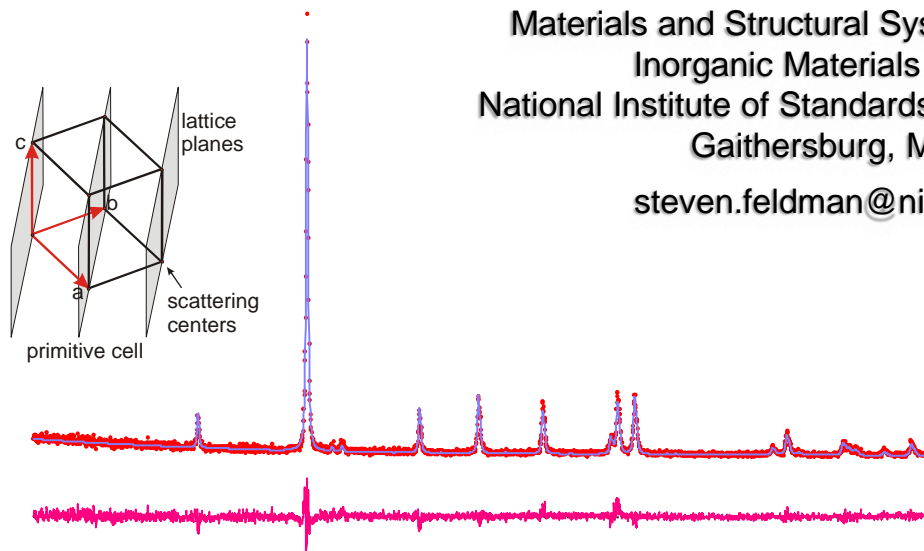
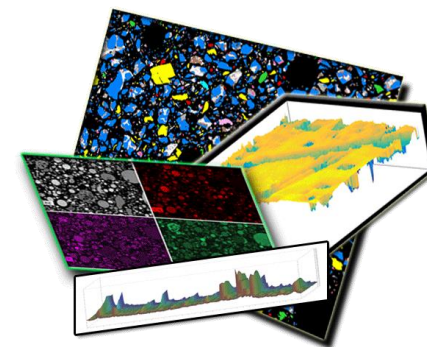


X-Ray Powder Diffraction and Rietveld Analysis with Applications to Cementitious Materials – II

Steve Feldman

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Inorganic Materials Group
National Institute of Standards and Technology
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steven.feldman@nist.gov



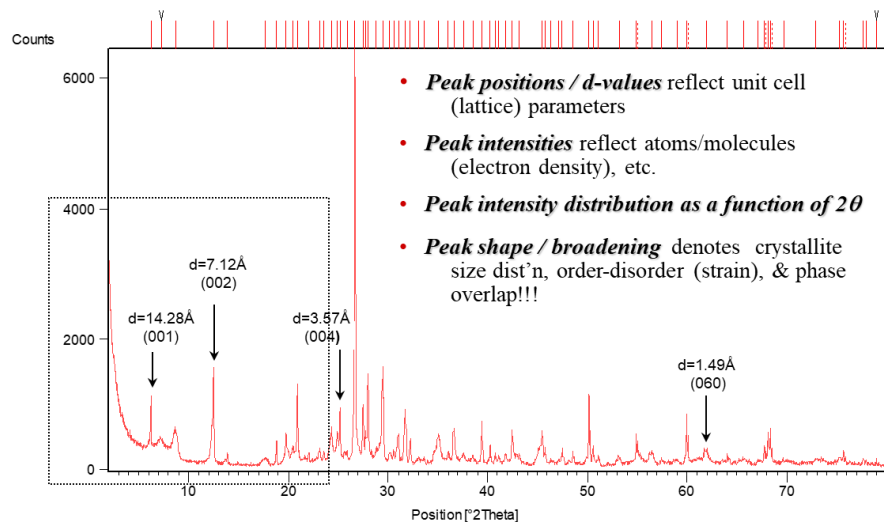
Optimizing Data Collection, and Sources of Error

Data Collection and Minimizing Error

Measurement considerations

Recall: Four parameters of special interest in an XRD Pattern

- ✓ *Position of the diffraction peaks*
- ✓ *Resolution of diffraction peaks*
- ✓ *Peak intensities*
- ✓ *Intensity distribution as a function of 2θ angle*



This requires accurate representation of the inherent scattering from the crystal lattices of all crystallites and phases present.

Data Collection and Minimizing Error

Measurement considerations

What is the optimum instrument configuration?

- ✓ choice of x-ray tube
- ✓ incident and diffracted beam optics
- ✓ low- or high-resolution

Collect data appropriate to the task at hand:

- ✓ qualitative or quantitative phase analysis
- ✓ unit cell determination / indexing
- ✓ solution of an unknown crystal structure
- ✓ refinement of a partially known structure

Data Collection and Minimizing Error

Sources of Error

- Measurement-dependent:
 - ✓ Resolution / step size
 - ✓ Counting statistics
- Specimen-dependent:
 - ✓ Particle-size and statistics
 - ✓ Preferred orientation
 - ✓ Absorption effects
 - ✓ Sample displacement
 - ✓ Phase composition (noncrystalline present?)
- Instrument-dependent
- Sample preparation (Paul S.)

Data Collection and Minimizing Error

Measurement considerations

What angular range must be covered?

- ✓ most intense lines of all phases should be measured

What step size must be used?

- ✓ step size \approx FWHM / 5 (minimum)

What count time should be used?

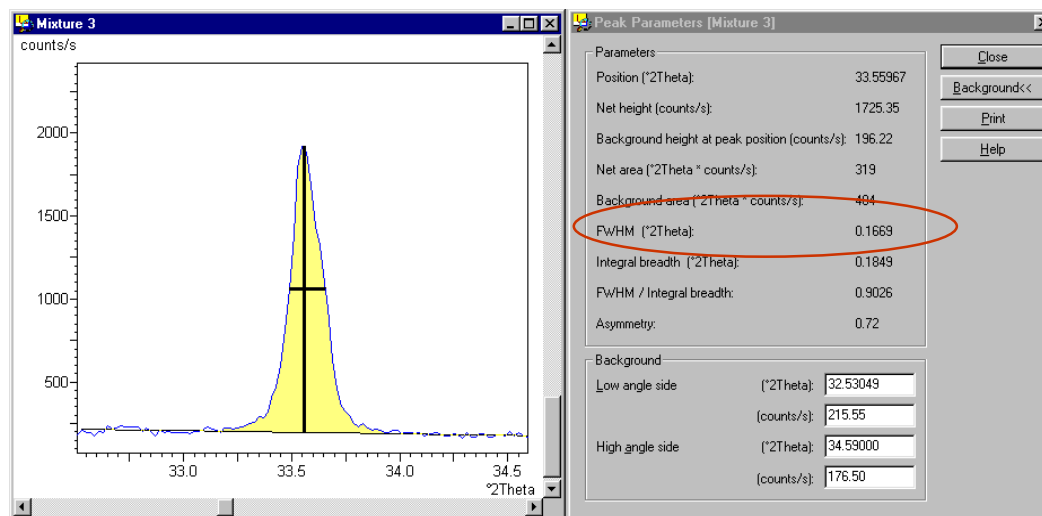
- ✓ ~10000+ counts in the main peak(s)

Data Collection and Minimizing Error

Measurement considerations

Data Collection: Step size example

Peak is 0.167°
($\sim 0.2^\circ$) FWHM



@ 0.02° step-1 = 10 steps across peak (above FWHM)

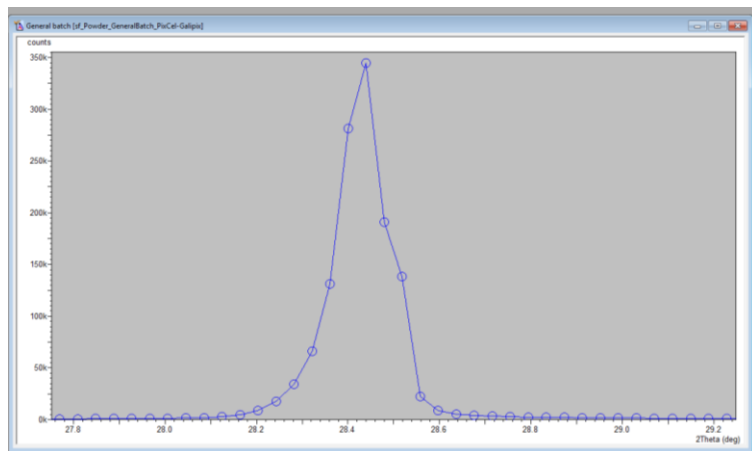
@ 0.03° step-1 = 7 steps across peak (above FWHM)

@ 0.04° step-1 = 5 steps across peak (above FWHM)

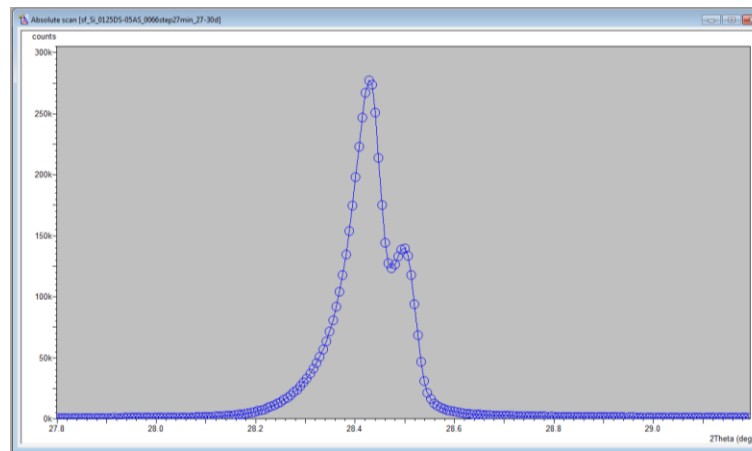
Data Collection and Minimizing Error

Measurement considerations

Data Collection: Step size example (FWHM = $0.167^\circ 2\theta$)



@ $0.04^\circ \text{ step}^{-1}$ = 4 steps across peak (above FWHM)



$0.015^\circ \text{ step}^{-1}$ = 10 steps across peak (above FWHM)

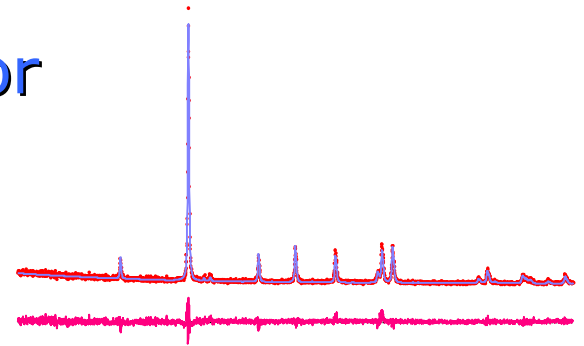
Which is better????

Data Collection and Minimizing Error

Measurement considerations

Counting Statistics

The magnitude of statistical counting error depends only on the *total number of counts* received at the detector.



$$\text{Std. Dev.} = \sqrt{\text{Counts}}$$

Ex 1: Peak intensity = 100 counts

$$\sqrt{100} = 10 \Rightarrow \text{Std. Err.} = 10 / 100 = 10\%$$

Ex 2: Peak intensity = 10000 counts

$$\sqrt{10000} = 100 \Rightarrow \text{Std. Err.} = 100 / 10000 = 1\%$$

<u>Desired σ (%)</u>	<u>N Required</u>
0.2	250,000
0.4	62,500
0.6	27,790
0.8	15,625
1.0	10,000
1.5	4,444
2.0	2,500
3.0	1,111
4.0	625
5.0	400

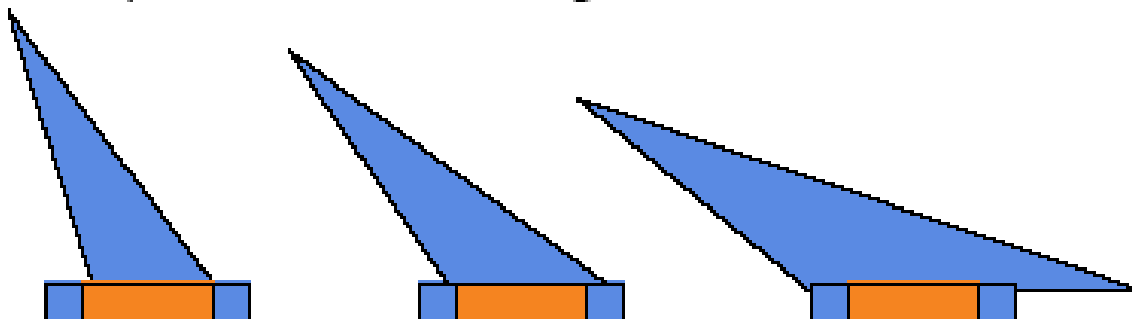
Data Collection and Minimizing Error

Measurement considerations

Sample length and thickness requirements

The sample must be equal to or longer than the spread of the incident beam at the lowest diffraction angle used.

- Make sure that you never over-irradiate the sample at low 2Theta angles...



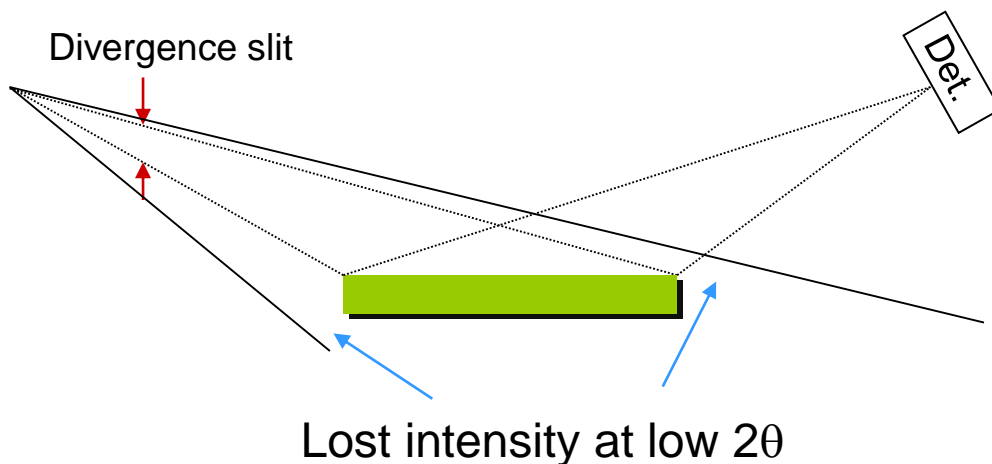
... it will give a very high background!

Data Collection and Minimizing Error

Measurement considerations

Sample length and thickness requirements

The sample must be equal to or longer than the spread of the incident beam at the lowest diffraction angle used.

