Methods in Phase Quantification with PXRD

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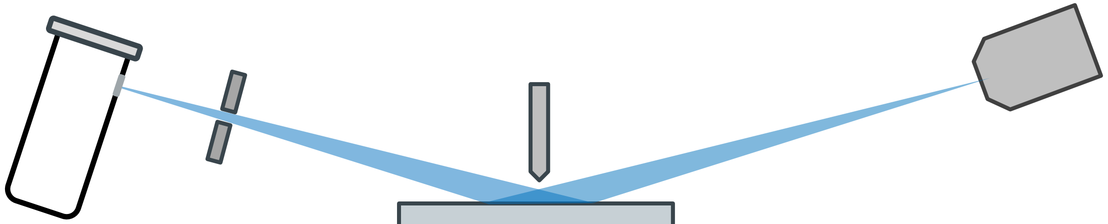
Reflection Geometry (Bragg-Brentano)

Line Geometry (1D Detector)



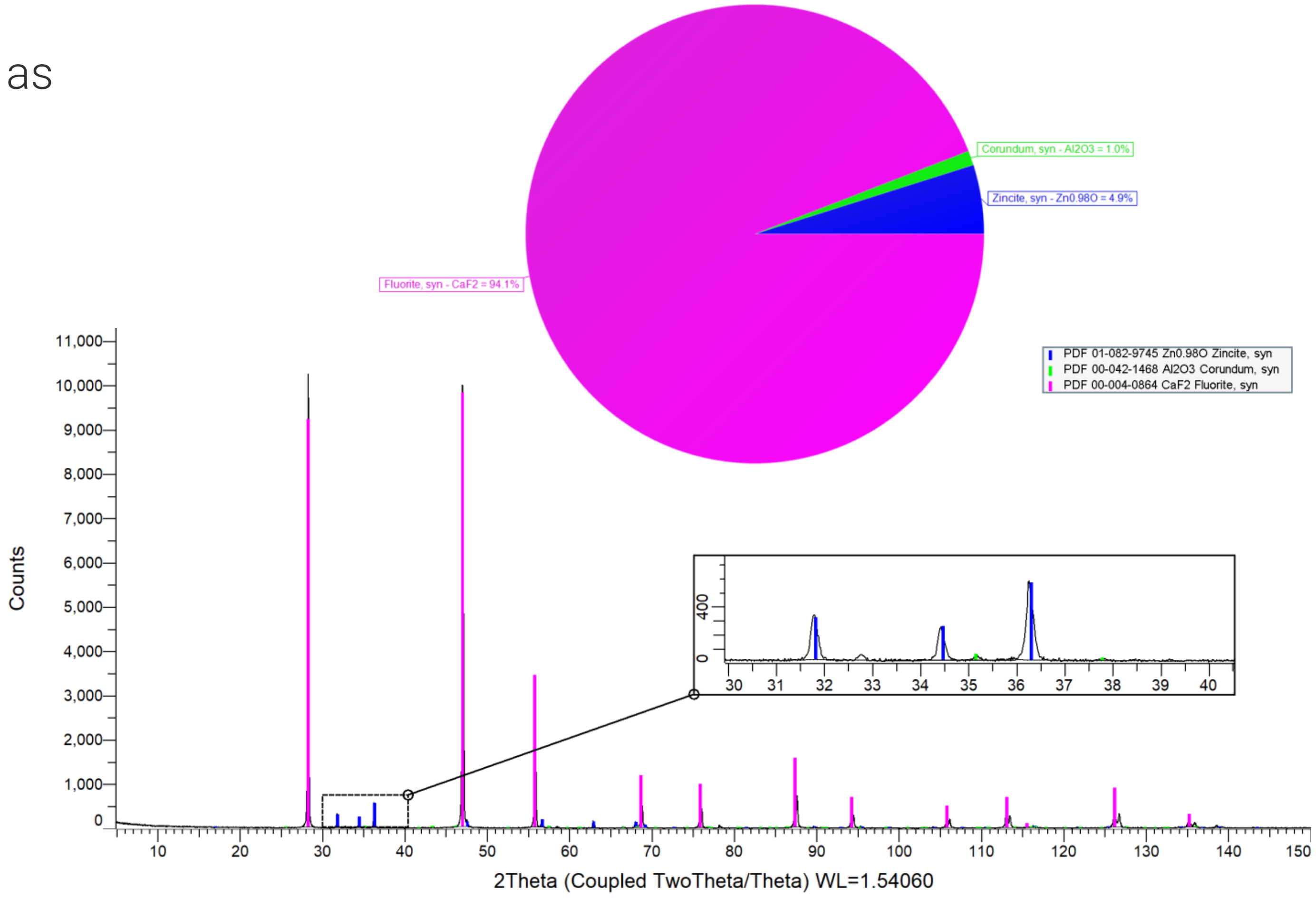
- Diverging beam geometry increases sampling statistics through large sample illumination
- Rapid data collection with linear detectors (1D)
- Generally preferred over spot beam analysis (2D) for quantification

Quantification Overview

- **Concentration** of crystalline phases calculated as a function of **intensity**
- Data quality is generally a limiting factor

