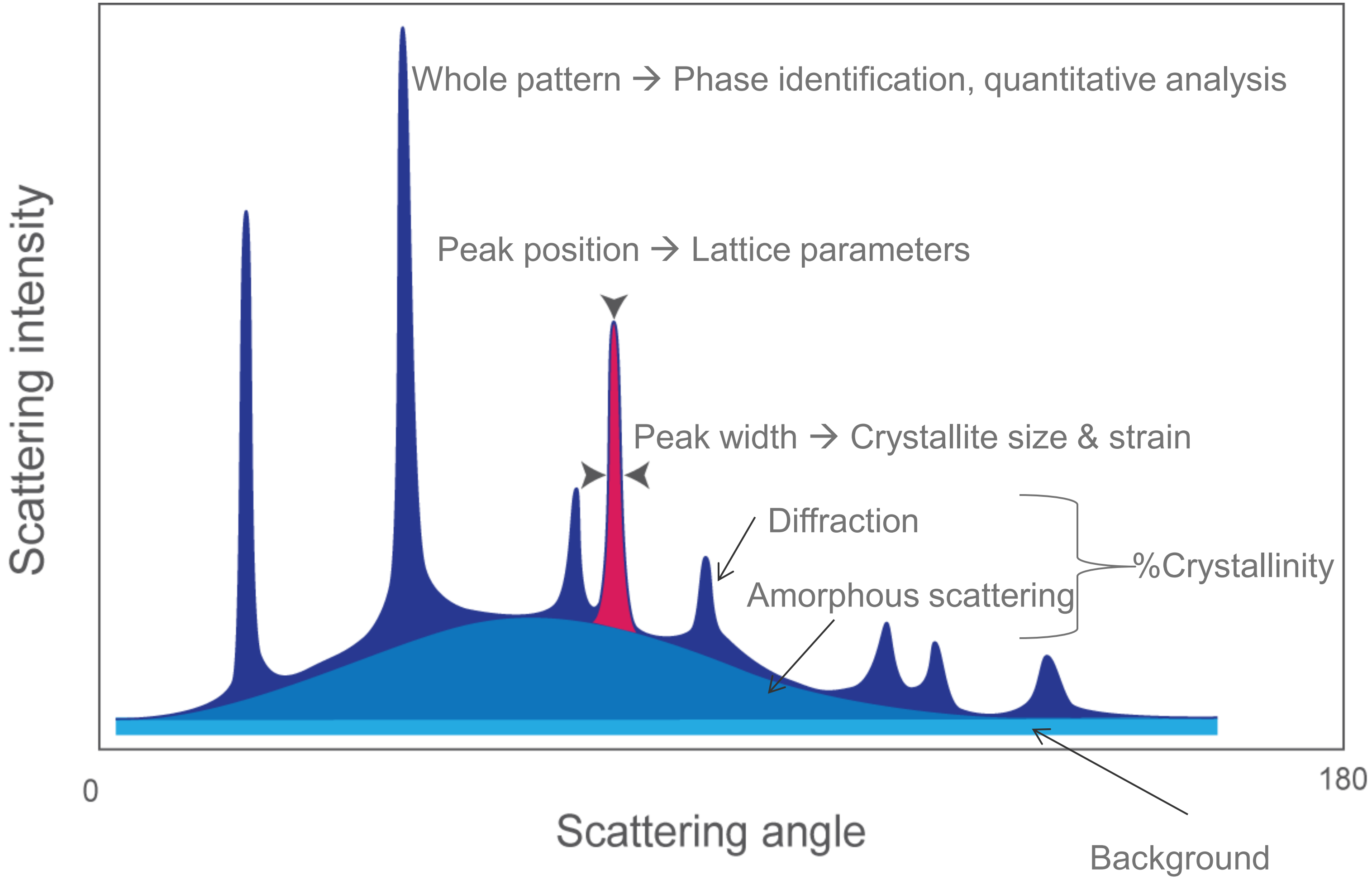
1. Recap of XRD basics
2. Common XRD quantitative techniques
3. Choosing the right method
4. Common mistakes
5. Case studies

1. Recap of XRD basics

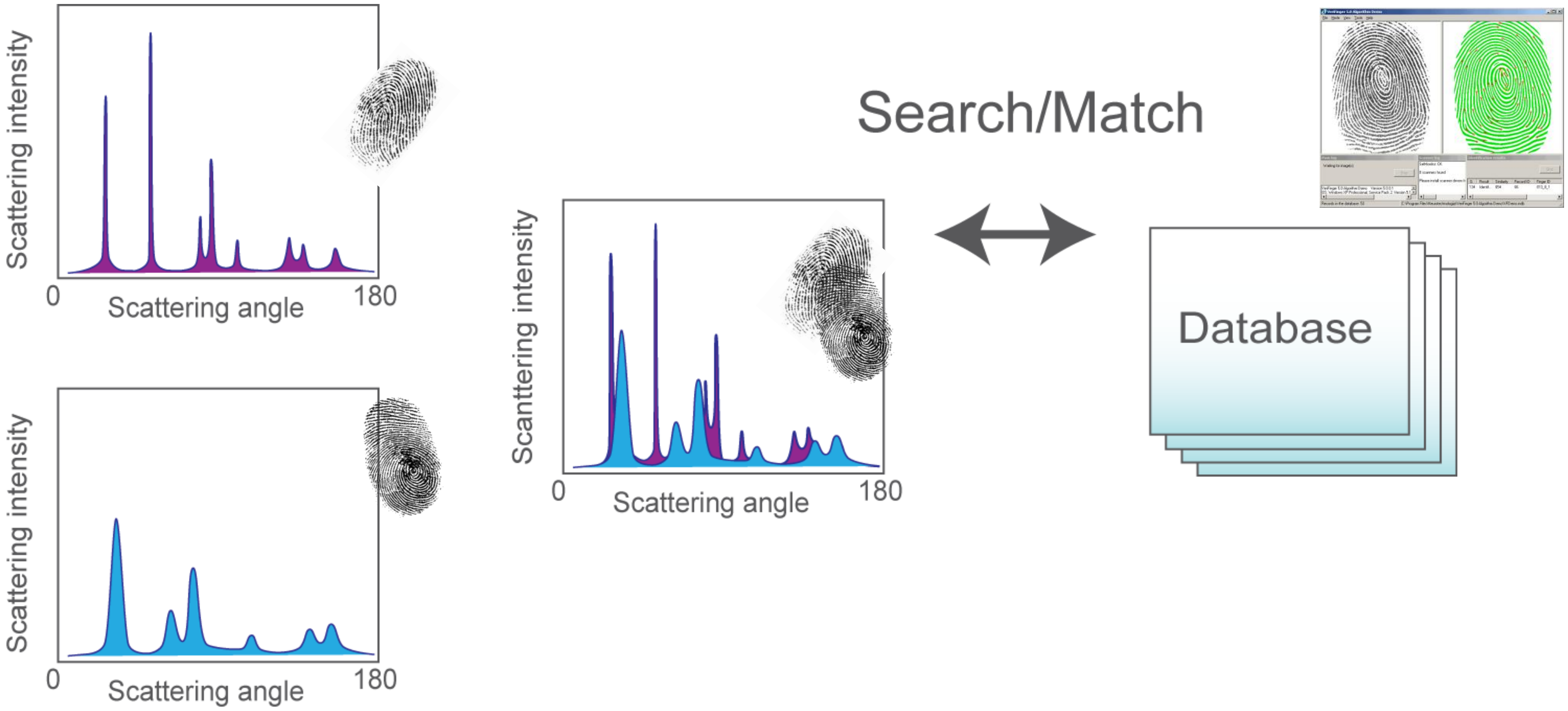
What is powder X-ray diffraction (XRD)?



Overall view of different analyses



Phase identification

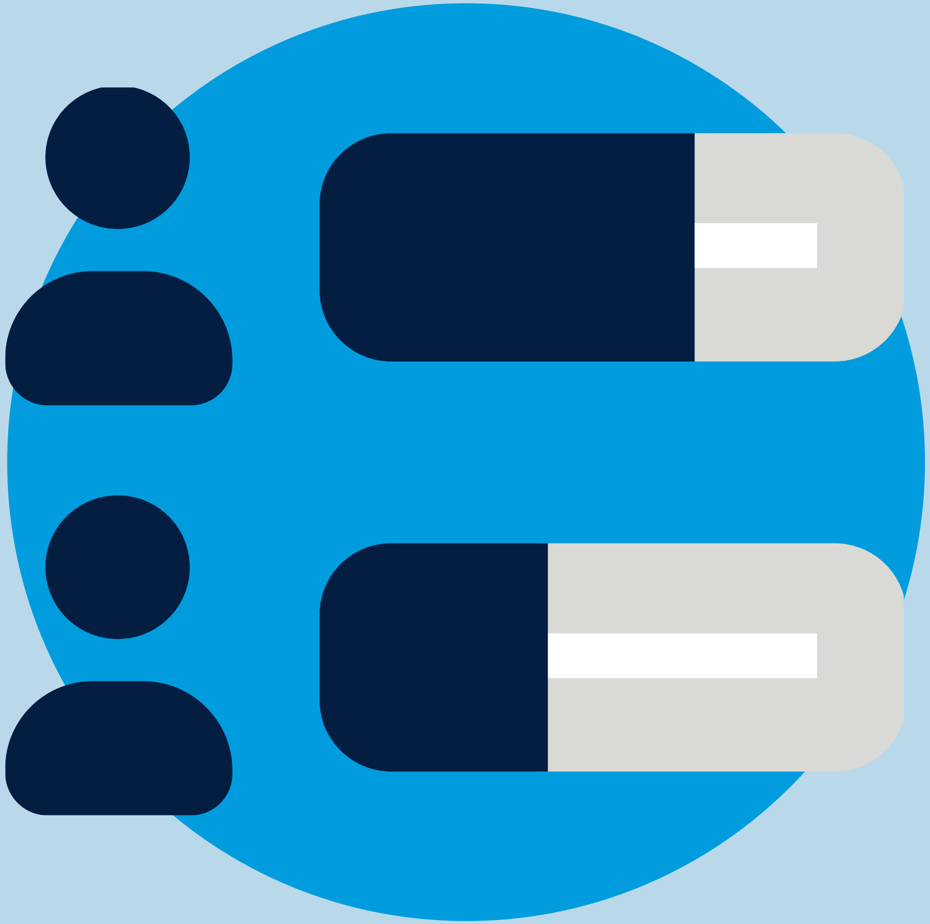


2. What are the most common quantitative XRD techniques?

Polling Question

#1 If you do quantitative analysis, what method do you currently use?

- ❖ Semi-quantitative methods (RIR)
- ❖ Whole powder pattern fitting (Rietveld) or DD
- ❖ Quantification using calibration curve
- ❖ Quantification of amorphous phases



Preparing sample for measurements

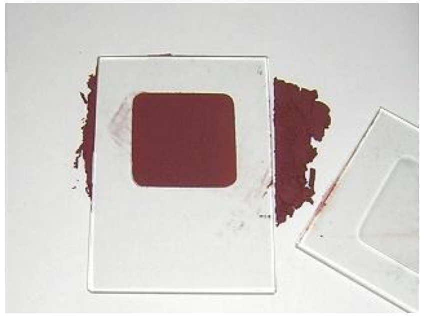
- ✓ The surface of the sample must be exactly level with the edge of the holder.
- ✓ The depression in the sample holder should be completely filled (unless you are using a low background holder).
- ✓ The particle size should be 10 - 40 µm (~ 635 mesh).
- ✓ The sample should be firmly packed.
- ✓ Footprint of X-ray
- ✓ Homogenously mixed sample
- ✓ Preferred orientation

Ref: A Practical Guide for the Preparation of Specimens for X-ray Fluorescence and X-ray Diffraction Analysis. V.E. Burke, R. Jenkins, D.K. Smith, 1998. ISBN: 0471194581.

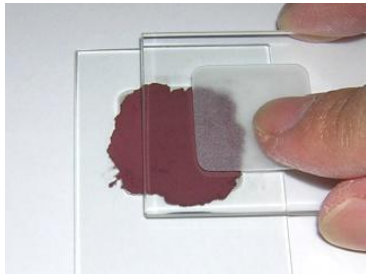
Sample preparation

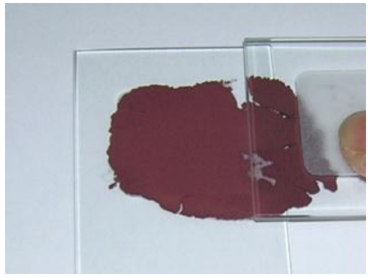
1. Pour the sample on the indented section of the holder.

3. Sample should be right up to the brim of sample holder

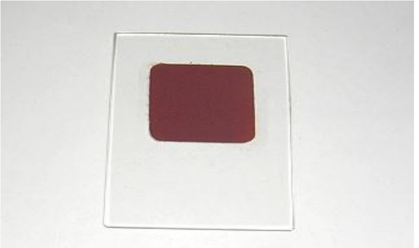


2. Spread and pack the sample evenly.

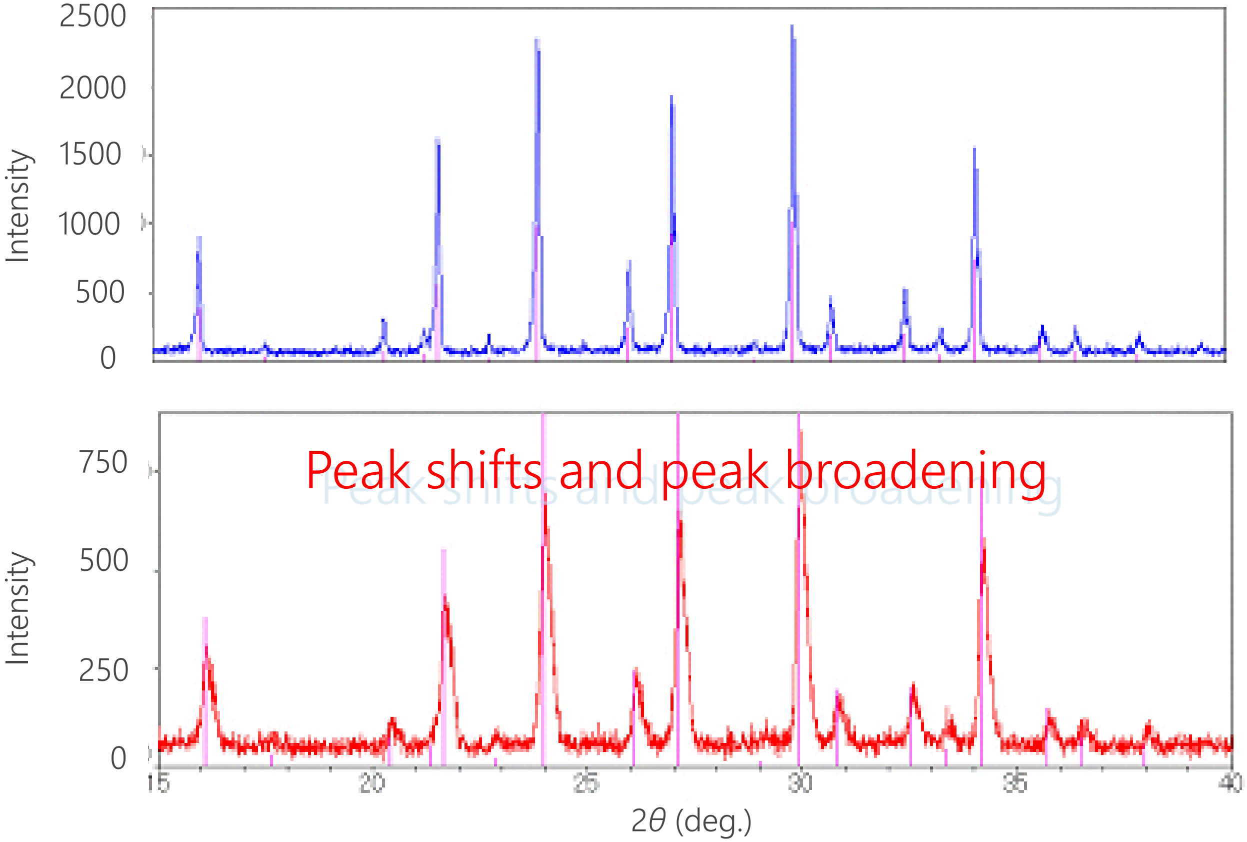




4. Clean the sample holder surface.



Sample displacement error: an example



Smooth & well packed surface

Rough surface

Comprehensive review of the quantitative XRD methods

- Semi-quantitative methods (RIR)
- Whole powder pattern fitting (Rietveld) and Direct Derivative (DD) analysis
- Quantification with calibration curve
- Quantification of amorphous phases

Examples of special quantitative applications

- Quantification of respirable silica (dust analysis)

  - Calculates contents of crystalline silica in workplace air or chrysotile asbestos in bulk sample

- Quantification of retained austenite

  - Calculates retained austenite in steel using X-ray diffraction intensities of α-iron and γ-iron.

