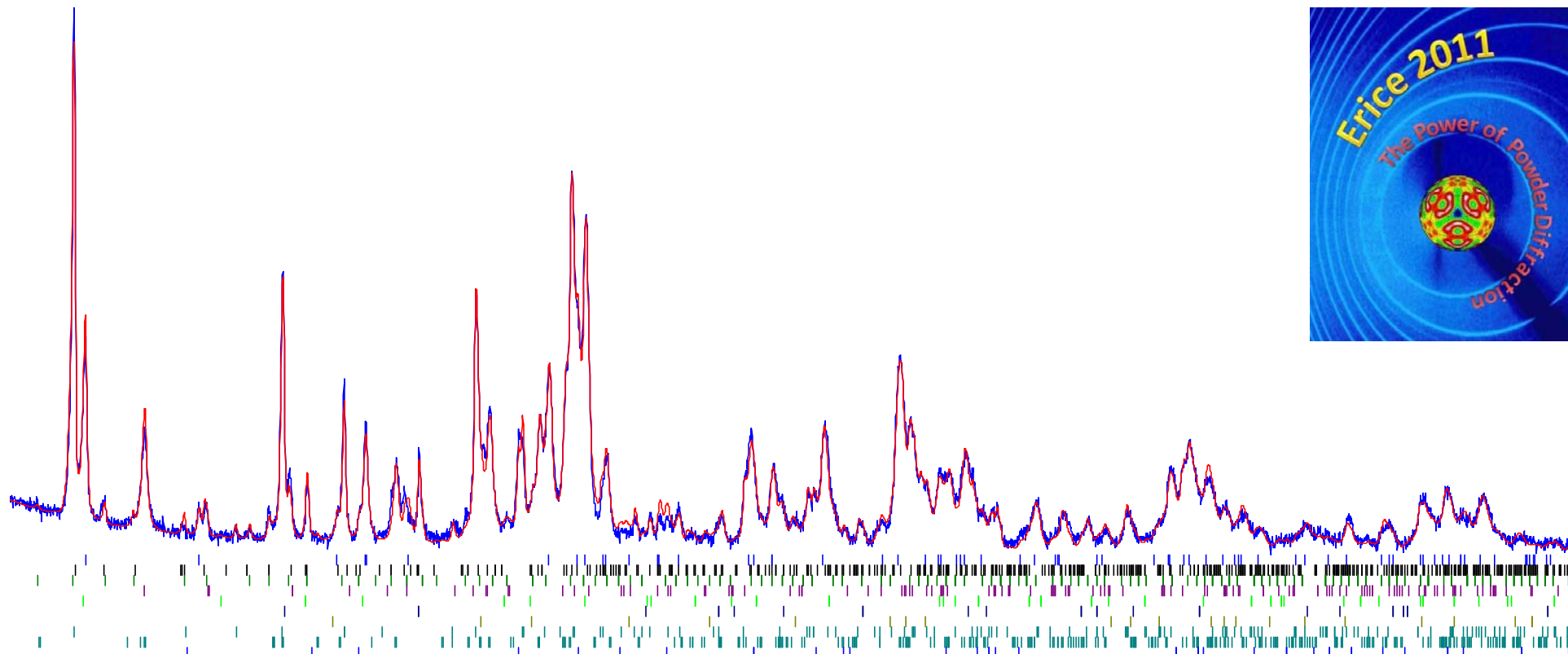




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Quantitative Phase Analysis Introduction and Standards

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Outline



- Basis of quantitative phase¹ analysis (QPA)
- How to select which method to use
- Analysis of phases with poorly defined crystal structures
- Use of Rietveld based methodology in QPA
 - Advantages & Disadvantages
- Selected outcomes of the round robin on QPA
- Issues in precision & accuracy

¹ Phase = a crystallographically distinct component of the sample – not to be confused with the “phase problem”

A Shameless Opportunity for Self Citation



- Most discussion will be on Rietveld-based QPA methodology
- 75% of returns to the IUCr Commission on Powder Diffraction (CPD) QPA round robin used Rietveld-based techniques

research papers

Outcomes of the International Union of Crystallography Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis: samples 1a to 1h

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The International Union of Crystallography (IUCr) Commission on Powder Diffraction (CPD) has sponsored a round robin on the determination of quantitative phase abundance from diffraction data. Specifically, the aims of the round robin were (i) to document the methods and strategies commonly employed in quantitative phase analysis (QPA), especially those involving powder diffraction, (ii) to assess levels of accuracy, precision and lower limits of detection, (iii) to identify specific problem areas and develop practical solutions, (iv) to formulate recommended procedures for QPA using diffraction data, and (v) to create a standard set of samples for future reference. Some of the analytical issues which have been addressed include (a) the type of analysis (integrated intensities or full-profile, Rietveld or full-profile, database of observed patterns) and (b) the type of instrument used, including geometry and radiation (X-ray, neutron or synchrotron). While the samples used in the round robin covered a wide range of analytical complexity, this paper reports the results for only the sample 1 mixtures. Sample 1 is a simple three-phase system prepared with eight different compositions covering a wide range of abundance for each phase. The component phases were chosen to minimize sample-related problems, such as the degree of crystallinity, preferred orientation and microabsorption. However, these were still issues that needed to be addressed by the analysts. The results returned indicate a great deal of variation in the ability of the participating laboratories to perform QPA of this simple three-

J. Appl. Cryst. (2001) Madsen *et al* , **34**, 409–426

research papers

Outcomes of the International Union of Crystallography Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis: samples 2, 3, 4, synthetic bauxite, natural granodiorite and pharmaceuticals

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The International Union of Crystallography (IUCr) Commission on Powder Diffraction (CPD) has sponsored a round robin on the determination of quantitative phase abundance from diffraction data. The aims of the round robin have been detailed by Madsen *et al.* [*J. Appl. Cryst.* (2001), **34**, 409–426]. In summary, they were (i) to document the methods and strategies commonly employed in quantitative phases analysis (QPA), especially those involving powder diffraction, (ii) to assess levels of accuracy, precision and lower limits of detection, (iii) to identify specific problem areas and develop practical solutions, (iv) to formulate recommended procedures for QPA using diffraction data, and (v) to create a standard set of samples for future reference. The first paper (Madsen *et al.*, 2001) covered the results of sample 1 (a simple three-phase mixture of corundum, fluorite and zincite). The remaining samples used in the round robin covered a wide range of analytical complexity, and presented a series of different problems to the analysts. These problems included preferred orientation (sample 2), the analysis of amorphous content (sample 3), microabsorption (sample 4), complex synthetic and natural mineral suites, along with pharmaceutical mixtures with and without an amorphous component. This paper forms the second part of the round-robin study and reports the results of samples 2 (corundum, fluorite, zincite, bauxite), 3 (corundum, fluorite

J. Appl. Cryst. (2002) Scarlett *et al* , **35**, 383–400

Basis of Quantitative Phase Analysis

Methods – Direct and Indirect

Merits of Different Approaches

Putting QPA on an Absolute Scale

Analytical Methods of Phase Analysis



- Indirect methods

- Measure e.g. bulk chemistry – apportion elemental abundances according to assumed composition of each phase
 - normative calculation (Bogue method for Portland cement)
- Potential for errors in assumed compositions
- Instability in method when phases have similar chemistry

- Direct Methods

- Magnetic susceptibility – limited to samples with magnetic phases
- Selective dissolution – rate of dissolution can be phase dependant
- Density measurements – physical separation of phases
- Image analysis – optical & e-beam images – issues with stereology
- Thermal analysis – magnitude of endo-/exo-thermic features during phase transitions relate to phase content
- Diffraction based methods