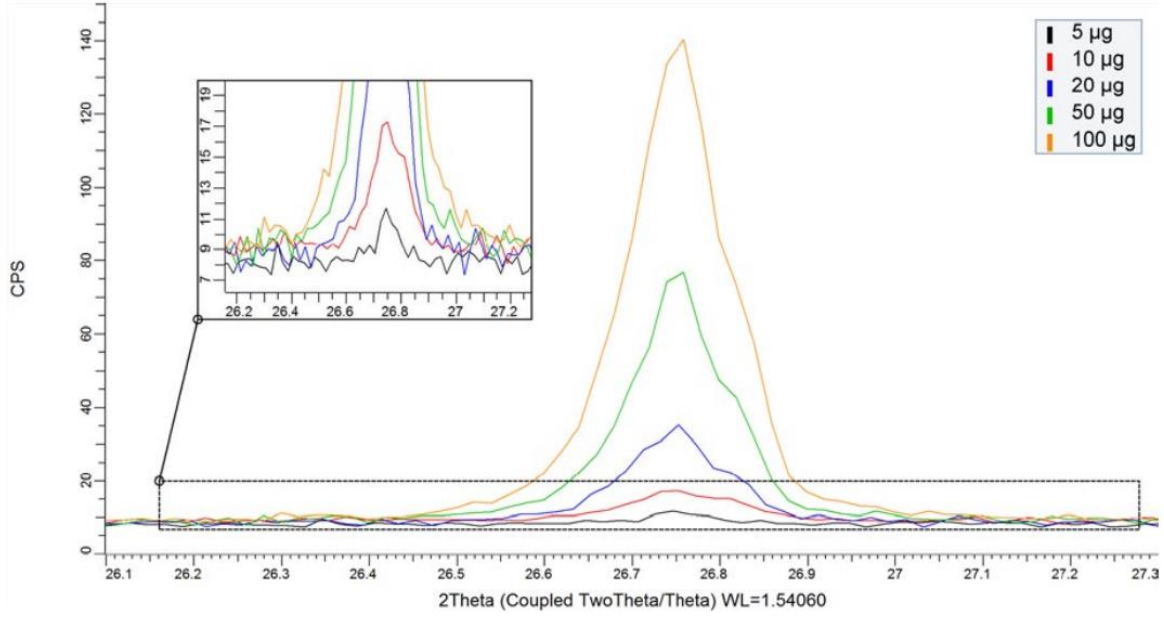
- Selected Methods:
  - Calibration Curve
  - Reference Intensity Ratio
  - Full Pattern Summation
  - Quantitative Rietveld Refinement

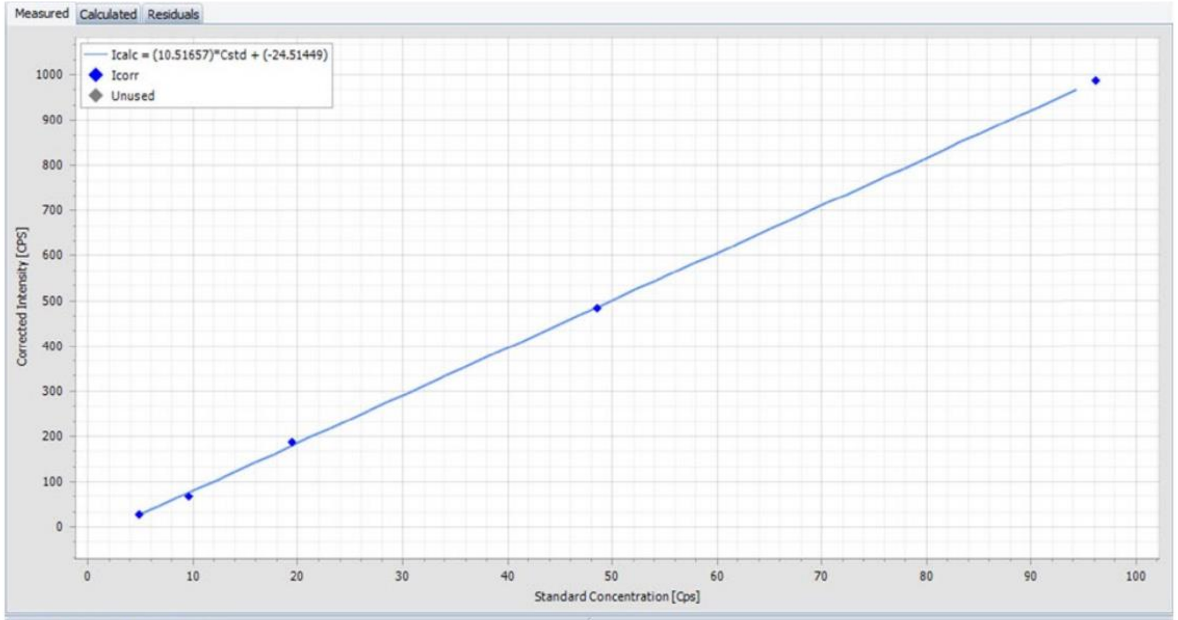
  - Degree of crystallinity / Percent Amorphous



Calibration Curve

Calibration standards provide an increase in instrument response with increased concentration