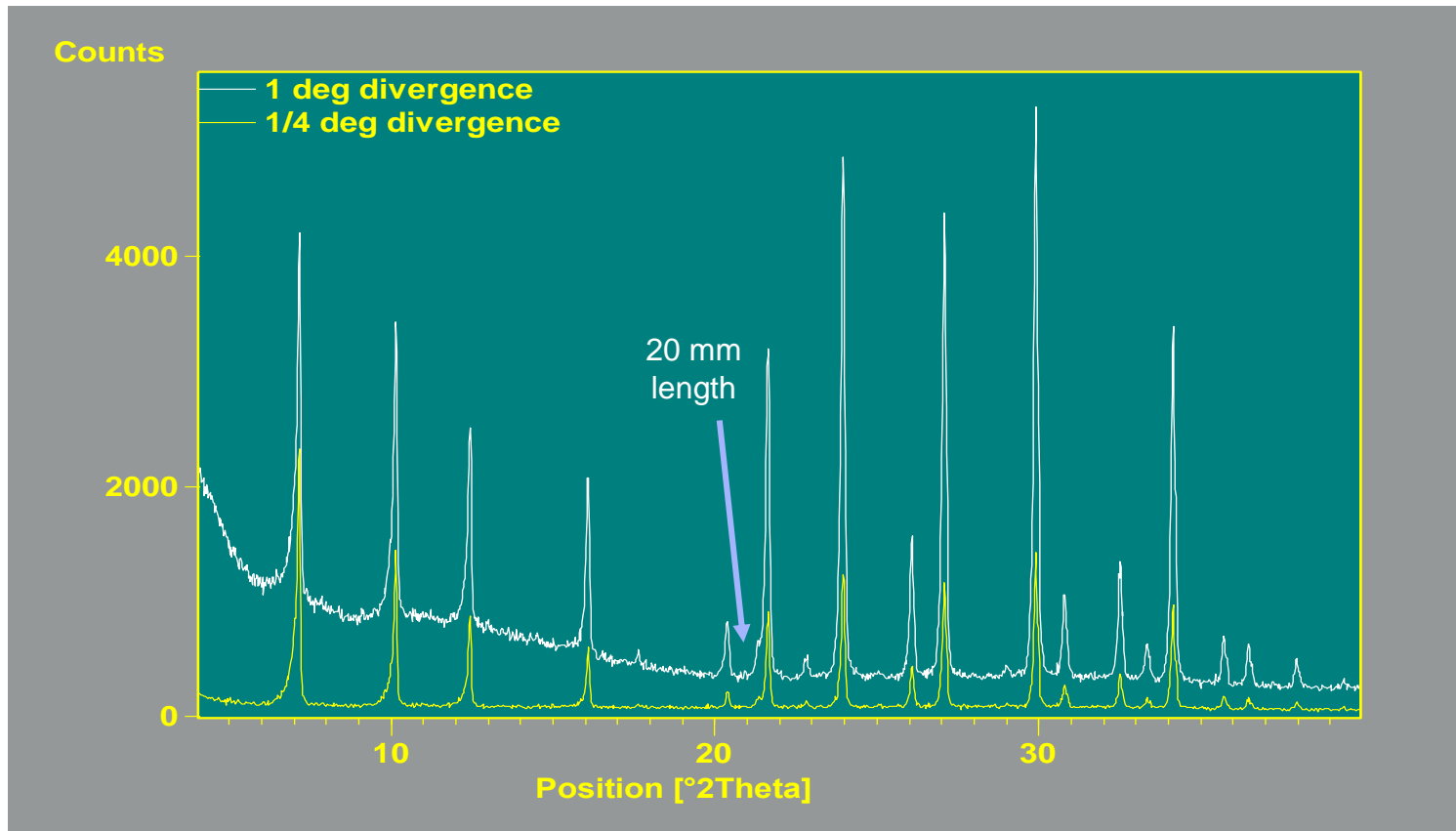


Therefore, select the proper fixed divergence slit

Data Collection and Minimizing Error

Measurement considerations

Divergence slits and peak intensities



Data Collection and Minimizing Error

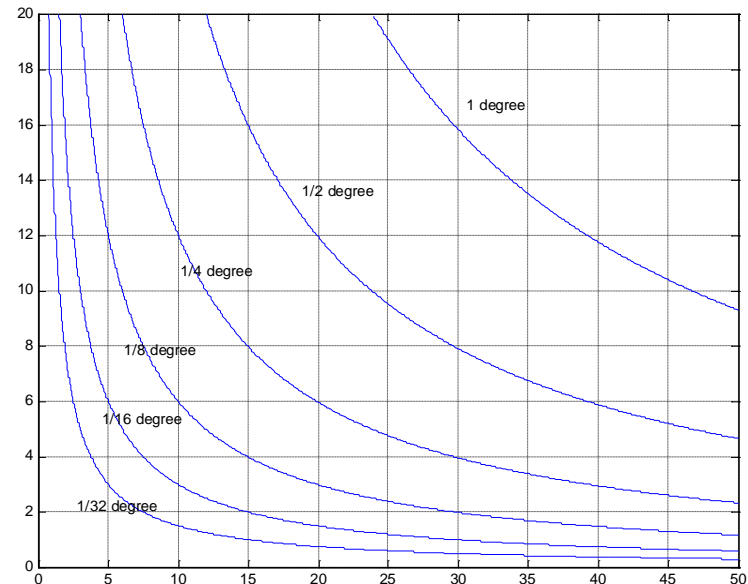
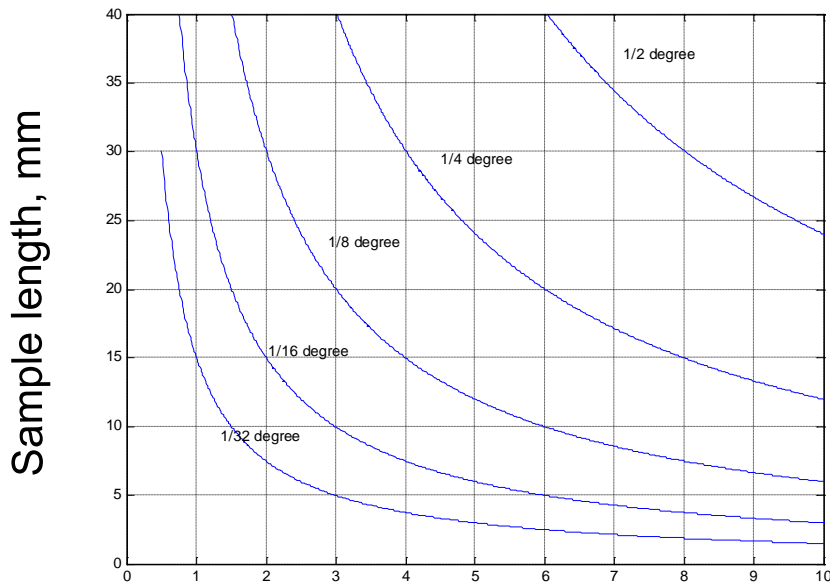
Measurement considerations

Sample illuminated length as a function of divergence slit and start angle
(240 mm radius goniometer)

Illuminated sample length:

$$L = R_o \tan \alpha / \sin \theta$$

where R_o is the goniometer radius in centimeters, and α is the angular aperture of the divergence slit in degrees.



Start angle, °2θ

Data Collection and Minimizing Error

Sources of Error

- Measurement-dependent:
 - ✓ Resolution / step size
 - ✓ Counting statistics
- Specimen-dependent:
 - ✓ Particle-size and statistics
 - ✓ Preferred orientation
 - ✓ Absorption effects
 - ✓ Sample displacement
 - ✓ Phase composition (noncrystalline present?)
- Instrument-dependent
- Sample preparation (Paul S.)

Data Collection and Minimizing Error

Specimen-dependent considerations

Particle-size, particle statistics, and relative intensities

Intensity Measurements on Different Size Fractions of <325-Mesh Quartz Powder (after Klug and Alexander [1974], p. 366)

Specimen No.	15-50 μ Fraction	5-50 μ Fraction	5- 15 μ Fraction	<5 μ Fraction
1	7.612	8.688	10.841	11.055
2	8.373	9.040	11.336	11.040
3	8.255	10.232	11.046	11.386
4	9.333	9.333	11.597	11.212
5	4.823	8.530	11.541	11.460
6	11.123	8.617	11.336	11.260
7	11.051	11.598	11.686	11.241
8	5.773	7.818	11.288	11.428
9	8.527	8.021	11.126	11.406
10	10.255	10.190	10.878	11.444
Mean area	8.513	9.227	11.268	11.293
Mean deviation	1.545	0.929	0.236	0.132
Mean % deviation	18.2	10.1	2.1	1.2

Large particle size (>50 μ) can lead to *poor particle statistics* and irreproducible *relative intensities*.



Reproducible intensities from pure quartz powders have been shown to be obtainable with Cu-K α radiation **only when size fractions <15 μ** were used.

Data Collection and Minimizing Error

Specimen-dependent considerations

Particle-size, particle statistics, and relative intensities

Only with sufficiently small particle-size will the theoretical relative intensity distribution of all diffraction lines from each mineral be present.

- ✓ With only large particles, there is an inadequate representation of all lattice planes, alignments, and orientations.

Data Collection and Minimizing Error

Specimen-dependent considerations

Particle-size, particle statistics, and relative intensities

<325-mesh (47μ) powders may not be sufficiently fine for anything but qualitative measurements.



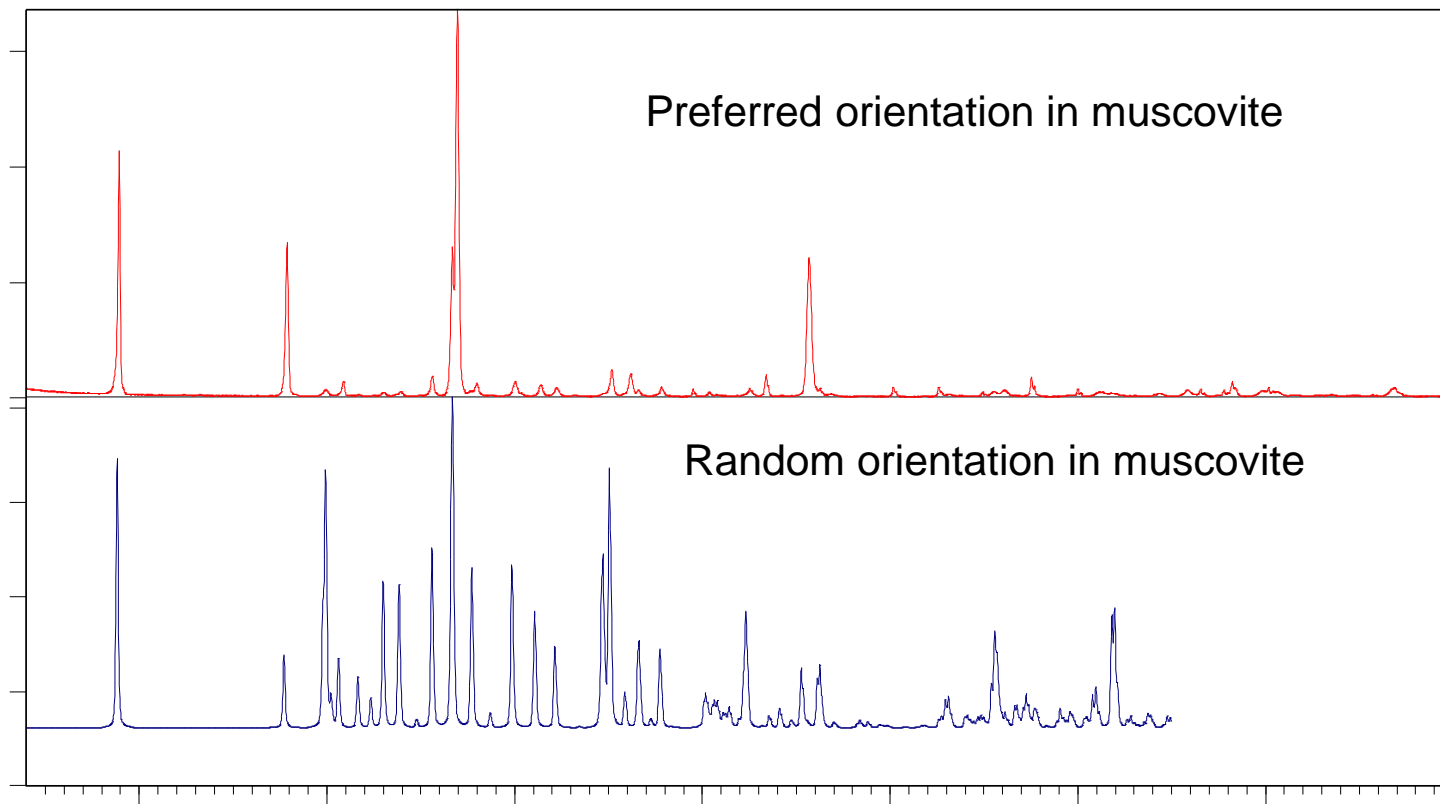
10μ powders are suitable for applications where a few percent error can be tolerated.

- ✓ Micronize important samples, preferably by wet milling.

Data Collection and Minimizing Error

Specimen-dependent considerations

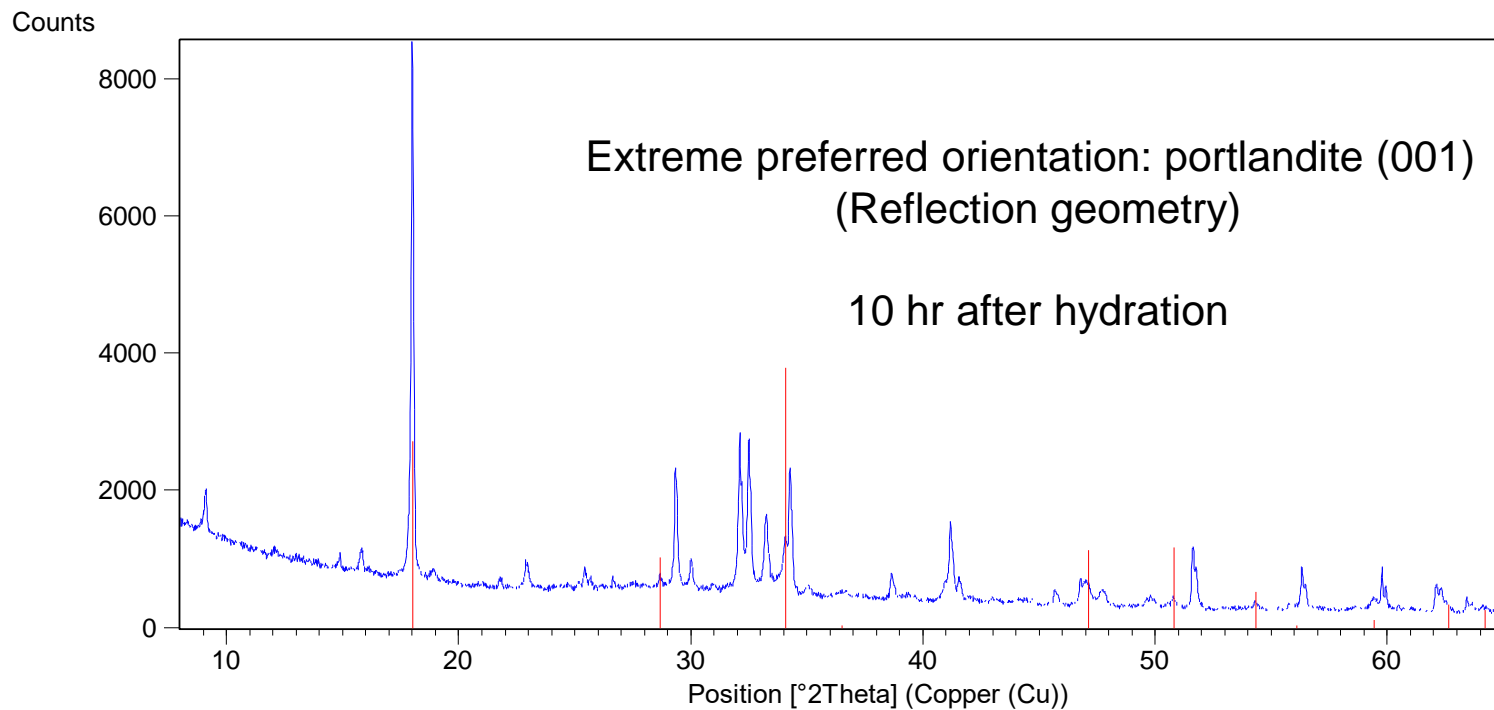
Preferred orientation: intensity artifact