XRD for Quantitative Phase Analysis

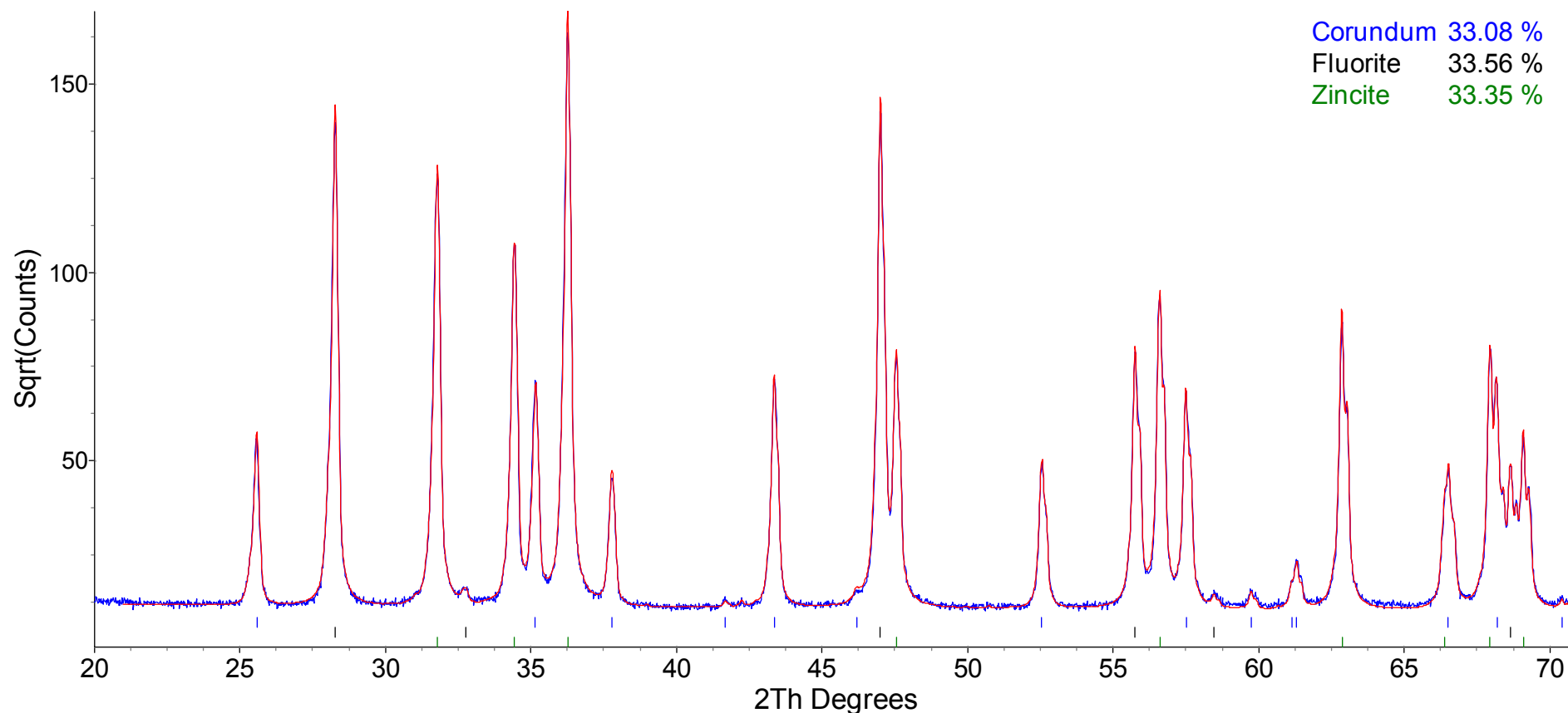


- “Quantitative phase analysis by X-ray diffraction (QXRD) is the only analytical technique that is truly phase sensitive” ¹
 - Diffraction data derived directly from the crystal structure of each phase
 - Results are not inferred via indirect measurement
 - Capable of analysing polymorphs
- Mathematical basis of QPA is well established, but
- Limitations on accuracy are mostly experimental
- Many sources of error
 - Instrument configuration
 - Particle statistics
 - Counting error
 - Preferred orientation
 - Microabsorption
 - Operator error ! → PICNIC → Problem In Chair, Not In Computer

Range of Complexity in QPA Synthetic Materials



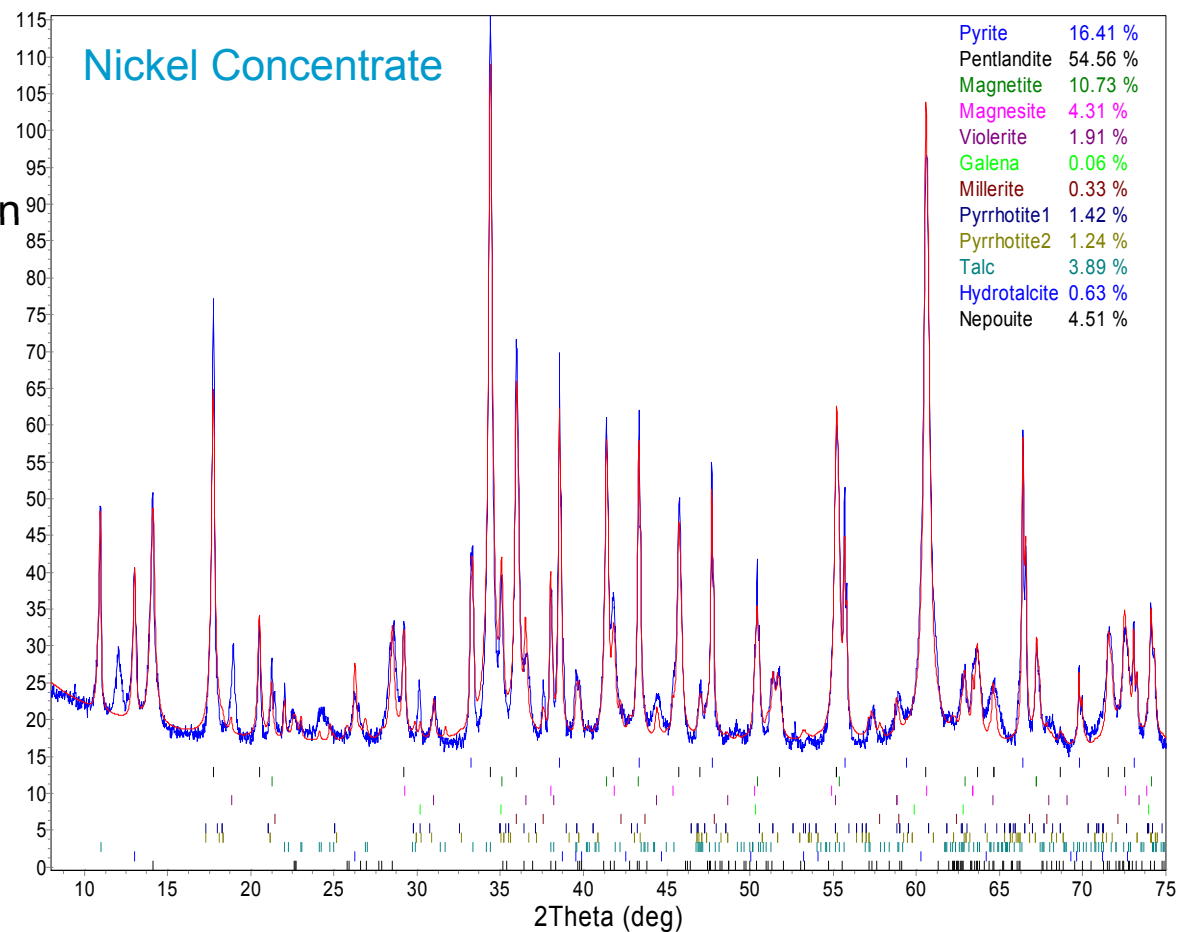
- Sample 1G from IUCr CPD round robin
 - 'Simple' – 3 well defined phases with high symmetry, small unit cells
 - Little peak overlap



Range of Complexity in QPA Mineralogical Samples



- Mineral samples are complex !
 - Multi-phase (20 not uncommon)
 - Inhomogeneous at all size ranges
- QPA of mineral samples is rarely a straight-forward exercise !
- Difficult to standardize methodology
- Sample related issues
 - Poorly crystallinity
 - Clays, goethite, nontronite
 - Variable chemical composition (solid solution) of phases
 - Preferred orientation, micro-absorption etc..



Complex Relationship Between Intensity of Diffracted Peaks & Phase Concentration



$$I_{(hkl)\alpha} = \left[\frac{I_0 \lambda^3}{32\pi r} \frac{e^4}{m_e^2 c^4} \right] \cdot \left[\frac{M_{hkl}}{2V_\alpha^2} |F_{(hkl)\alpha}|^2 \cdot \left(\frac{1 + \cos^2 2\theta \cos^2 2\theta_m}{\sin^2 \theta \cos \theta} \right) \cdot \text{Exp} \left(-2B \left(\frac{\sin \theta}{\lambda} \right)^2 \right) \right] \cdot \left[\frac{W_\alpha}{\rho_\alpha \mu_m^*} \right]$$

Experiment / Instrument Dependant

$I_{(hkl)\alpha}$ = Intensity of reflection of hkl in phase α
 I_0 = incident beam intensity
 r = distance from specimen to detector
 λ = X-ray wavelength
 $(e^2/m_e c^2)$ = square of classical electron radius

Phase Dependant

M_{hkl} = multiplicity of reflection hkl of phase α
 V_α = volume of unit cell phase α
 $F_{(hkl)\alpha}$ = structure factor - reflection hkl of phase α
 2θ = diffraction angle of reflection hkl of phase α
 $2\theta_m$ = diffraction angle of the monochromator
 ρ_α = density of phase α
 B = atomic displacement (thermal) parameter

Sample Dependant

W_α = weight fraction of phase α in sample
 μ_m^* = mass absorption coefficient (MAC) of the entire sample

Quantitative Phase Analysis

Factors Affecting Observed Intensities



- **Instrument-sensitive**

- Source configuration (lab & synchrotron) – drift of intensity (synchrotron),
- Optical path
 - Divergence slit
 - Receiving slit width
 - Anti-scatter slits
 - Axial divergence
 - Detector efficiency
 - Detector dead time
- Lorentz and polarization factors (L_p)

- **Structure-sensitive**

- Atomic scattering factor
- Structure factor
- Reflection multiplicity
- Atomic displacement (thermal) parameter

- **Measurement-sensitive**

- Counting time
- d-spacing range
- Angular step width

- **Sample-sensitive**

- Bulk sample absorption
- Crystallite size
- Micro stress/strain
- Degree of crystallinity
- Residual stress
- Particle statistics
- Absorption contrast between phases (microabsorption)

Relationship Between Intensity of Diffracted Peaks & Phase Concentration



$$I_{(hkl)\alpha} = \underbrace{\left[\frac{I_0 \lambda^3}{32\pi r} \frac{e^4}{m_e^2 c^4} \right]}_{\text{Constant for experimental setup}} \cdot \underbrace{\left[\frac{M_{hkl}}{2V_\alpha^2} |F_{(hkl)\alpha}|^2 \cdot \left(\frac{1 + \cos^2 2\theta \cos^2 2\theta_m}{\sin^2 \theta \cos \theta} \right) \cdot \text{Exp} \left(-2B \left(\frac{\sin \theta}{\lambda} \right)^2 \right) \right]}_{\text{Constant for intensity of peak (hkl) for phase } \alpha} \cdot \underbrace{\left[\frac{W_\alpha}{\rho_\alpha \mu_m^*} \right]}_{\text{Sample effects}}$$