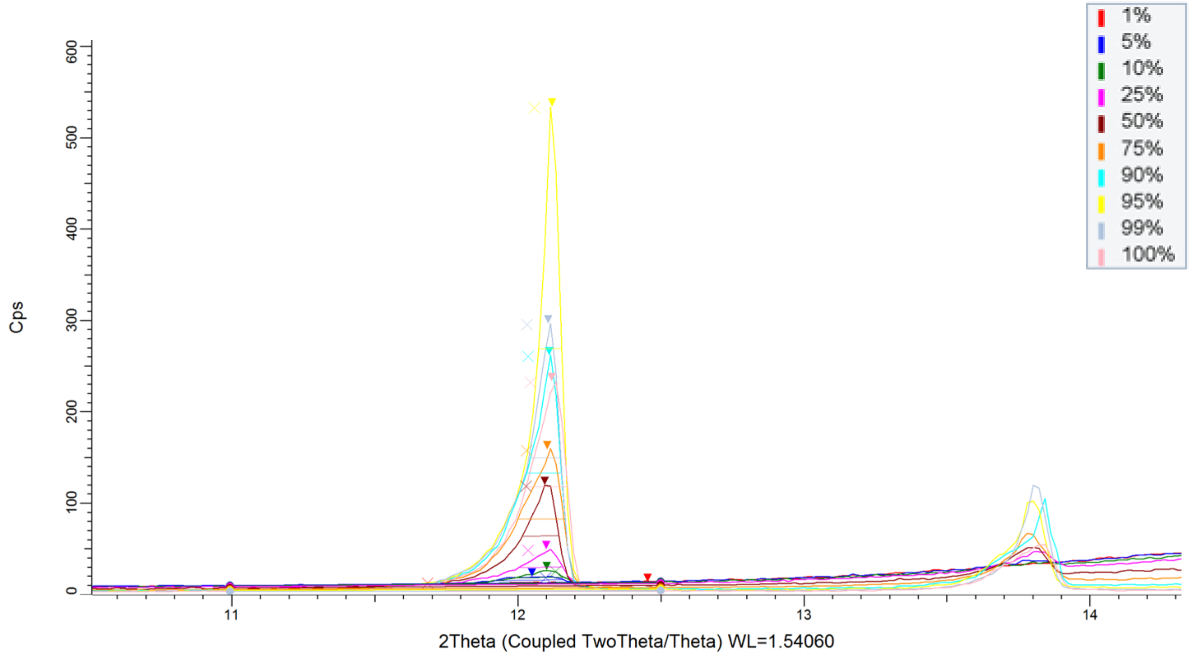


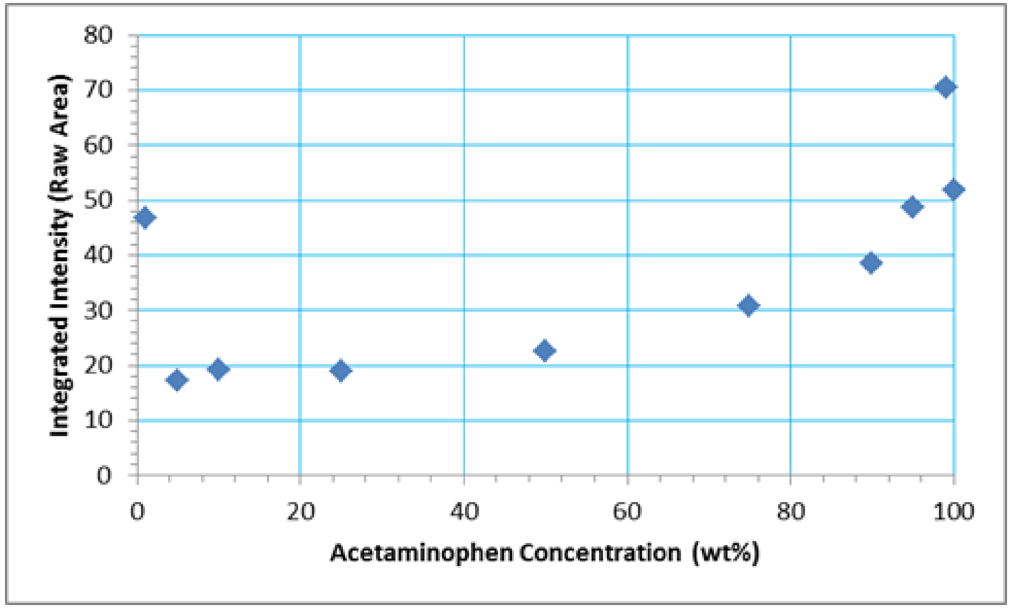
Results [Quartz_Primary_Peak]

Use	Standard	Corr. Intensity	σ(Ic)	Std. Conc.	Calc. Conc.
☑	5 microgram	28.221	0.0000	4.850	**5.015**
☑	10 microgram	68.867	0.0000	9.600	**8.880**
☑	20 microgram	187.884	0.0000	19.400	**20.197**
☑	50 microgram	483.815	0.0000	48.600	**48.336**
☑	100 microgram	986.373	0.0000	96.100	**96.123**

Calibration Curve

Non-reproducible preferred orientation leads to poor quality calibration curve





Calibration Curve

Benefits

- Sensitive to low concentrations (micrograms under controlled conditions)
- Simple, straight-forward concept

Challenges

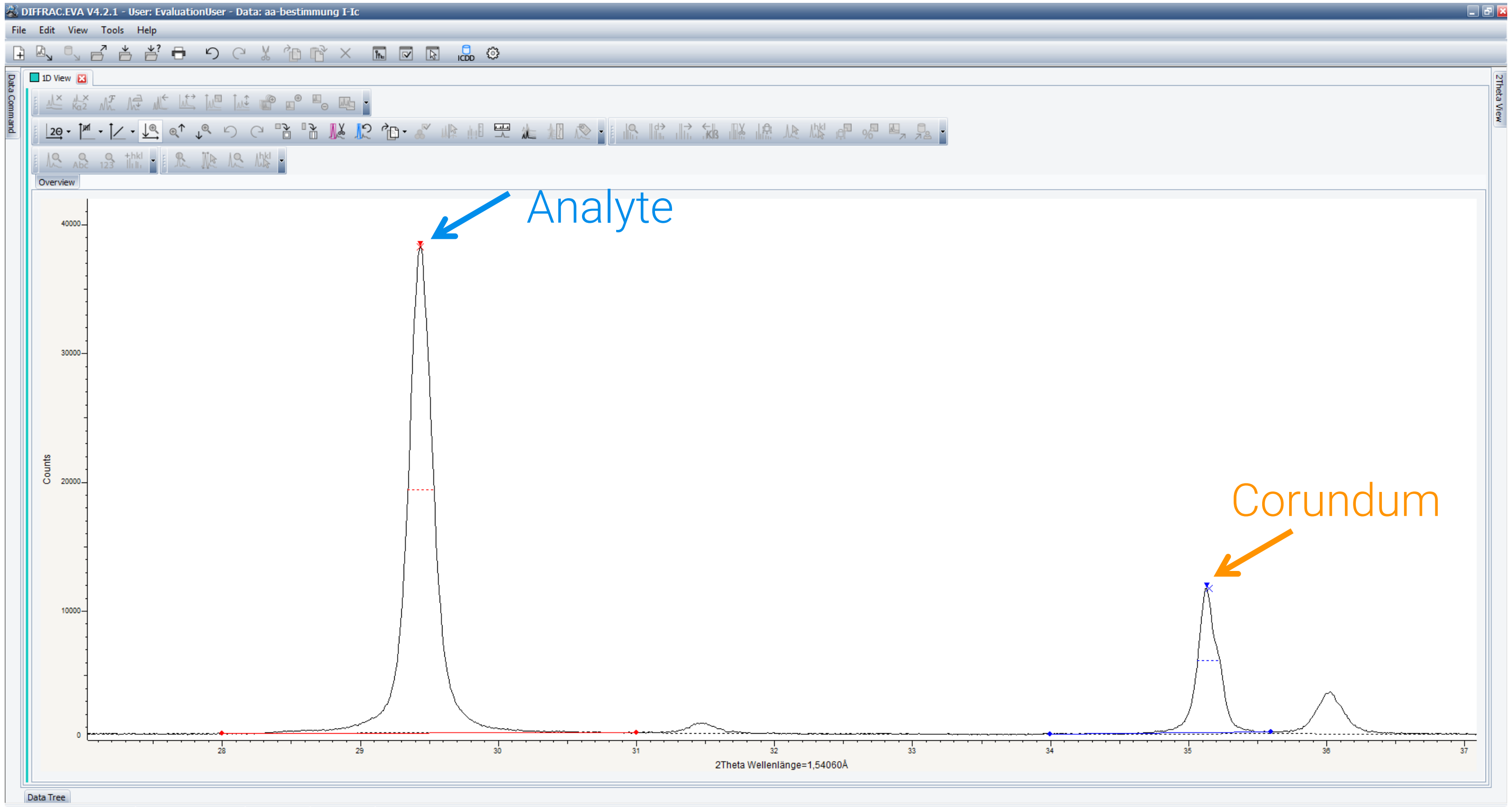
- Requires availability of standards
- Requires intensity monitoring for tube aging
- Susceptible to preferred orientation