Data Collection and Minimizing Error

Specimen-dependent considerations

Preferred orientation: intensity artifact

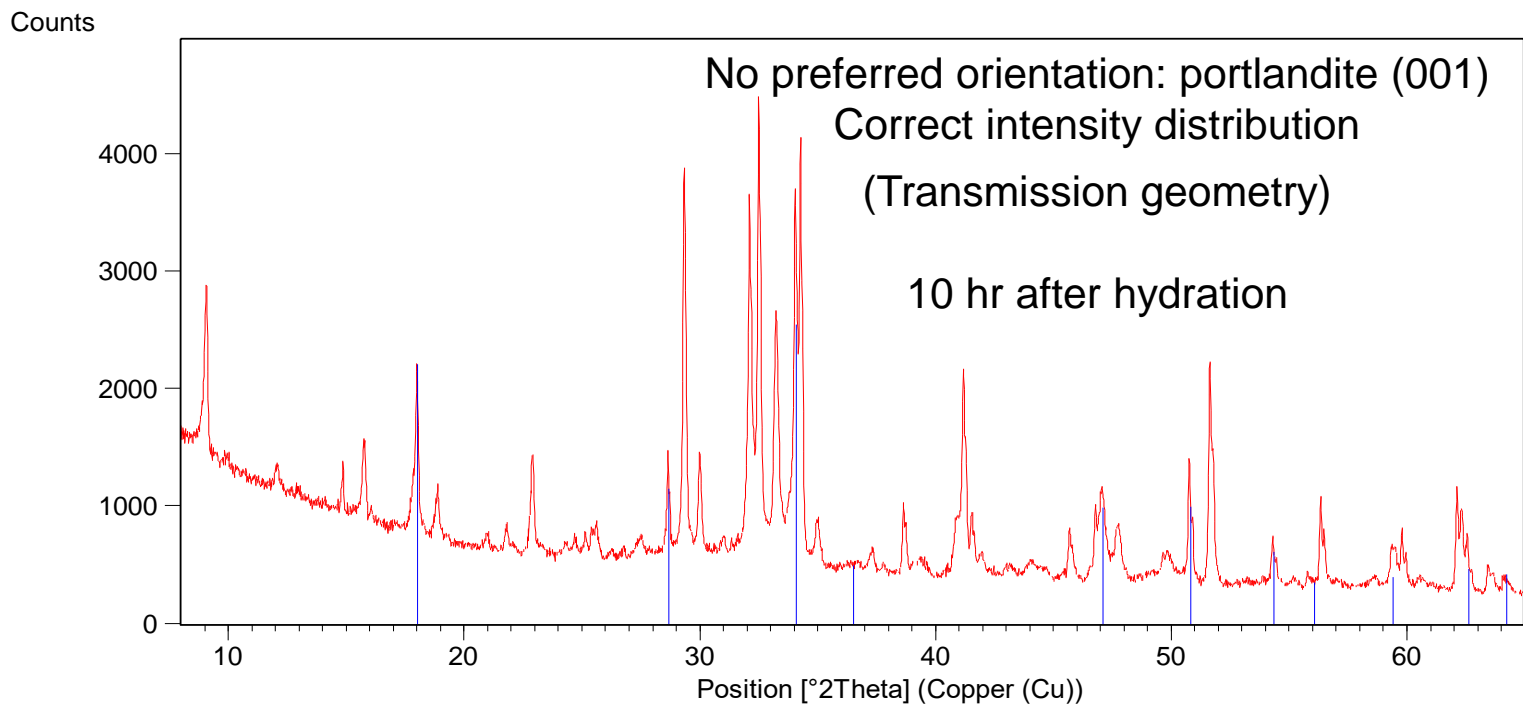


00-044-1481; Portlandite, syn; $\text{Ca}(\text{OH})_2$

Data Collection and Minimizing Error

Specimen-dependent considerations

Preferred orientation: intensity artifact

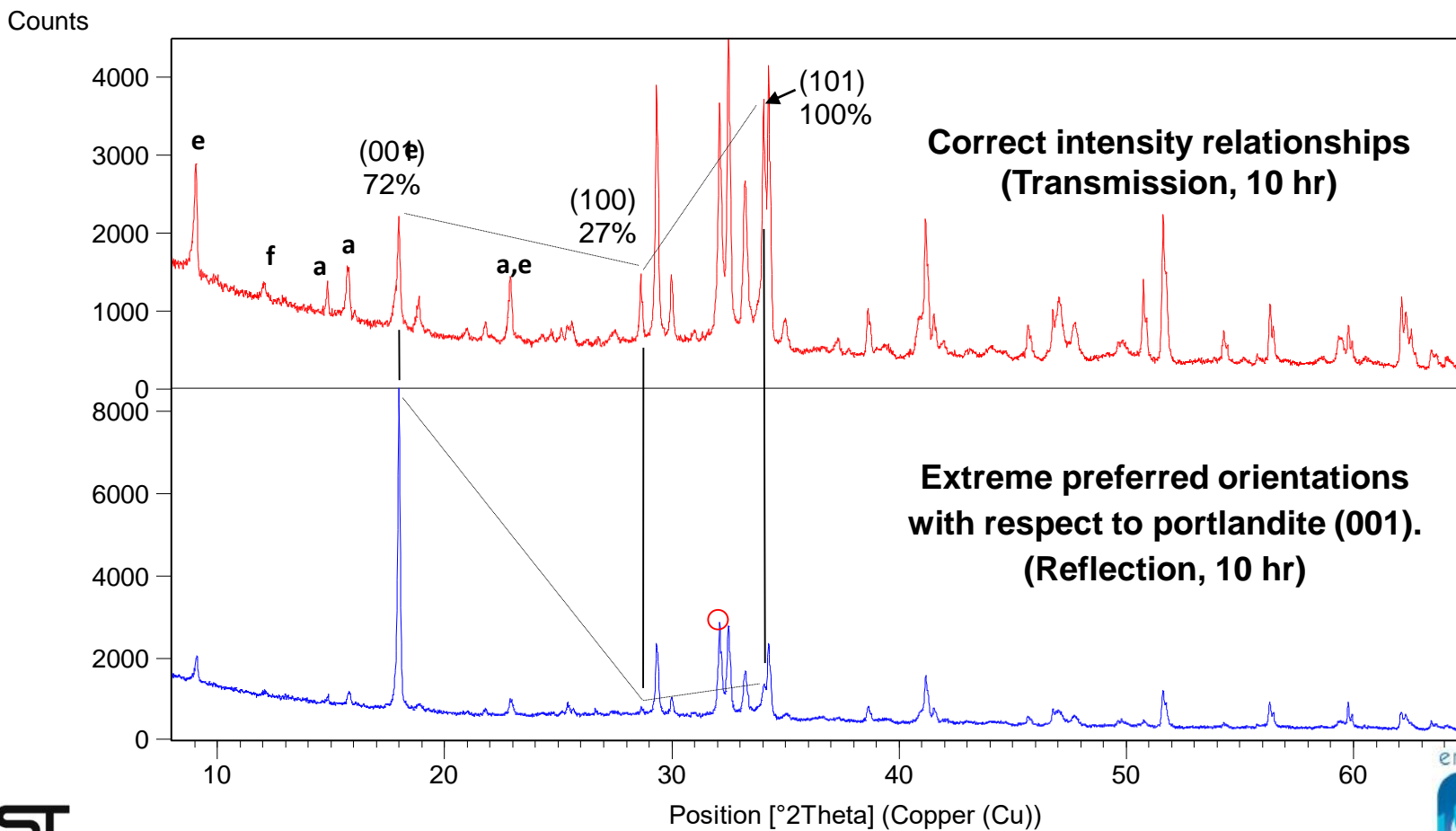


Peak List
00-044-1481; Portlandite, syn; Ca (OH) ₂

Data Collection and Minimizing Error

Specimen-dependent considerations

Preferred orientation: intensity artifact



Data Collection and Minimizing Error

Specimen-dependent considerations

Microabsorption

The loss (attenuation) of scattered intensity inside a particle. If this loss is different between two phases, the quantitative phase analysis will be affected.

--- *Brindley (1945)*

- Depends on grain diameter and linear absorption coefficient, μD
- Mitigate absorption contrast by grinding to particle size $<1\mu$
- Can be ignored if the product μD is equal for all phases
- Apply Brindley correction during Rietveld
- Use appropriate wavelength for the experiment

Data Collection and Minimizing Error

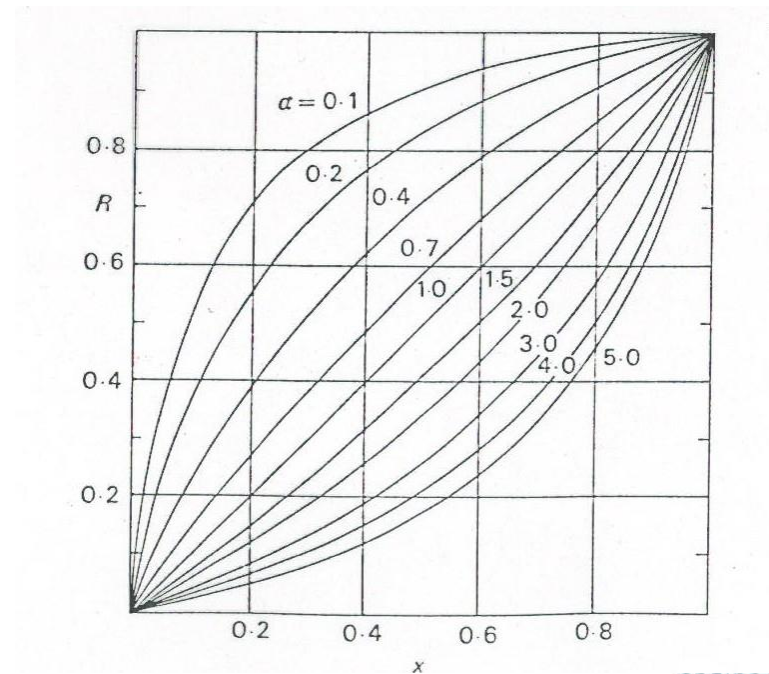
Specimen-dependent considerations

Microabsorption

Quantity:intensity relationships are seldom linear for highly variable mixtures!!!

Mass Absorption Coefficients (MAC) For Selected Elements (with CuK α radiation)

<u>Element</u>	<u>MAC</u>
Al	50.2
Si	65.3
K	148
Ca	171
Fe	304

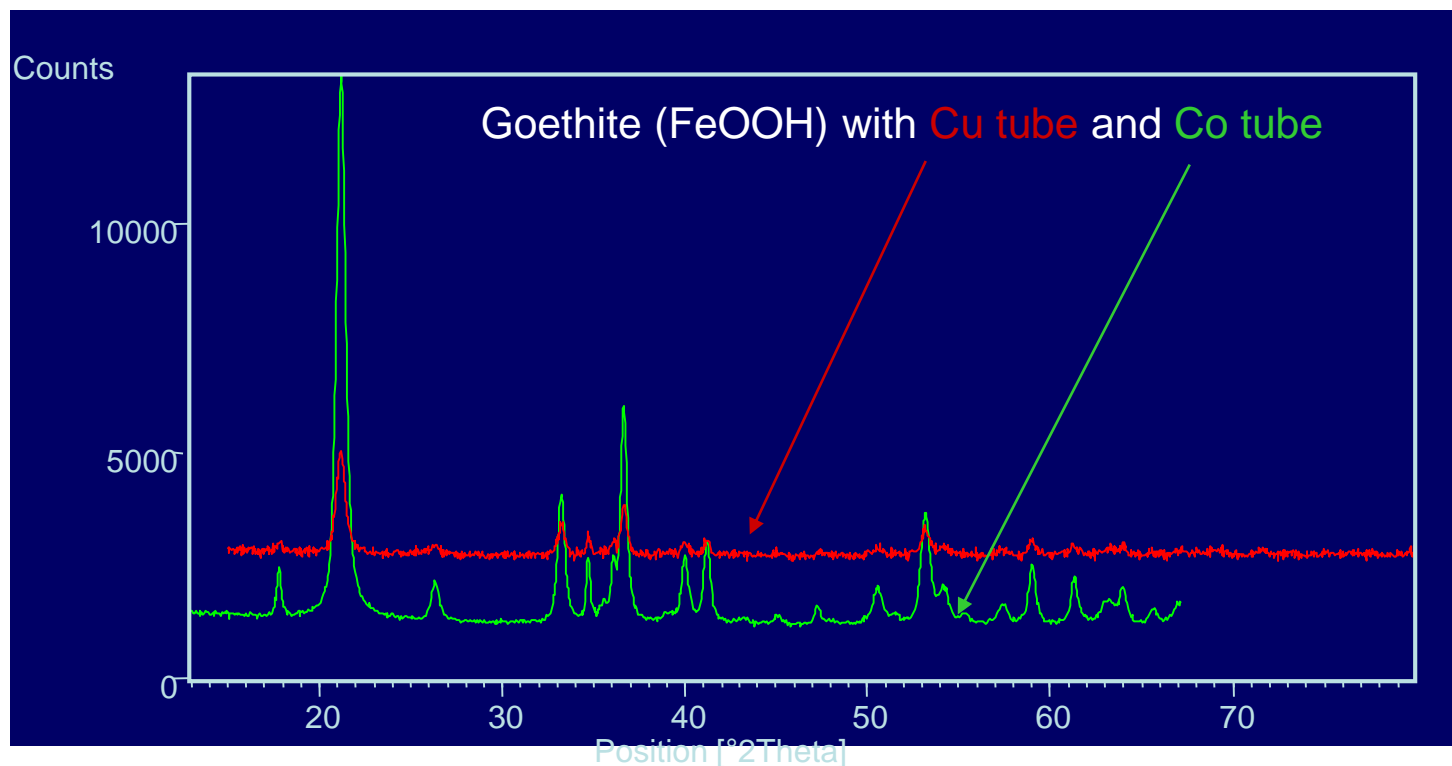


Data Collection and Minimizing Error

Specimen-dependent considerations

Microabsorption

Quantity:intensity relationships are seldom linear for highly variable mixtures!!!



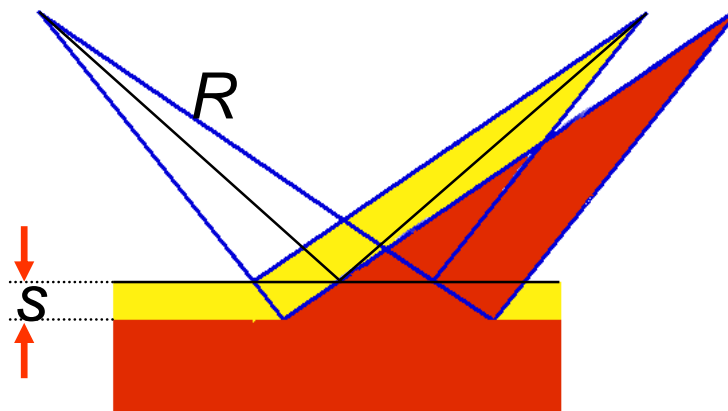
Data Collection and Minimizing Error

Specimen-dependent considerations

Sample (height) displacement

Displacement error (or transparency) in focusing geometry:

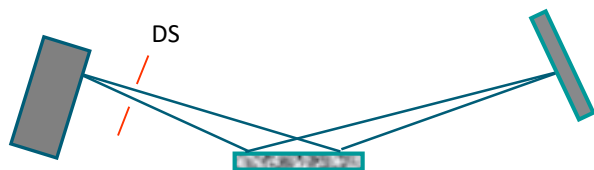
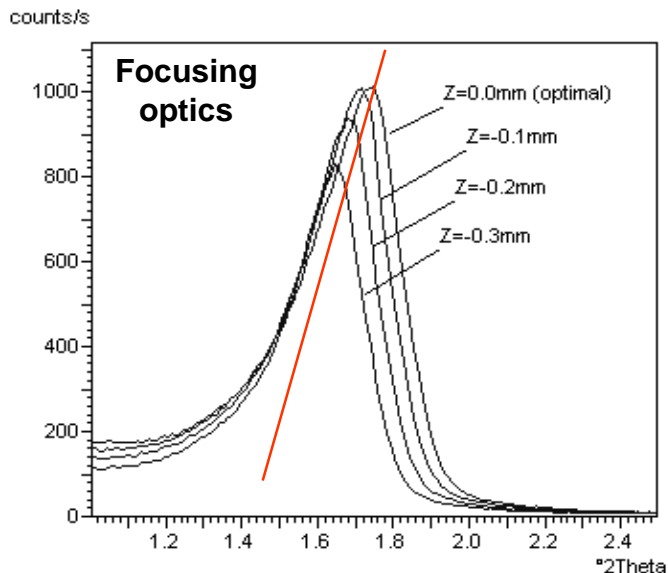
Sample stage and/or sample above or below diffraction plane: peaks are displaced from original position by