Constant for
experimental
setup

Constant for intensity
of peak (hkl) for phase α

Sample
effects

$$I_{(hkl)\alpha} = C_1 \cdot C_2 \cdot \frac{W_\alpha}{\rho_\alpha} \cdot \frac{1}{\mu_m^*} \cdot \frac{1}{V_\alpha^2}$$

- Combine constants together into a single constant K , and
- Equate $I_{(hkl)\alpha}$ with the Rietveld scale factor S_α

$$S_\alpha = \left[\frac{K}{V_\alpha^2} \right] \cdot \left[\frac{W_\alpha}{\rho_\alpha} \right] \cdot \frac{1}{\mu_m^*}$$

- Where

- S_α = Rietveld scale factor for phase α
- W_α = weight fraction of phase α
- ρ_α = density of phase α
- μ_m^* = mixture mass absorption coefficient (MAC)
- V_α = volume of the unit cell for phase α

- This equation inherently contains the weight fraction information

Extracting Phase Abundances

- Rearrange

$$W_{\alpha} = \frac{S_{\alpha} \rho_{\alpha} V_{\alpha}^2 \mu_m^*}{K}$$

- Phase density can be calculated from crystallographic parameters

$$\rho_{\alpha} = \frac{ZM_{\alpha}}{V_{\alpha}} \cdot 1.66054$$

- Where
 - ZM = the mass of the unit cell contents
 - V = the unit cell volume

1.66054 = $10^{24} / 6.022 \times 10^{23}$
converts ρ in AMU/Å³ to g/cm³

Substitute for Density



$$W_{\alpha} = \frac{S_{\alpha} (ZMV)_{\alpha} \mu_m^*}{K}$$

- K is an 'experiment constant' for the instrumental setup ^{1,2}
 - Used to put W_{α} on an absolute basis
 - Dependant only on instrumental and data collection conditions
 - Independent of individual phase and overall sample-related parameters
 - A single measurement is (usually) sufficient to determine K
- ZMV_{α} becomes a 'dynamic calibration constant' for phase α
 - Can be determined from published/refined crystal structure parameters
 - It is updated as the structure is refined
- This approach is referred to hereafter as the *External Standard* method

¹ O'Connor & Raven (1988) Powder Diffraction, **3**(1), 2-6. – Rec'd 31/03/1987

² Bish & Howard (1988) *J. Applied Crystallogr.*, **21**, 86-91. – Rec'd 30/03/1987

Issues in the Application of the External Standard Approach



- Need to measure K and ensure that instrumental conditions do not change between measurement of K and data collection from samples
- Need to measure or calculate μ_m^*
 - Difficult to measure directly
 - Need total chemistry or QPA for calculation
- Can eliminate the need to know K and μ_m^* by
 - Adding a known amount W_s of a well characterised standard s to the sample

$$W_s = \frac{S_s (ZMV)_s \mu_m^*}{K}$$

Eliminating K and μ_m^*

- Divide equation for phase α by equation for standard s ,

$$\frac{W_\alpha}{W_s} = \frac{S_\alpha(ZMV)_\alpha \mu_m^*}{K} \frac{K}{S_s(ZMV)_s \mu_m^*}$$

- Rearrange , eliminate K, μ_m^*

$$W_\alpha = W_s \cdot \frac{S_\alpha(ZMV)_\alpha}{S_s(ZMV)_s}$$

- Issues relating to sample MAC & experiment conditions are eliminated
- This approach is referred to hereafter as the *Internal Standard* method

How to Choose an Internal Standard

- Material should be stable & unreactive (especially for *in situ* studies)
- Simple diffraction pattern – minimal overlap with sample peaks
- Standard *MAC* should be similar to sample *MAC*
 - Avoid introducing microabsorption effects
- Minimal sample related effect on observed intensities
 - No preferred orientation
 - 100% (or known) crystallinity
 - Minimal 'graininess'
- Possibilities
 - α -Al₂O₃ (corundum) TiO₂ (rutile) ZnO (zincite) Cr₂O₃ (eskolaite)
 - α -Fe₂O₃ (hematite) CeO₂ (cerianite) CaF₂ (fluorite) C (diamond)
- Alternate approach
 - Use an independent measure (e.g. chemical analysis) to derive the concentration of a phase already present in the sample
 - Designate it as the internal standard

Advantages in Internal and External Standard Approach to QPA



- Within the limits of experimental accuracy, the internal and external standard approaches produce *absolute phase abundances*
- Possible to estimate the amount of amorphous / non-determined material $W_{unknown}$ in the sample
 - Equals the difference between unity & sum of the (absolute) analysed phases

$$W_{(unknown)} = 1.0 - \sum_{j=1}^n W_{j(absolute)}$$

Matrix Flushing Method (*MFM*)^{1, 2}

Rietveld Context (*ZMV* method)



- *MFM* applies an additional constraint
 - Σ of analysed weight fractions = 1.0
- Put *MFM* into Rietveld context^{3,4}
 - Weight fraction of phase α in an n phase system is :-

$$W_{\alpha} = \frac{S_{\alpha}(ZMV)_{\alpha}}{\sum_{j=1}^n S_j(ZMV)_j}$$

- Where
 - S = the Rietveld scale factor
 - ZM = mass of unit cell contents
 - V = unit cell volume

¹ Chung (1974a) ² Chung (1974b)

³ Hill & Howard (1987) *J. Appl. Cryst.*, **20**, 467-474. – Rec'd 02/04/1987

⁴ Bish & Howard (1988) *J. Appl. Cryst.*, **21**, 86-91. – Rec'd 30/03/1987

Matrix Flushing Method (*MFM*)^{1, 2}

Rietveld Context (cont'd)



- This approach is the most widely used for Rietveld based QPA
 - Almost universally coded into Rietveld analysis programs
 - This is probably the default QPA reported
- BUT, only produces the correct *relative phase abundances*.
 - If the sample contains amorphous phases and/or unidentified crystalline phases → analysed weight fractions will be overestimated
- If absolute abundances are required ..
 - Reaction kinetics in *in situ* studies
 - Measurement of amorphous content
 - etc...
 - etc...
- ... then this method is not suitable

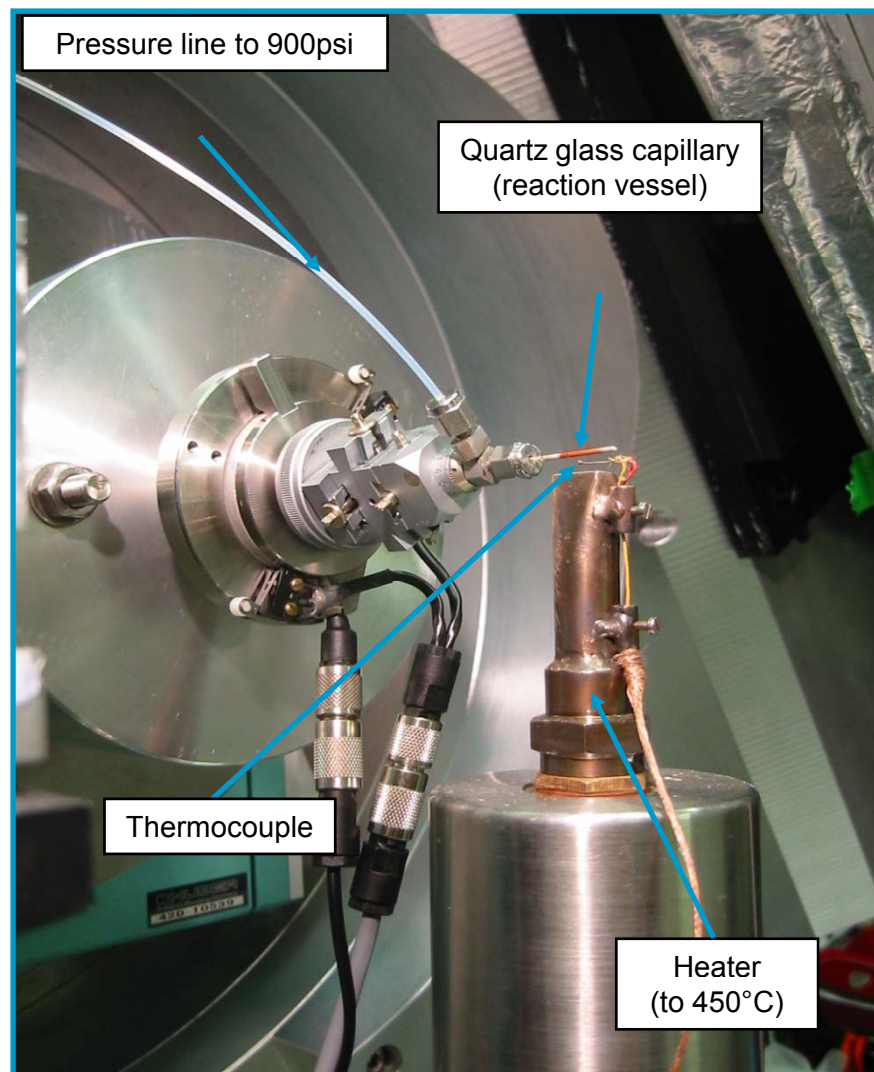
How to Select Which QPA Method to Use

- Experiment at the Australian Synchrotron by Webster *et al.* ¹
 - Study of nucleation & crystal growth of gibbsite $\text{Al}(\text{OH})_3$
 - Context – Bayer process (extraction of Al from bauxite ores)
- Synthetic Bayer liquors (Al-loaded caustic solutions)
 - Seeded with various Fe-oxides – in this example, goethite ($\alpha\text{-FeOOH}$)
 - Use S-XRD to follow mechanism & kinetics of phase formation

¹ Webster, N.A.S. *et al*, *J. Appl. Cryst.*, **43**: 466-472.