When to use RIR or Rietveld or Calibration curve methods

RIR

- Easy to use, no crystal structure needed
- Relatively low accuracy
- Preferred orientation can cause incorrect results
- Not much useful when you have more than 4 phases

Rietveld

- Relatively high accuracy
- Reflection overlaps are best handled
- The effect of preferred orientation can be corrected
- Best when crystal structure of all phases are known
- Has a learning curve

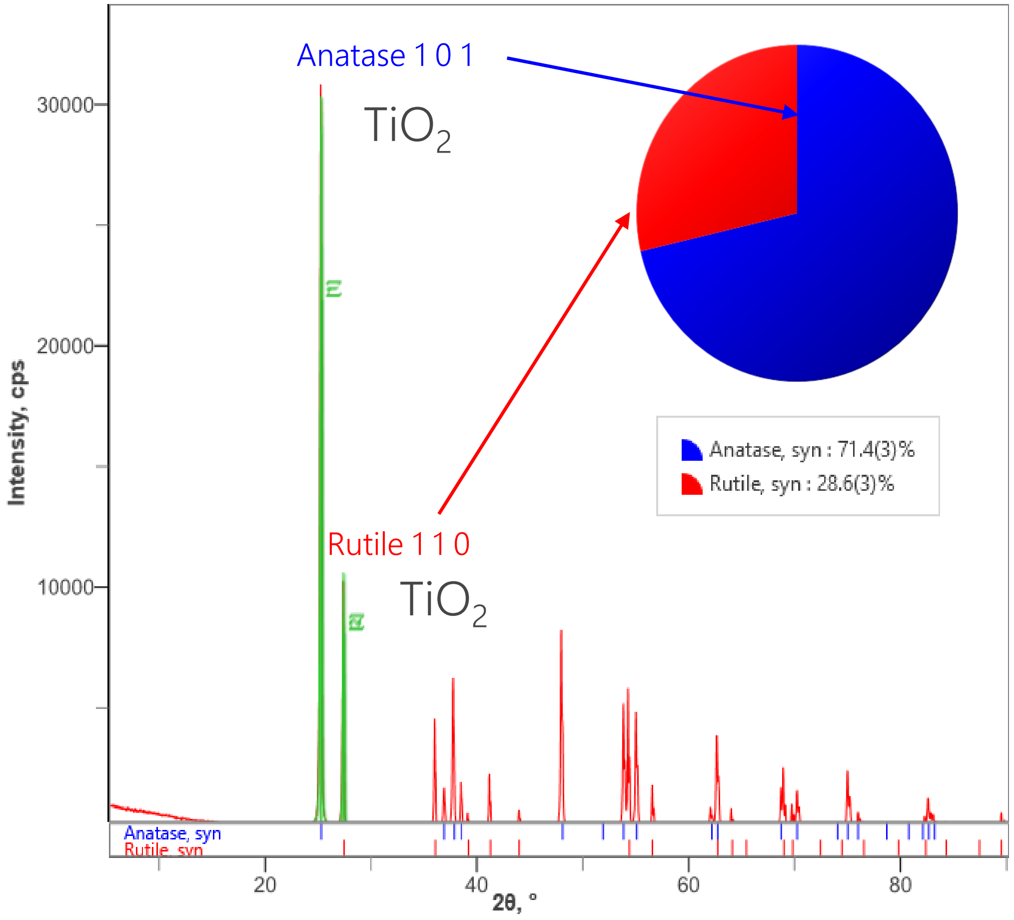
Calibration curve

- Highest accuracy
- Requires a set of calibration samples
- Constructing calibration curve can be time-consuming
- Absorption and matrix effect can cause errors

Relative intensity ratio (RIR) method

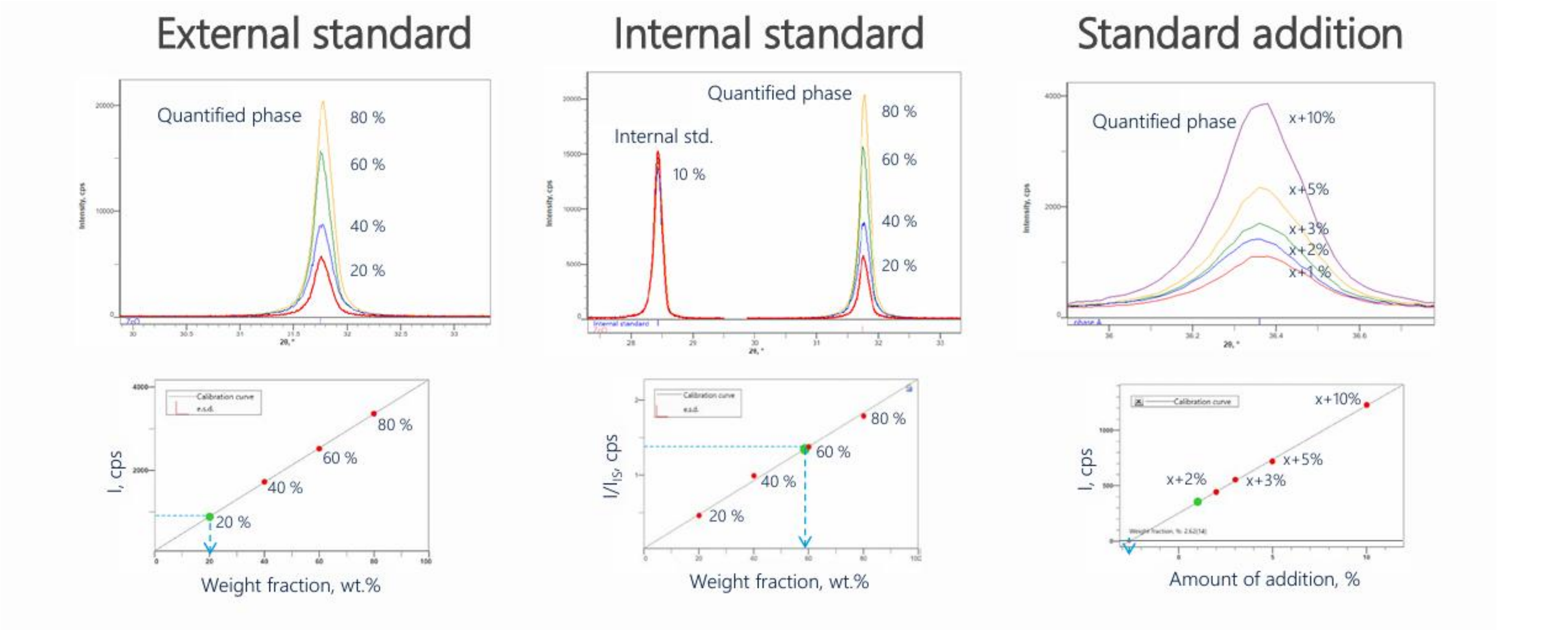
Semi-quantitative methods

- Quantitative values are calculated using RIR numbers from a database from the integrated intensity of the highest peak.

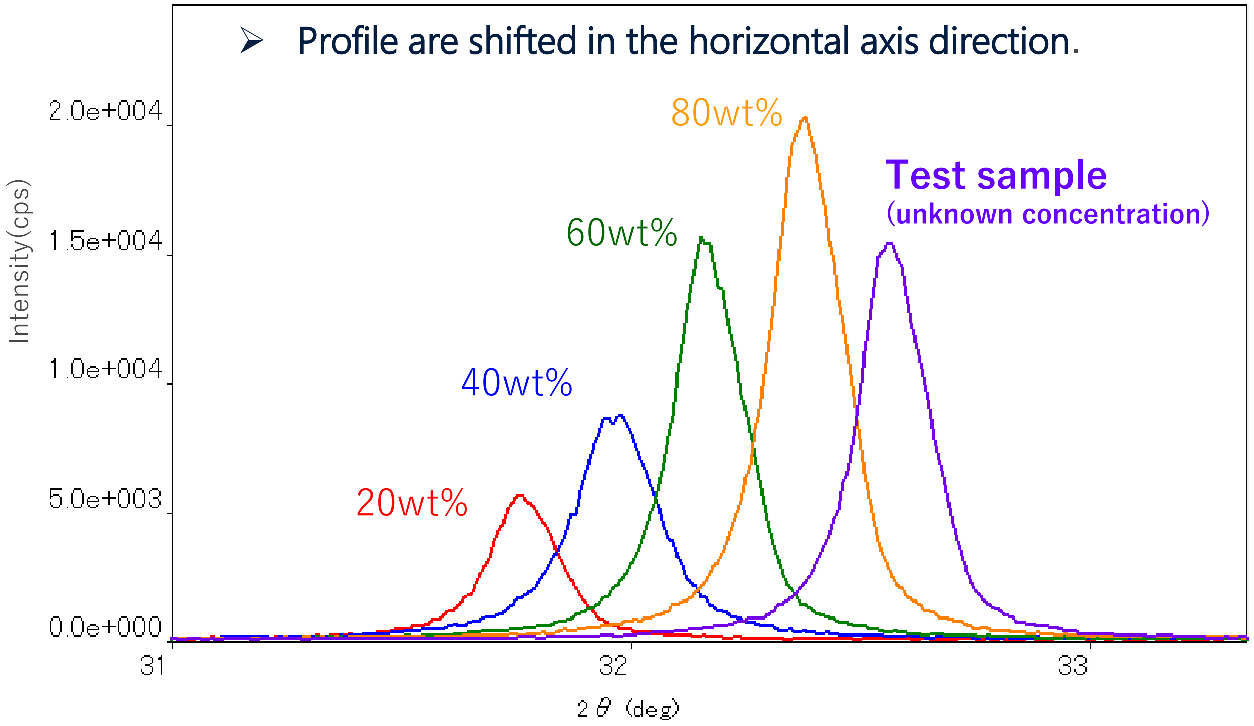


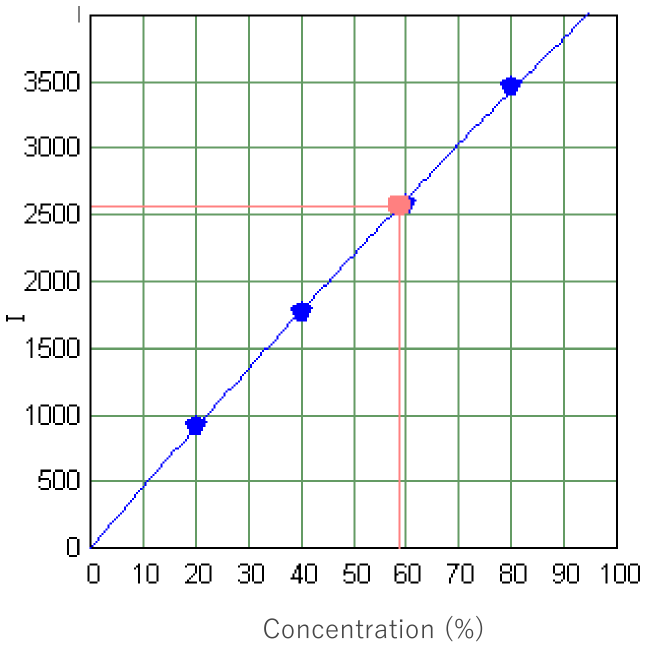
Calibration curve methods

Calibration curve methods details



External standard



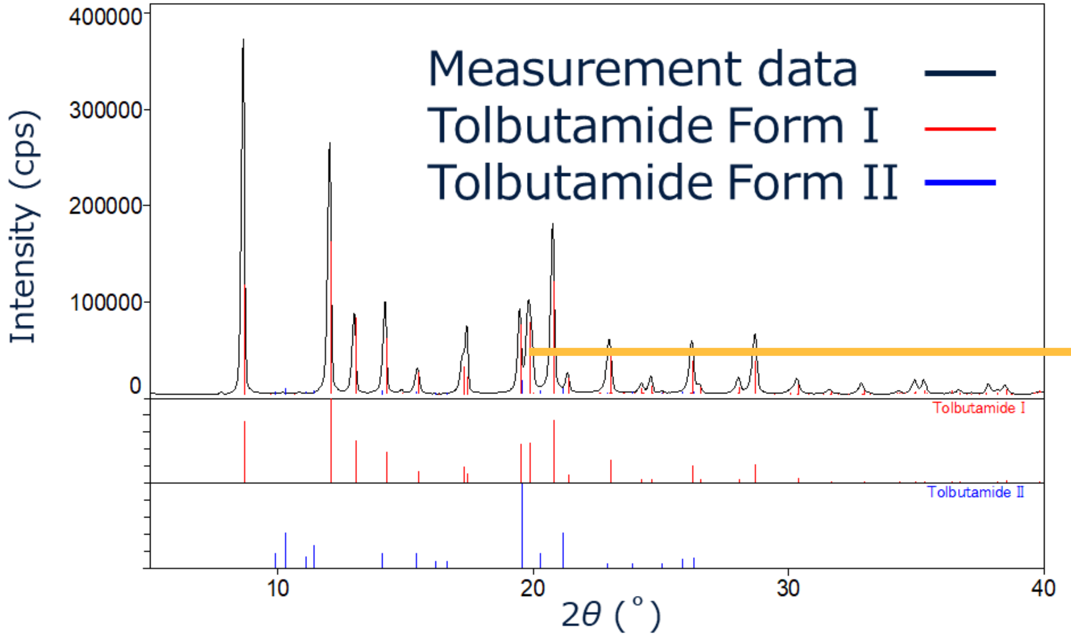


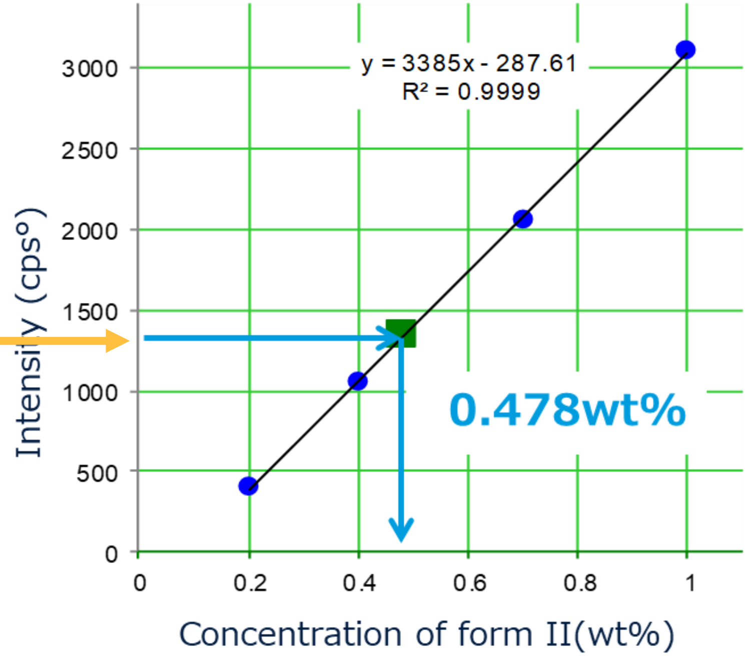
Test sample =58.6(5)wt%

External standard is a method of quantifying an unknown sample by creating the calibration curve with known samples.

Standard addition (spiking method)

Standard Addition (spiking) methods





How much is the form II wt %?

Whole powder pattern fitting (WPPF): Rietveld analysis

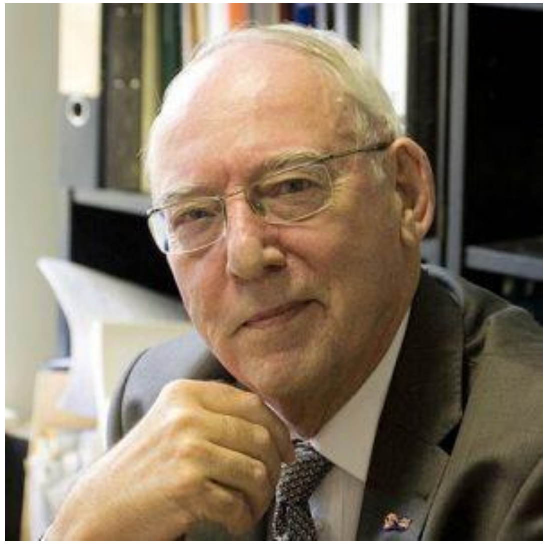
Rietveld analysis

- ❑ Non- linear least square function: $R = \Sigma W_i [Y_i^{obs.} - Y_j^{calc.}]^2$

$Y_i^{obs.}$ background-corrected observed counts

Y_i^{calc} calculated counts,

W_i is a weighting factor given by $1/Y_i^{obs.}$.

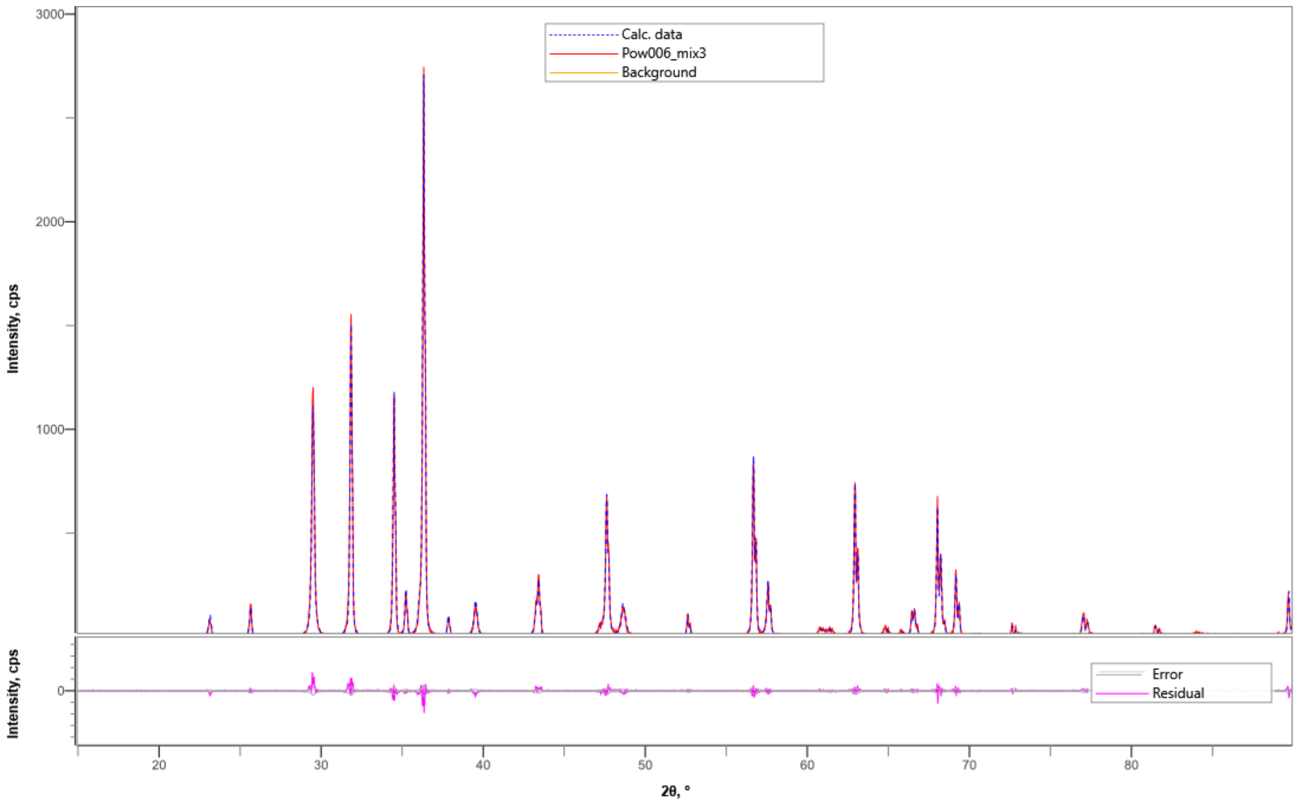


Dr. H. M. Rietveld

Rietveld, H. M. *J. Appl. Crystallogr.* 1969, *2*, 65.