Data Collection and Minimizing Error

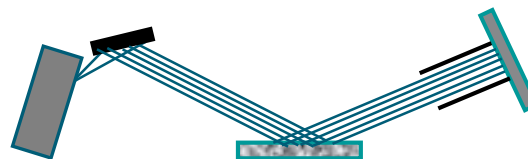
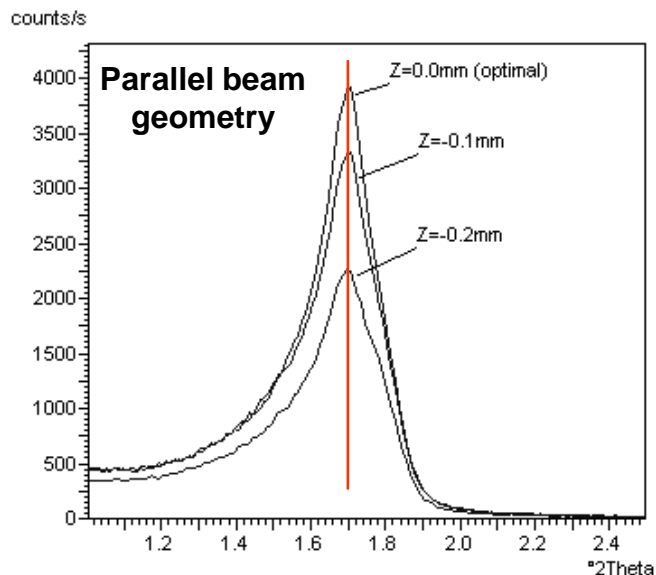
Specimen-dependent considerations

Sample (height) displacement



Reflection (focusing): flat samples

Intensity, resolution, and peak position are height dependent



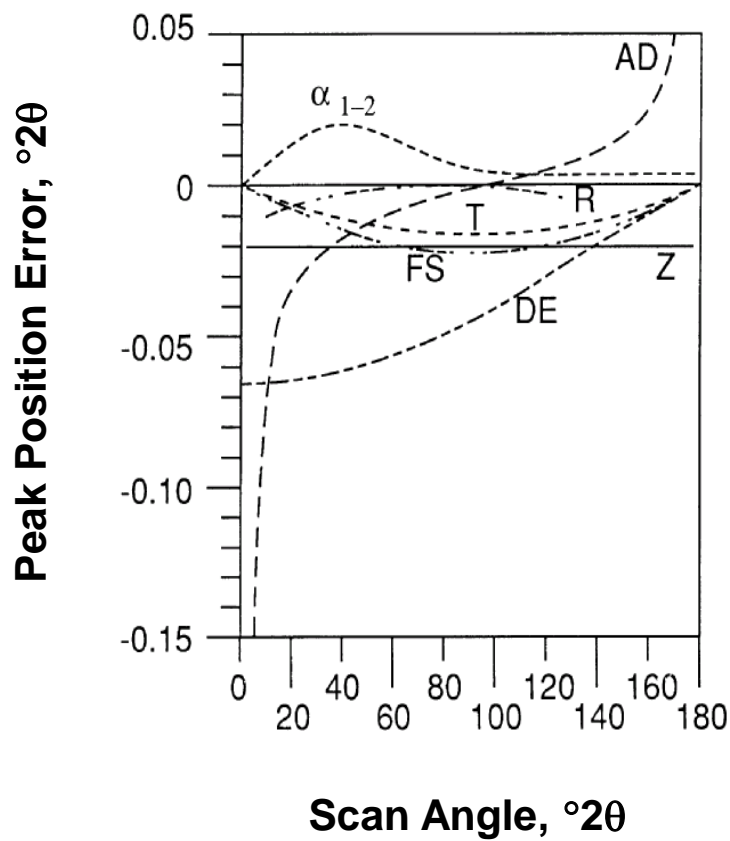
Parallel Beam: uneven surfaces

Resolution limited; intensity is height dependent

Data Collection and Minimizing Error

Instrument-dependent considerations

Summary of positional errors as a function of 2θ



$\alpha_{1-2} = \alpha_1$ shift due to α_2
AD = Axial Divergence
DE = 100 mm sample displ.
FS = Flat sample
R = -1 mm rec. slit position
T = 100 cm⁻¹ transparency
Z = 0.02° zero angle offset

Quantitative Phase Analysis

Quantitative Phase Analysis

Established methods of phase analysis in the cement industry

1. Microscopy / Point Counting

- ✓ Accurate, but time-intensive, subjective, and interstitial phases cannot be easily distinguished; limited use for plant control

2. Bogue Method

- ✓ Gives theoretical (potential) compositions based on calculation from elemental analysis (with inherent limitations)

3. XRD Analysis

- ✓ Actual (not Bogue) clinker phase composition
- ✓ Determination of free lime (CaO and Ca-sulfates)
- ✓ Limited historical use, but **many modern benefits**

Quantitative Phase Analysis

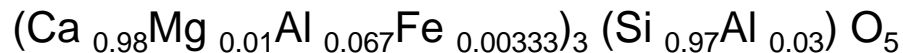
Established methods of phase analysis in the cement industry

The Bogue Method

Assumption 1: The composition of clinker phases are chemically pure (ideal stoichiometry); weight % can be calculated based on elemental analysis.

Fact: Actual clinker composition typically differs appreciably from that of pure C3S, C2S, C4AF, and C3A compounds.

Example: Alite (C3S)



vs.



(also large Al/Fe variation in ferrites)

Quantitative Phase Analysis

Established methods of phase analysis in the cement industry

The Bogue Method

Assumption 2: The clinker melt crystallizes to form solid phases under conditions of thermodynamic equilibrium at high temperature.

Fact: Equilibrium conditions are rarely achieved in industrial production and therefore ideal (pure) phases seldom result.

Assumption 3: Measured concentrations of CaO are all attributable to C3S, C2S, C4AF, or C3A.

Fact: Bogue calculations are typically not corrected for free lime and minor phases are ignored

Quantitative Phase Analysis

Established methods of phase analysis in the cement industry

The Bogue Method

Additionally:

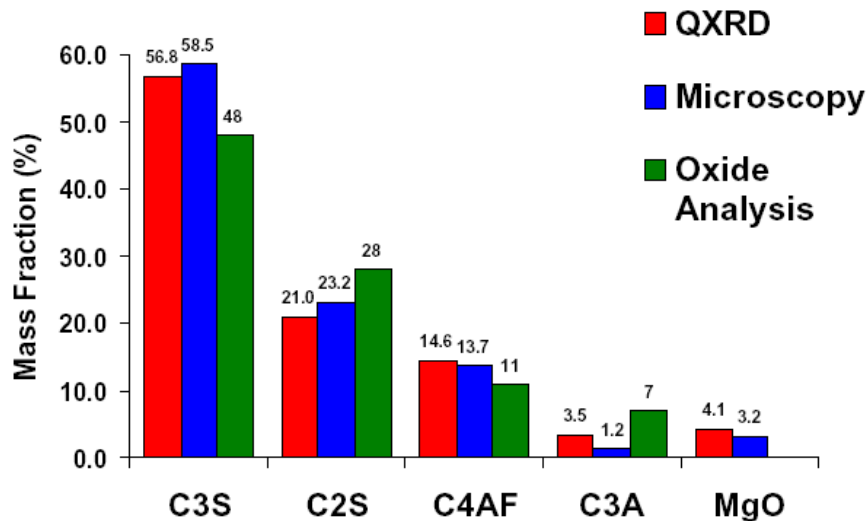
- ✓ No information is provided about polymorphs
(*e.g.*, o-C3A vs c-C3A)
- ✓ Elemental data poorly correlated with setting time, and strength
- ✓ Minor phases (*e.g.*, alkalis) are neglected

Quantitative Phase Analysis

Established methods of phase analysis in the cement industry

The Bogue Method

Phase Analysis of RM 8486 by QXRD,
Microscopy, and Calculation from Oxide
Analysis



Bogue:

- C₃S overestimated
- C₂S underestimated
- C₃A overestimated
- MgO ignored

-- P. Stutzman

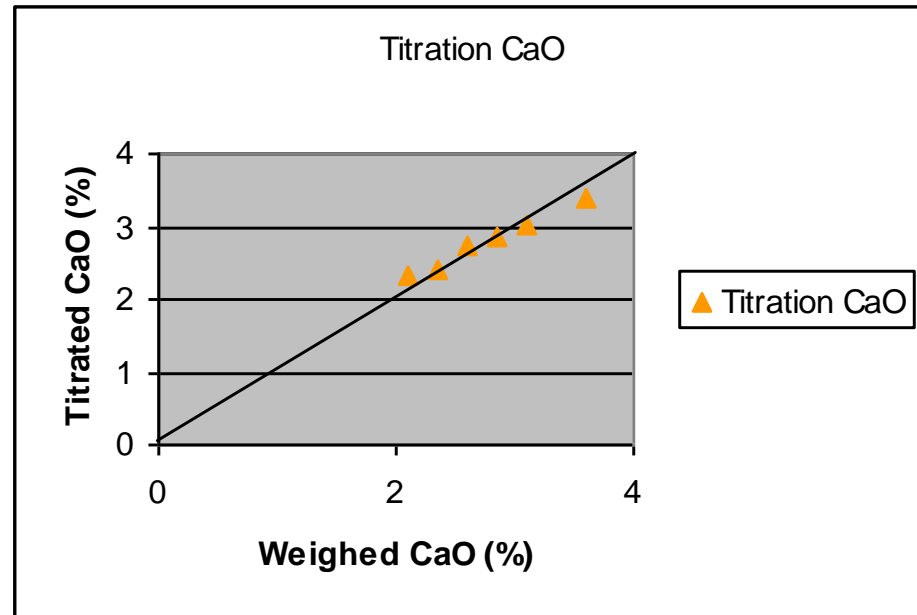
Quantitative Phase Analysis

Established methods of phase analysis in the cement industry

'Traditional' XRD methods: Free lime by calibration

Free Lime: Titration

Can be very accurate.....



Quantitative Phase Analysis

Established methods of phase analysis in the cement industry

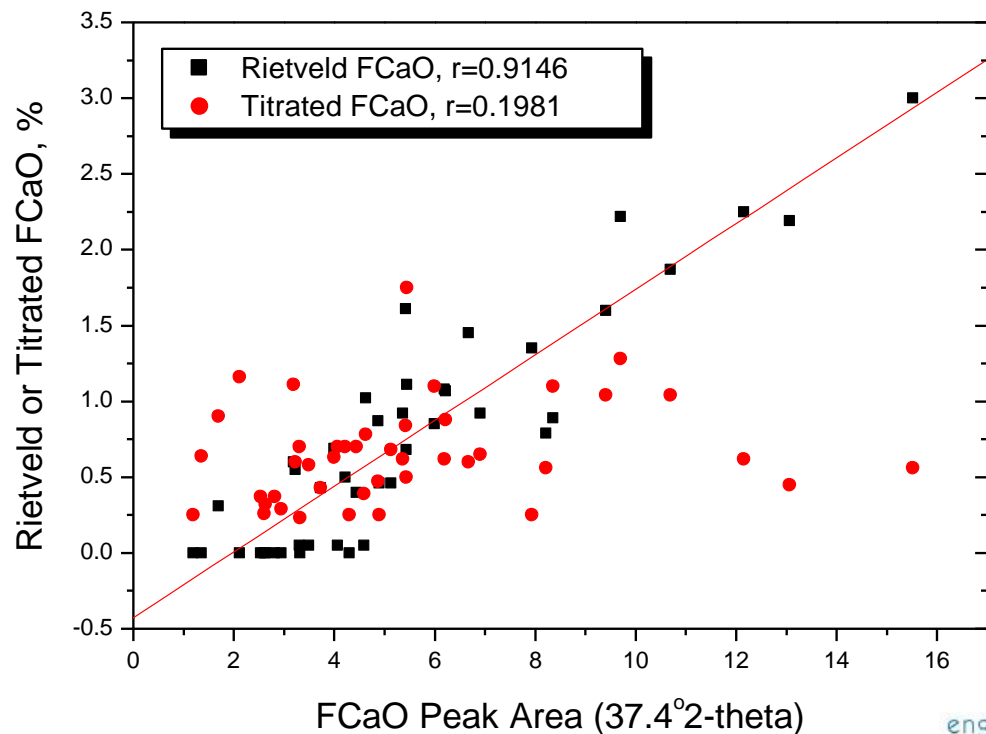
'Traditional' XRD methods: Free lime by calibration

Can be very accurate.....

...but not always

Titration *can be* highly variable.

Free Lime: XRD vs. titration



Quantitative Phase Analysis

Established methods of phase analysis in the cement industry

'Traditional' XRD methods: Free lime by calibration

Quantity (x) – Intensity (I)
relationship in XRD:

$$I_i = K_i \frac{X_i}{\rho_i \mu_m}$$

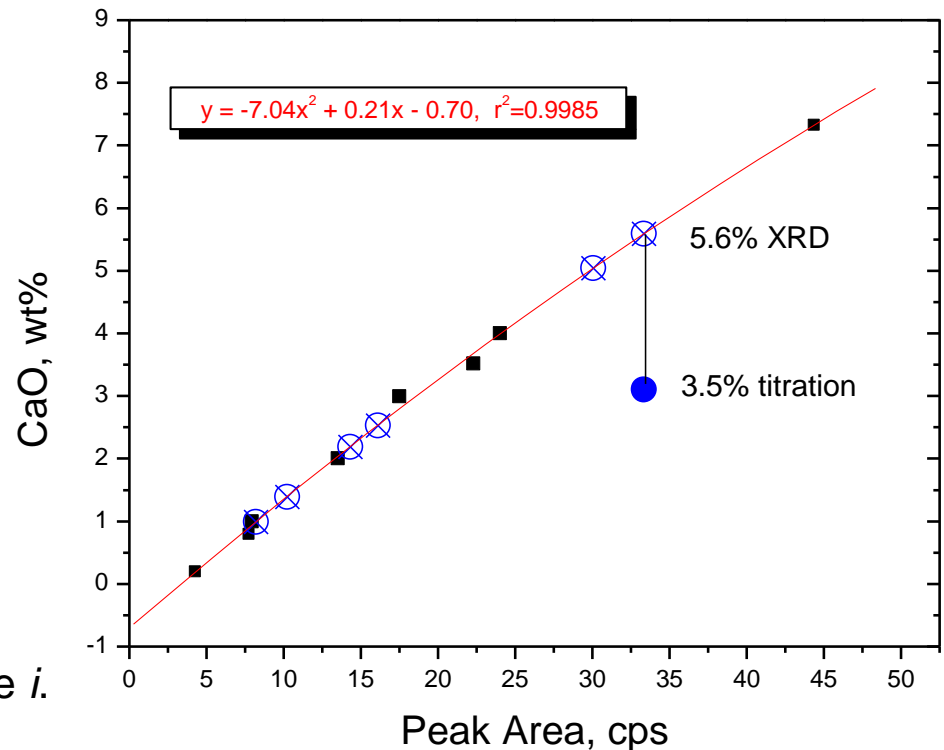
where

I_i = peak intensity of phase i ,

X_i = weight percent of phase i ,

ρ_i = density of phase i , and

μ_i = mass absorption coefficient of phase i .