BRUKER

Reference Intensity Ratio (RIR Method)

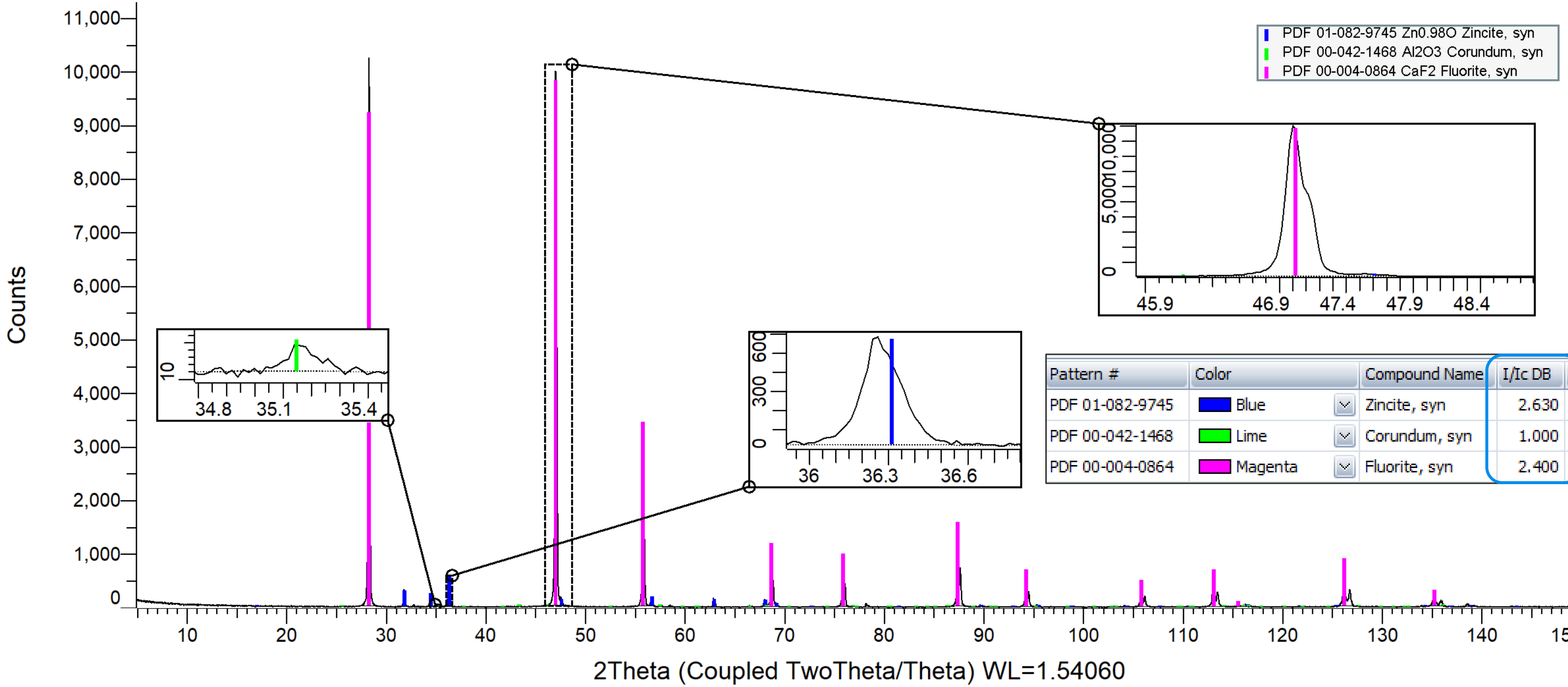
I/I_C is measured or calculated with a 50/50 wt% mixture of a given material with corundum (Al_2O_3)

$$\frac{I_a}{I_b} = \frac{\left(I/I_c\right)_a}{\left(I/I_c\right)_b}\,\frac{x_a}{x_b}$$



Reference Intensity Ratio (RIR Method)

Scaling of largest reflections (100% peak) for each phase provides concentration



Pattern #	Color	Compound Name	I/Ic DB	I/Ic User	S-Q
PDF 01-082-9745	Blue	Zincite, syn	2.630	0.000	4.9%
PDF 00-042-1468	Lime	Corundum, syn	1.000	0.000	1.0%
PDF 00-004-0864	Magenta	Fluorite, syn	2.400	0.000	94.1%

Reference Intensity Ratio (RIR Method)