Rietveld analysis

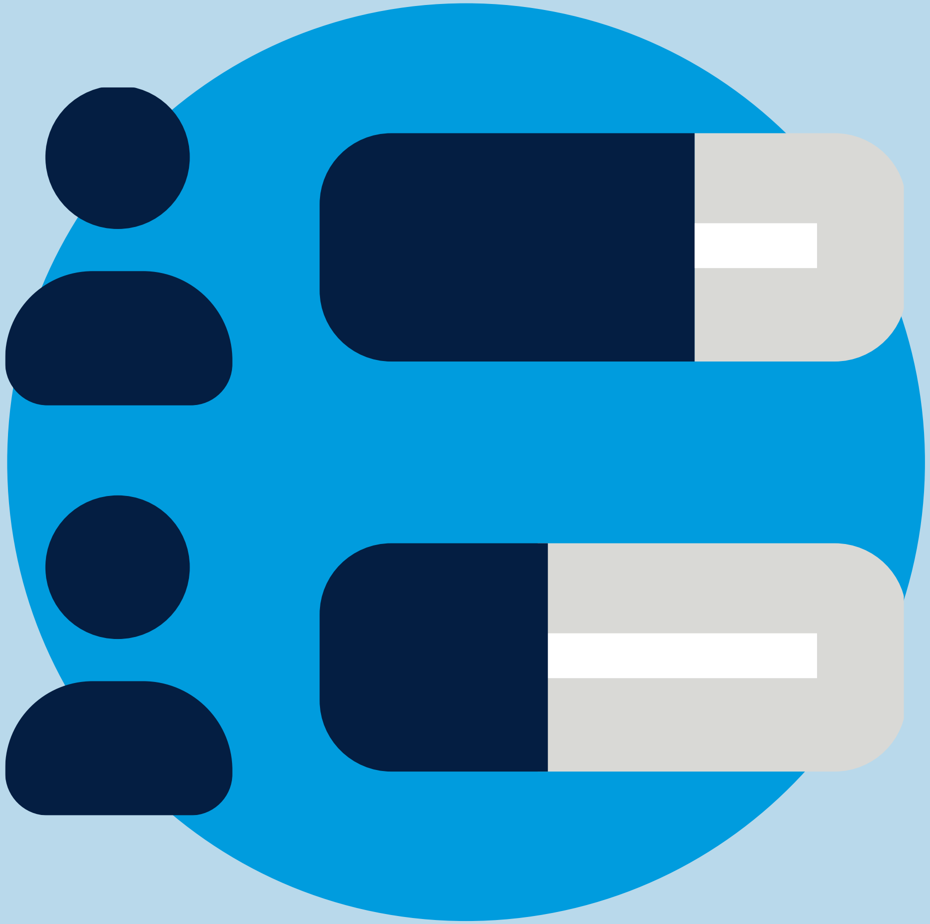
The least-squares refinements are carried out until the best fit is obtained between the **entire** observed powder diffraction pattern and the entire calculated pattern



Polling Question

If you do Quantitative Analysis how many Phases do you typically analyze?

1
2
3
4
5+



What makes a good Rietveld analysis?

1. **Measurement data**

   - ✓ Good 2θ range
   - ✓ Well grounded powder
   - ✓ It is essential that data be collected appropriately.
   - ✓ Do not try to smooth the diffraction data.
   - ✓ Do not remove background.

2. **Phase identification (crystal structure information)**

Crystal structure and diffraction data

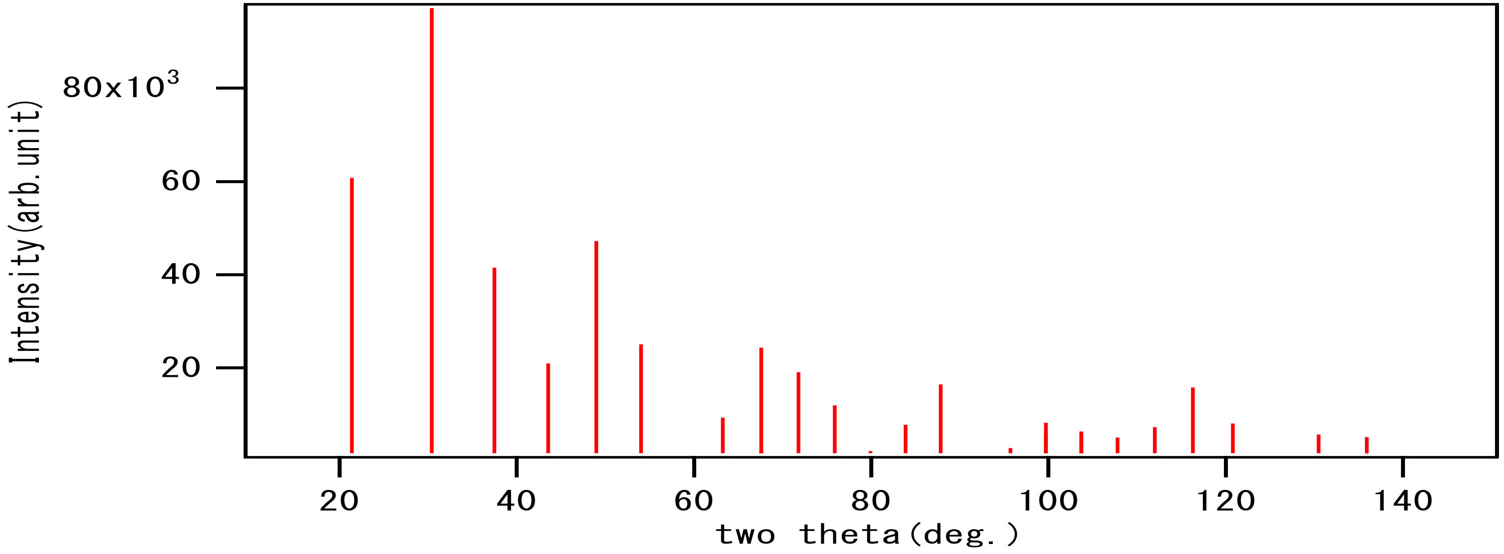
XRD Feature	What it Represents	Controlled By
Position (2θ)	Crystal structure	Crystal system, space group, lattice parameters
Width (FWHM)	Microstructure	Crystallite size, lattice strain, defects
Intensity	Atomic arrangement	Atomic positions, occupancy, composition, thermal vibration

Integrated intensities

- Structure factor:

$$F_{hkl} = \sum_{j}^{atom} f_0^j\left(\frac{\sin\theta_{hkl}}{\lambda}\right)\exp\{2\pi i(h\cdot x_j + k\cdot y_j + l\cdot z_j)\}$$

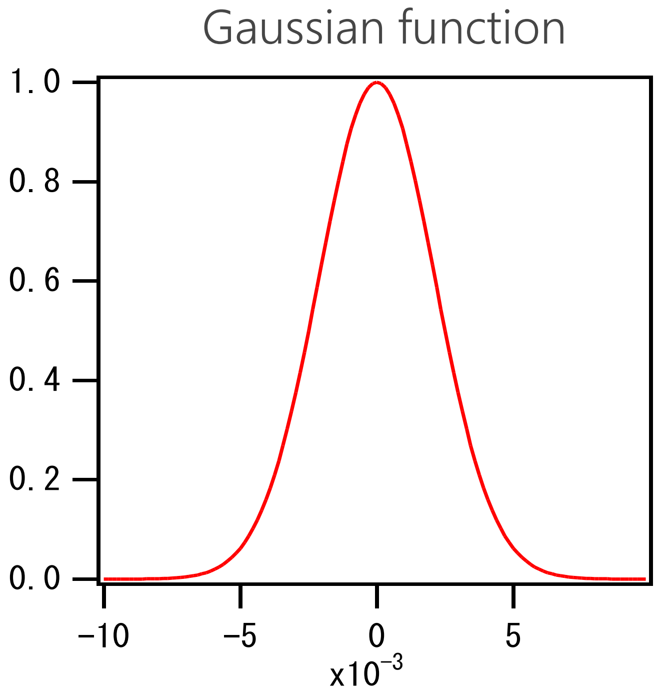
Symbol	Meaning
F_{hkl}	Structure factor
j	Atom index
f_j^0	Atomic scattering factor
θ_{hkl}	Bragg angle
λ	X-ray wavelength
h, k, l	Miller indices
x_j, y_j, z_j	Atomic positions
exp term	Phase factor (interference)

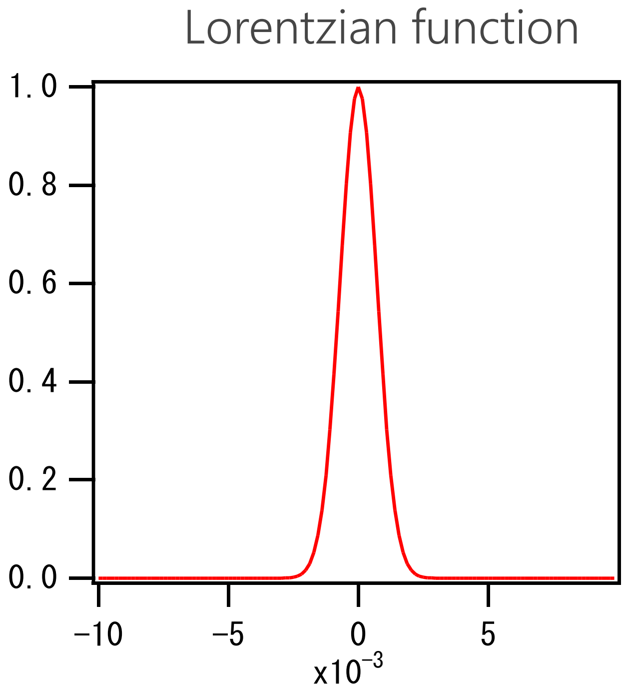


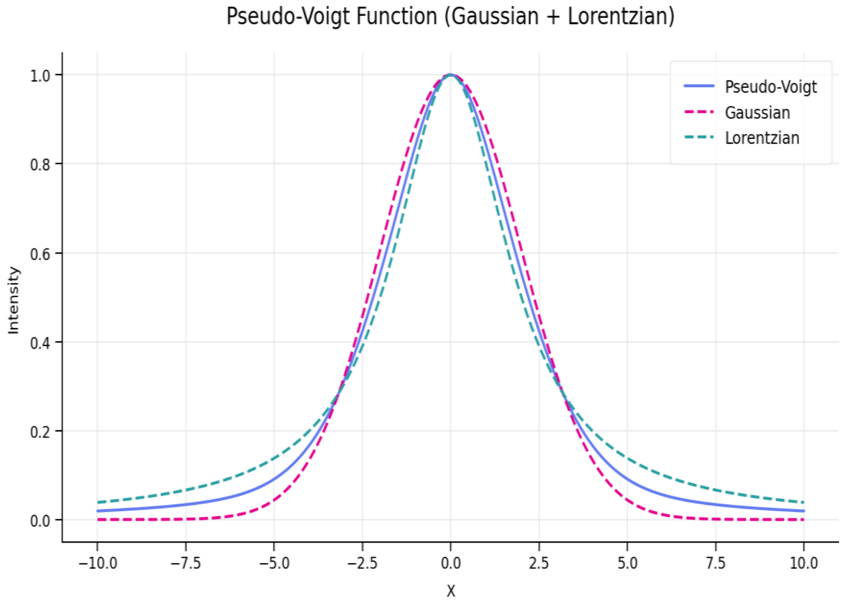
- Integrated Intensities:

$$I_{hkl} \propto |F_{hkl}|^2$$

Profile shape functions

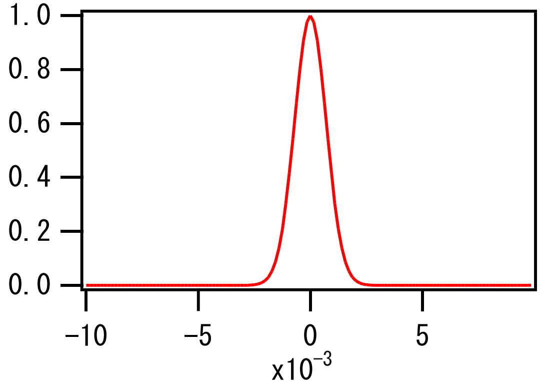




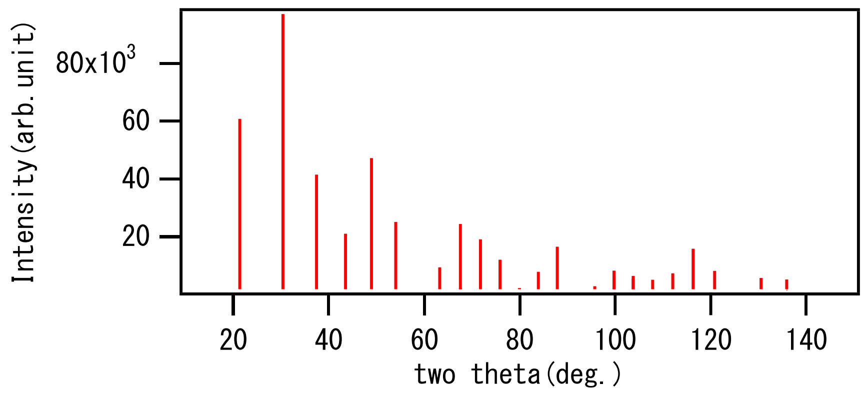


Calculated diffraction pattern

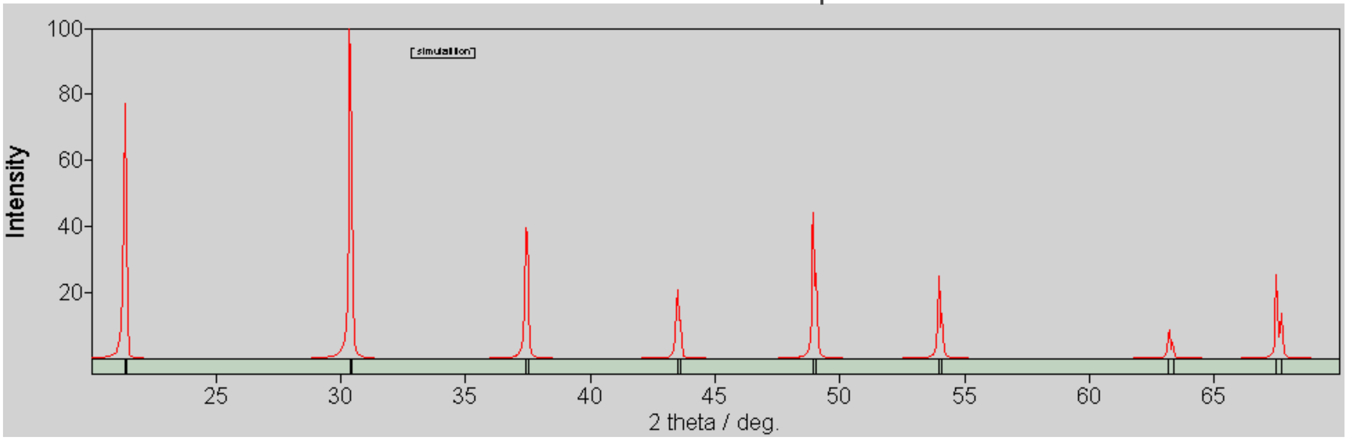
Profile function



Integrated intensities



Calculated diffraction pattern

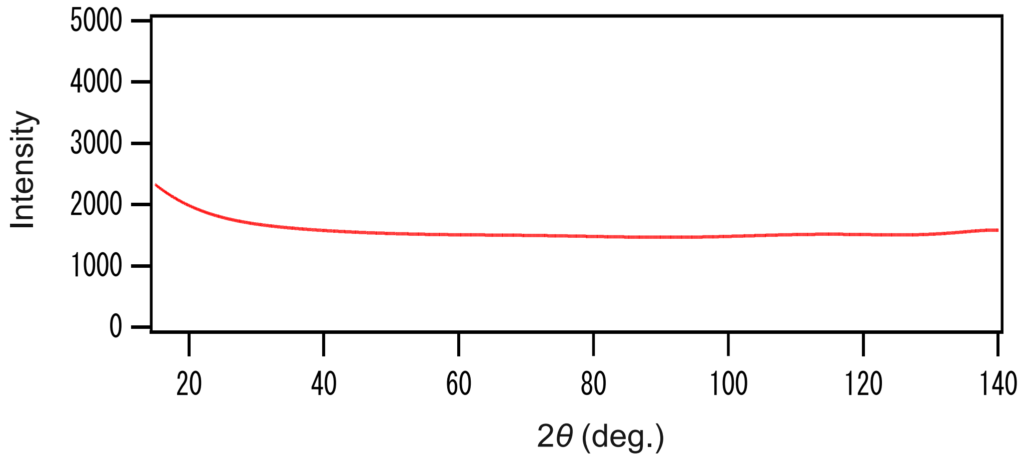


Background

- Compton scattering etc.
- Amorphous phase
- Sample holder and capillary
- Electrical noise of counting circuit

e.g. Polynomial background curve

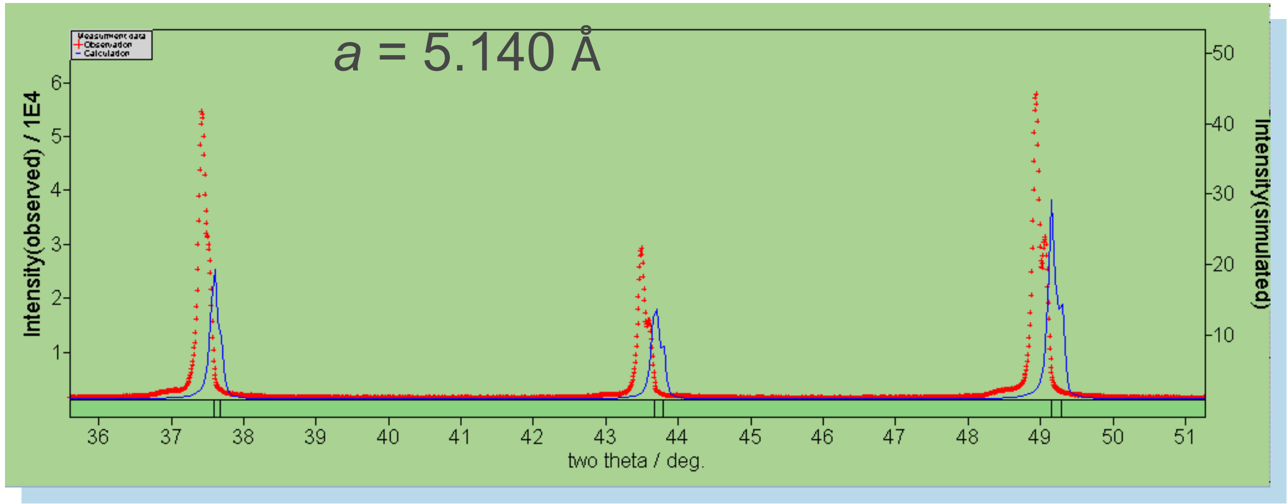
$$y_b(2\theta_i) = B_0 + B_1 \cdot 2\theta_i + B_2 \cdot 2\theta_i^2 + \cdots + b_n \cdot 2\theta_i^n$$