Experimental Configuration for Seeding Studies

- **Sample environment**
 - 1 mm quartz glass capillary
 - Heated to 60 - 75° C using hot air blower
 - Slight pressure to prevent evaporation of fluid
- **Simultaneous data collection**
 - Mythen multistrip detector, Australian Synchrotron
 - 2 minutes per data set for ~ 3 hours
- **Rietveld based data analysis**
 - Three different QPA methods used to extract phase abundance at each stage of the reaction

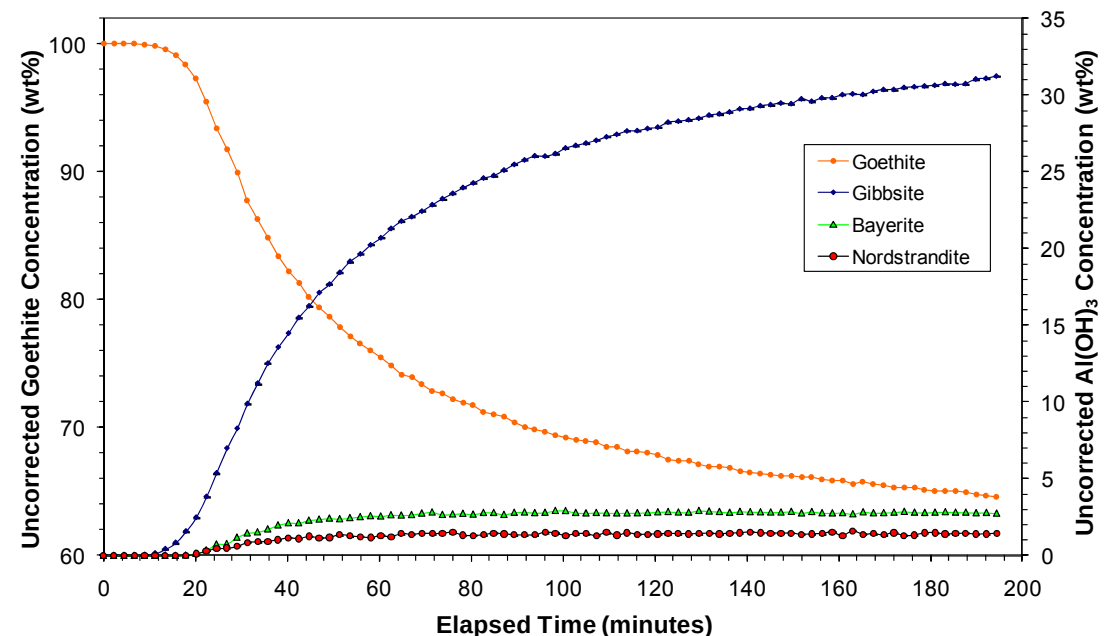


Method #1

QPA Derived Using ZMV (Hill & Howard) Algorithm



- This is the most commonly used Rietveld based QPA methodology
- Reported goethite conc'n starts at 100wt%
 - Normalised to 100wt% as it is the only phase in the analysis
 - But, goethite added at 14.13wt% in total sample (solid + fluid)
- Apparent decrease in goethite conc'n as $\text{Al}(\text{OH})_3$ polymorphs crystallise
 - But, goethite will not dissolve or react in this environment
 - Total $\text{Al}(\text{OH})_3 \rightarrow 35\text{wt}\%$
 - Exceeds known Al addition
- Behaviour of goethite & $\text{Al}(\text{OH})_3$ phases is an artefact of the analysis
 - We are not considering the entire sample – only the crystalline components

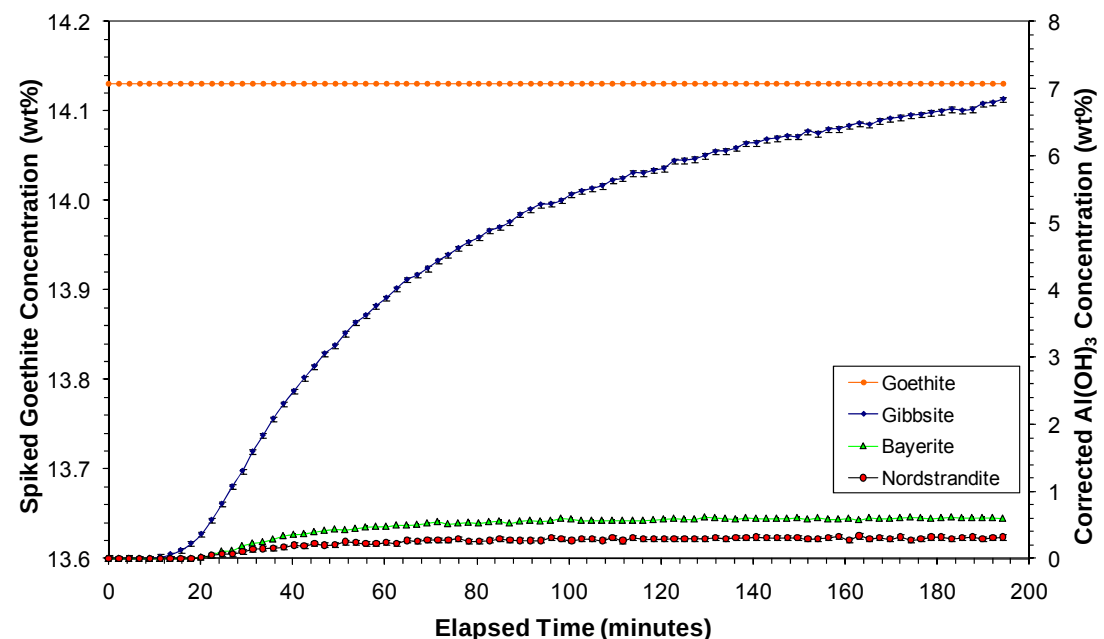


Method #2

QPA Derived Using Internal Standard Method



- Goethite seed added in known amount – 14.13wt%
 - Assume that it does not change during experiment
 - Correct concentrations of other phases using internal standard equation
- $\text{Al}(\text{OH})_3$ phase conc'n now $\sim 7.5\text{wt}\%$ = $\sim \frac{1}{2}$ of the known Al addition
 - In agreement with performance from independent estimates
- Must consider the entire sample (solid & liquid)
- Now have ability to derive reaction kinetics from absolute QPA



Method #3

QPA Derived Using External Standard Method



- Need to determine experimental constant K
- K determined from analysis of first data set
 - Use goethite scale factor, ZMV and known addition (= 14.13wt%)
 - Ignore μ_m^* – sealed system – chemistry, therefore μ_m^* , will not change
- But – synchrotron beam current decays during data collection
 - Instrument conditions have changed
 - Need to allow for what amounts to a change in K

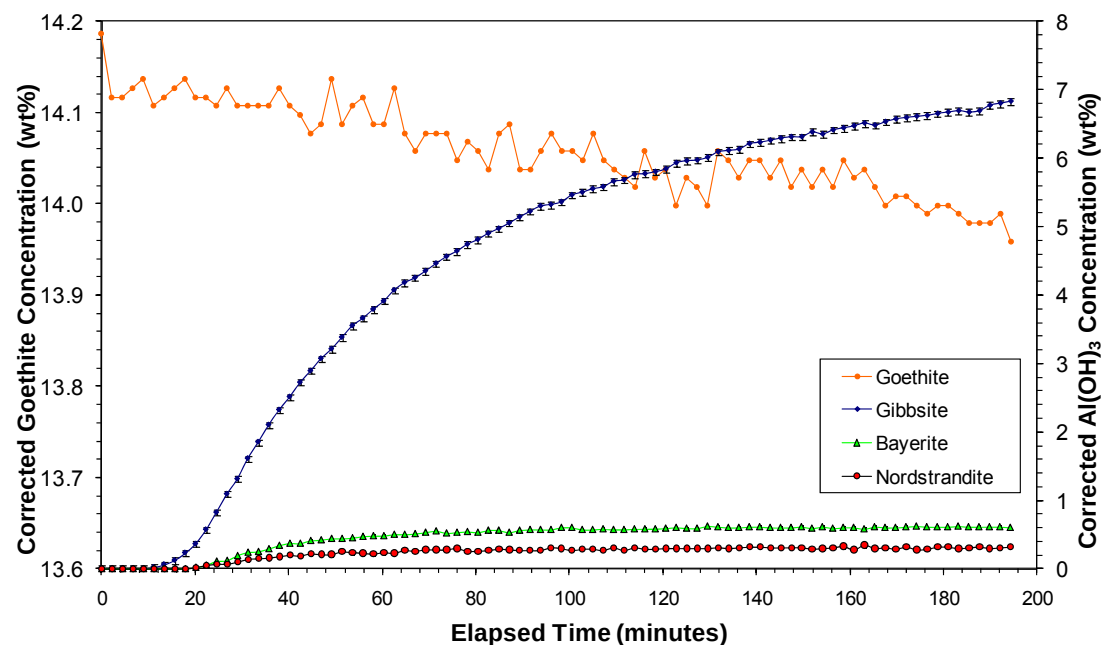
$$W_{\alpha i} = \frac{S_{\alpha i} (ZMV)_{\alpha} \mu_m^*}{K} \cdot \frac{I_0}{I_i}$$

- Where
 - I_0 & I_i = monitor count (or beam current) at start & in data set i respectively

QPA Derived Using External Standard Method



- Absolute phase abundances derived
- $\text{Al}(\text{OH})_3$ conc'n ~same as internal standard estimates
- Now observe a slight decrease in goethite QPA (<1% relative)
 - What could be the cause ?