Benefits

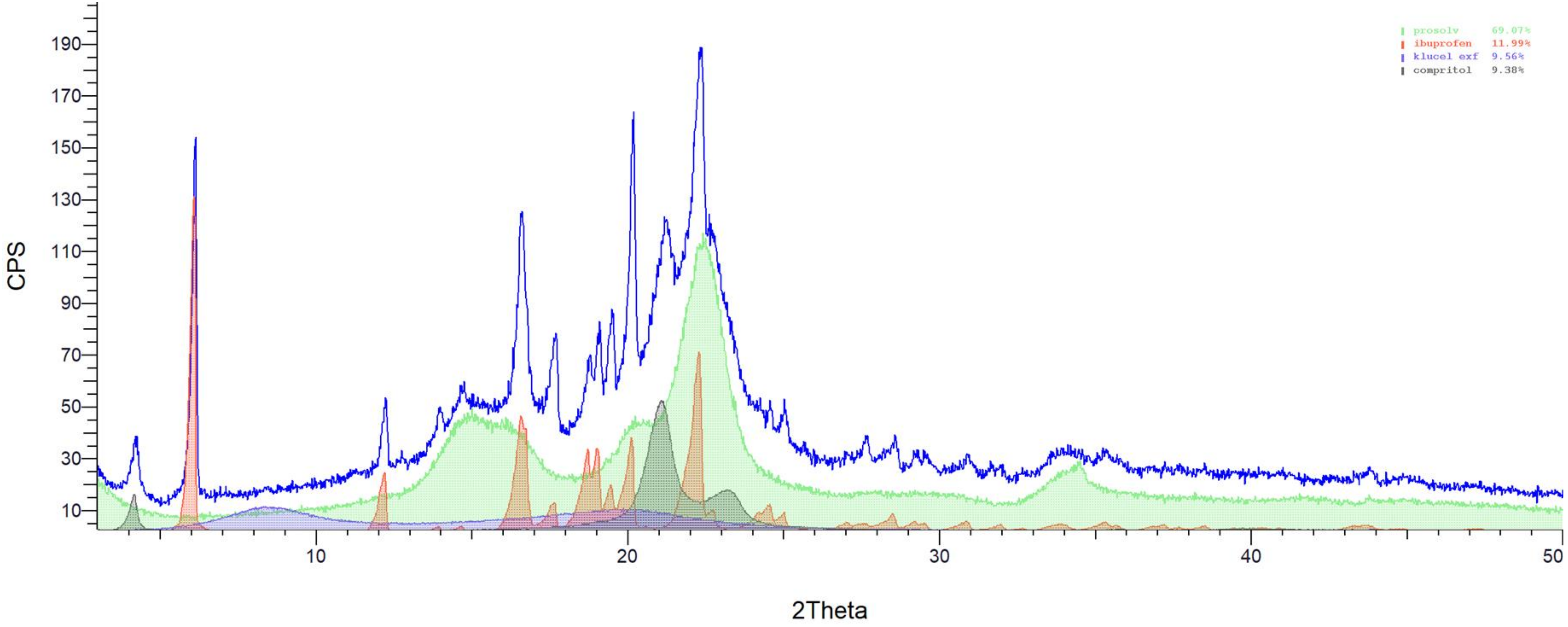
- Quick and simple process
- Widely implemented in XRD software packages
- I/Ic values widely available or easily obtainable by user

Challenges

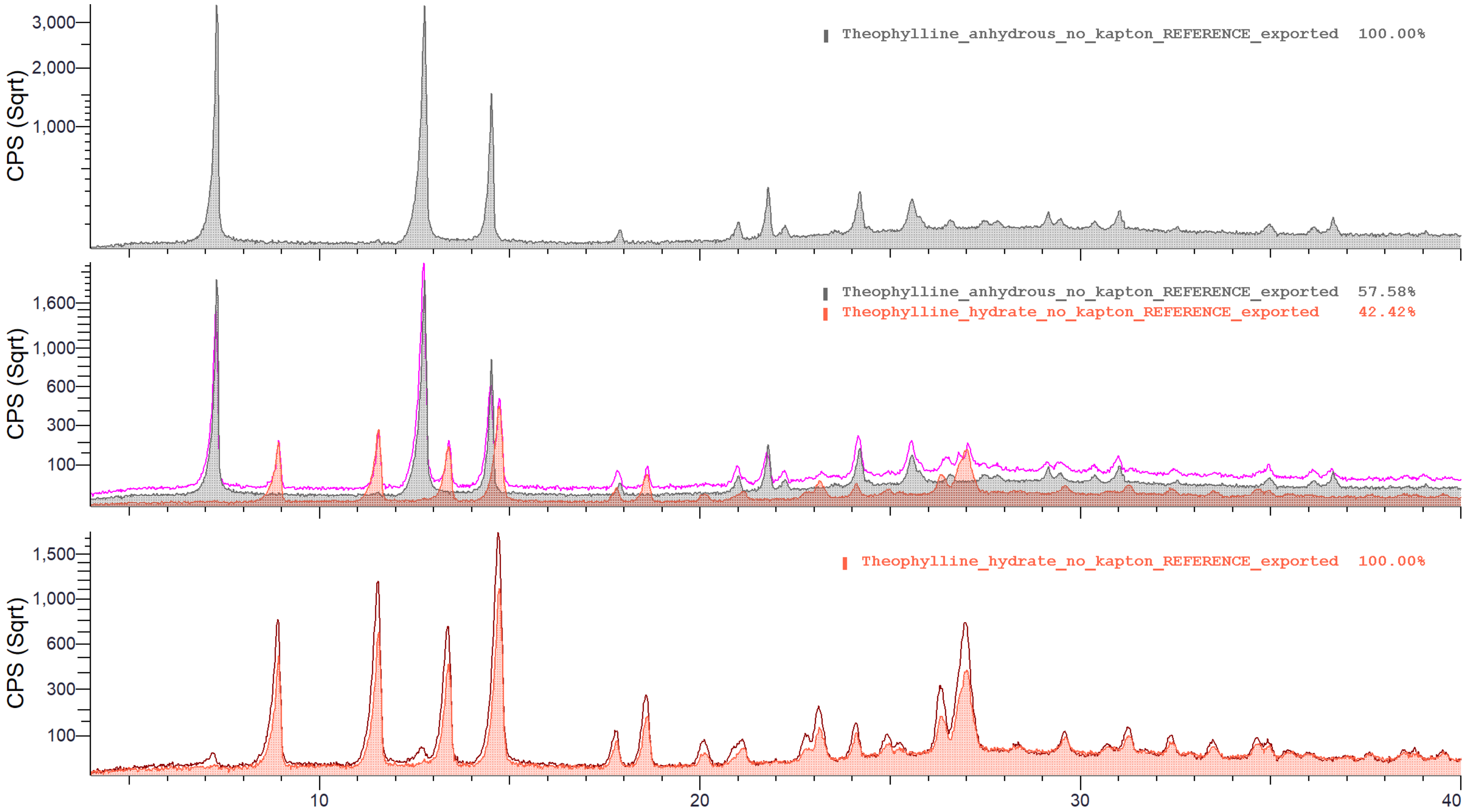
- Susceptible to errors in data quality from preferred orientation and graininess
- Relies on availability of DB values for I/Ic or ability of user to derive independently
- Errors with crystallite size broadening (changes to observed peak maximum)

Full Pattern Summation

Summation of user-collected reference patterns (both crystalline and amorphous possible)