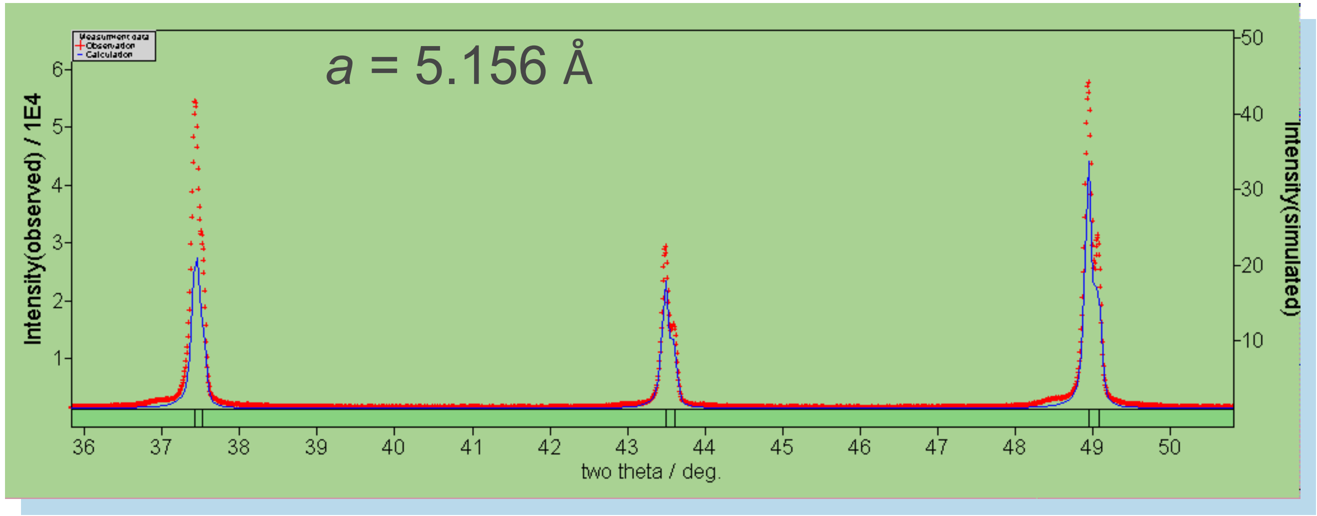


Refinable parameters

- ❑ Crystal structure parameters
  - Lattice constant (Peak positions)
  - Atomic coordinates (Peak intensities)
- ❑ Profile parameters (Peak shape)
- ❑ Background parameters (Background shape)
- ❑ Thermal parameters (Temperature factors)
- ❑ Occupancies
- ❑ Preferred orientation function

Lattice parameter





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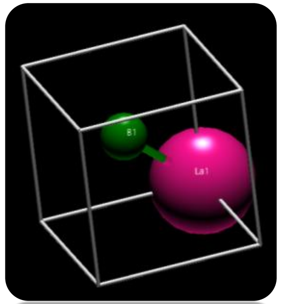
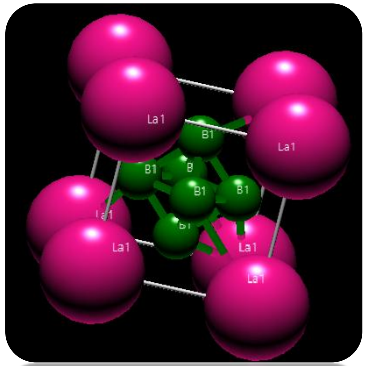
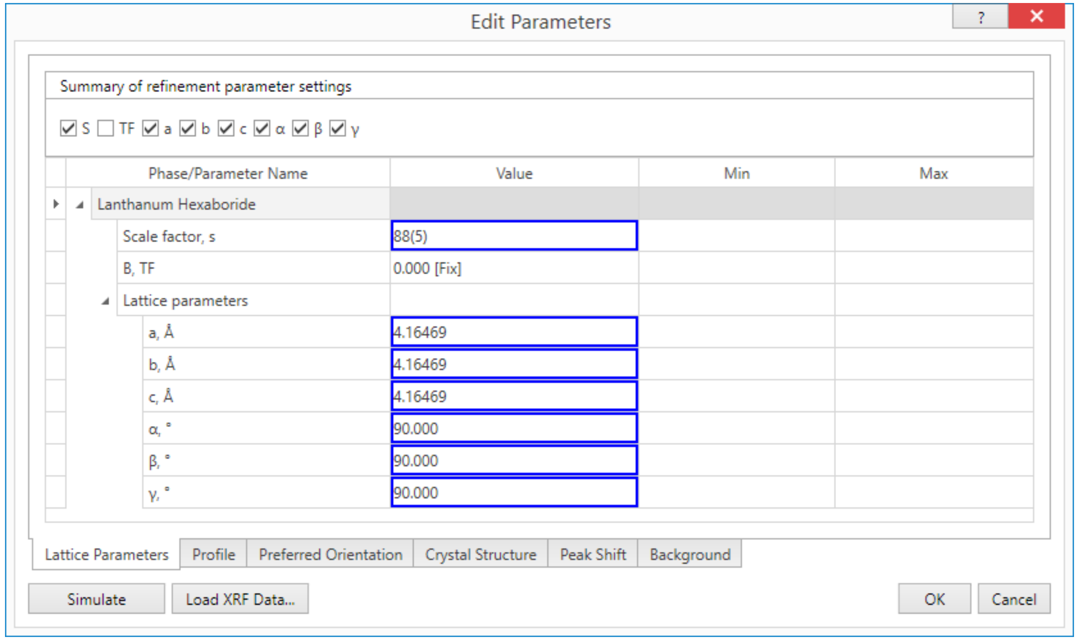
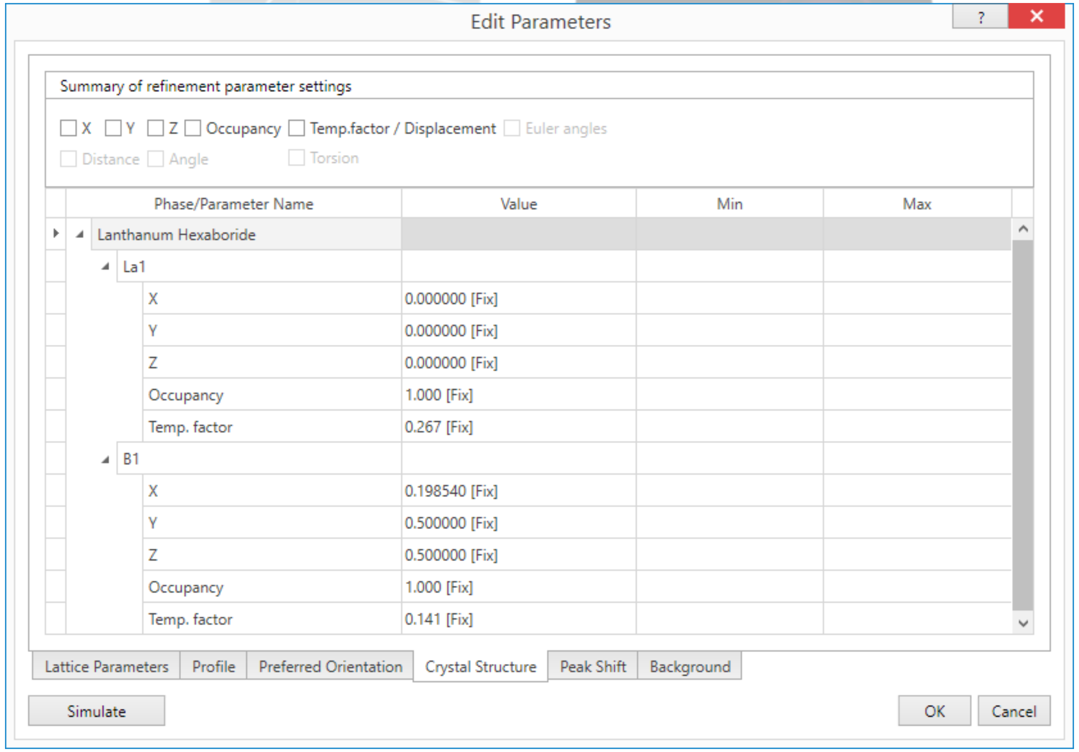
Atomic coordinates

Coordinates, unit cell, and scale factors

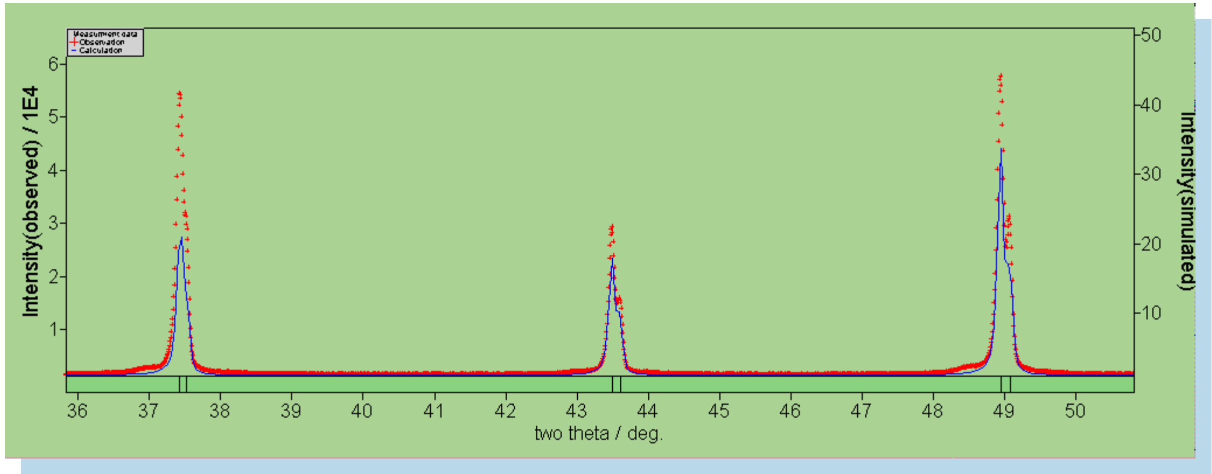


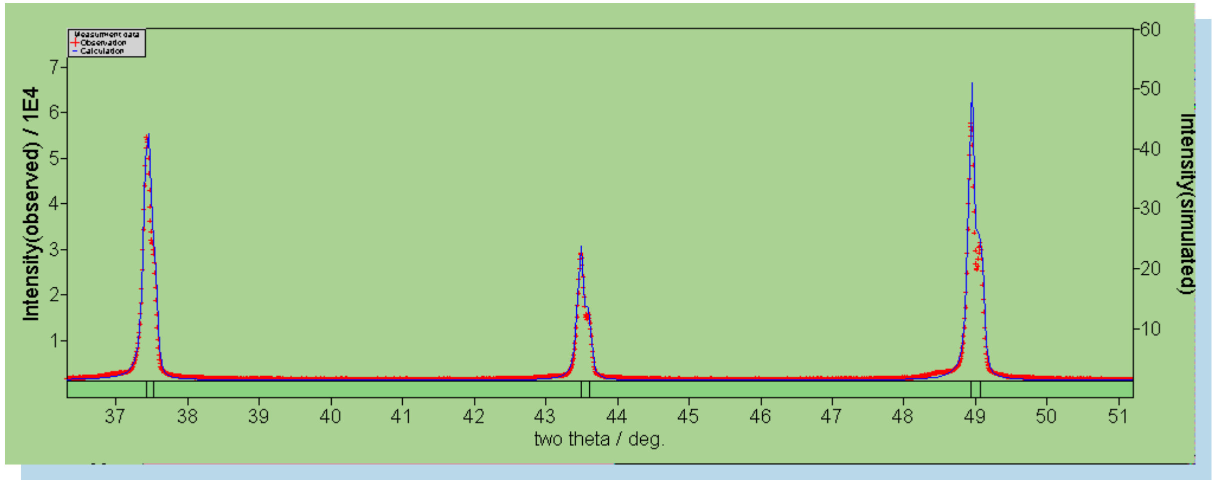






Atomic coordinates





Finally, the Rietveld refined model (SLSII pic)