SEM Image of Goethite Seeded Gibbsite Crystallisation



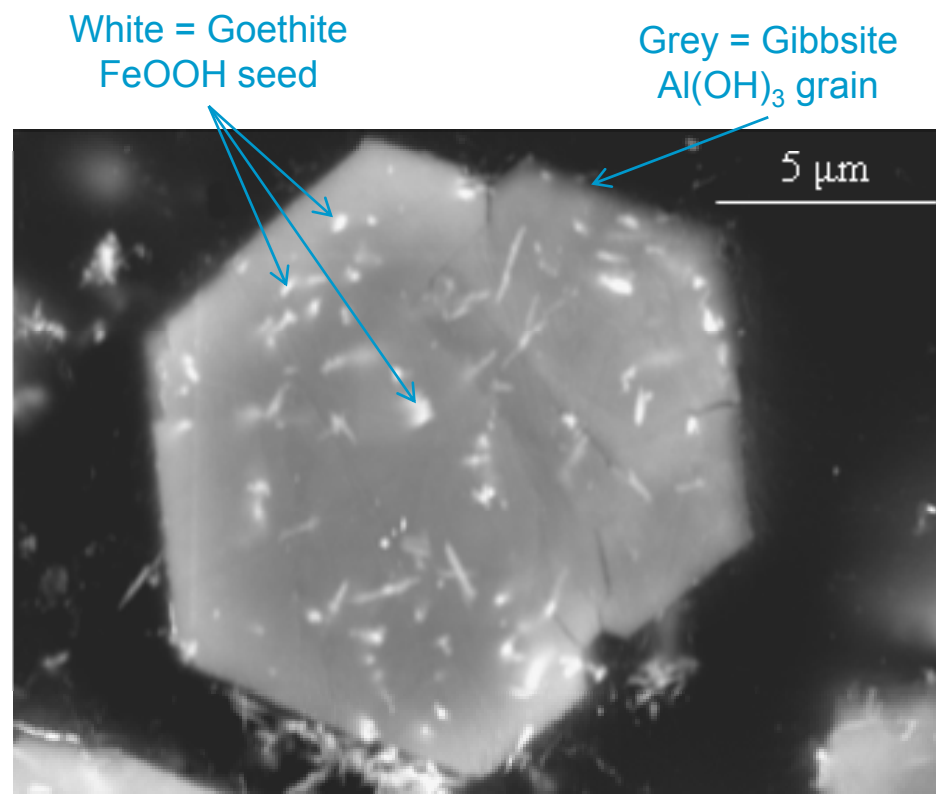
- Initial goethite seed has particle size of $\sim 0.1 \times 0.6 \mu\text{m}$
- During growth, gibbsite envelopes goethite seed
 - Progressively 'shields' goethite from X-ray beam
- Gibbsite particles $\sim 10\mu\text{m}$
 - In general agreement with size calculated from decrease in observed intensity

$$\frac{I_{(t)}}{I_0} = \text{Exp}(-\mu t) \quad *$$

μ = linear absorption coefficient of gibbsite at selected wavelength

t = thickness

* Beer's Law



PONKCS¹

*QPA of phases with
Partial Or No Known Crystal Structure*

¹ Scarlett, N.V.Y. and Madsen, I.C., (2006), "Quantification of phases with partial or no known crystal structures", *Powder Diffraction*, **21(4)**, 278-284.

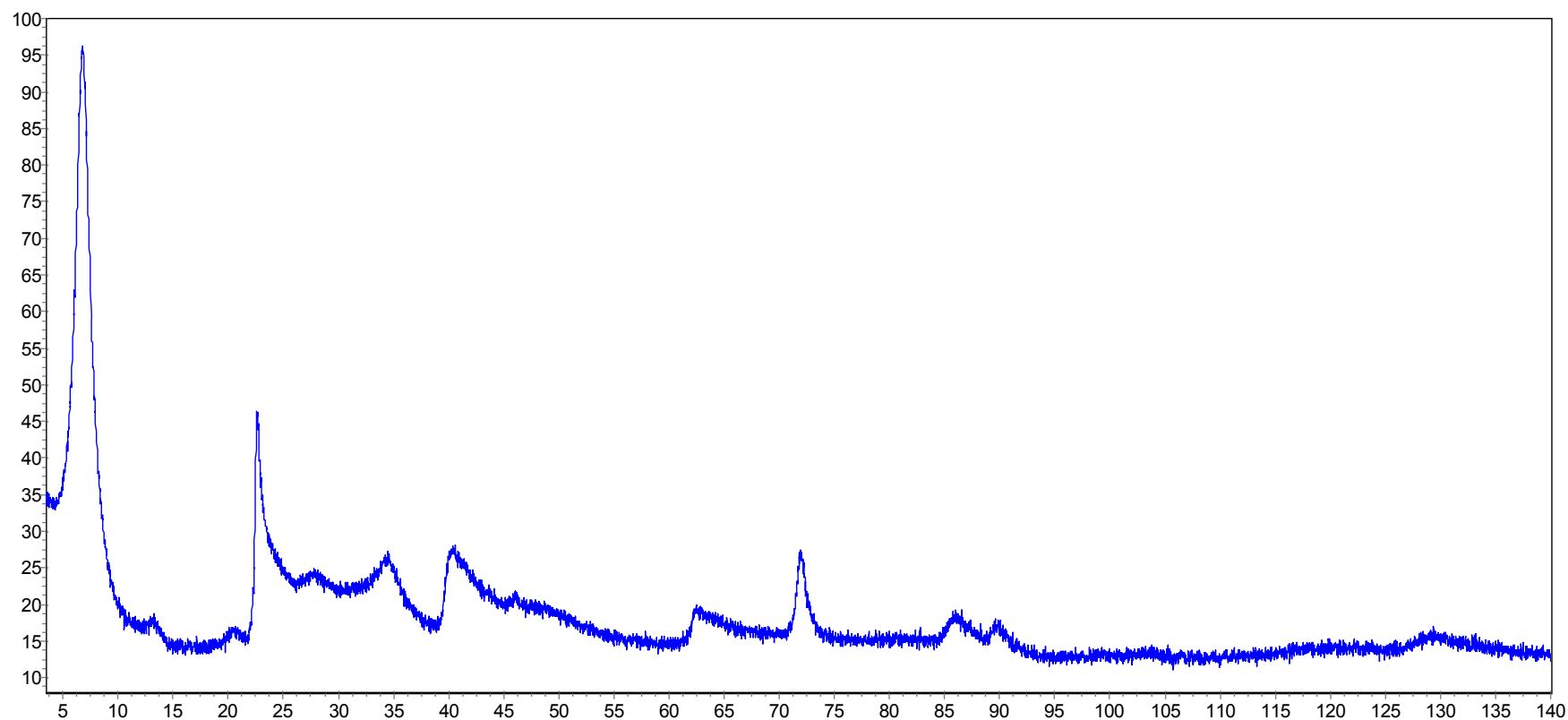
Issues in the Analysis of 'Real' Materials

- Sometimes, materials (esp. mineralogical) contain phases for which the crystal structure is not well defined
 - May be crystalline but with new and unknown structure, or
 - Poorly ordered or even amorphous
- Structure may change with the weather!
 - XRD pattern for some clay minerals affected by humidity

Diffraction Pattern of Nontronite (Co K α)