Quantitative Phase Analysis

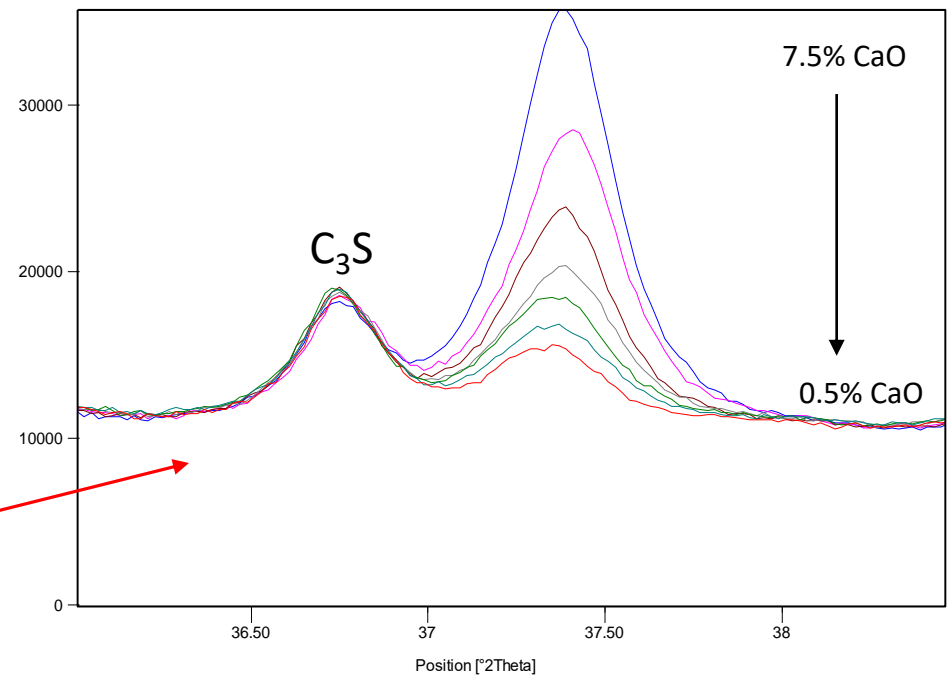
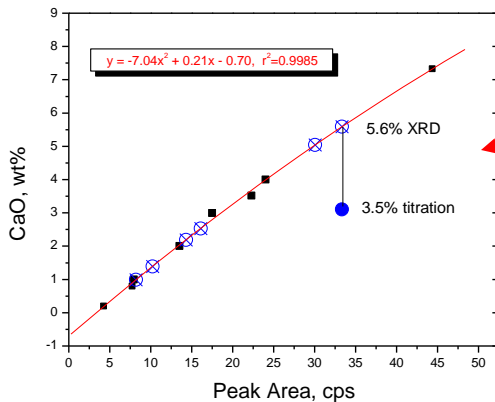
Established methods of phase analysis in the cement industry

'Traditional' XRD methods: Free lime by calibration

Fast, accurate, and sensitive at low concentrations with no interference from other 'lime' phases (CaOH_2)

Suitable standards are required.

Free-standing peak needed!!



Quantitative Phase Analysis

Established methods of phase analysis in the cement industry

'Traditional' XRD methods: **Limitations**

Classical methods for clinker/cement analysis are limited by:

- ✓ Substantial peak overlap among major phases
- ✓ Peak position and/or intensity shifts
- ✓ *Calibration standards* are unstable, difficult to obtain, or impure

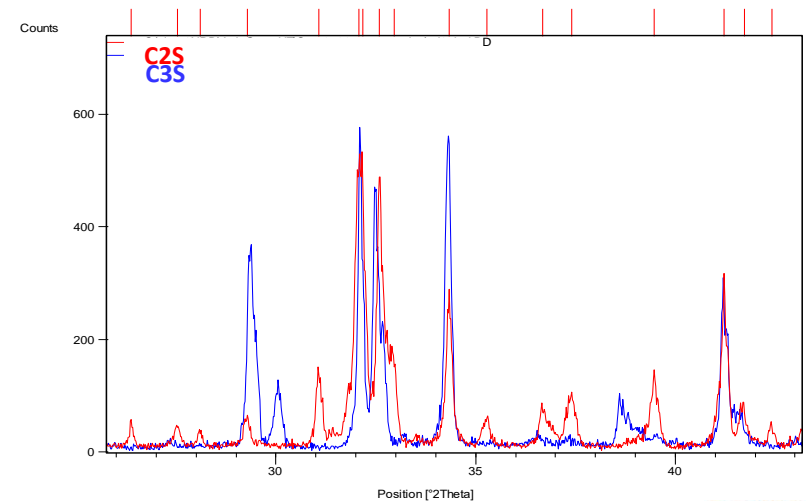
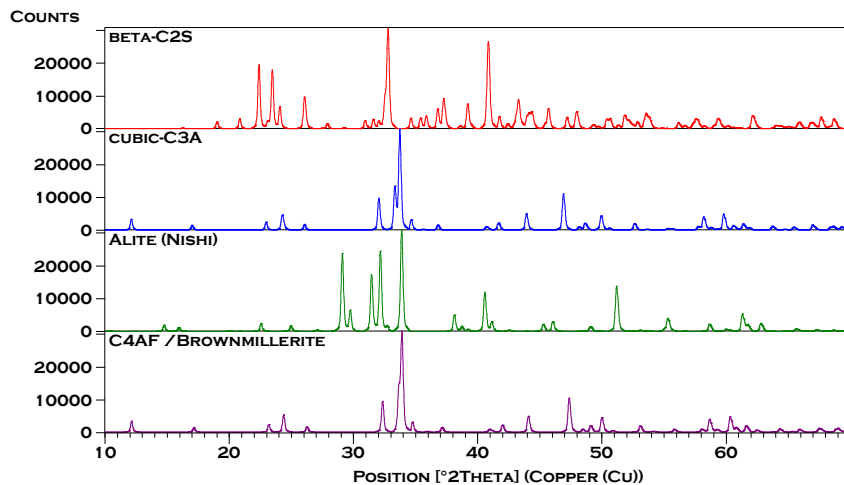
Quantitative Phase Analysis

Established methods of phase analysis in the cement industry

'Traditional' XRD methods: **Limitations**

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Quantitative Phase Analysis

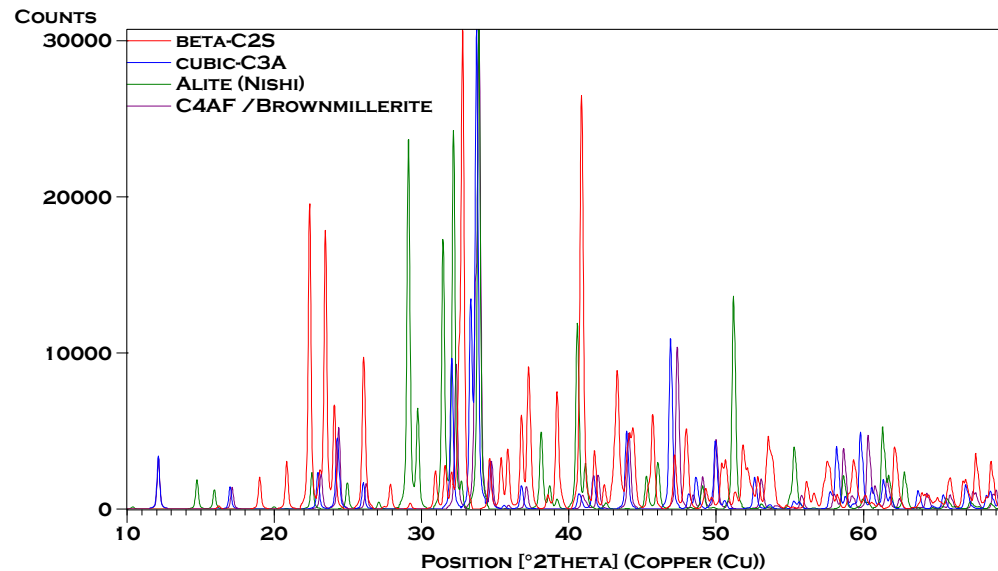
Established methods of phase analysis in the cement industry

'Traditional' XRD methods: **Limitations**

Classical methods for clinker/cement analysis are limited by:

- ✓ Substantial peak overlap among major phases

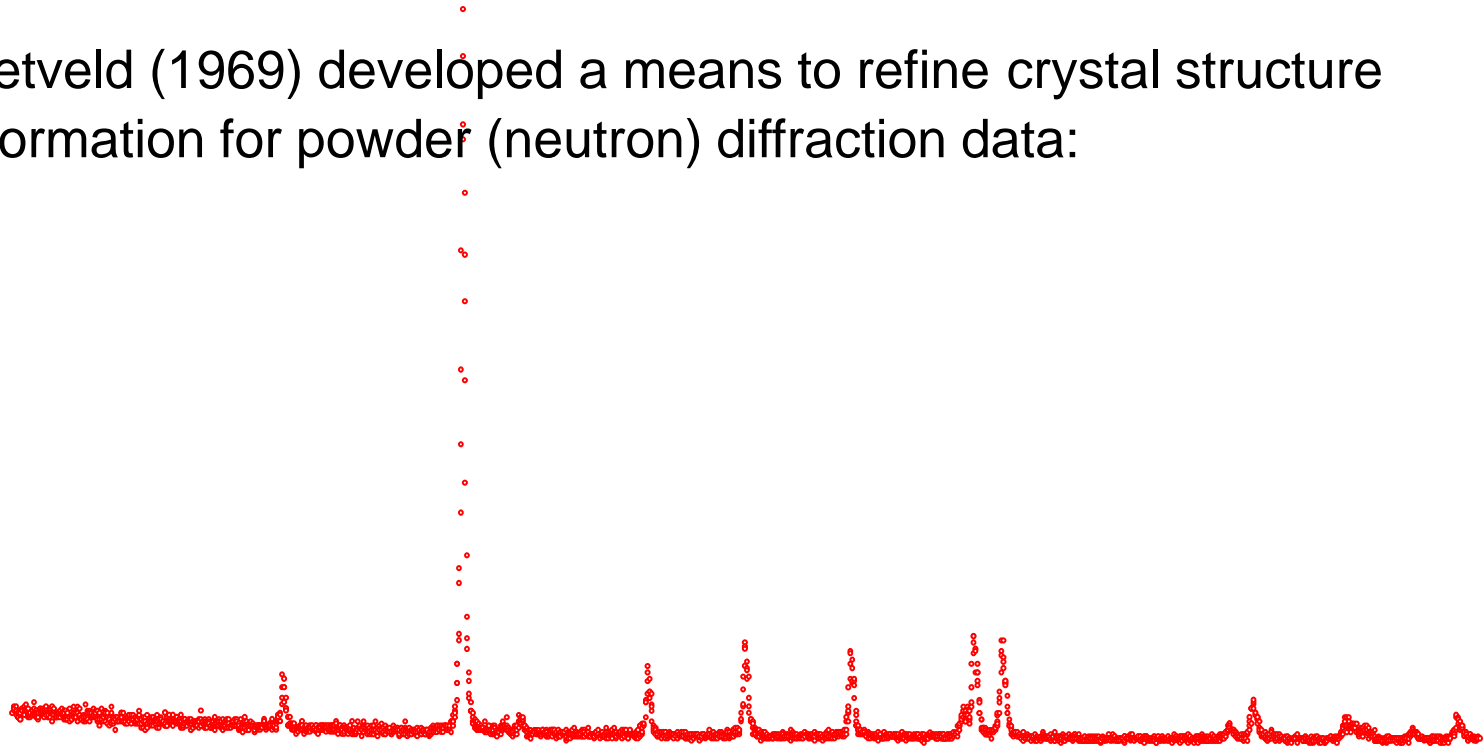
All 4 major
clinker phases:



Quantitative Phase Analysis

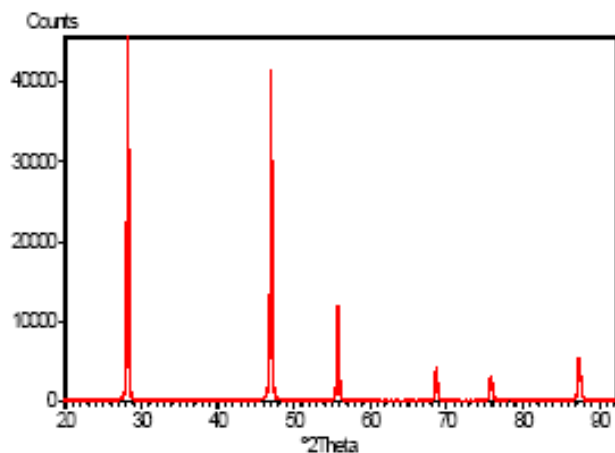
The Rietveld Method

Rietveld (1969) developed a means to refine crystal structure information for powder (neutron) diffraction data:

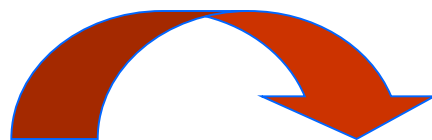


Quantitative Phase Analysis

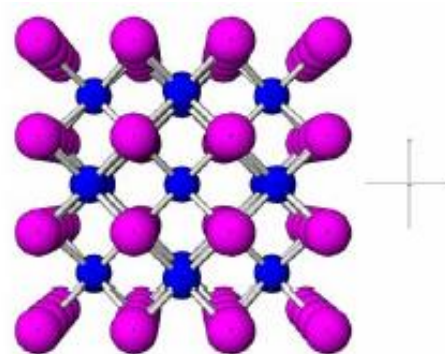
The Rietveld Method



NaCl calculated

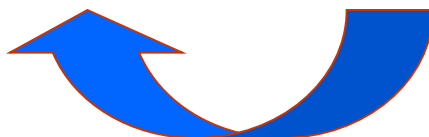


Structure Solution



NaCl

Rietveld (simulation)

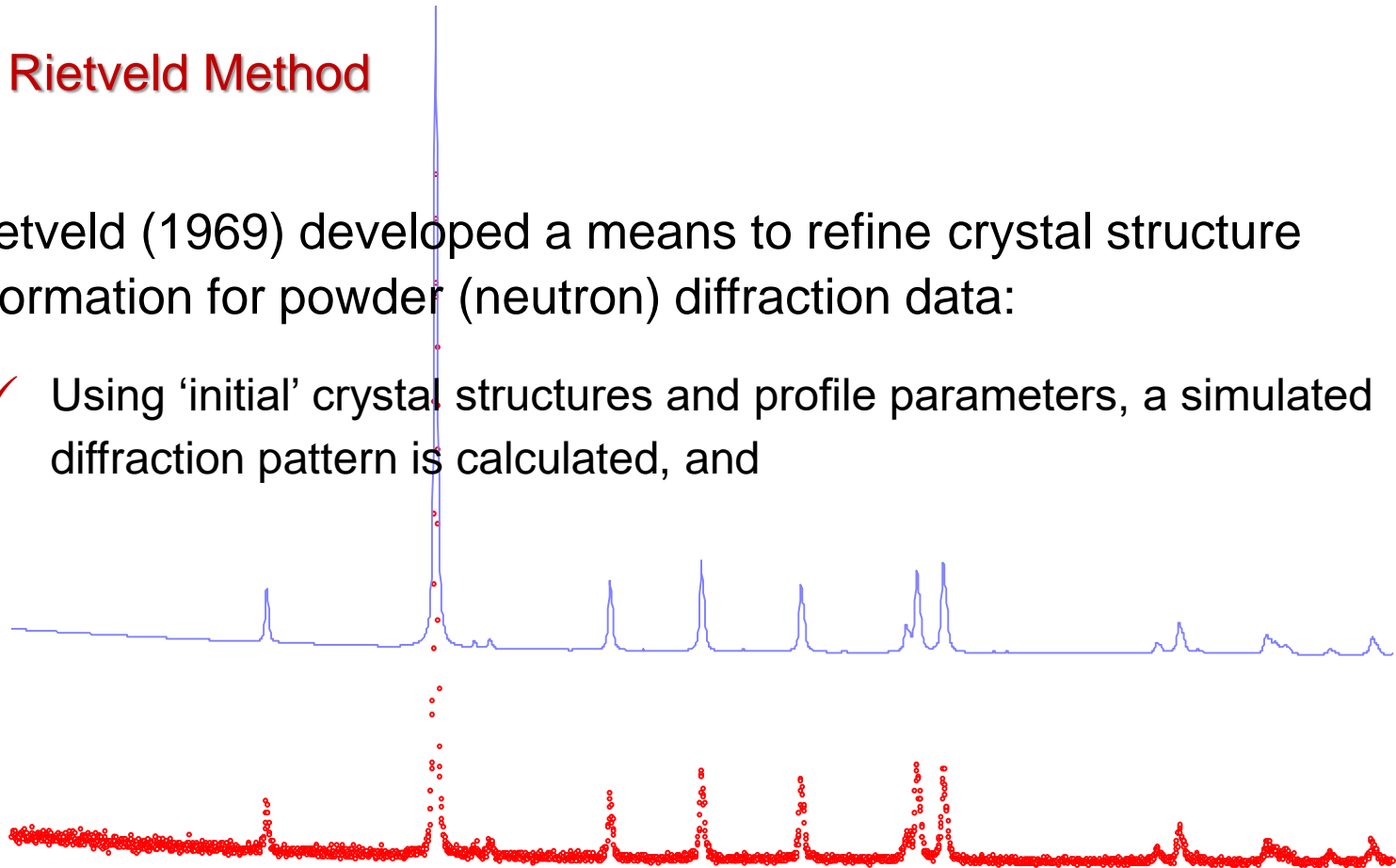


Quantitative Phase Analysis

The Rietveld Method

Rietveld (1969) developed a means to refine crystal structure information for powder (neutron) diffraction data:

- ✓ Using 'initial' crystal structures and profile parameters, a simulated diffraction pattern is calculated, and

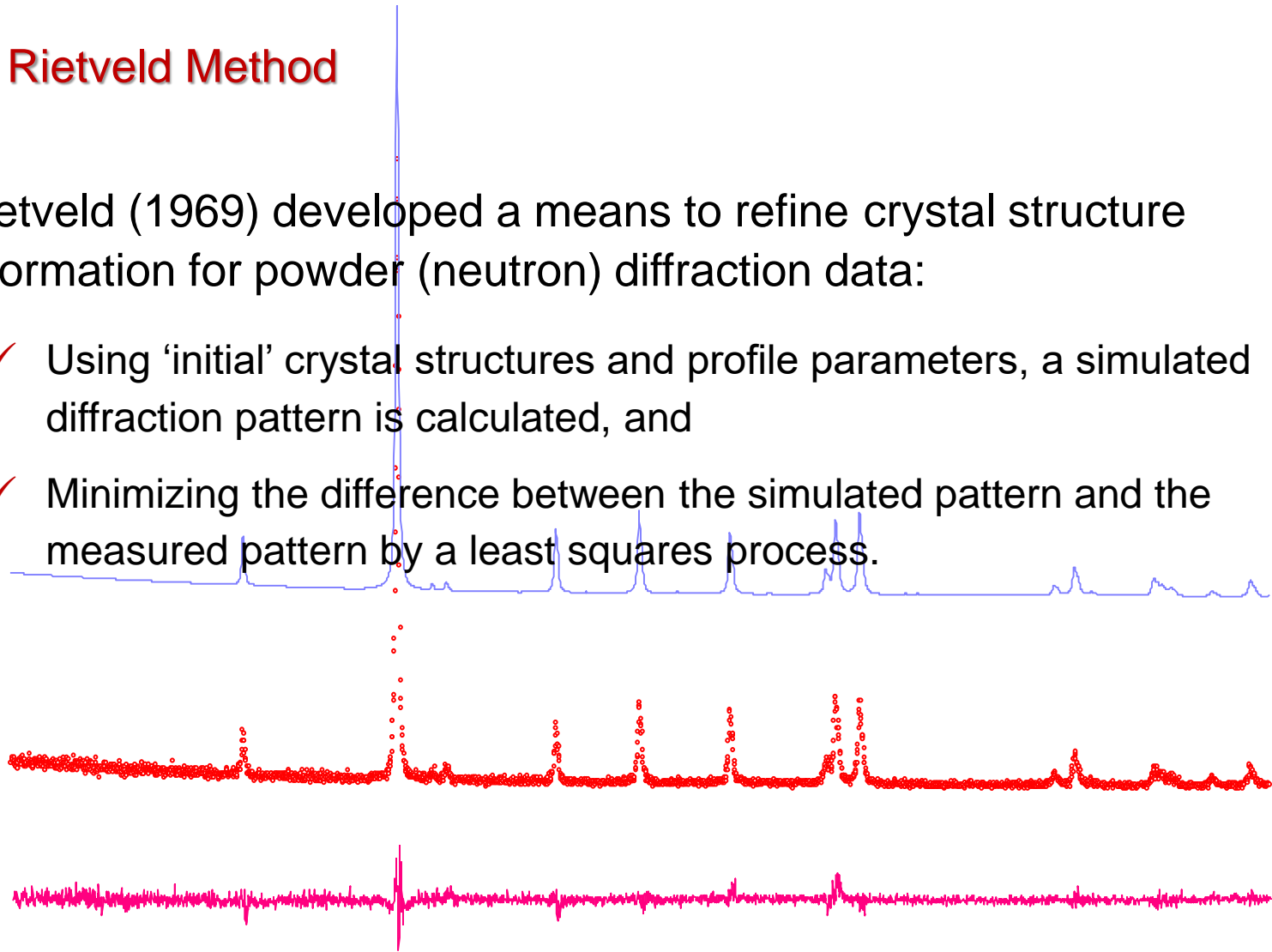


Quantitative Phase Analysis

The Rietveld Method

Rietveld (1969) developed a means to refine crystal structure information for powder (neutron) diffraction data:

- ✓ Using 'initial' crystal structures and profile parameters, a simulated diffraction pattern is calculated, and
- ✓ Minimizing the difference between the simulated pattern and the measured pattern by a least squares process.



Quantitative Phase Analysis

The Rietveld Method

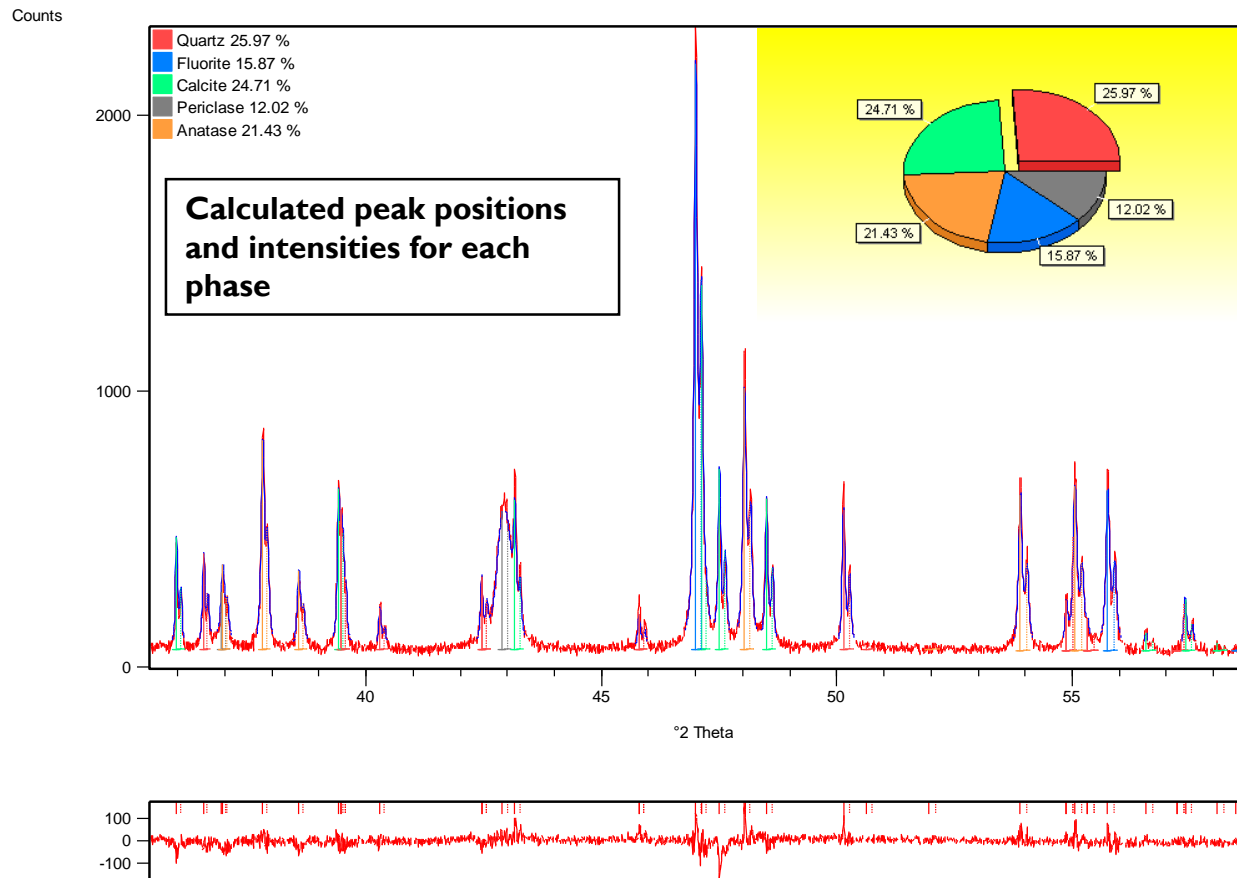
Advantages

- ✓ Models each phase independently \therefore overlapped peaks and complex mixtures can be analyzed,
- ✓ Is not limited by the unavailability of suitable calibration standards,
- ✓ Can refine site occupancies (solid-solution effects),
- ✓ Can model and correct orientation and other errors,
- ✓ Can calculate amorphous content

Quantitative Phase Analysis

The Rietveld Method


Rietveld uses all peaks and the complete profile (all data points) for the analysis




Quantitative Phase Analysis

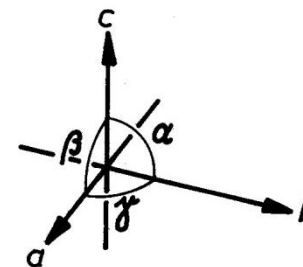
The Rietveld Method: Required input

Structural parameters: Crystal structures for calculation of the diffraction pattern

- ✓ Space group information  Generation of reflections (peak positions)
 - Symmetry and translation vectors
 - Unit cell parameters

- ✓ Atom types and positions  Peak intensities
 - Site occupancy
 - Electron density / scattering

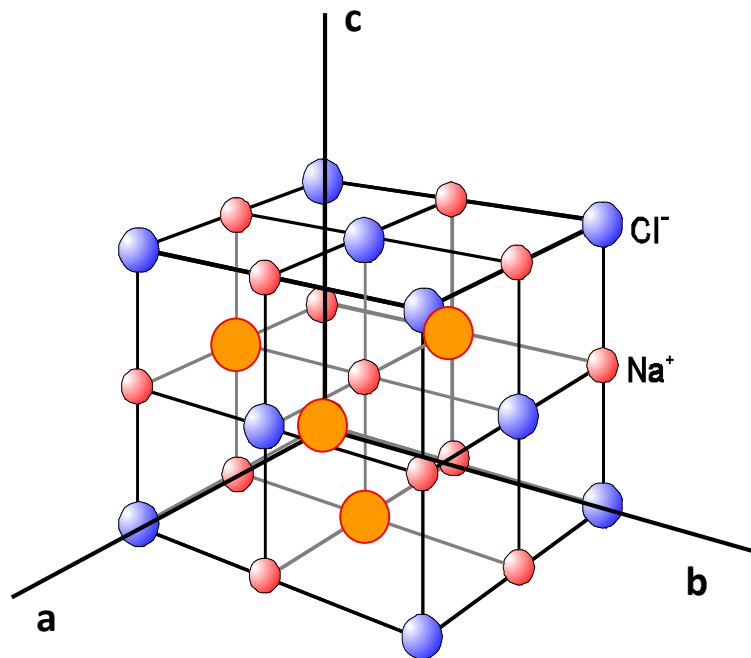
Space Group P 32 2 1; SG Number 154								
Red Cell P 4.912 4.912 5.404 90 90 120 112.959								
Atom	#	OX	SITE	x	y	z	SOF	
Si	1	+4	3 a	0.4705(3)	0	0.6667	1.	
O	1	-2	6 c	0.4152(7)	0.2678(6)	0.7851(4)	1.	



Quantitative Phase Analysis

The Rietveld Method: Required input

Halite: Face-Centered Cubic Structure (FCC)



<u>Cl⁻</u>	<u>Na⁺</u>
(0, 0, 0)	(1/2, 1/2, 1/2)
(1/2, 1/2, 0)	(0, 0, 1/2)
(1/2, 0, 1/2)	(0, 1/2, 0)
(0, 1/2, 1/2)	(1/2, 0, 0)

Quantitative Phase Analysis

The Rietveld Method: Required input

Overview

1. Accurate phase ID is required
2. Input crystal structures for each phase
3. A calculated pattern for all phases is generated from the crystal structure data.

Quantitative Phase Analysis

The Rietveld Method: Required input

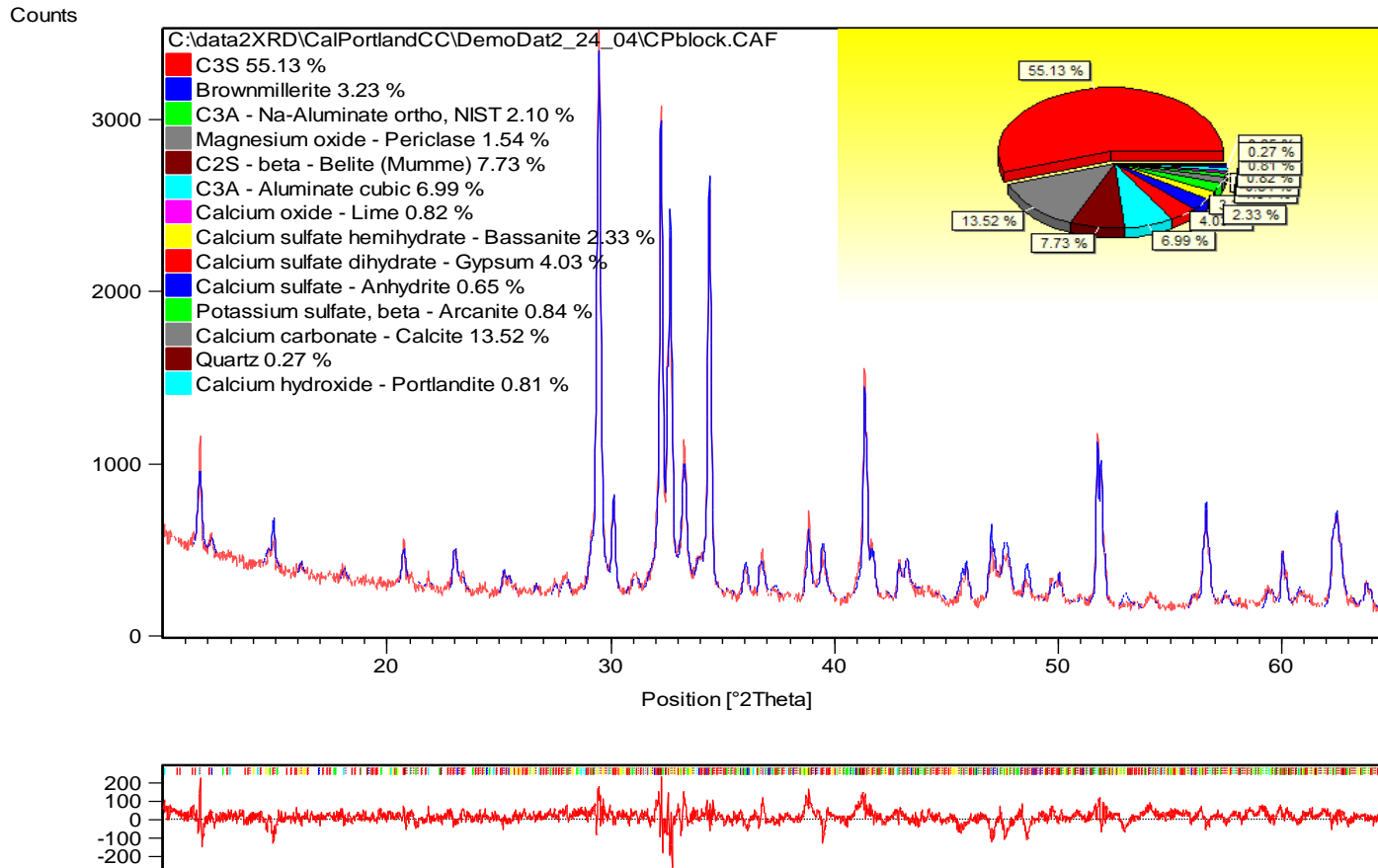
Overview

1. Accurate phase ID is required
2. Input crystal structures
3. A calculated pattern for all phases is generated from the crystal structure data.
4. The calculated pattern is fit to the raw data ('refined') by modifying the appropriate:
 - ✓ unit cell parameters,
 - ✓ scale factor,
 - ✓ peak shape and profile parameters, *etc.*