Full Pattern Summation



Full Pattern Summation

Benefits

- Extends quantification to amorphous phases and textured phases that are highly reproducible
- Can be implemented for multiple amorphous phases

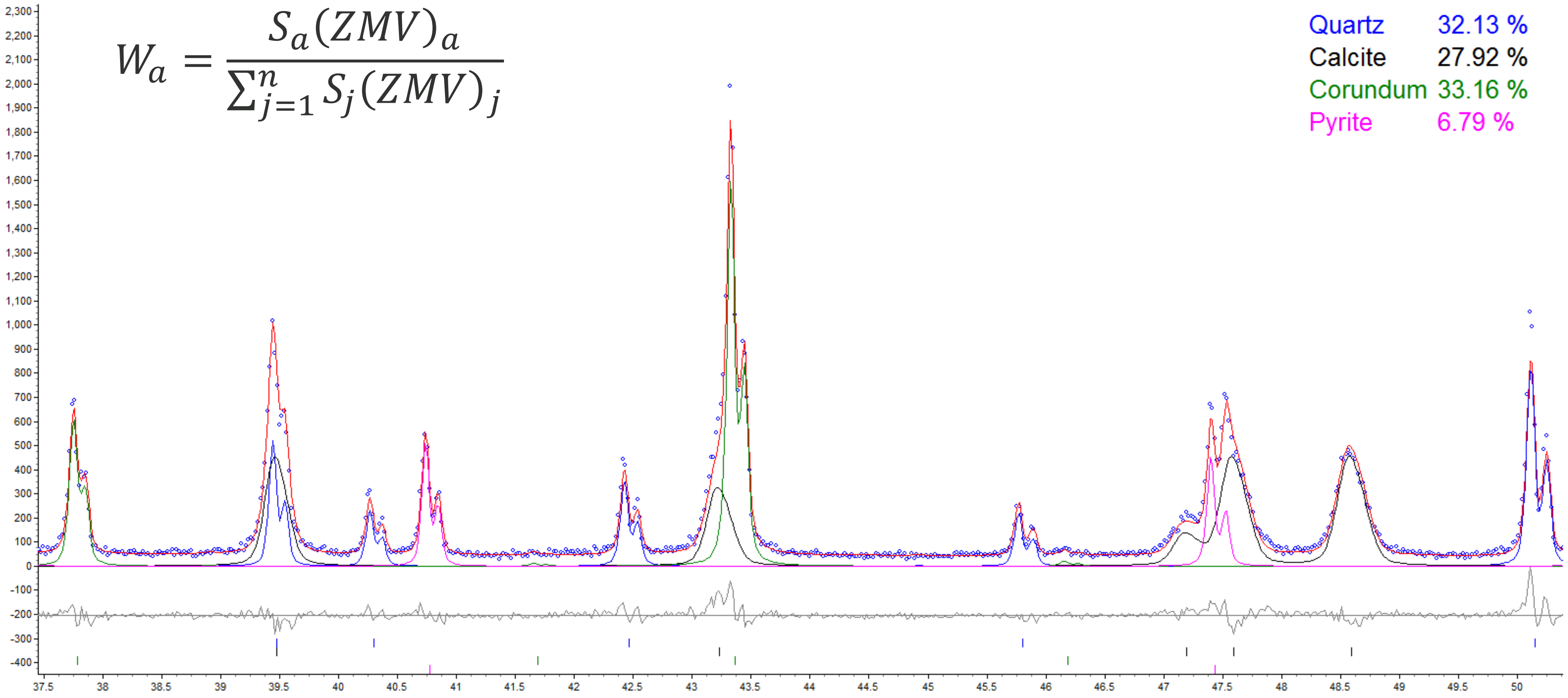
Challenges

- Requires characterization of pure phases for baseline “fingerprint”
- Requires similar data collection parameters
- Susceptible to variations in non-reproducible preferred orientation

Quantitative Rietveld Refinement

Standardless, least-squares modeling using scaling of calculated, known crystal structures

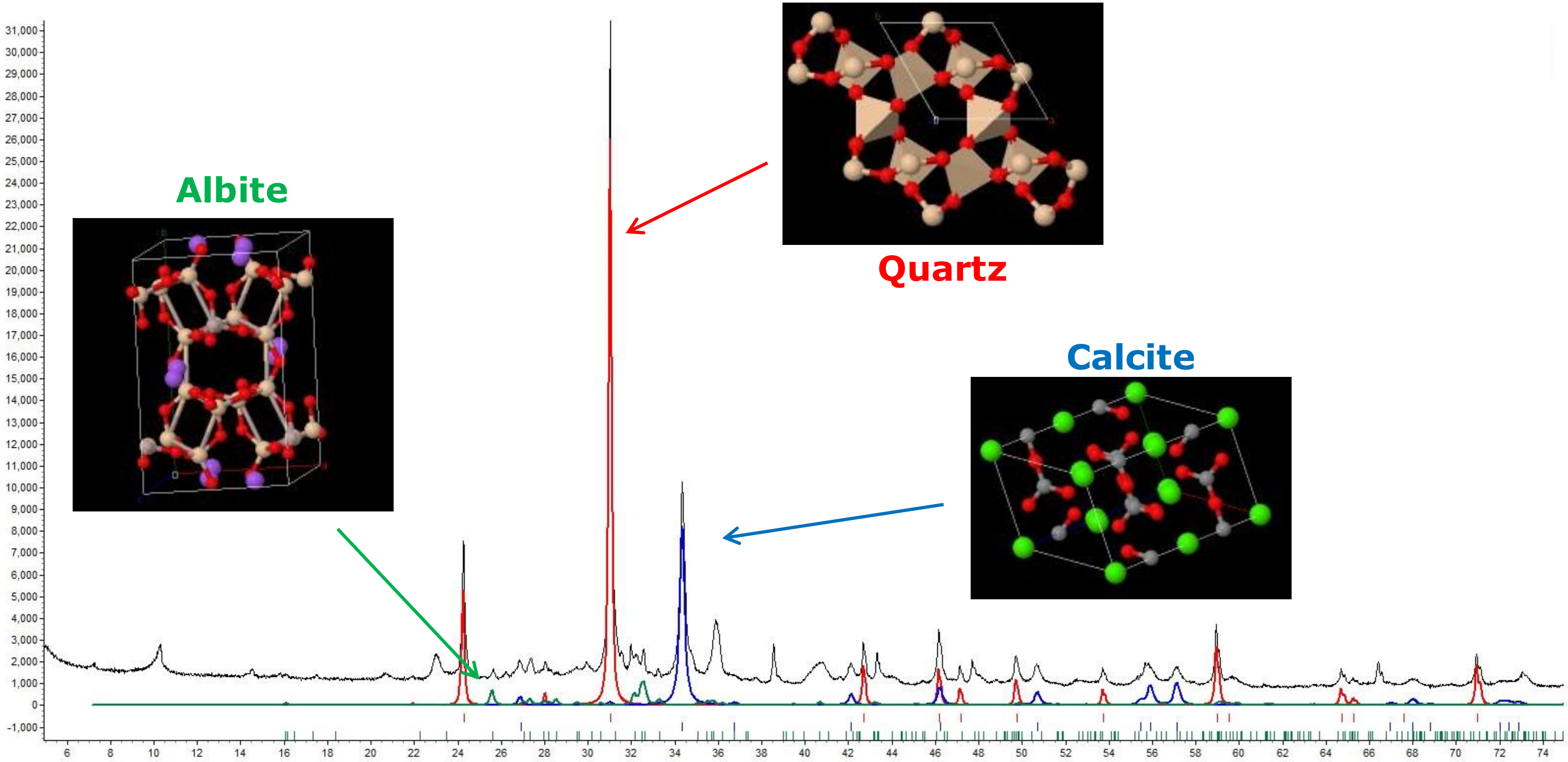
$$W_a = \frac{S_a(ZMV)_a}{\sum_{j=1}^{n} S_j(ZMV)_j}$$