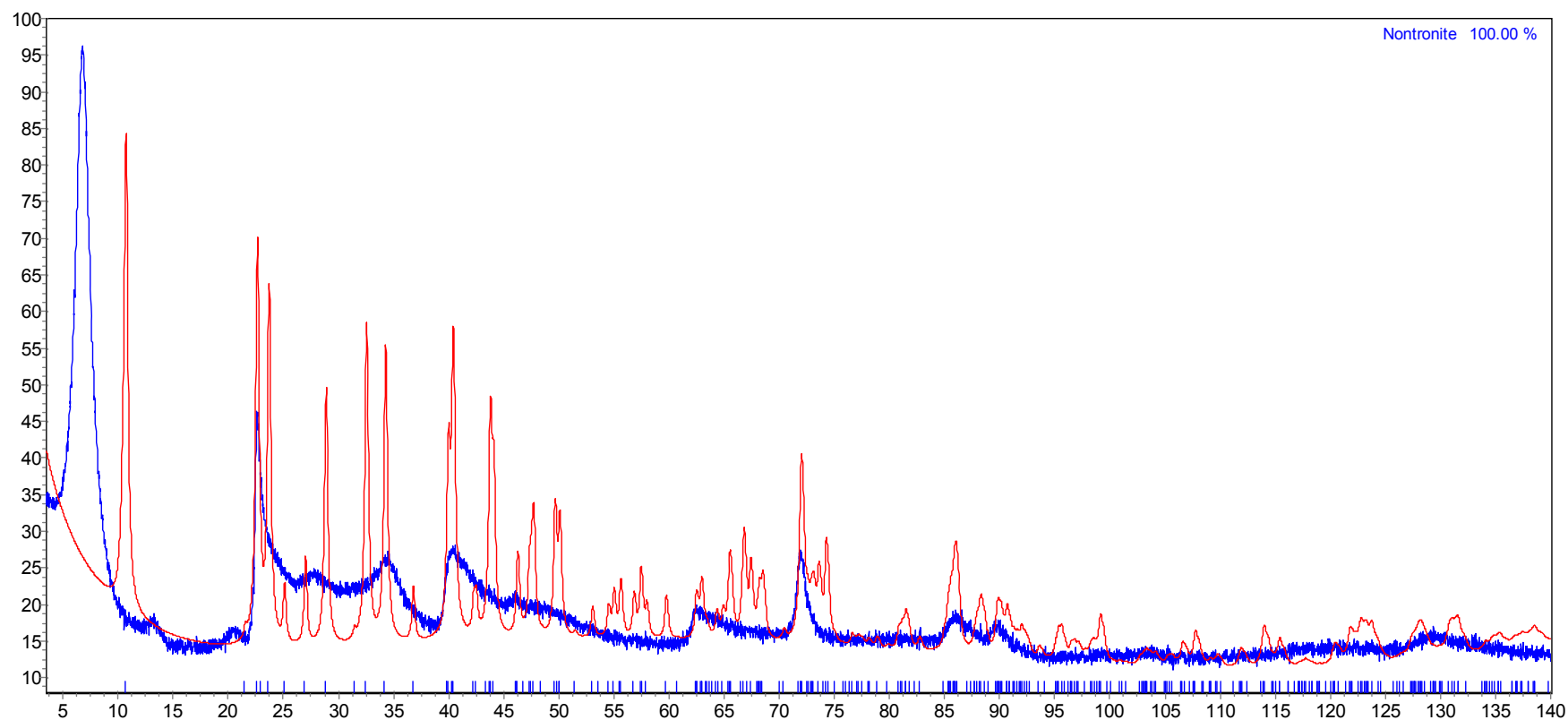
Component of many materials
of interest e.g. Nickel laterites



Nontronite (Co $K\alpha$)



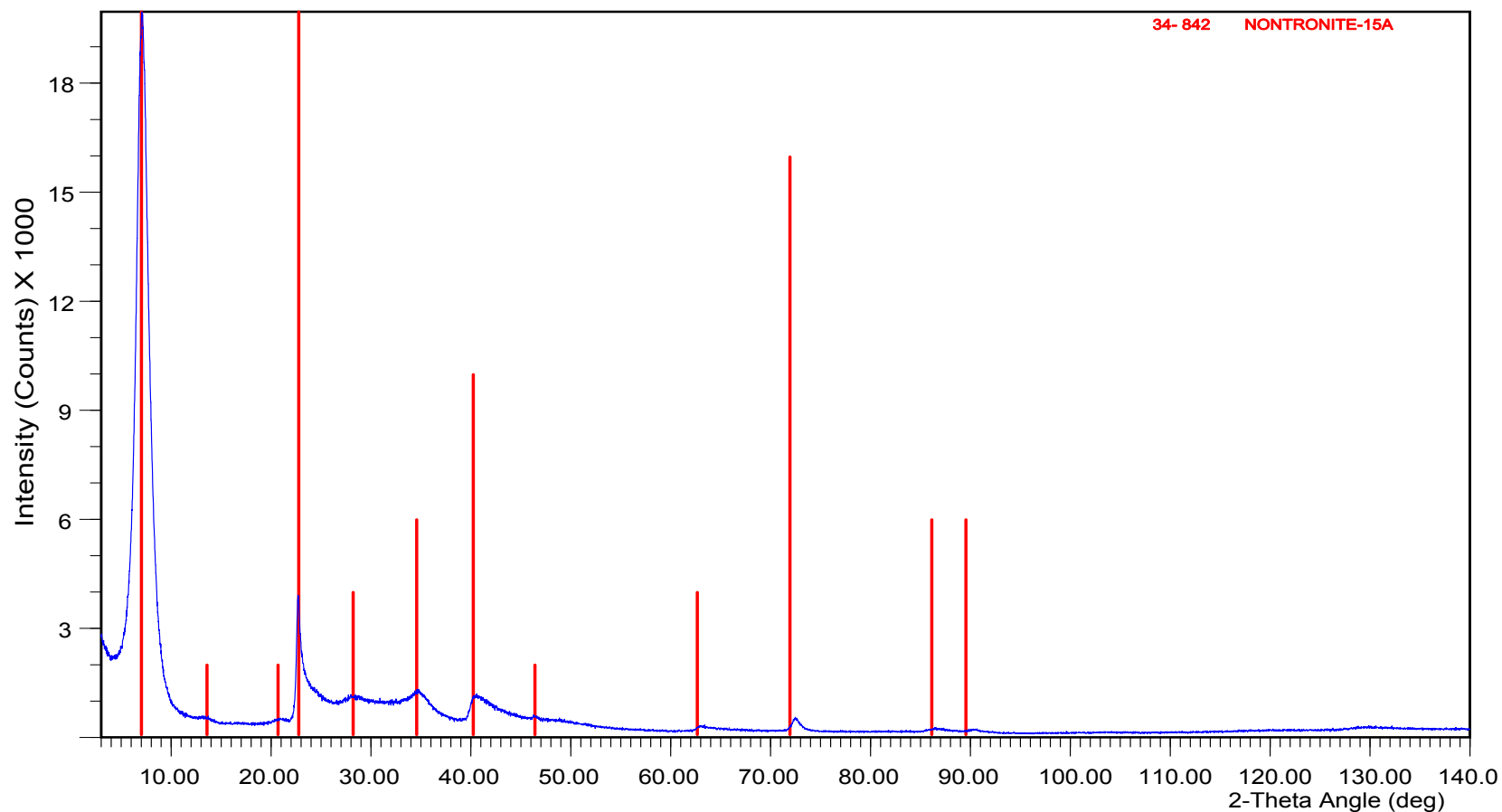
Calculated pattern using the only published structure of nontronite (Manceau et al., 1998)



Nontronite (Co K α)



- ICDD (34-842) contains an indexed pattern which is a much better match
 - Note differences in relative intensities



Modelling a Phase with “Unknown” Structure



- QPA can still be achieved
 - Use *measured peak intensities* in place of *calculated structure factors*
- 1. If the phase can be indexed (SG & unit cell) → “*hkl phase*”
 - Use Le Bail or Pawley fit to constrain peak positions via SG & unit cell
 - Individual peak intensities varied to achieve best fit to observed pattern
- 2. If phase cannot be indexed → “*peaks phase*”
 - Define it as a group of individual peaks
 - Scale the group as a single entity during analysis
- In both cases:-
 - The relative peak intensities can be derived through peak fitting to a diffraction pattern in which the phase is a major component

ZMV “Calibration Constant”

- QPA via Hill/Howard algorithm requires the calculation of the ZMV “calibration constant”

$$W_{\alpha} = \frac{S_{\alpha} (ZMV)_{\alpha}}{\sum_{k=1}^n S_k (ZMV)_k}$$

Where:

***W* = wt%**

***S* = Rietveld scale factor**

***Z* = No. formula units in unit cell**

***M* = molecular mass of formula unit**

***V* = unit cell volume**

- Fitting an unknown with either an ‘*hkl phase*’ or a ‘*peaks phase*’ does not provide ZMV – this due to the lack of crystal structure information

Derivation of an Empirical ZMV

- Calibration may be achieved via a mixture in which there are known amounts of the unknown (W_α) and a standard material (W_s)
- In this mixture, the ratio of the known weight fractions is given by:

$$\frac{W_\alpha}{W_s} = \frac{S_\alpha (ZMV)_\alpha}{S_s (ZMV)_s}$$

- In such a mixture some things are known
 - Weight fractions of W_α and W_s of phase α and standard s
 - Scale factors S_α and S_s
 - Unit cell mass & volume of standard ZMV_s

Derivation of an Empirical ZMV (cont'd)

- A empirical value for the *ZM* or *ZMV* of the unknown can be calculated by rearranging thus:

- For an *hkl* phase
$$(ZM)_{\alpha} = \frac{W_{\alpha}}{W_s} \cdot \frac{S_s}{S_{\alpha}} \cdot \frac{(ZMV)_s}{V_{\alpha}}$$

- For a *peaks* phase
$$(ZMV)_{\alpha} = \frac{W_{\alpha}}{W_s} \cdot \frac{S_s}{S_{\alpha}} \cdot (ZMV)_s$$

- Note

- *ZM* and *ZMV* derived in this way are arbitrary and do not equate to crystallographically derived values

Requirements for Application of PONKCS



- Quantification of phases of unknown or partially known structure can be achieved given the following:
- Phase is available as pure specimen or as the major phase of a sample
 - Any impurity phases can be quantified by some means (XRD, chemistry)
- A mixture can be prepared in which the amount of the unknown and an internal standard are known
- The unknown in question does not vary in its relative intensities due to preferred orientation or other sample related effects
 - Preferred orientation/solid solution/etc may be compensated for to some degree in an *hkl* phase

Quantitative Phase Analysis Using the Rietveld Method

Advantages, Disadvantages, Precision & Accuracy

Advantages of the Rietveld Method for QPA



- Whole diffraction pattern used in analysis
 - c.f. single peak methods which cannot accommodate sample related problems such as peak overlap, preferred orientation
- Additional information gained from the refinement
 - Crystal structure – unit cell dimensions & atom location & site occupancies
 - Chemical composition
 - Solid solution
 - Profile parameters (peak shape & width)
 - Crystallite size
 - Crystallite strain
 - Preferred orientation parameter → 'texture'
 - Plating conditions in electro-deposited thin films
 - Crystal morphology