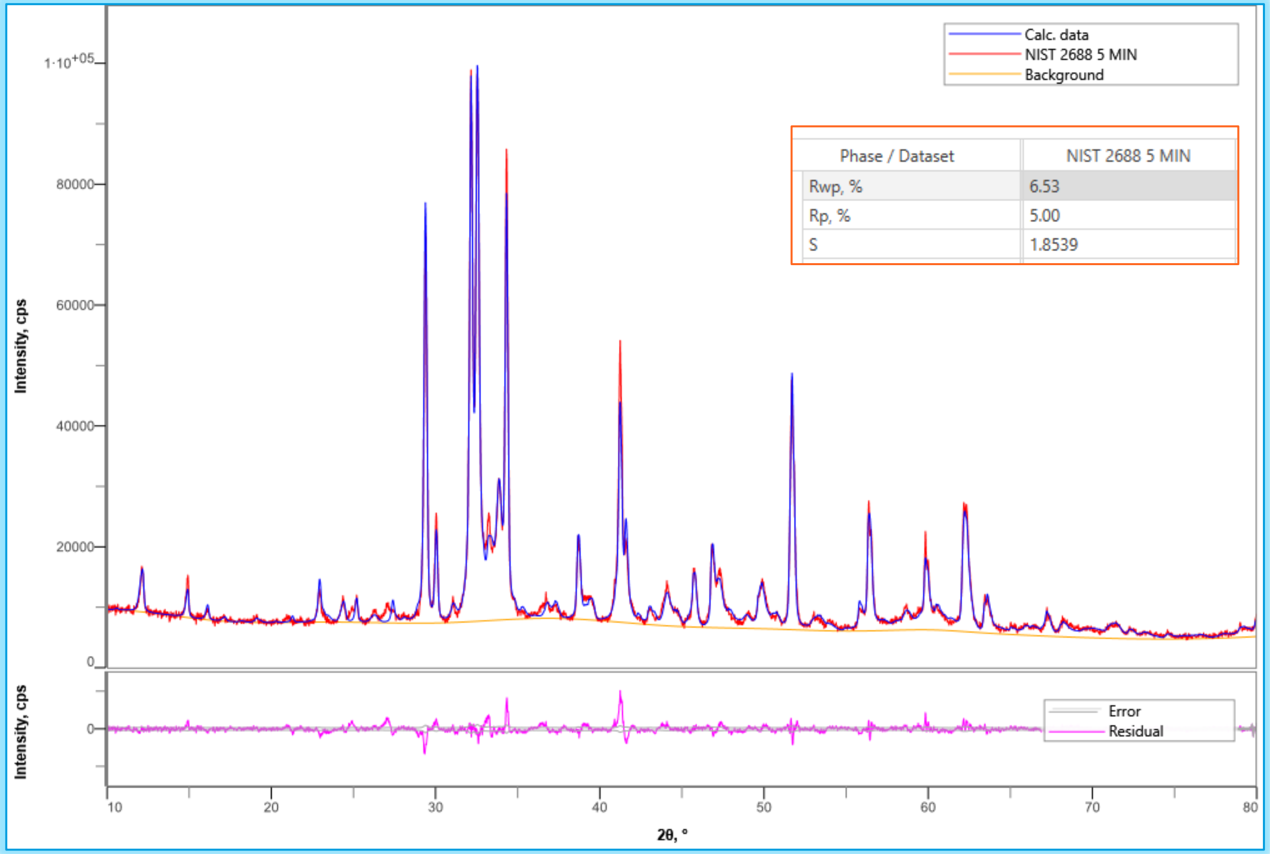
Refinement method: Least square

Refining parameter settings

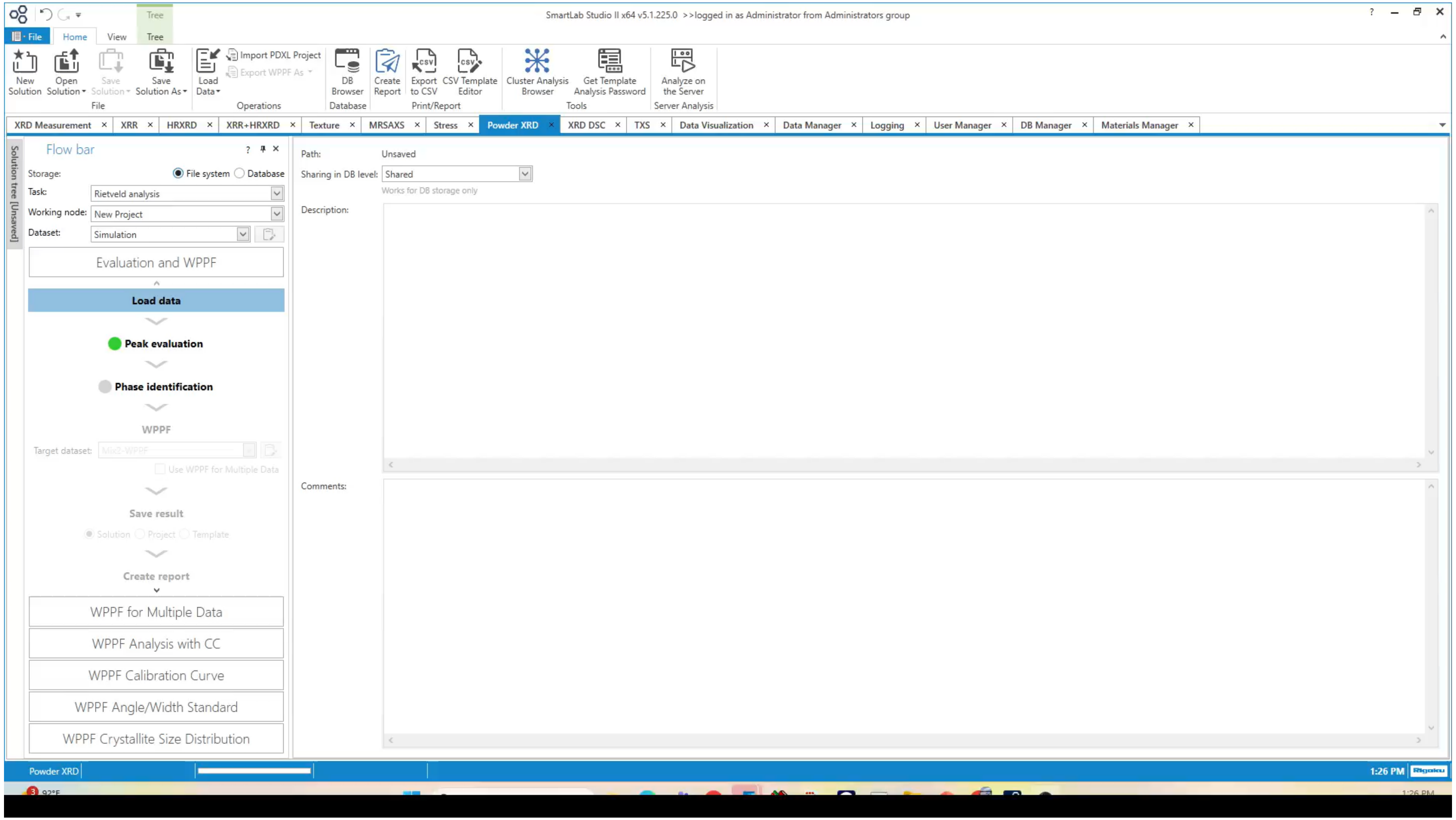
Phase Name	Scale	Lattice	Profile	Texture	Structure	Method
C3S-Mono.	Refine	Refine	Refine	Fix	Fix	Rietveld/d-I pattern
C3A-Cubic	Refine	Refine	Refine	Fix	Fix	Rietveld/d-I pattern
C4AF-Ortho.	Refine	Refine	Refine	Fix	Fix	Rietveld/d-I pattern
C2S-Mono.	Refine	Refine	Refine	Fix	Fix	Rietveld/d-I pattern

Model function

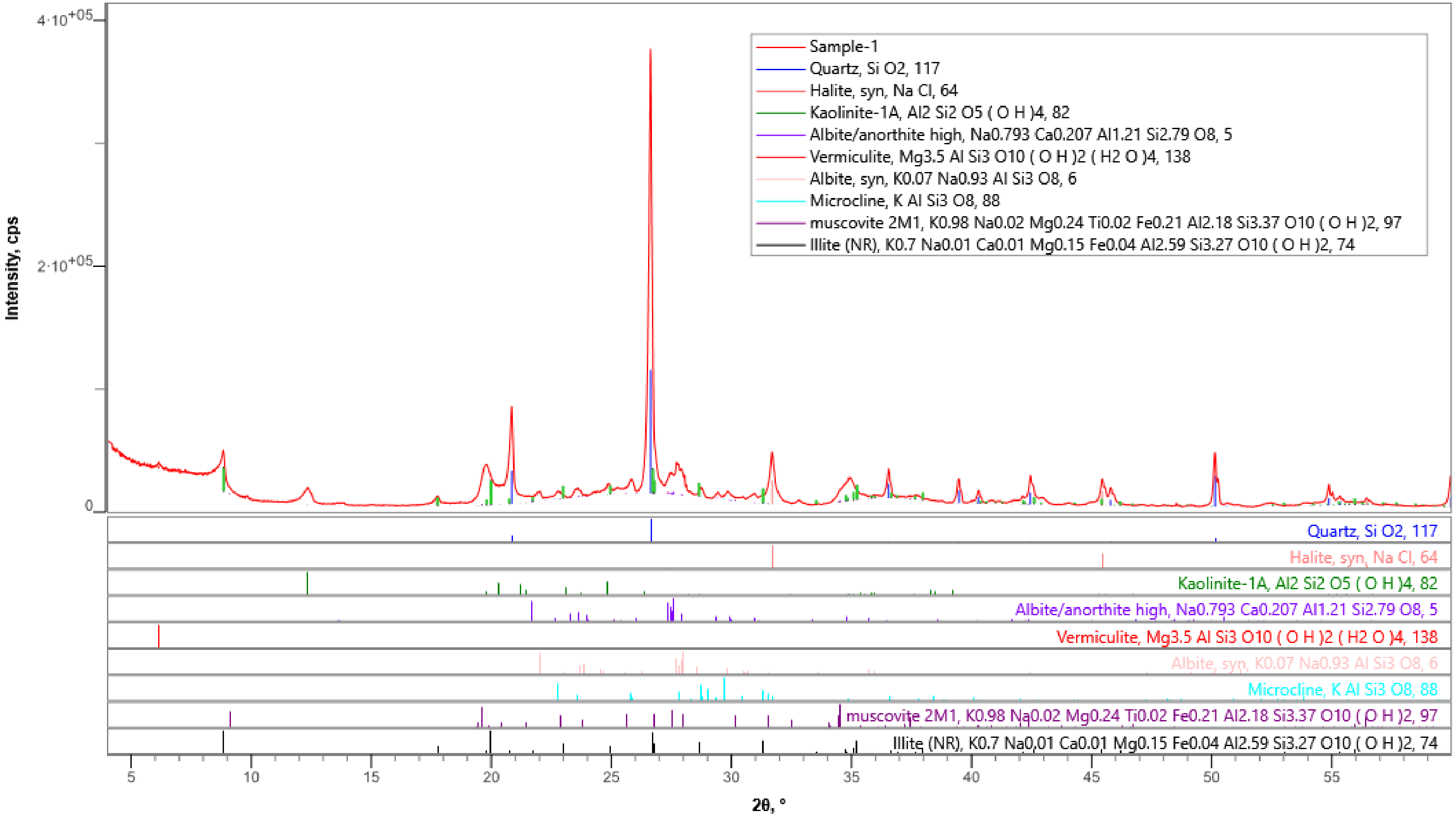
Model Name	Function Name	Degree
Background	B-spline	-
Peak shift	Shift axial displac...	-
Profile type	Split pseudo-...	-



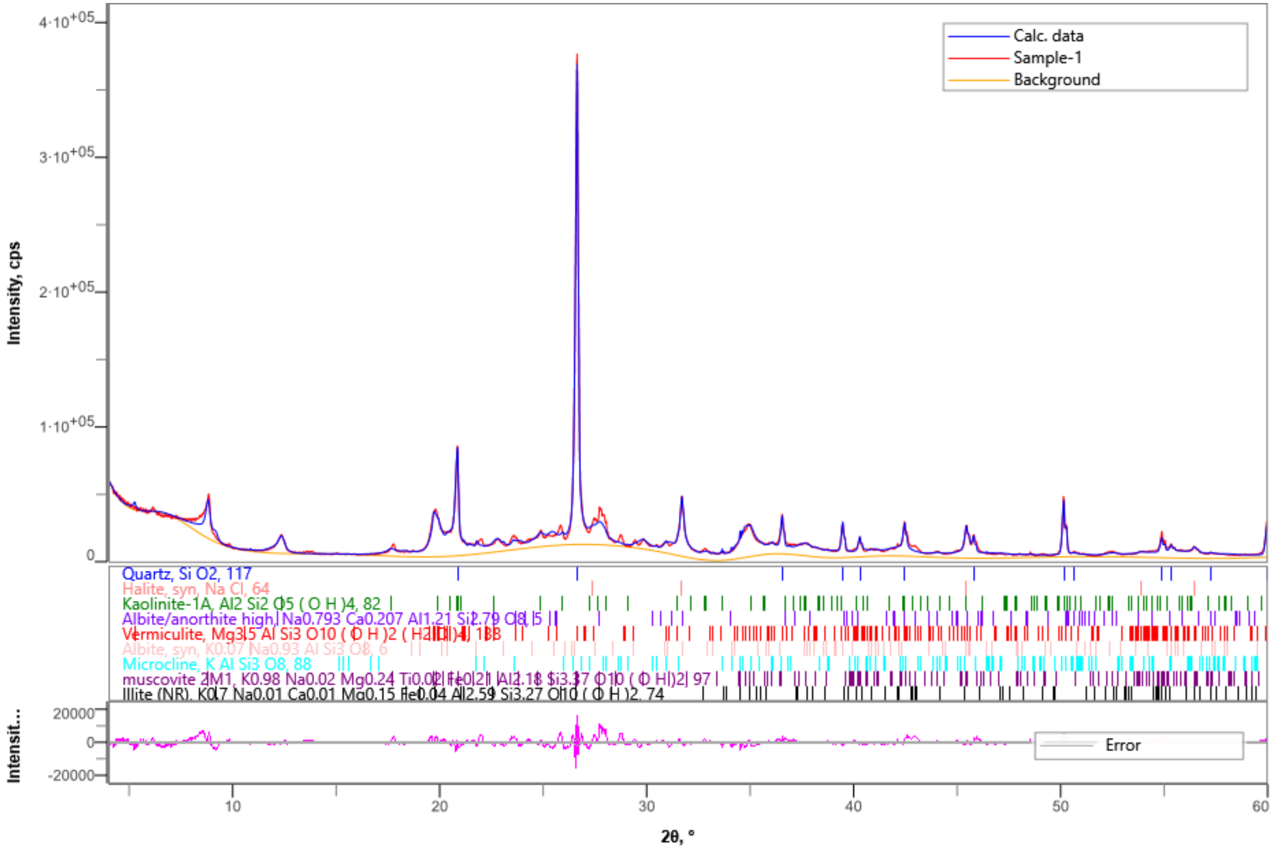
Quantitative techniques: Rietveld analysis

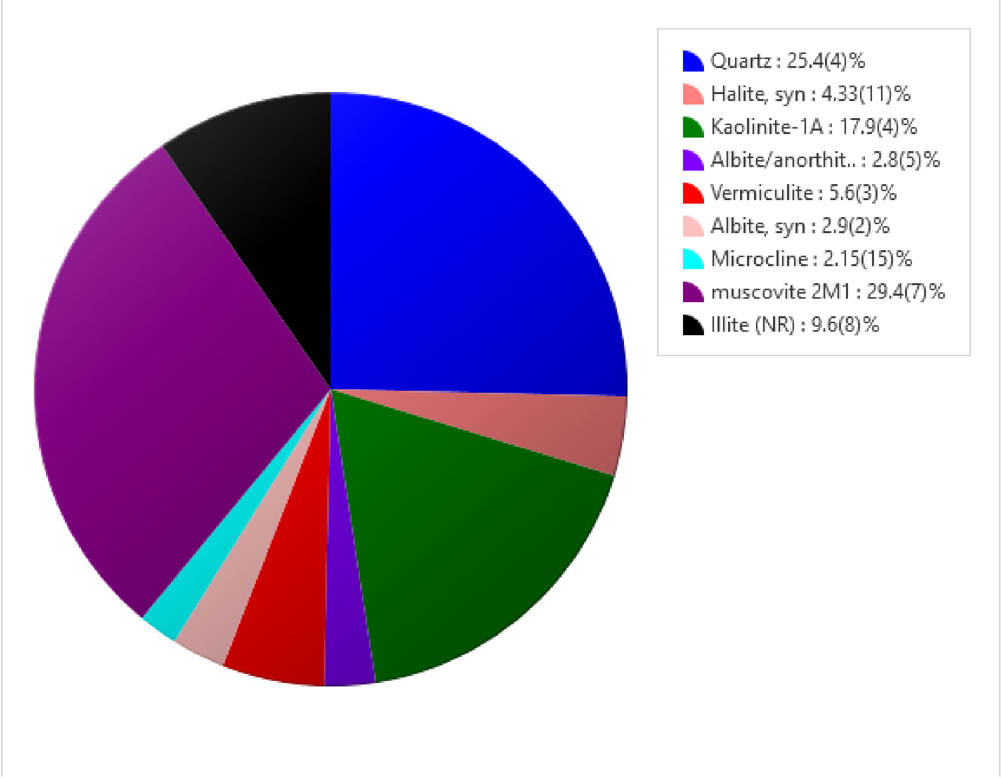


Phase identification: Sample-1 - Clay/mineral



Rietveld Quantification: Sample – Clay/mineral





3. Choosing the right method

When to use RIR or Rietveld or Calibration curve methods

RIR

- Easy to use, no crystal structure needed
- Relatively low accuracy
- Preferred orientation can cause incorrect results
- Not much useful when you have more than 4 phases

Rietveld

- Relatively high accuracy
- Reflection overlaps are best handled
- The effect of preferred orientation can be corrected
- Best when crystal structure of all phases are known
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Calibration curve

- Highest accuracy
- Requires a set of calibration samples
- Constructing calibration curve can be time-consuming
- Absorption and matrix effect can cause errors

Questions?

Direct Derivative (DD) method

Basic principle behind the method

$$\sum |F_{hkl}|^2 \propto \sum \rho^2$$

- $\sum |F_{hkl}|^2$: Sum of square of structure factor
  - Integrated intensity of all diffraction peaks, which includes corrections, e.g. LP and absorption.
- $\sum \rho^2$: Sum of square of electron density
  - Total number of electrons is proportional to total weight of atoms

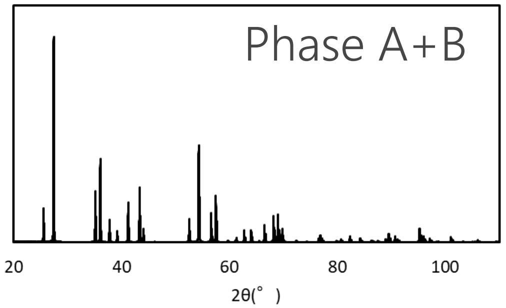
➔ The weight fraction is calculated by the chemical formula and the integrated intensity.

Hideo Toraya (2016), *J. Appl. Cryst.*, **49**, 1508-1516.

The DD method

"Extracted" profiles with or without background of each phase are fixed and scale factors are refined

Experimental data – (BKG)



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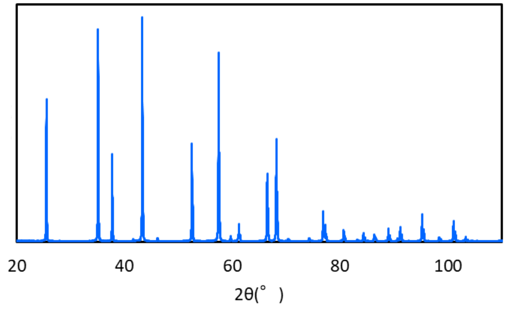
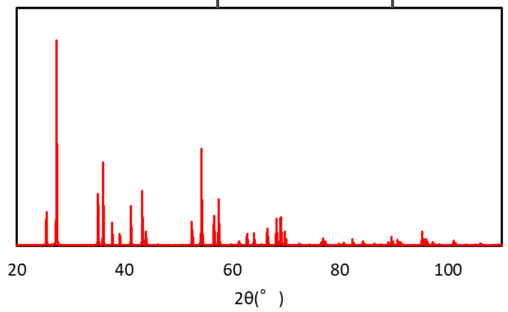
Extracted phase A profile



Fixed

Extracted phase B profile



$\times\ Scale\ factor_A$

Refined

$\times\ Scale\ factor_B$

DD Method: in a nutshell

- The DD method requires either single-phase XRD patterns with defined chemical formulas or the deconvolution/extraction of individual phase profiles from complex multi-phase diffraction data.