Hill and Howard, 1987

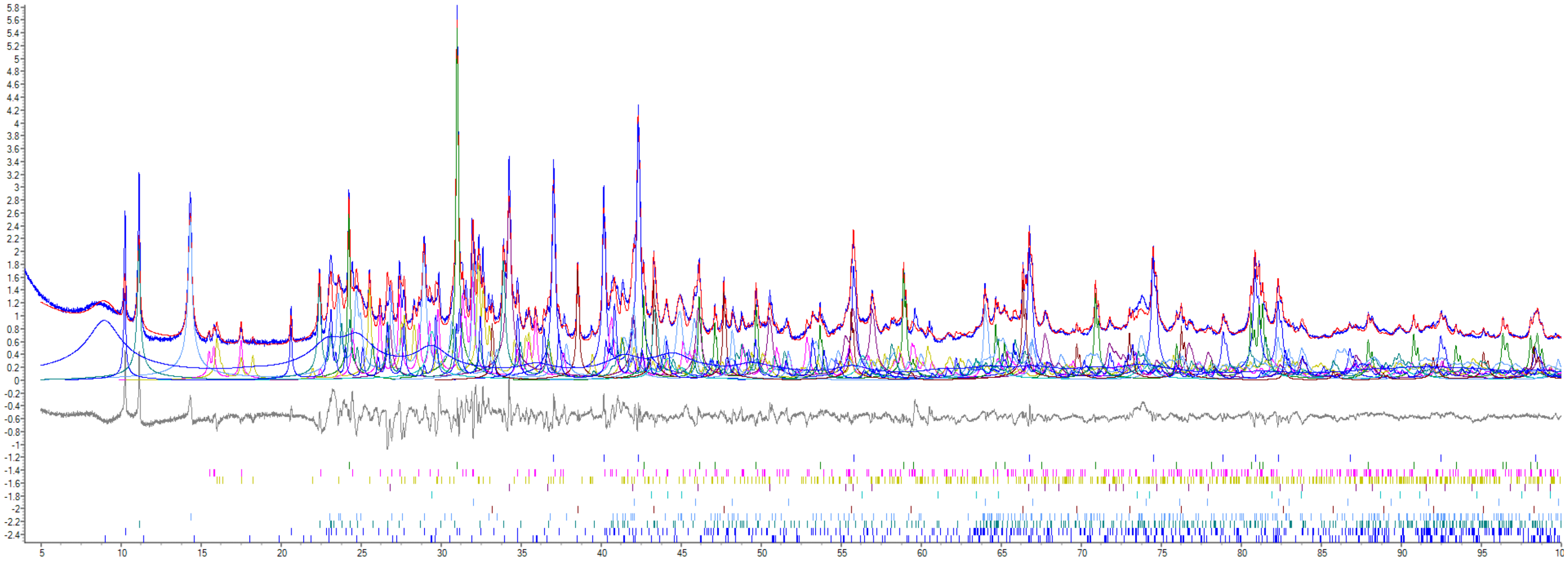
Quantitative Rietveld Refinement

Refinement model can be modified and extended by adding additional structures as needed



Quantitative Rietveld Refinement

Complex mixtures can be refined with high quality data and thorough phase identification



Phase	Actual (wt%)	Refined (wt%)	Difference
Quartz	15.3	16.2	0.9
K-Feldspar	8.6	8.1	0.5
Plagioclase	10.9	10.0	0.9
Calcite	10.6	12.5	1.9
Pyrite	3.9	3.6	0.3
Rutile	3.0	3.2	0.2
Anatase	1.3	1.1	0.2
Amphibole	0.1	-	0.1
Chloritoid	0.3	-	0.3
Zircon	0.1	-	0.1
Kaolinite	21.6	17.7	3.9
Muscovite	4.9	8.2	3.3
Montmorillonite	9.8	10.5	0.7
Pyrophyllite	9.6	8.9	0.7