Disadvantages of the Rietveld Method for QPA



- Before you can quantify, you must first identify !
 - Failure to identify a phase or incorrect assignment affects QPA
 - May require additional information (SEM, EPMA, optical microscopy)
- Knowledge of crystal structure
 - However, calibration methods have been developed¹ which are helping to overcome this requirement → PONCKS
 - Not suitable for one-off, multi-phase sample in which the unknown phase is only a small component
- Difficulty in using Rietveld software (even with sophisticated interfaces !)
 - NOT a black box
 - Requires some crystallographic & diffraction understanding for success
- Not all sample related problems are adequately modelled
 - Preferred orientation
 - Microabsorption
 - Biggest impediment to accurate QPA via XRD

¹ Scarlett, N.V.Y. and Madsen I.C. (2006)

IUCr Commission on Powder Diffraction

Round Robin on Quantitative Phase Analysis



- Run between 1996 – 2002
- Aims of the round robin
 - Document methods (esp. powder diffraction) & strategies employed in QPA
 - Assess accuracy, precision and lower limits of detection
 - Identify problem areas and develop practical solutions
 - Formulate recommended procedures for QPA using diffraction data
 - Create a standard set of samples for future reference
- Two published papers on outcomes ^{1,2}

¹ Madsen I.C. *et al* (2001)

² Scarlett, N.V.Y. *et al* (2002)

IUCr Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis

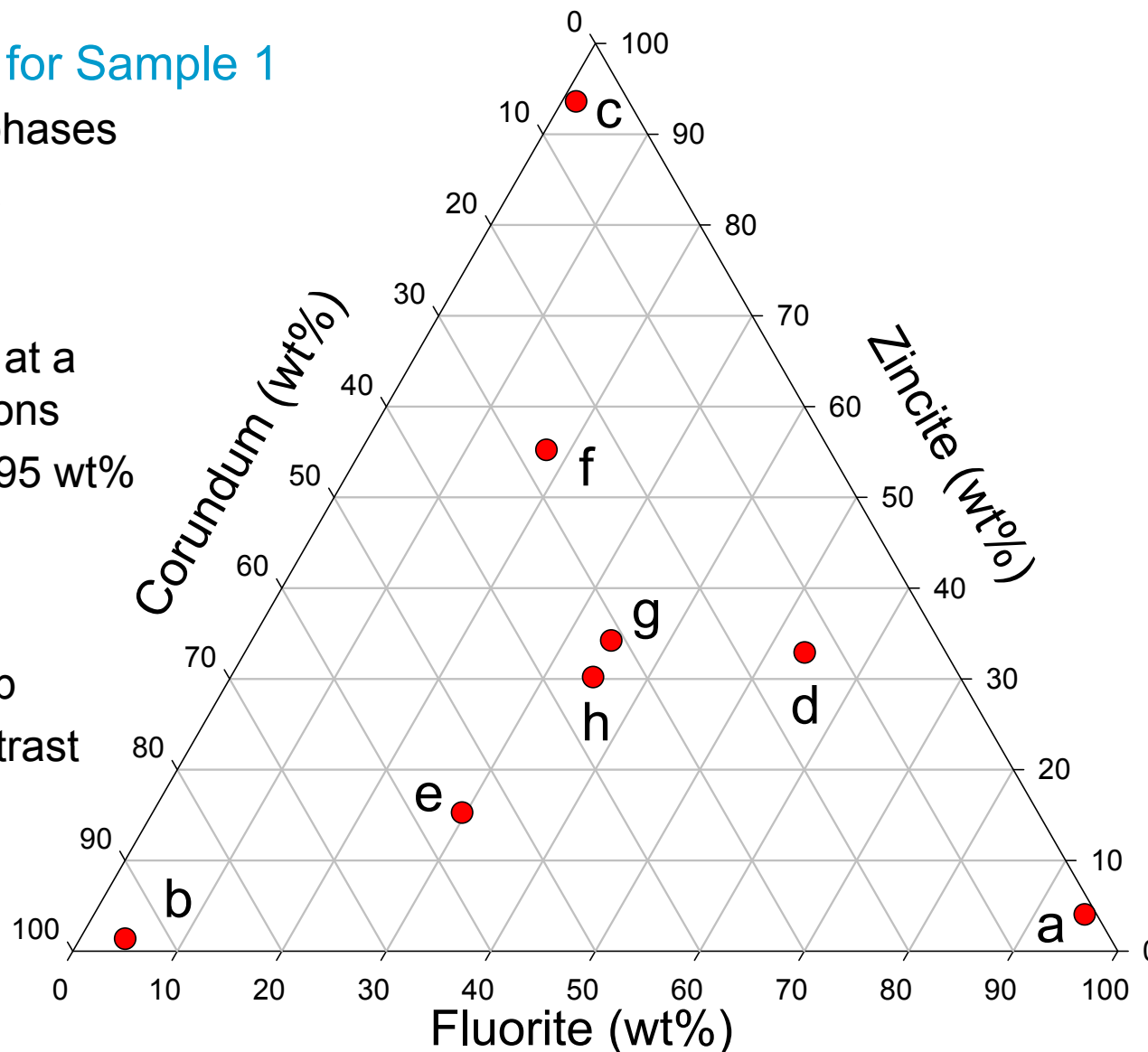


- Experimental design for Sample 1

- Eight mixtures of 3 phases
 - Corundum – $\alpha\text{-Al}_2\text{O}_3$
 - Fluorite – CaF_2
 - Zincite – ZnO
- Each phase present at a range of concentrations
- ~ 1.5, 5, 15, 30, 55, 95 wt%

- 'Simple' system

- Well defined phases
- Minimal peak overlap
- Little absorption contrast



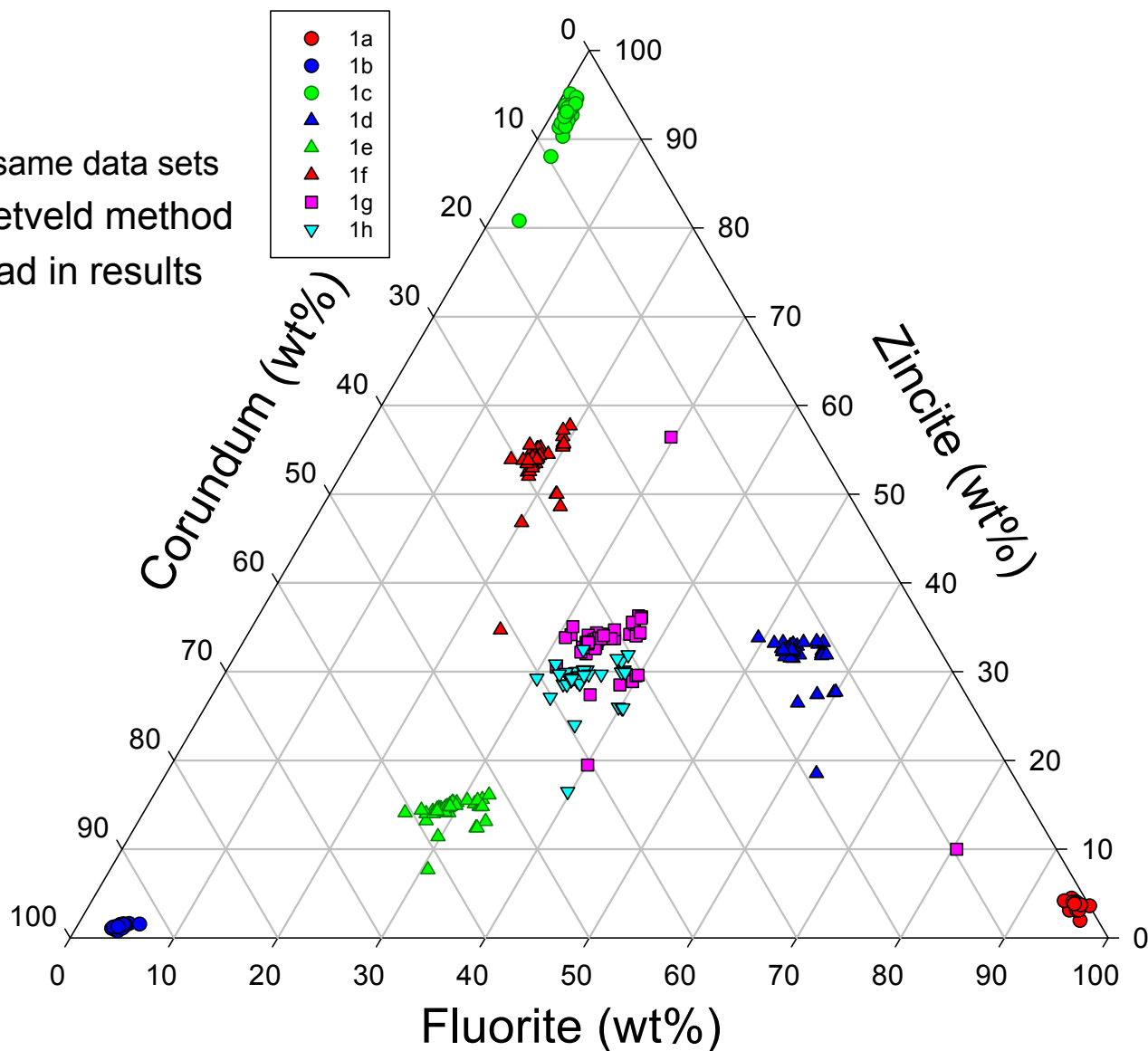
IUCr CPD Round Robin on QPA

CPD Supplied Data



- Participant's results

- CPD-supplied data
 - Everyone analysed the same data sets
- 92% of returns used Rietveld method
- Note considerable spread in results