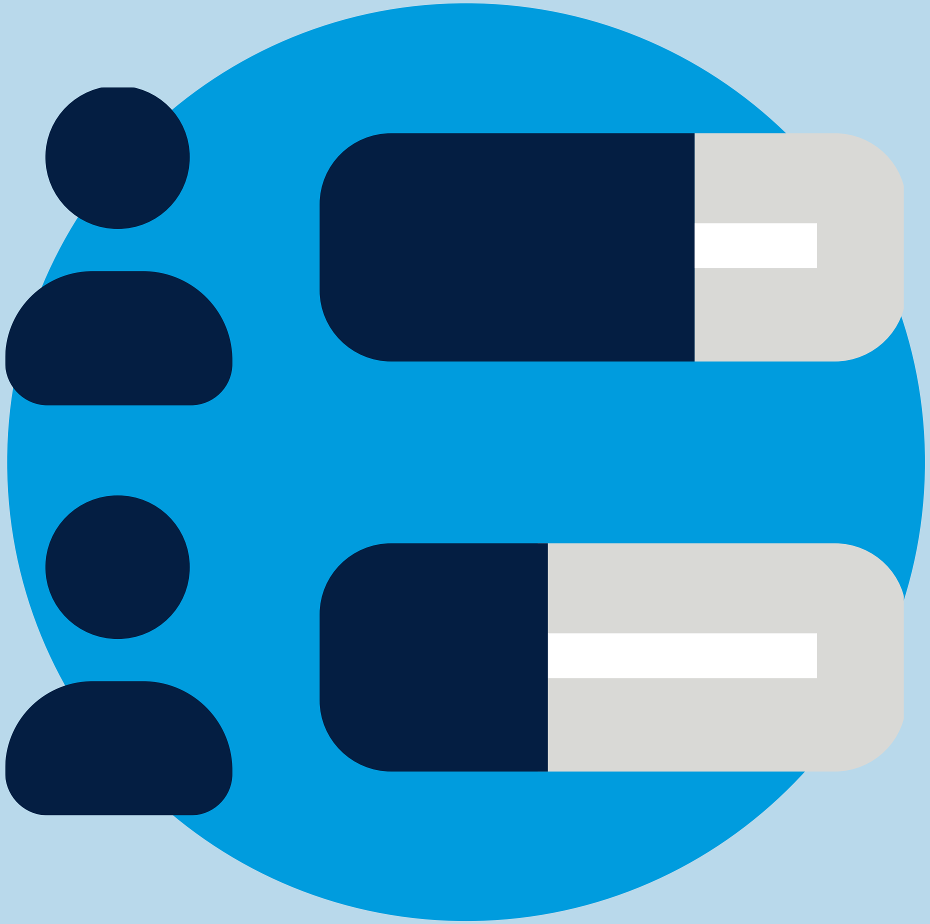
- **Where DD method helps: Application examples**

1. Textured or large crystallite size sample
2. Crystal structure database or RIR isn't available
3. Amorphous or trace phase, where WPPF is difficult to be applied

Polling Question

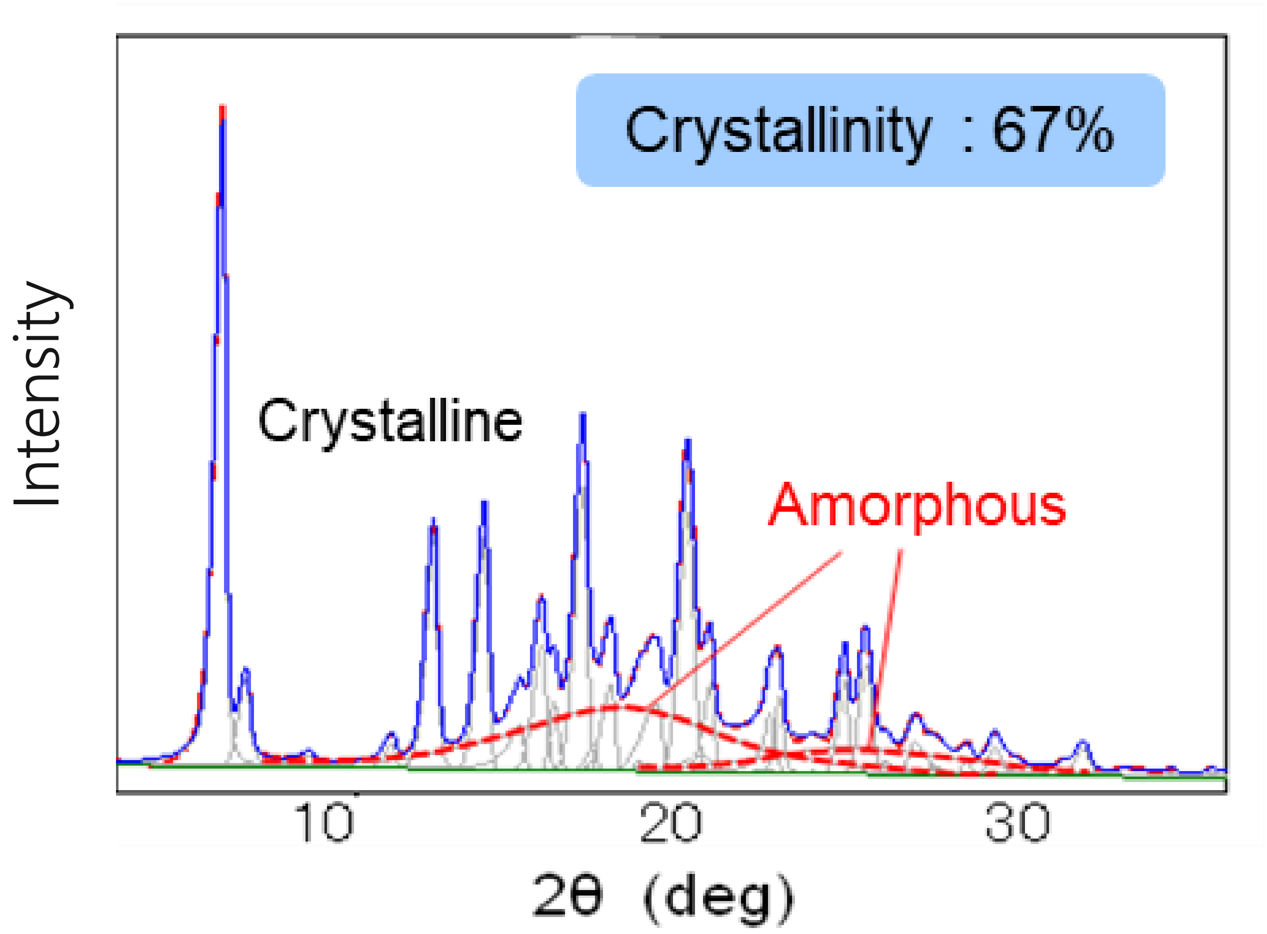
Have you ever used the DD method?

1. Yes
2. No
3. Haven’t heard of it before this webinar



Quantification of amorphous phases

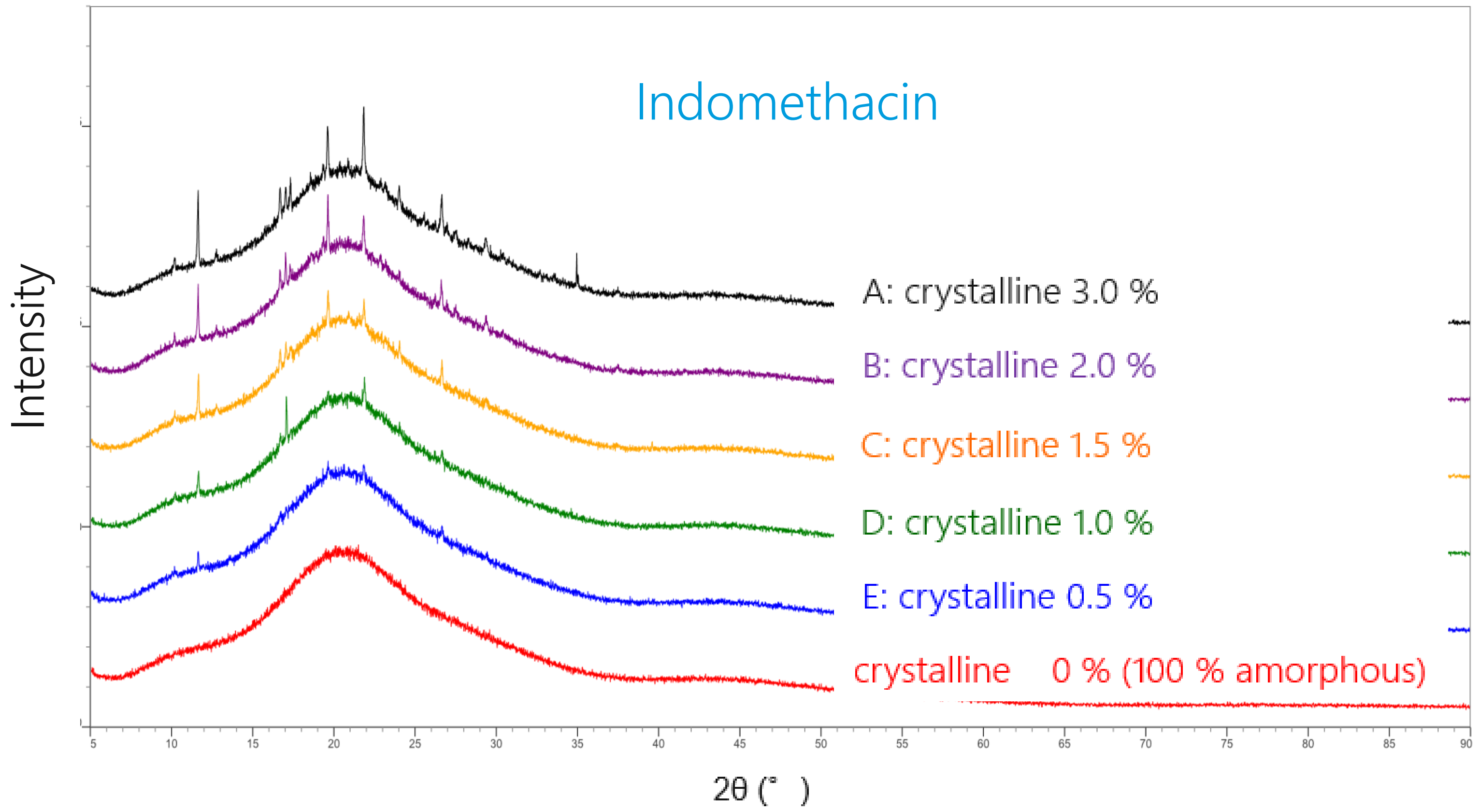
Percent crystallinity



How much is the crystallinity?

Limit of quantitation (LOQ)

Amorphous quantification by DD method type C_2 function

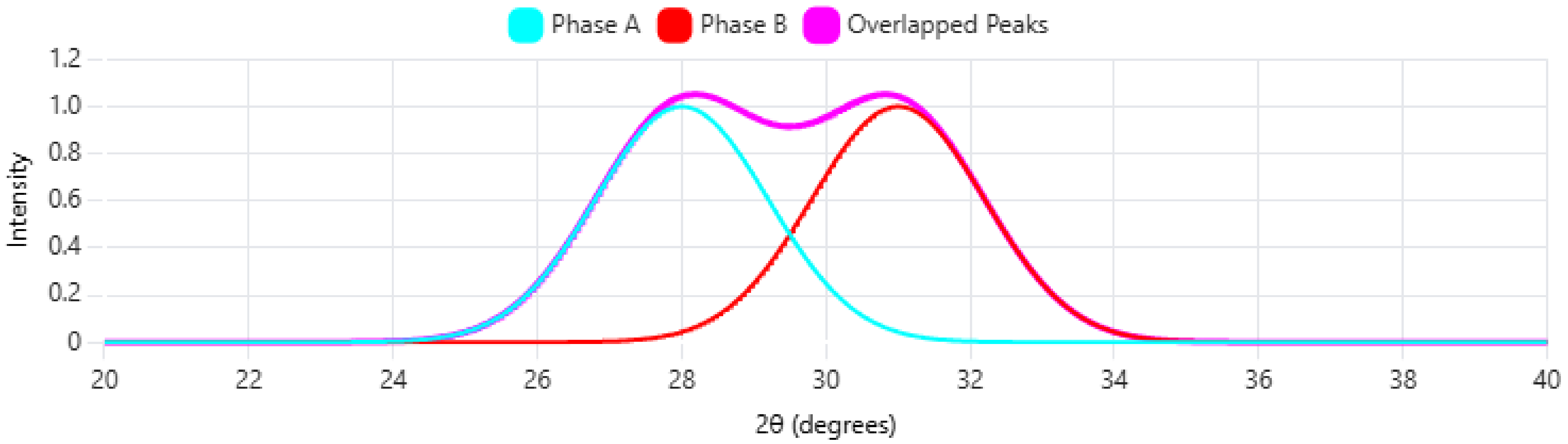


Crystalline phase (wt. %)		
Sample	Expected	Measured
A	3.0	3.20 (4)
B	2.0	2.18 (4)
C	1.5	1.65 (4)
D	1.0	1.09 (4)
E	0.5	0.71 (3)

4. Common mistakes and solutions

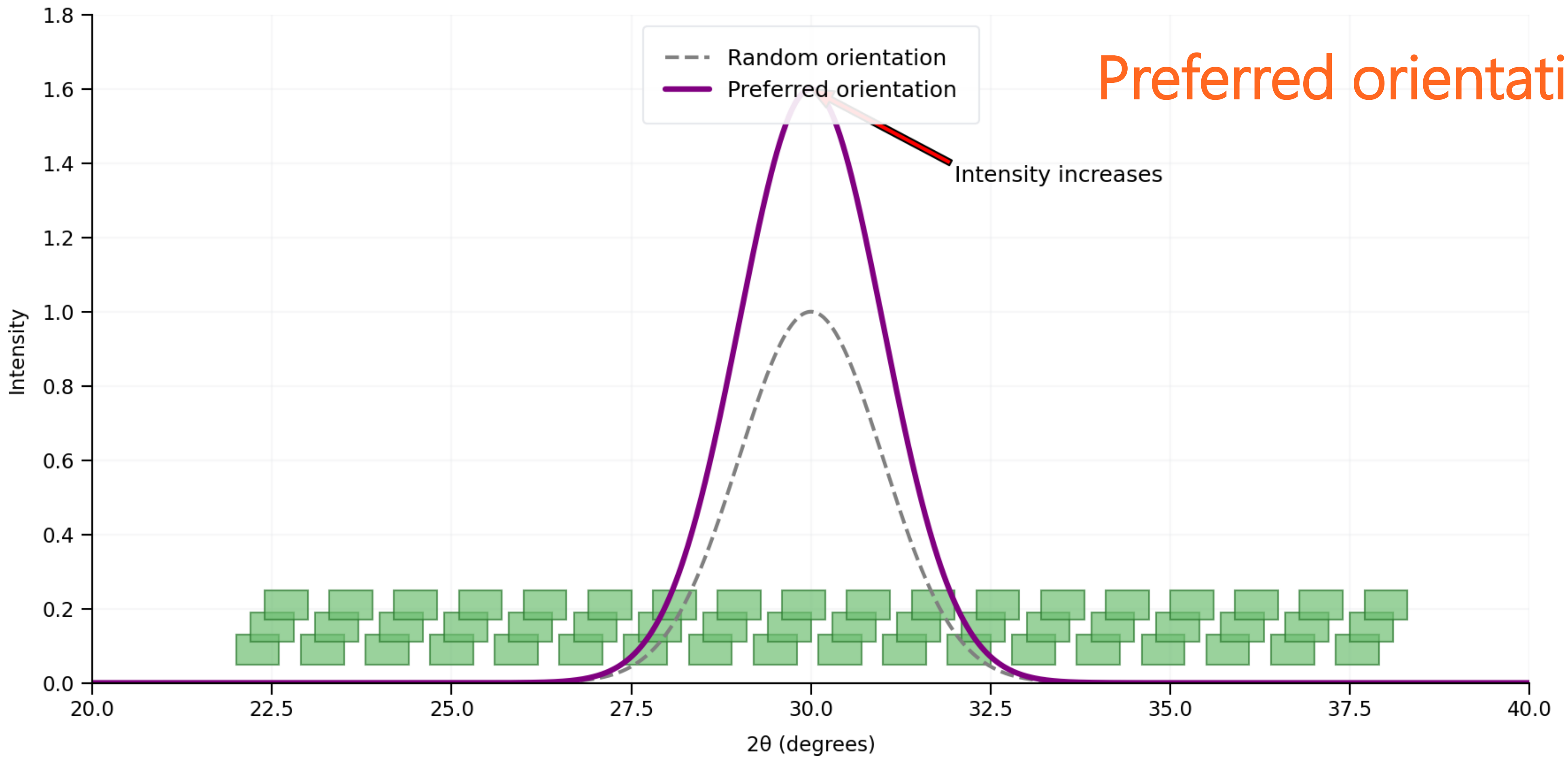
How to handle peak overlap, preferred orientation, and microstructure effects?