Kaduk et al. Nature Reviews Methods Primer 2021

Quantitative Rietveld Refinement

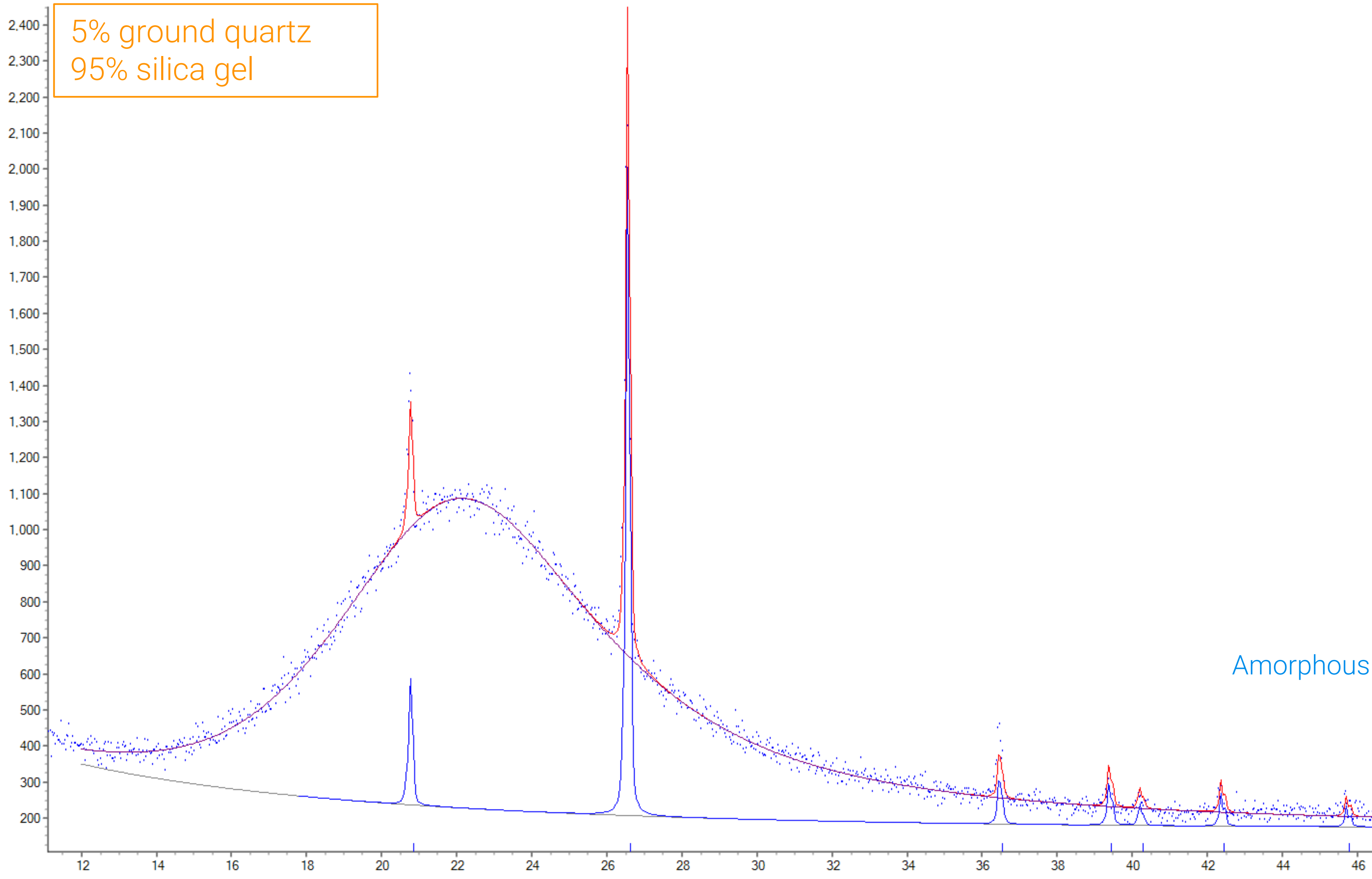
Benefits

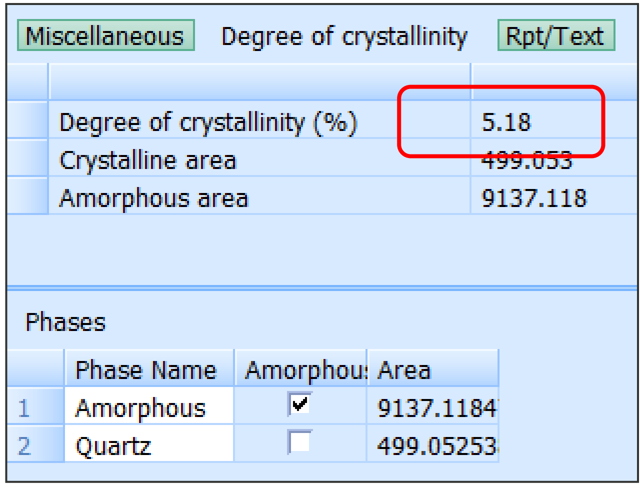
- Generally regarded as gold standard for quantification via PXRD
- No standards required
- Robust quantification method with ability to deconvolve overlapping reflections in complex mixtures
- Modeling possible for almost any definable parameter (e.g., preferred orientation, crystallite size broadening, anisotropic peak broadening, etc.)

Challenges

- Requires known crystal structures for building refinement model
- Potential error due to microabsorption (contrast in densities)
- Steeper learning curve with more advanced understanding on diffraction experiment

Degree of Crystallinity (Ratio of Integrated Areas)





Amorphous signal modeled with a single peak (type PV)

Degree of Crystallinity (Ratio of Integrated Areas)

Benefits

- Simple, rapid calculation
- Widely implemented in XRD software packages
- Can analyze multiple amorphous phases in a single diffraction specimen

Challenges

- Susceptible to user bias in integration and background fitting
- Inaccuracies possible with aggressive background modeling
- Decreased accuracies with large difference in scattering potential between amorphous and crystalline phases (different chemical compositions)

Supplemental Reading

- Madsen, I.C.; Scarlett, N.V.Y.; Kleeberg, R.; Knorr, K.
  Chapter 3.9: Quantitative Phase Analysis
  in *International Tables for Crystallography, Volume H, Powder Diffraction*
  Eds. Gilmore, Kaduk, and Schenk, Wiley, 2019
- Madsen, I.C. and Scarlett, N.V.Y.
  Chapter 11: Quantitative Phase Analysis
  in *Powder Diffraction: Theory and Practice*
  Eds. Dinnebier and Billinge, Royal Society of Chemistry, 2008.
- Madsen, I.C.; Scarlett, N.V.Y.; Kern, A.
  Description and survey of methodologies for the determination of amorphous content via X-ray powder diffraction.
  Z. Krist. *226*, 2011, 944.
- Madsen, I.C.; Scarlett, N.V.Y.; Riley, D.P.; Raven, M.D.
  Quantitative Phase Analysis using the Rietveld Method
  in *Modern Diffraction Methods*
  Eds. Mittemeijer and Welzel, Wiley, 2012.

Innovation with Integrity