Quantitative Phase Analysis

The Rietveld Method: Example

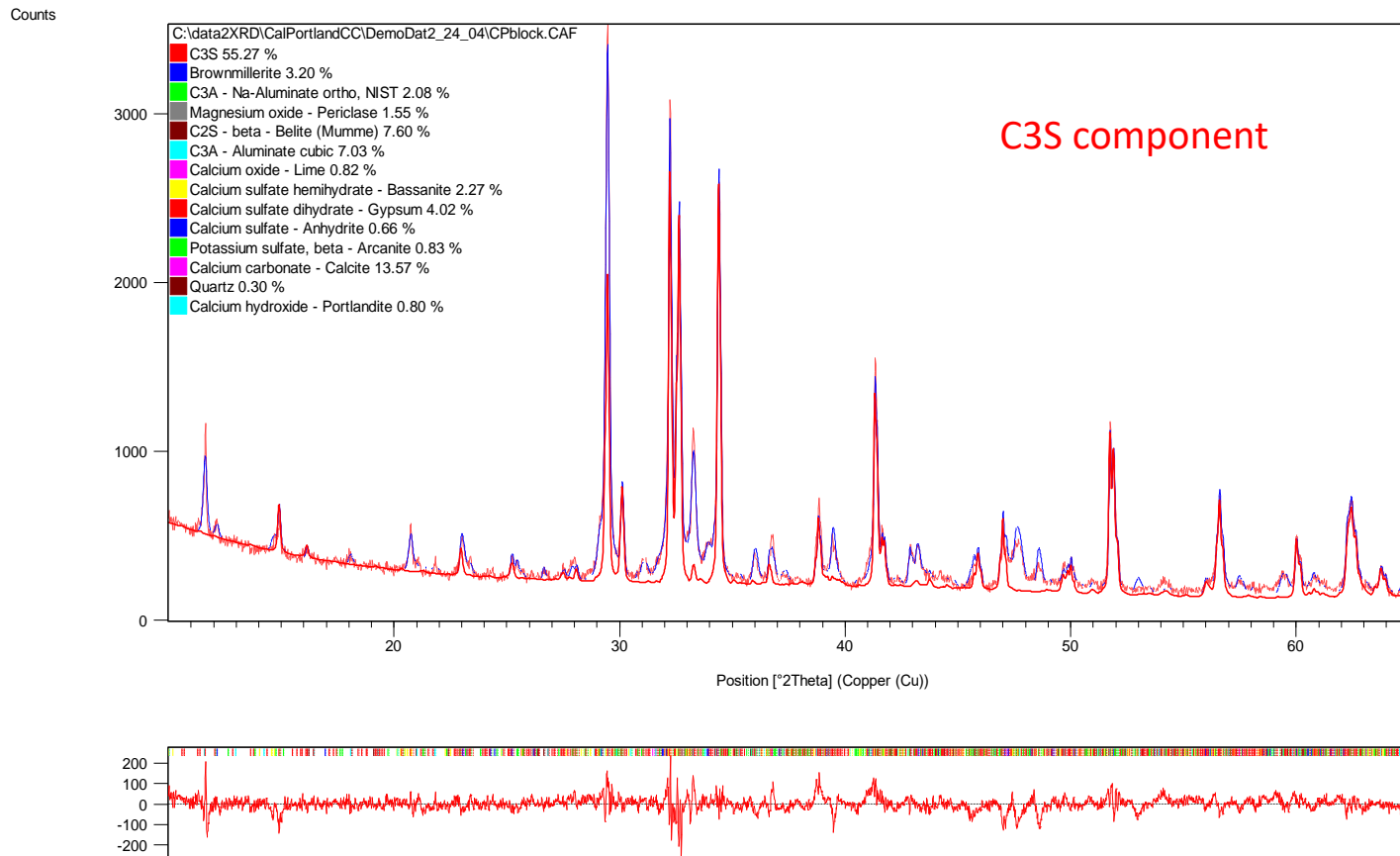
A Refined Cement Sample 'A' with Quantitative Data Shown



Quantitative Phase Analysis

The Rietveld Method: Examples

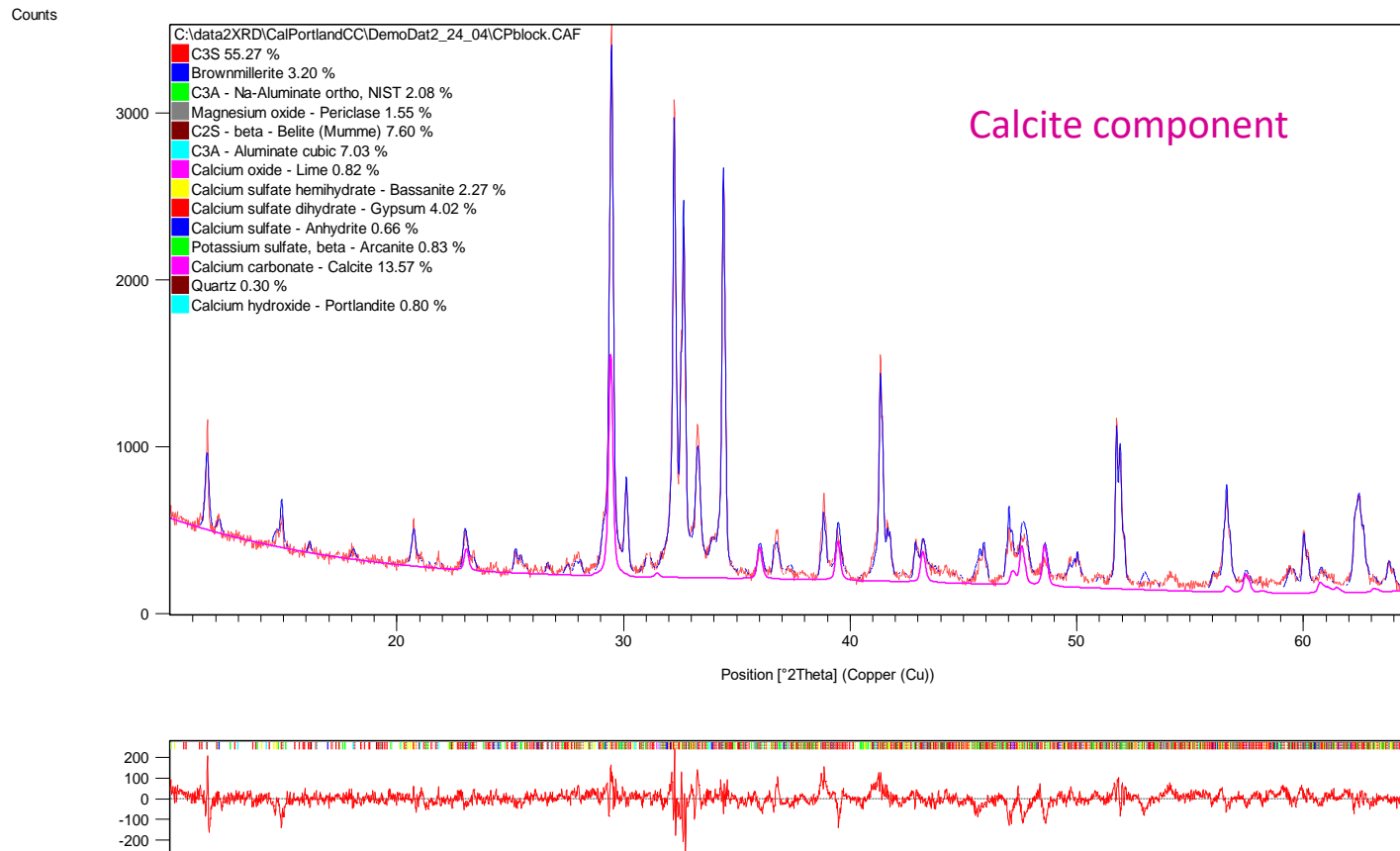
A Refined Cement Sample 'A' with Quantitative Data Shown



Quantitative Phase Analysis

The Rietveld Method: Example

A Refined Cement Sample 'A' with Quantitative Data Shown



Quantitative Phase Analysis

The Rietveld Method: Refinement procedures

The starting model consists of :

1. **Global parameters:** affect the entire pattern, regardless of phase(s)
2. **Structure parameters:** describe the crystallographic parameters
3. **Profile parameters:** describe the width and shape of diffracted peaks

Quantitative Phase Analysis

The Rietveld Method: Refinement procedures

1. Global Parameters (Phase independent)

- ✓ Pattern background
 - Typically refinement of some polynomial function, or
 - Chebechev II, or
 - Manually fit (user-defined background)
- ✓ Error correction
 - Zero point (OR sample displacement)
 - Absorption
 - Extinction
- ✓ Wavelength

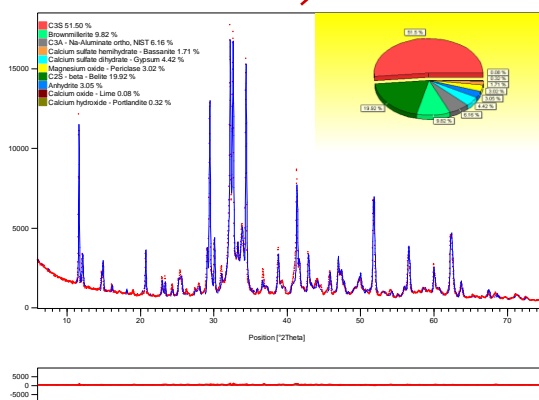
Quantitative Phase Analysis

The Rietveld Method: Refinement procedures

2. Structure Parameters (Phase specific)

- ✓ Space group
- ✓ Lattice parameters
- ✓ Atom co-ordinates
- ✓ Site occupation factors
- ✓ Displacement factors (temperature factors)

Name	Info	Refine	Value	Deviation
Global Parameters				
C3S				
Scale factor		<input checked="" type="checkbox"/>	0.000004	0.000000
Preferred Orientation	1.00 0...	<input checked="" type="checkbox"/>	0.961730	0.002695
B overall		<input type="checkbox"/>	0.000000	0.000000
Extinction		<input type="checkbox"/>	0.000000	0.000000
Flat Plate Absorption ...		<input type="checkbox"/>	0.000000	0.000000
Porosity		<input type="checkbox"/>	0.000000	0.000000
Roughness		<input type="checkbox"/>	0.000000	0.000000
Unit Cell C 1 m 1				
Atomic coordinates				
CA1	2a			
X		<input type="checkbox"/>	0.007490	0.000000
Y		<input type="checkbox"/>	0.000000	0.000000
Z		<input type="checkbox"/>	0.008980	0.000000
B isotropic		<input type="checkbox"/>	4.000000	0.000000
Occupancy		<input type="checkbox"/>	0.500000	0.000000
B anisotropic				
CA2	2a			
CA3	2a			
CA4	2a			
CA5	2a			
CA6	2a			
CA7	2a			
CA8	2a			
CA9	2a			
CA10	2a			



Partial list of atom positions for a C3S structure

Quantitative Phase Analysis

The Rietveld Method: Refinement procedures

3. Profile Parameters (Phase specific)

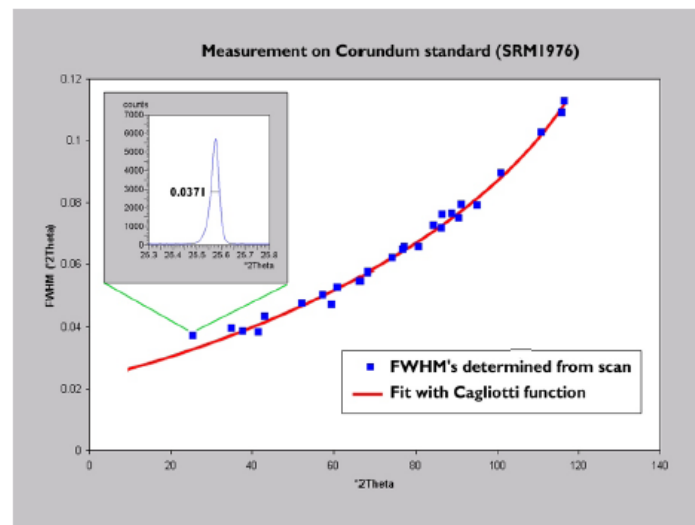
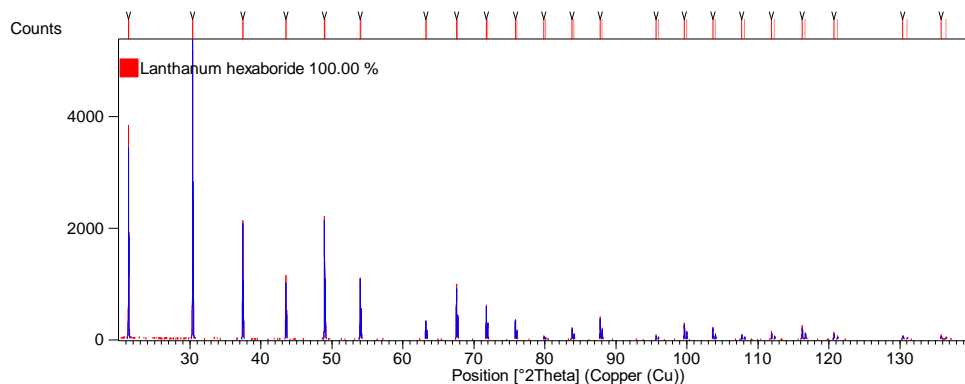
- ✓ Peak shape – will change peak intensities
 - Pseudo-Voigt profile function (refinable Gaussian or Lorentzian profile contributions)
- ✓ Peak width
 - Cagliotti function (FWHM calculation)
- ✓ Peak asymmetry
- ✓ Anisotropic broadening

e.g., how the data is distributed around the peaks

Quantitative Phase Analysis

The Rietveld Method: Refinement procedures

Instrument resolution and contribution to peak broadening



H_k is the Cagliotti function where u , v and w are refinable parameters:

$$H_k = (U \tan^2 \theta + V \tan \theta + W)^{1/2}$$

Quantitative Phase Analysis

The Rietveld Method: Refinement procedures

4. Miscellaneous Parameters

- ✓ Scale factor: ~proportional to weight % of phase
- ✓ Preferred orientation
- ✓ Absorption correction
- ✓ Extinction correction
- ✓ etc.

Quantitative Phase Analysis

The Rietveld Method: Algorithms

We can calculate the net intensity of a diffraction pattern, Y_{ic} , at each point i in the pattern according to:

$$Y_{ic} = Y_{ib} + \sum_p \sum_{k=k_1^p}^{k_2^p} G_{ik}^p I_k$$

Where:

Y_{ib} = the intensity of the background at point i in the pattern,

G_{ik} = the normalized peak profile function,

I_k = the intensity of Bragg reflection k , and

$K_1 - K_2$ = reflections contributing to the i^{th} point in the pattern.

(subnote 'c' stands for calculated and superscript 'p' stands for possible phases present)

- or, in plain English -

The intensity at any given point in the diffraction pattern is equal to the **Background Contribution + Profile Shape + Bragg Peak Intensity** for all possible phases and peak shapes.