Peak overlap

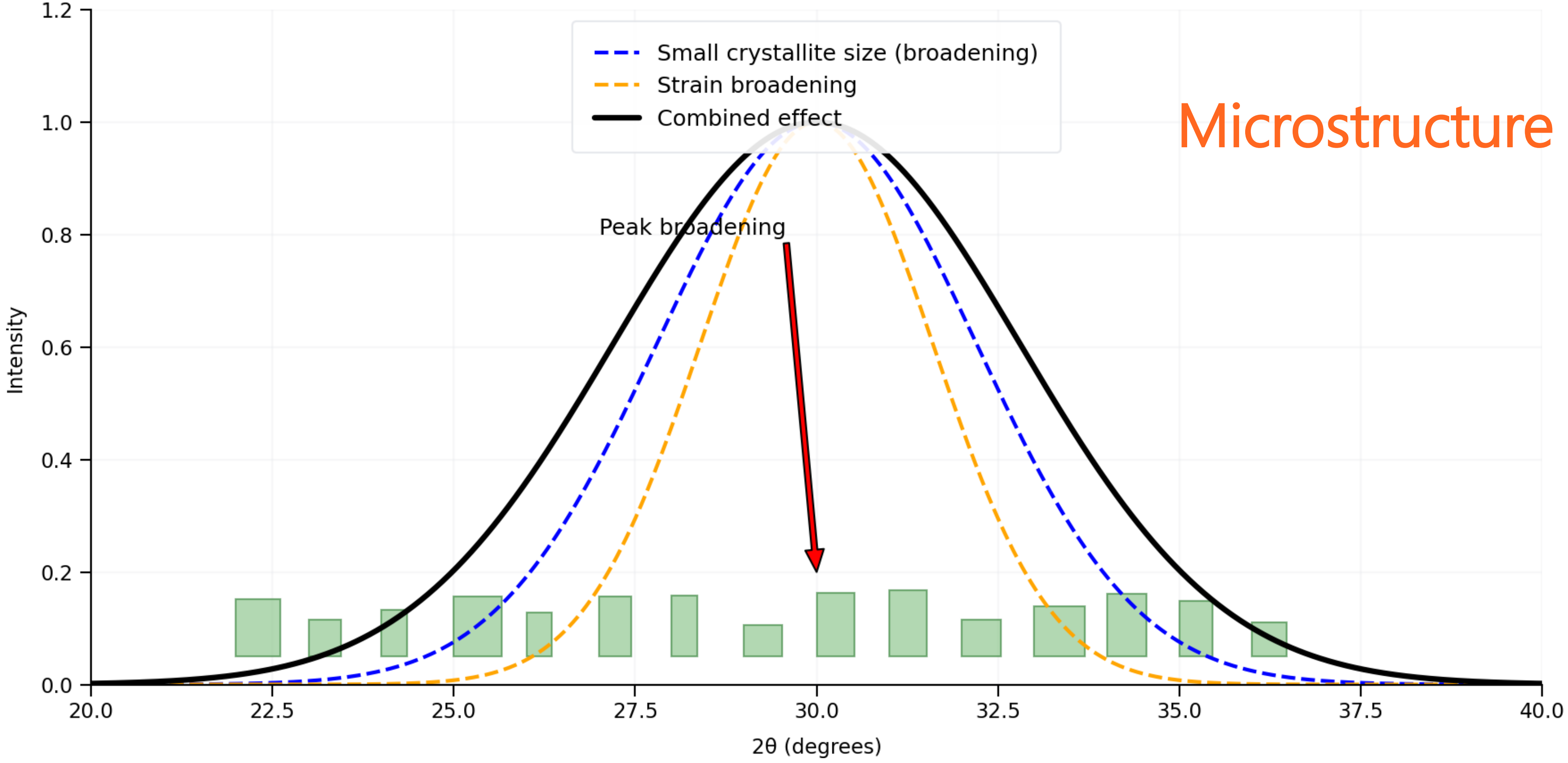


How to handle preferred orientation

Preferred orientation

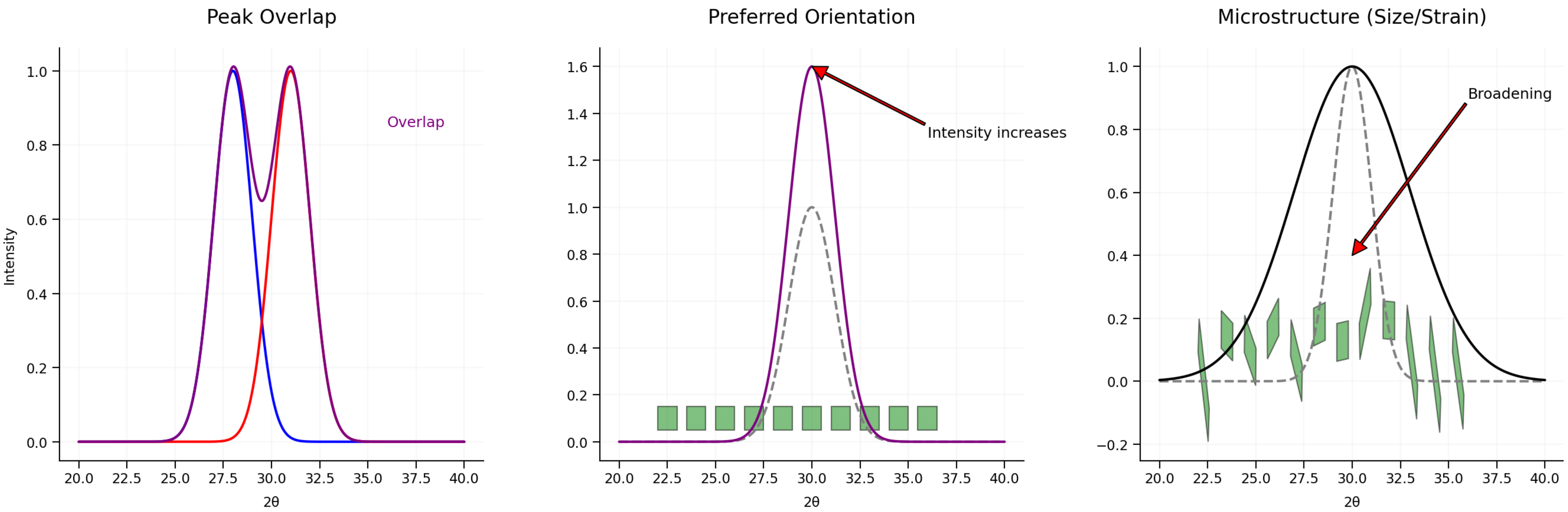


How to handle microstructure effects



Microstructure effects

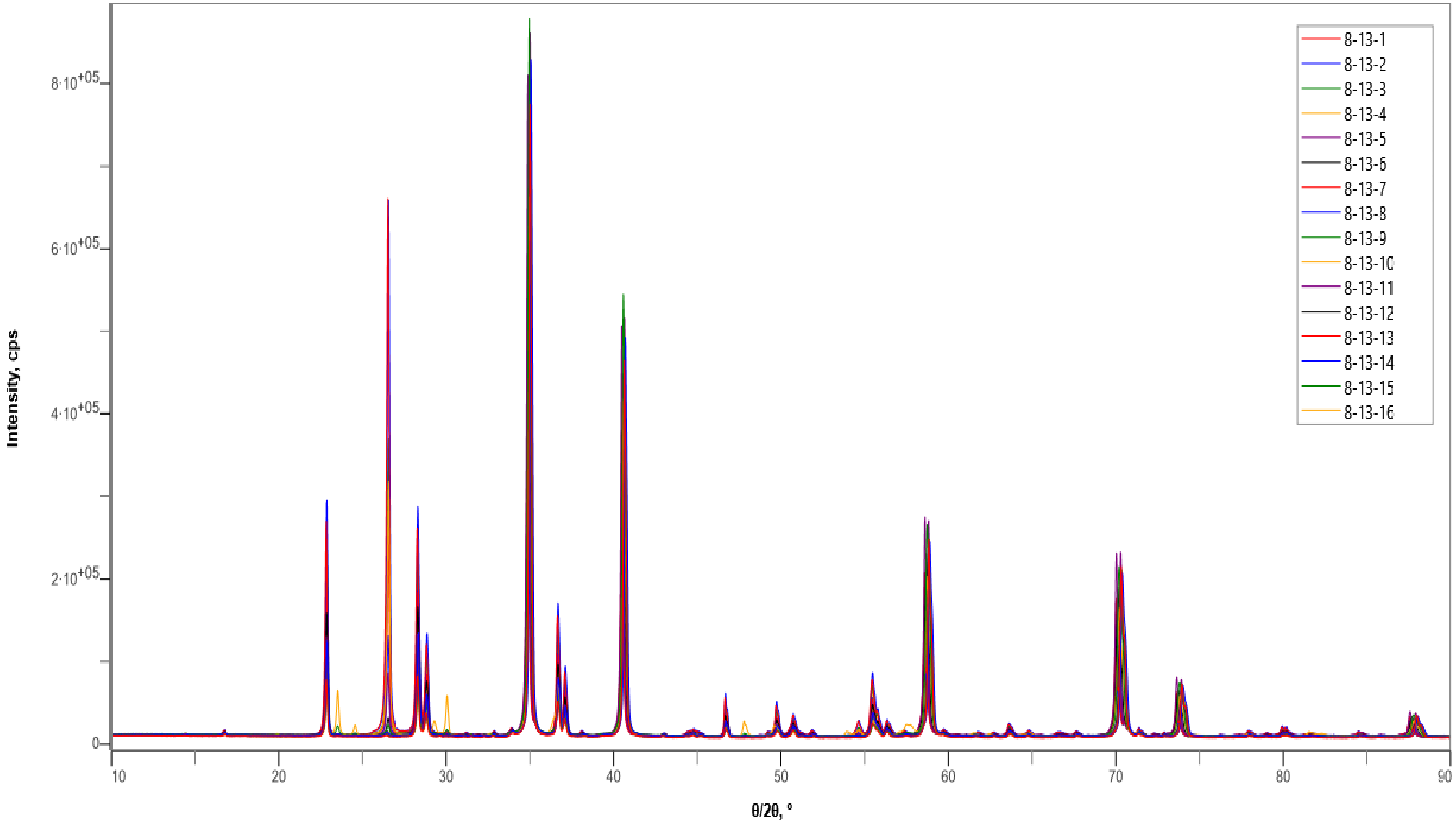
All three together

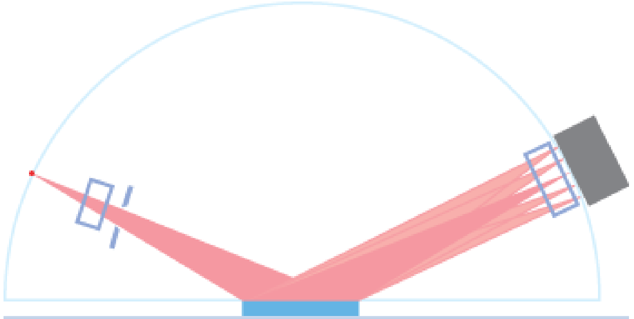


5. Case Studies…

Case Study 1: An example using cluster analysis and template approach, for example: mining and cement industry

Raw data 16 samples : Ta samples 8-13-(1-16)

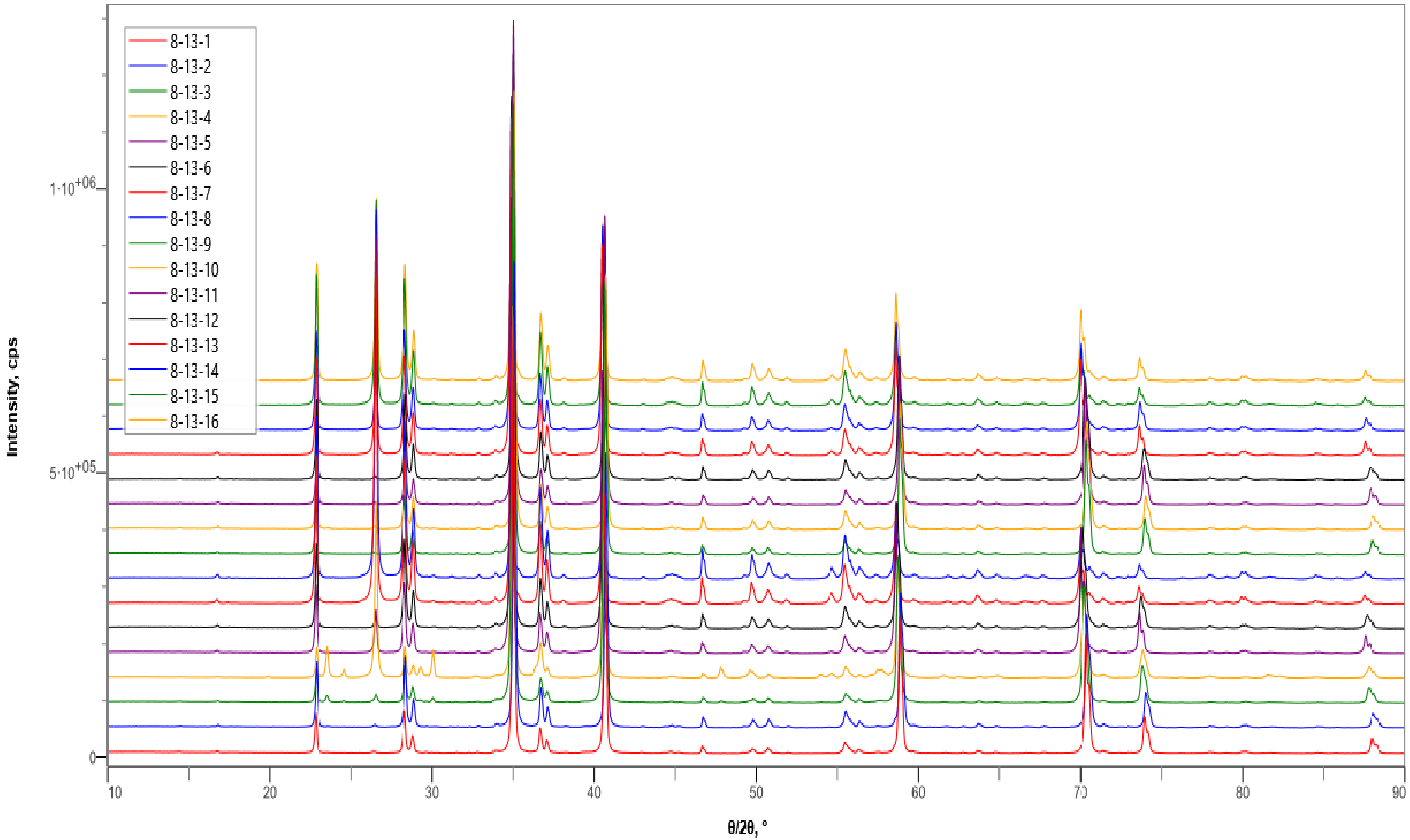


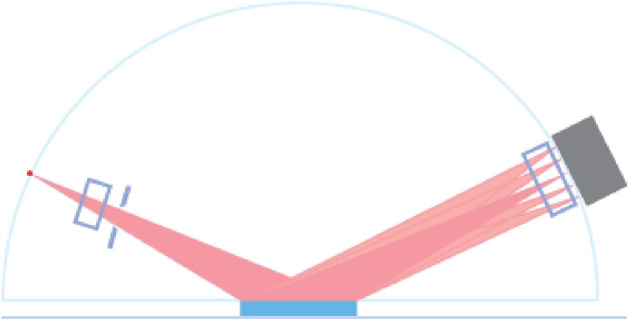


Att.: ASC-8
X-ray tube: Glass tube-Cu NF
XG: 40 kV – 15 mA
IS: 1.25 °
LLS: 10 mm
Soller S.: 5 °
RS1: 13 mm
RS2: Open
Detector: D/teX

Axis: θ / 2θ scan
Range: 10.0 – 90.0 °
Step: 0.02 °
Speed: 5 ° / min.
Duration: 16 min.

Raw data 16 samples : Ta samples 8-13-(1-16)





Att.: ASC-8
X-ray tube: Glass tube-Cu NF
XG: 40 kV – 15 mA
IS: 1.25 °
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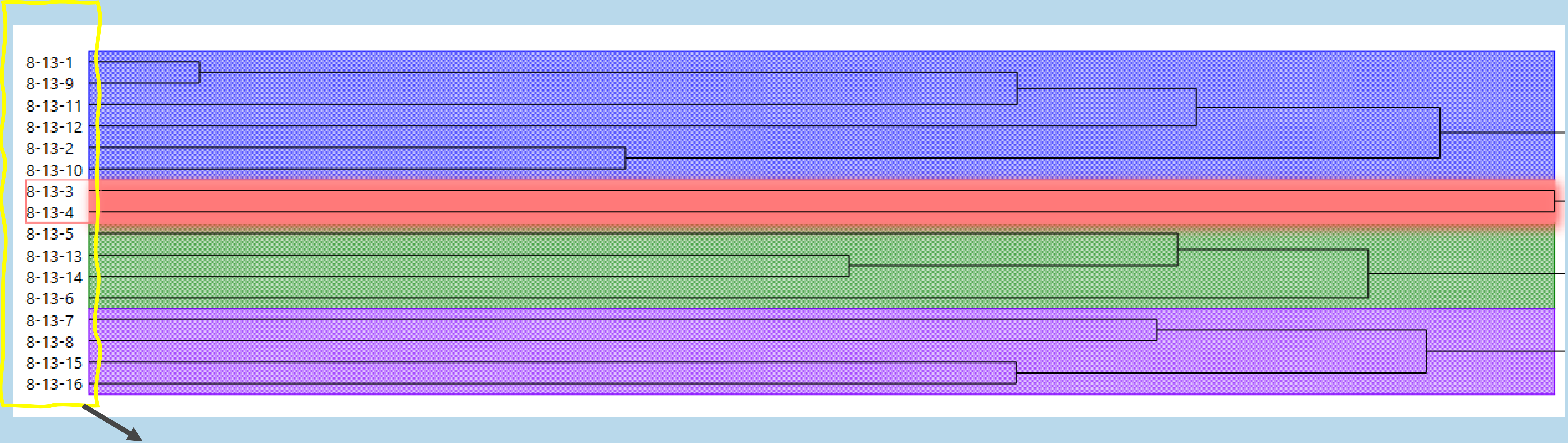
Axis: θ / 2θ scan
Range: 10.0 – 90.0 °
Step: 0.02 °
Speed: 5 ° / min.
Duration: 16 min.

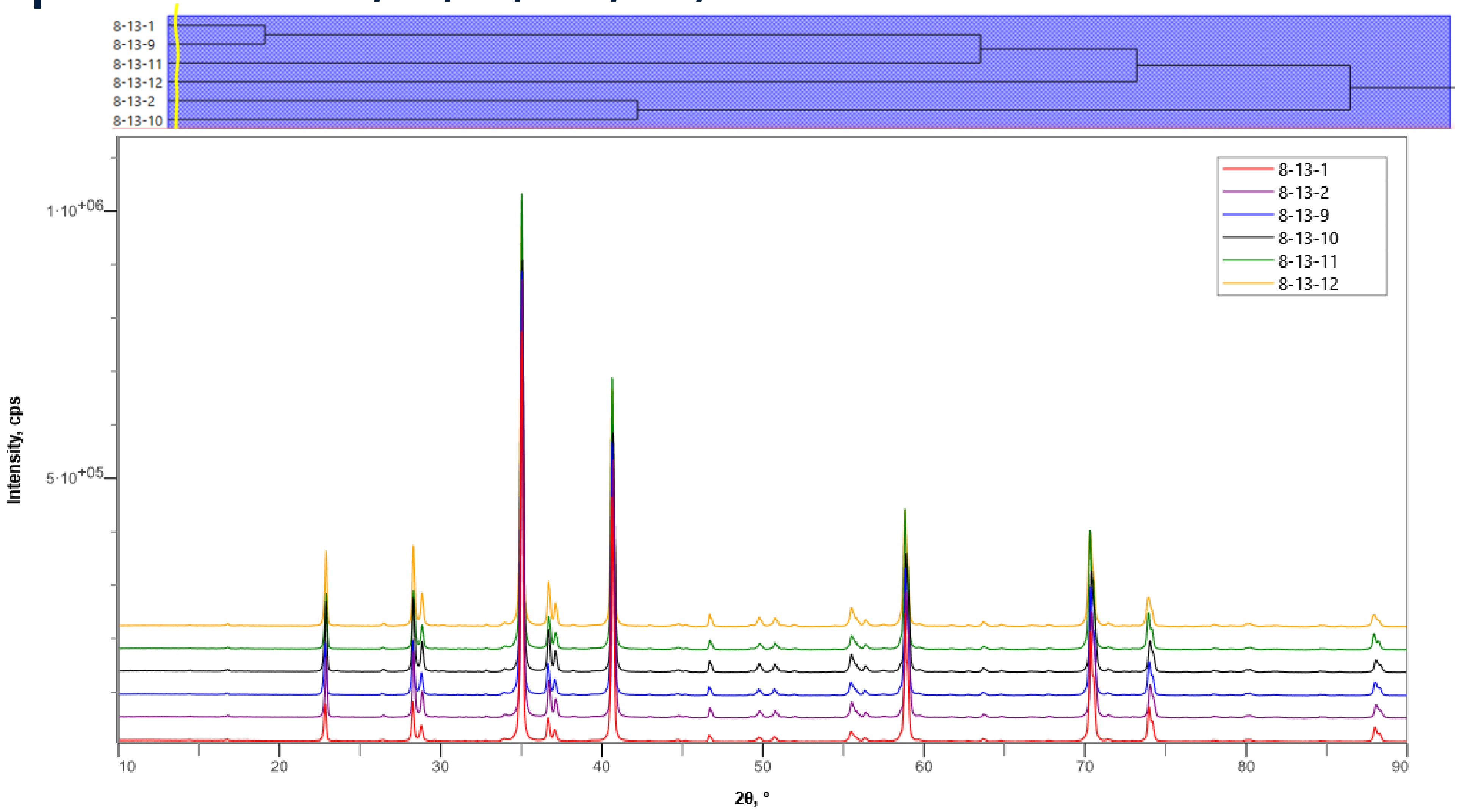
Segregating the 16 datasets into similar types using Cluster Analysis for making templates



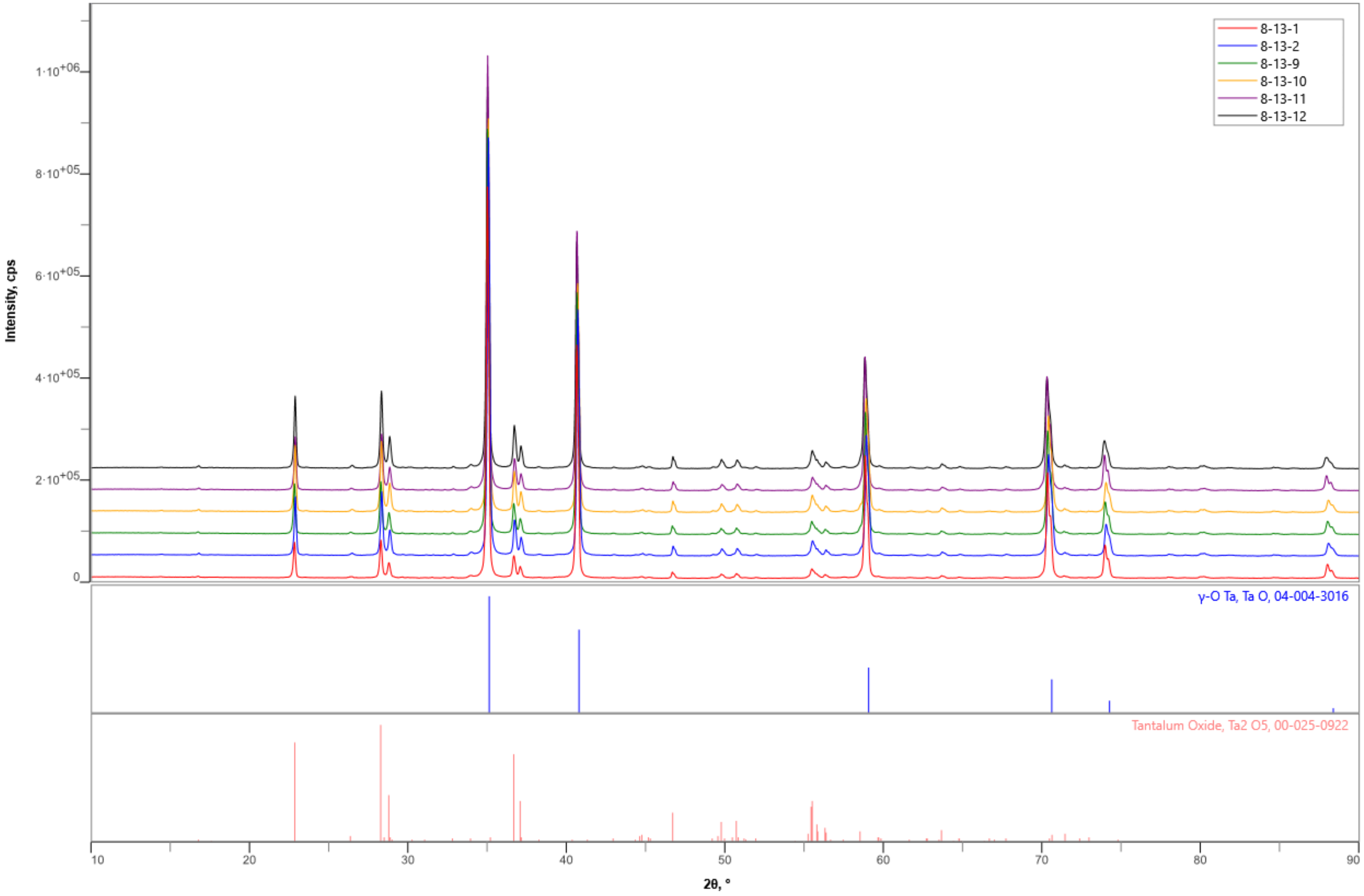
Dendrogram: data divided into 4 sets (A, B, C, D)

By using a macro (template) the Rietveld refinement can be carried out in batches now

Samples set A: 1, 2, 9, 10, 11, 12



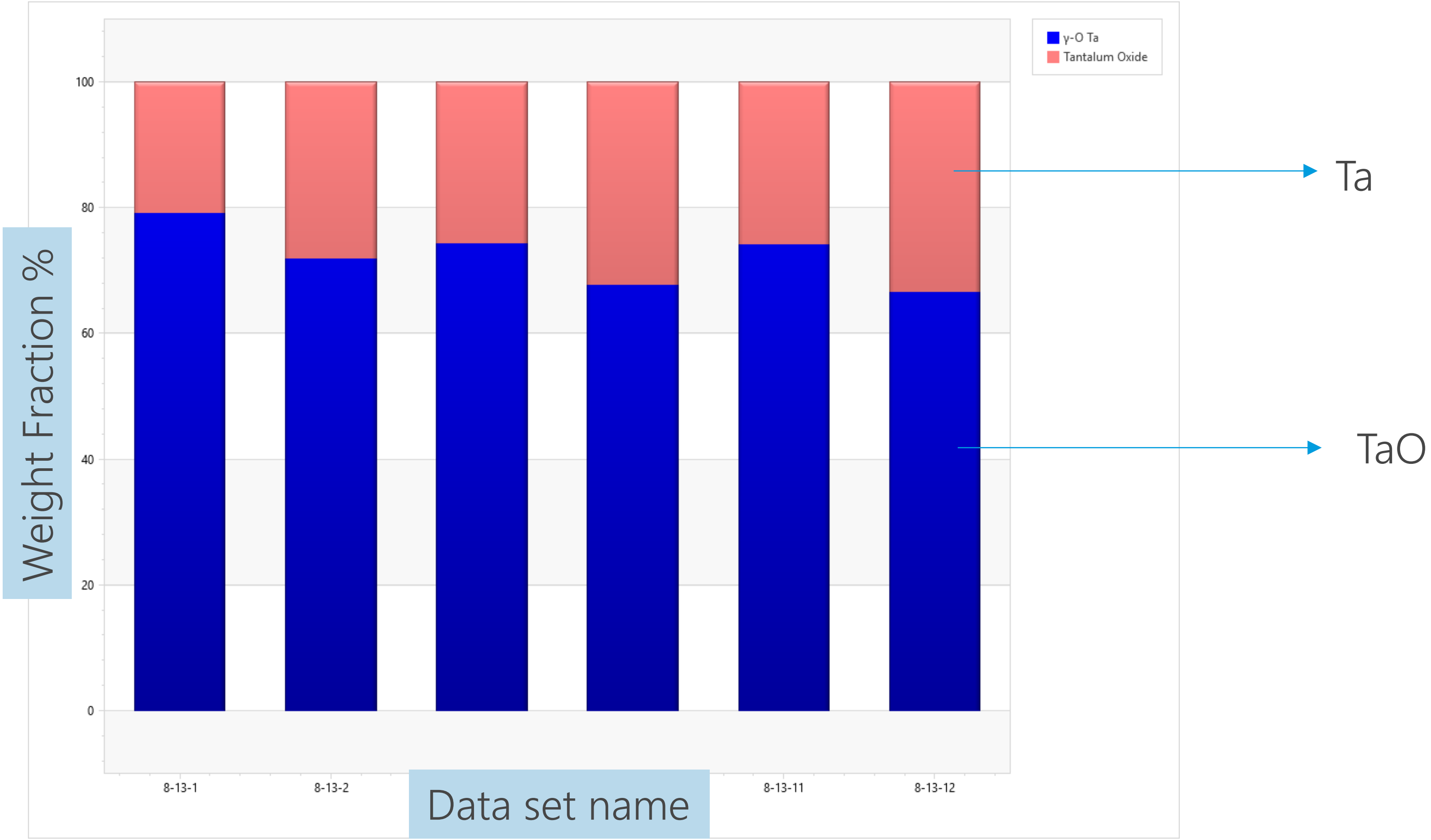
Samples set A: 1, 2, 9, 10, 11, 12; Phase id



Samples set A: 1, 2, 9, 10, 11, 12; Rietveld quant pie charts

Sample		8-13-1	8-13-2	8-13-9	8-13-10	8-13-11	8-13-12
Rwp, %		8.33	9.74	9.11	10.22	9.03	7.89
S		2.113	2.145	3.142	2.98	2.451	2.476
Ta, weight %		79.25(15)	71.93(18)	74.42(17)	67.85(19)	74.27(16)	66.64(19)
Unit Cell	a, Å	4.43714(19)	4.4368(3)	4.4363(2)	4.4366(3)	4.4414(2)	4.4410(3)
	b, Å	4.43714(19)	4.4368(3)	4.4363(2)	4.4366(3)	4.4414(2)	4.4410(3)
	c, Å	4.43714(19)	4.4368(3)	4.4363(2)	4.4366(3)	4.4414(2)	4.4410(3)
	α, °	90.000	90.000	90.000	90.000	90.000	90.000
	β, °	90.000	90.000	90.000	90.000	90.000	90.000
	γ, °	90.000	90.000	90.000	90.000	90.000	90.000
	Lattice volume, $Å^3$	87.359	87.341	87.308	87.327	87.610	87.587
TaO, weight %		20.75(15)	28.07(18)	25.58(17)	32.15(19)	25.73(16)	33.36(19)
Unit Cell	a, Å	6.2057(10)	6.2051(9)	6.2039(9)	6.2043(9)	6.2059(9)	6.2030(10)
	b, Å	40.290(4)	40.306(5)	40.293(4)	40.309(5)	40.294(4)	40.298(5)
	c, Å	3.8915(4)	3.8923(4)	3.8912(4)	3.8922(4)	3.8918(4)	3.8911(5)
	α, °	90.000	90.000	90.000	90.000	90.000	90.000
	β, °	90.000	90.000	90.000	90.000	90.000	90.000
	γ, °	90.000	90.000	90.000	90.000	90.000	90.000
	Lattice volume, $Å^3$	972.998	973.465	972.695	973.386	973.187	972.658

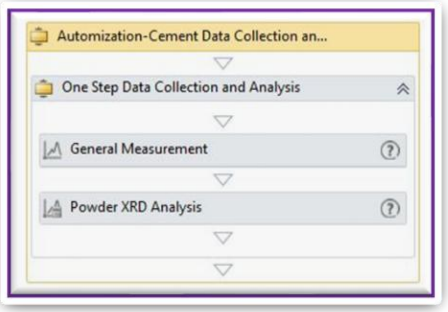
Samples set A: 1, 2, 9, 10, 11, 12; Rietveld quant using a template: load all data and auto run

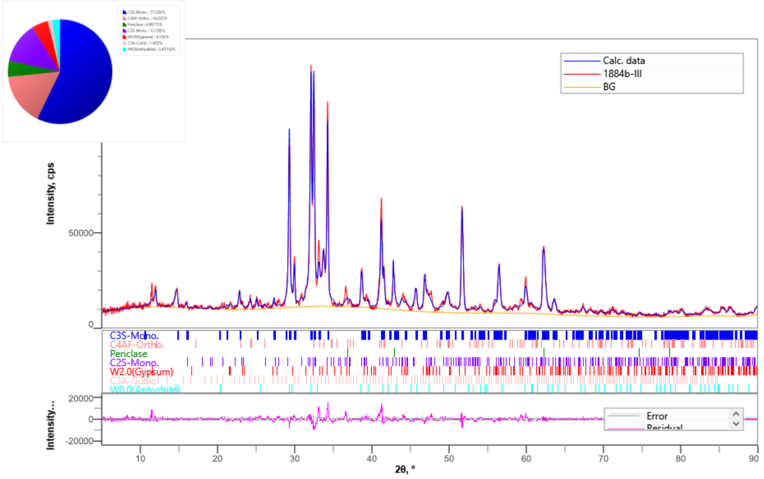


Rigaku

Automated quantification technique for QC

- Usually done by making a relevant macro (template).
- Most common using Rietveld method.
- The quant work is performed automatically using the phases present in the template file
- For example : Cement, battery materials etc.





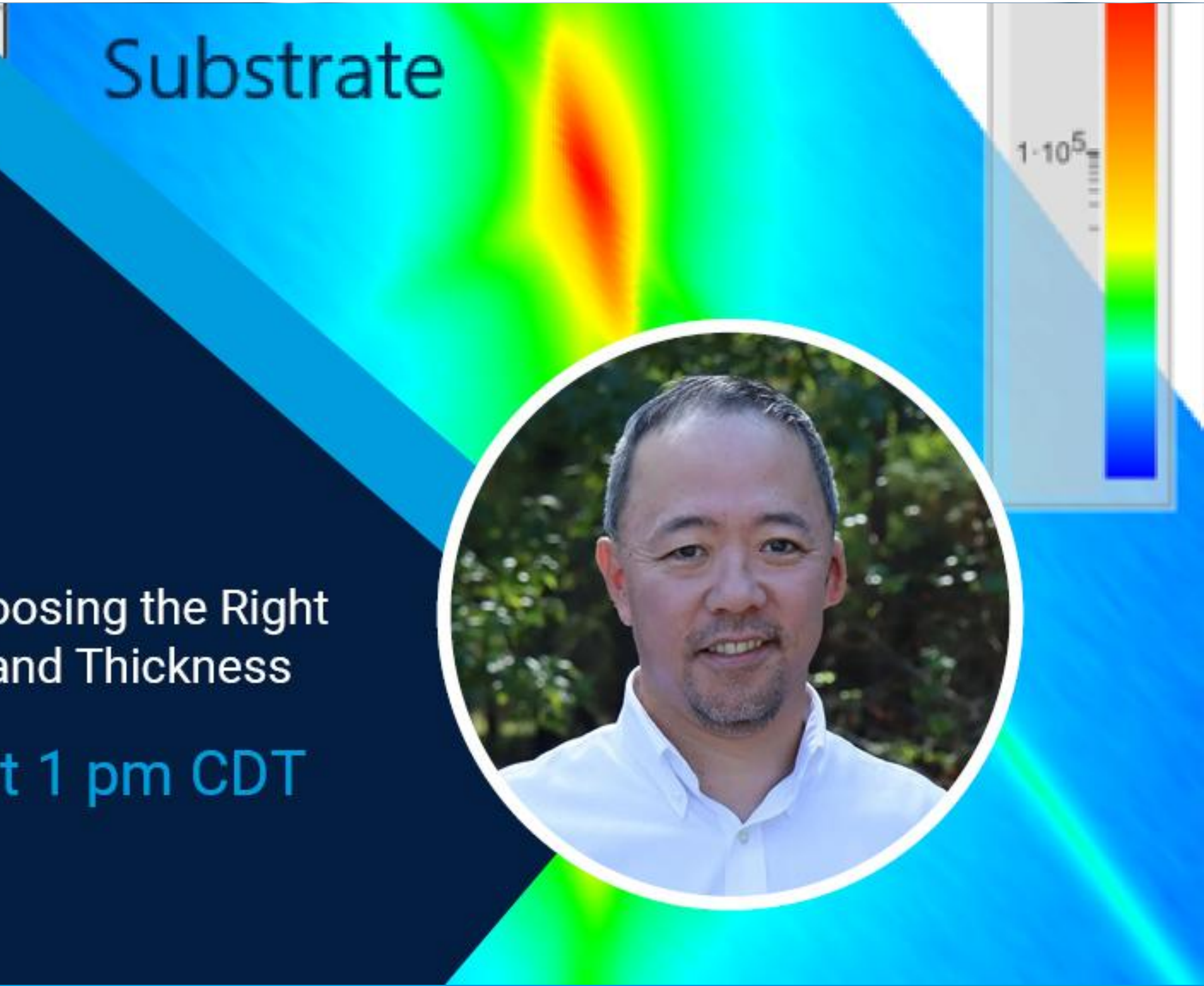
Questions?

We'll follow up with your questions.

Recording will be available tomorrow.

Register for webinar.

Rigaku



Practical XRD with Confidence

Episode 3 – XRD for Thin Films: Choosing the Right Measurement for Structure, Strain, and Thickness

Wednesday, June 3, 2026, at 1 pm CDT

Presenter: Keisuke Saito, PhD

Host: Tom Concolino, PhD