Quantitative Phase Analysis

The Rietveld Method: Algorithms

The intensity I_k is given by the expression:

$$I_{hkl} = |F_{hkl}|^2$$

- OR -

$$I_k = SM_k L_k |F_k|^2 P_k A_k E_k$$

Where

S = Scale factor

M_k = Reflection multiplicity,

L_k = Lorentz-Polarization factor

P_k = Preferred orientation

A_k = Absorption

E_k = Extinction

F = Structure Factor

Quantitative Phase Analysis

The Rietveld Method: Algorithms

The Structure Factor F_k is given by the expression:

$$F_k = \sum_{j=1}^n f_j \exp[2\pi i(\mathbf{h}_r^t \mathbf{r}_j - \mathbf{h}_k^t \mathbf{B}_j \mathbf{h}_k)]$$

Where:

N_j is the site occupancy factor (0,1) for the j th atom,

f_j is the atomic scattering factor for the j th atom,

h , k , and l are the Miller indices, and x_j , y_j , and z_j are the positional coordinates for the j th atom in the unit cell.

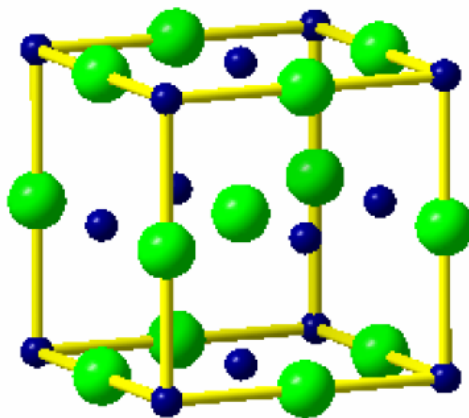
Quantitative Phase Analysis

The **intensity of an x-ray peak** is a function of the type and position of the atoms in the unit cell – *i.e.*, electron density and therefore **scattering power** ('Form Factor, f)

Amplitude

- Amplitude f_i of a scattered wave
 - represents the scattering power of an atom
 - varies with $(\sin\vartheta)/\lambda$
 - for $2\vartheta = 0$: f_i = number of electrons of the scattering atom

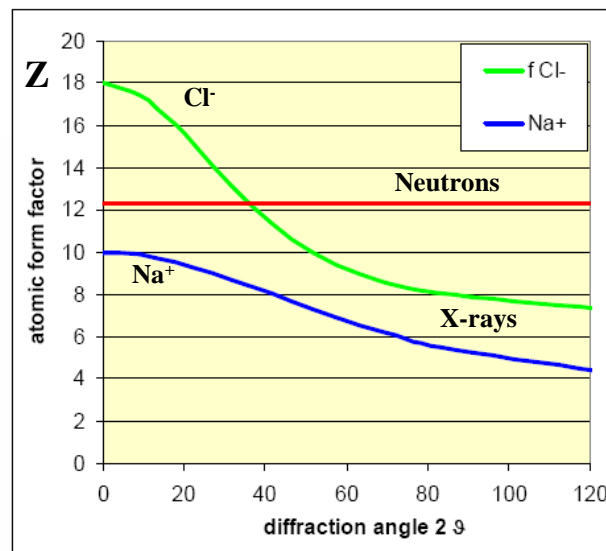
Reduces the intensities of peaks at higher angles.



NaCl-structure

Na⁺ : 10 electrons: $f_{\text{Na}^+} = 10$ ($\vartheta = 0$)

Cl⁻ : 18 electrons: $f_{\text{Cl}^-} = 18$ ($\vartheta = 0$)



Quantitative Phase Analysis

The Rietveld Method: Algorithms

Rietveld scale factor \propto wt.% phase present in the sample:

The weight fraction of phase p can then be derived as:

$$W_p = \frac{(SZMV)_p}{\sum_i (SZMV)_i}$$

analyte phase
all phases

where:

W_p is the weight percent of phase p

S is the refined Rietveld scale factor,

Z is the number of formula units per unit cell

M is the mass of the formula unit,

V is the volume of the unit cell.

Quantitative Phase Analysis

The Rietveld Method: Agreement indices and quality of the refinement

1. Best method is to evaluate the difference plot,
2. Agreement indices or 'R' values are the quantities that are minimized during the refinement.

Weighted profile R-factor (R_{wp}) is perhaps the most useful:

R_{wp} is a measure of the fit between the observed and calculated patterns

R_{exp} reflects the quality (statistics) of the data.

$$X^2 = R_{wp}/R_{exp} = \text{GOF}$$

$$R_{wp} = \left[\frac{\sum w_i (Y_{io} - Y_{ic})^2}{\sum w_i Y_{io}^2} \right]^{\frac{1}{2}}$$

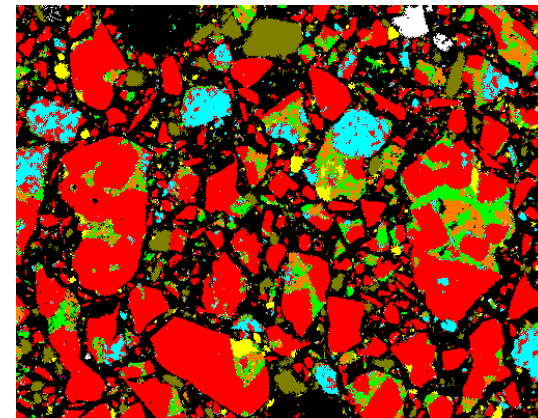
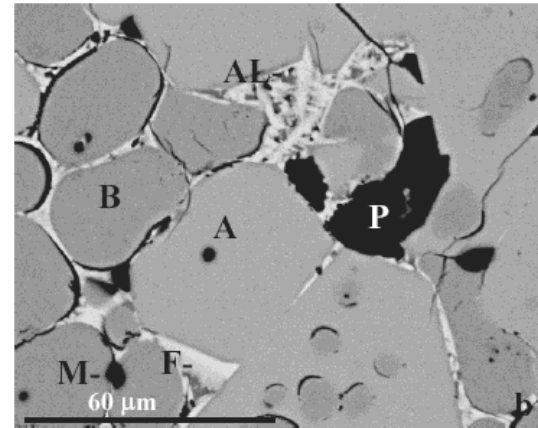
$$R_{exp} = \left[\frac{N - P}{\sum_i w_i y_i(\text{obs})^2} \right]^{\frac{1}{2}}$$

Quantitative Phase Analysis

The Rietveld Method: Agreement indices and quality of the refinement

'Independent calibration': Why it's needed

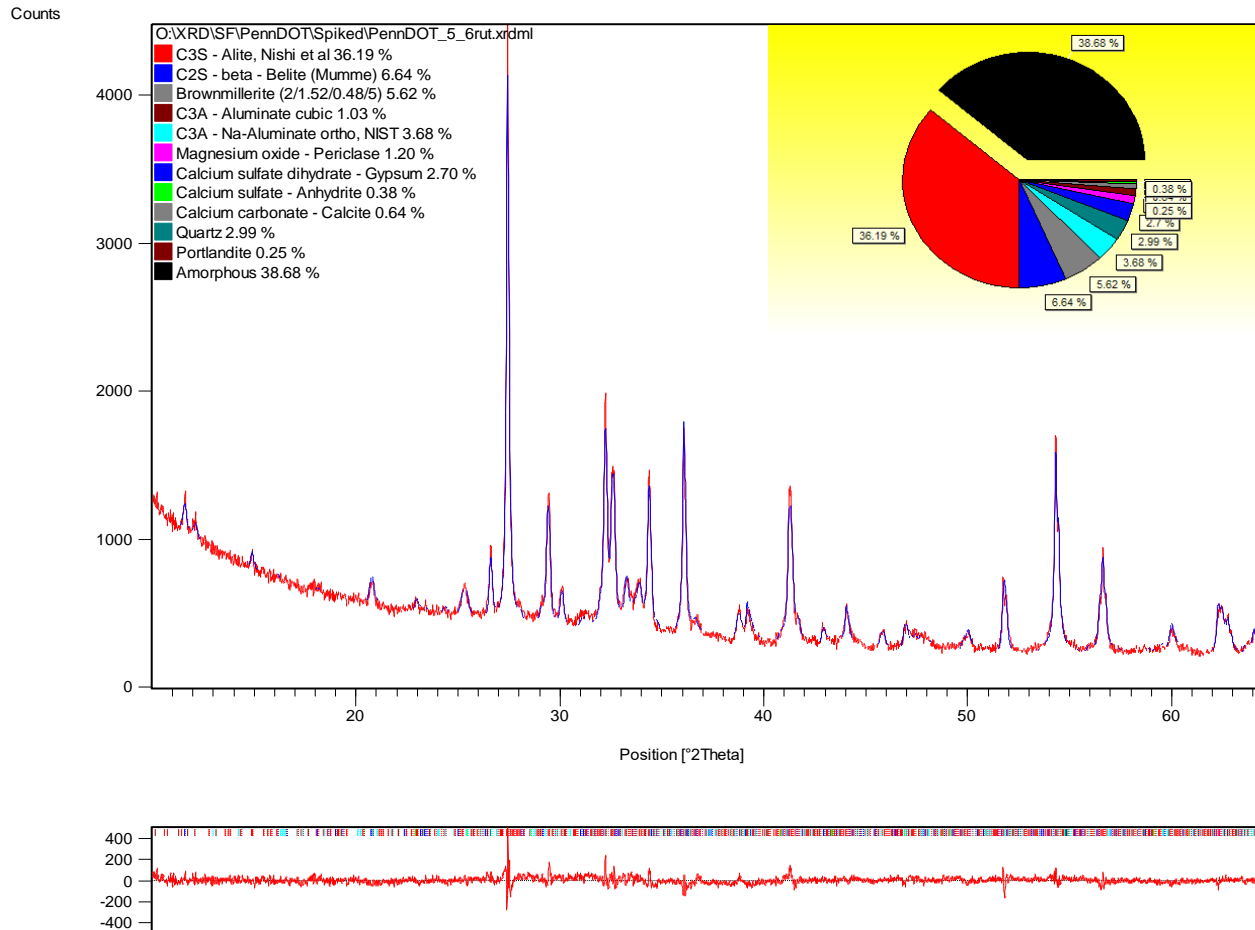
Rietveld is very precise, but in order to obtain the most accurate absolute concentrations, it is best to obtain independent characterization data for construction of control files to obtain true, 'referenced' phase concentrations.



Additional Rietveld Examples

Quantitative Phase Analysis

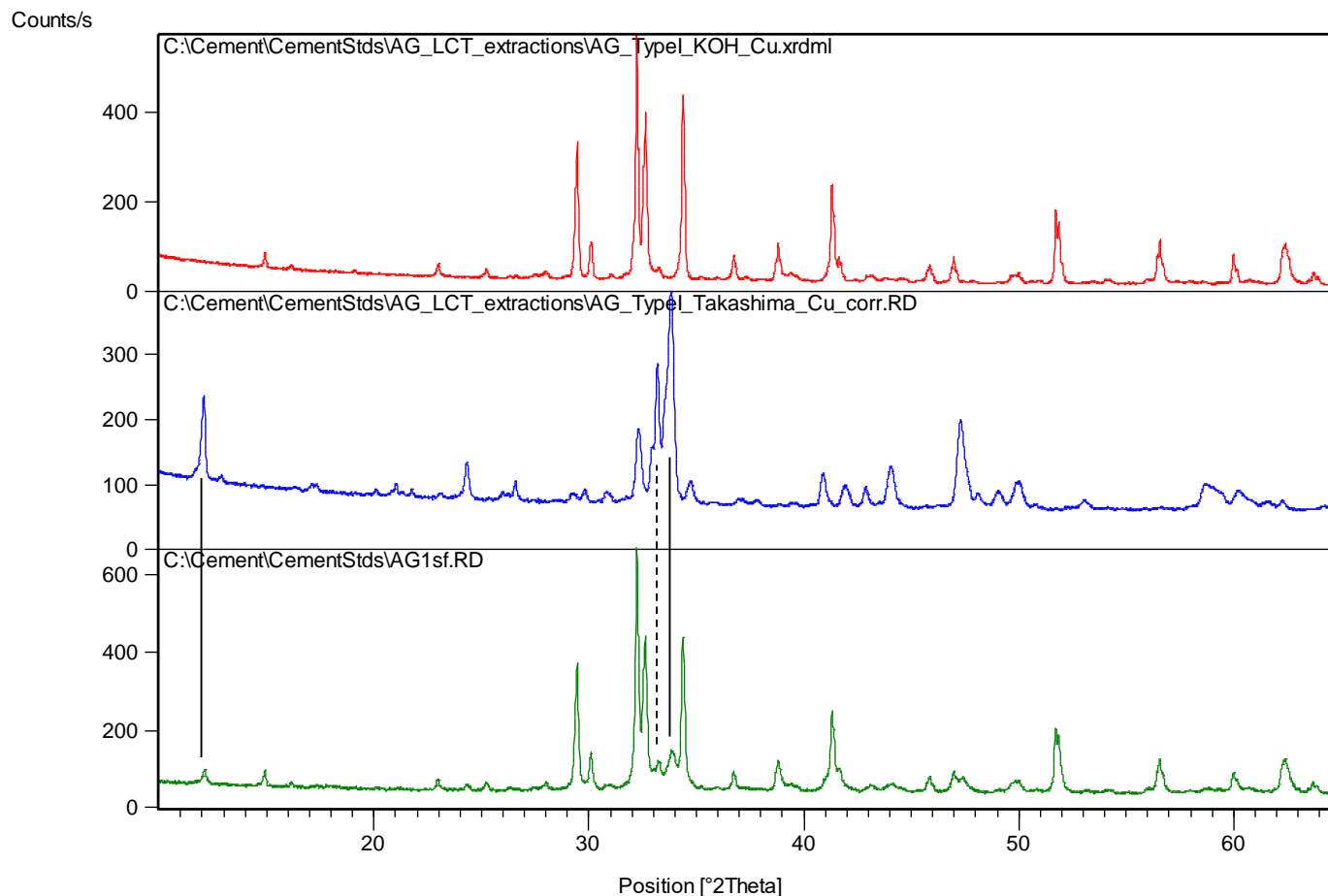
The Rietveld Method: Additional examples



Cement / Fly Ash
blend with 24%
rutile added as
internal standard for
amorphous
calculation

Quantitative Phase Analysis

The Rietveld Method: Additional examples



Selective extraction of interstitial phases (red) and silicates (blue). Bulk sample is shown in green.

Summary

Quantitative Phase Analysis

The Rietveld Method: Refinement strategies and tips

What parameters *can* be refined?

- Lattice parameters
- Atomic positions
- Site occupancy
- Isotropic temperature factor (B)
- Profile parameters (u, v, w , & other peak shape parameters)
- Preferred orientation
- Background contribution
- Zero point (or sample height)

Quantitative Phase Analysis

The Rietveld Method: Refinement strategies and tips

What parameters *should* be refined (for QPA)?

- Scale factor - all phases
- Lattice parameters – *all phases* (or at least major phases)
- Atomic positions - *never*
- Site occupation – rarely (only if needed)
- Temperature factors – *rarely* (never)
- Profile parameters - *major phases only*
- Preferred orientation – *as needed*, constrained to direction
- Background contribution – *always* (noncrystalline?...)
- Zero point (or sample height) - *always*

Summary

Rietveld analysis provides:

- Refined unit cell dimensions - phase chemistry and solid solutions (zoning)
- Crystal structure parameters/atom site occupancy and structural disorder
- Peak width and shapes - coherent domain size (*i.e.*, crystallite size)
- Preferred orientation - crystal texture
- Background modeling - characterization of amorphous material,
- Determination of polymorphic forms,
- Independent measure of CaO, Ca(OH)₂, CaCO₃, etc.
- AND...

...Standardless quantification (wt %) for each phase

Thank-you!

WHAT ON EARTH AM I
DOING IN HERE ON THIS
BEAUTIFUL DAY?!
THIS IS THE ONLY LIFE
I'VE GOT!!