IUCr CPD Round Robin on QPA

Participant Collected Data

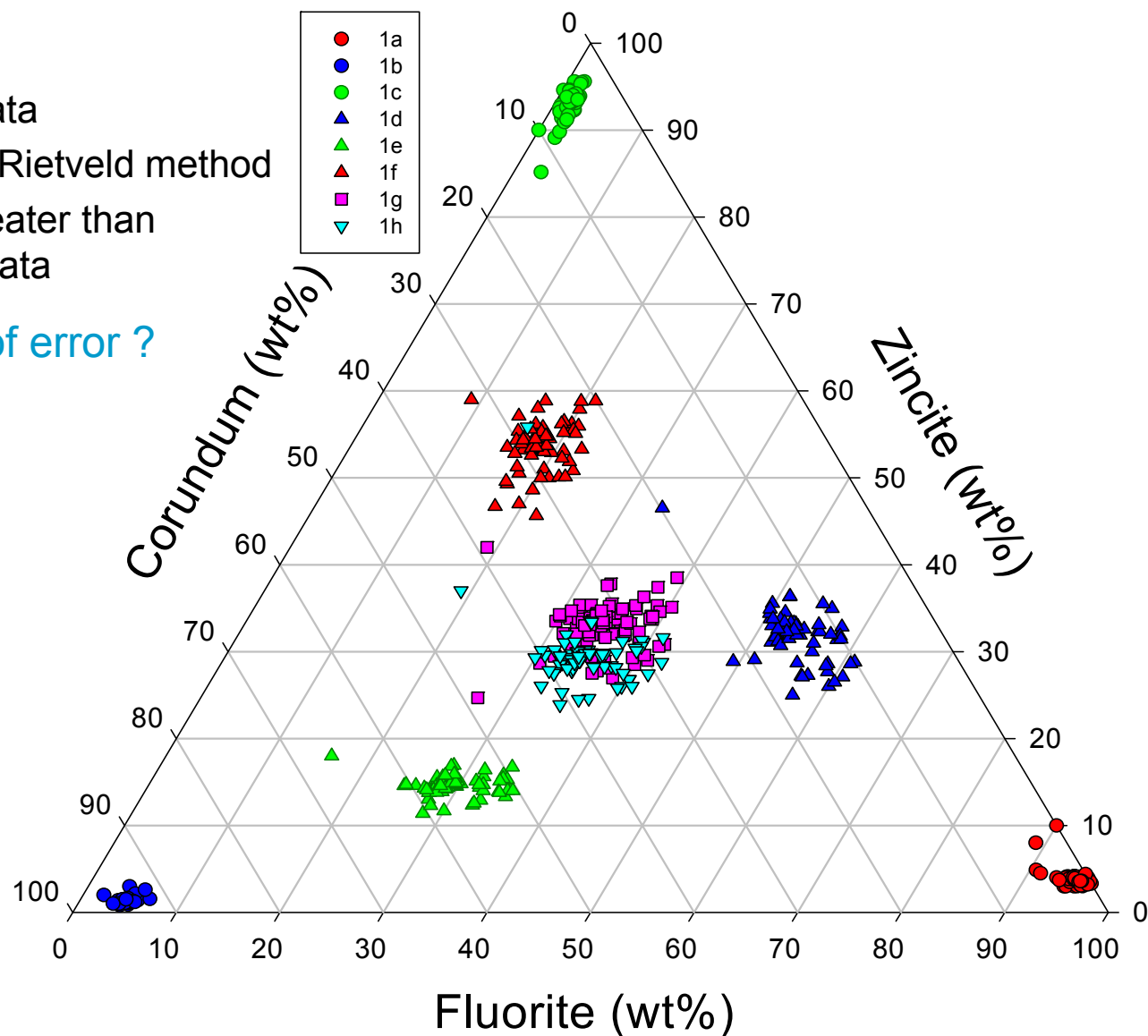


- Participant's results

- Participant collected data
- 75% of returns used a Rietveld method
- Spread of results is greater than for the CPD-supplied data

- What are the sources of error ?

- Methods ?
- Sample preparation ?
- Data collection ?
- Data analysis ?



IUCr CPD Round Robin on QPA

Test of Various Methods



- Samples analysed in CSIRO labs

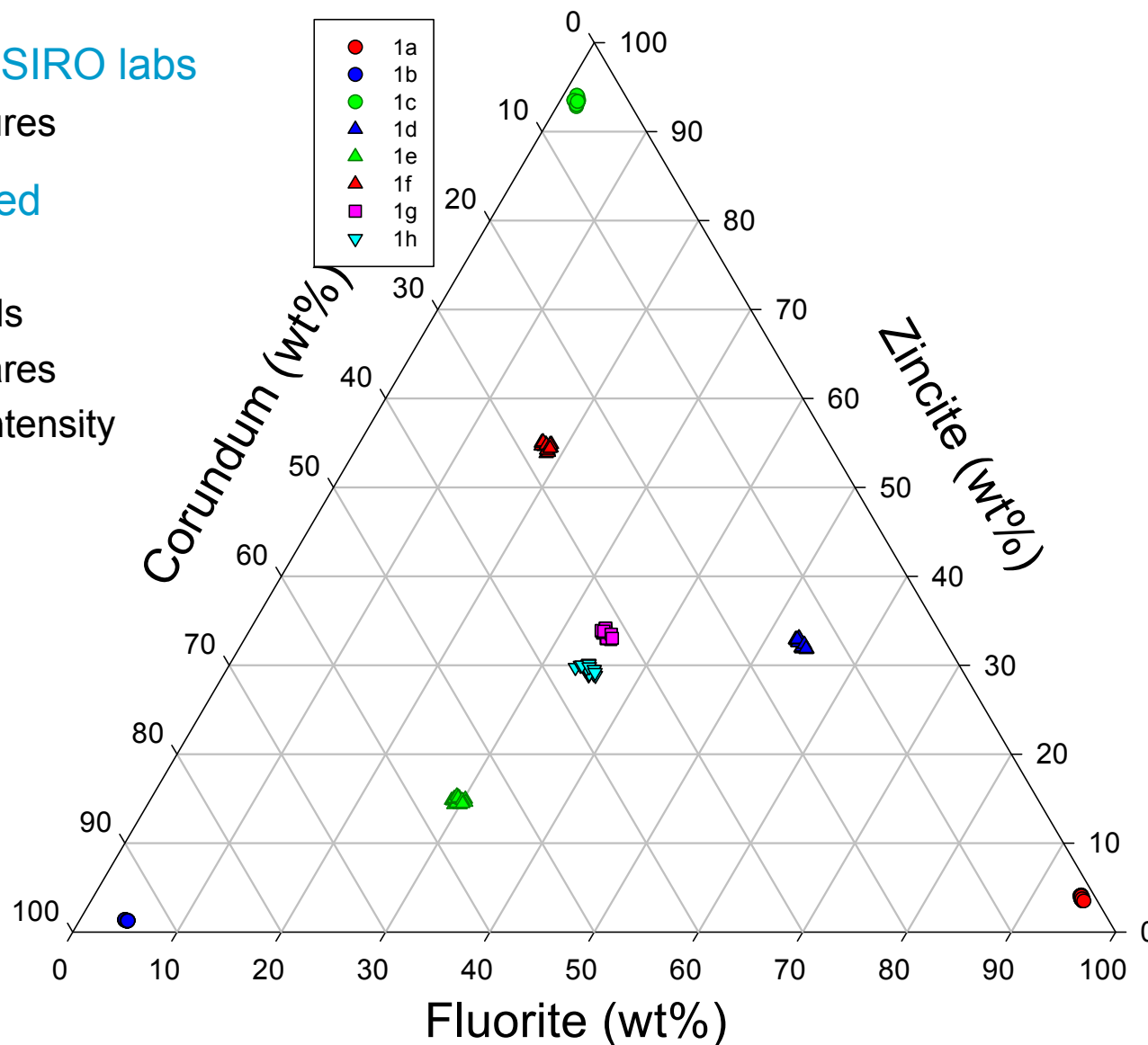
- 3x replicates of 8 mixtures

- A range of methods used

- 2x Rietveld packages
- 2x Single Peak methods
- 2x Iterative Least Squares
- 1x Mean Normalised Intensity
- XRF

- Summary

- Methods work OK
- Errors arise during application of methods



Sources of Error in QPA Rietveld Analysis Procedures



- Largest & most common sources of error are related to the carbon-based life forms involved in the analysis...
 - The dreaded “operator error”
- Some sources of error
 - Incorrect crystal structures: space group, atom coords, occupancies, Beq's
 - Use of poor profile models
 - Omission of phase(s) from the analysis
 - Errors in phase ID
 - Failure to refine parameters
 - Unit cell, thermal, etc..
 - Refinement of parameters which are not supported by the data !
 - Inappropriate use of correction models – just because you CAN doesn't mean you SHOULD!
 - Preferred orientation correction
 - Microabsorption correction

Sources of Error in QPA

Rietveld Analysis Procedures (cont'd)



- Poor assessment of output
 - Acceptance of physically unrealistic parameters (esp. thermal parameters)
 - Acceptance of incomplete refinements
 - High values of R-factors
 - Refined parameters not checked
 - Visual fit of model not checked
- Poor understanding of issues in data collection and analysis procedures
 - Rietveld software often treated as 'black-box'

These issues can only be solved through continuing education of users of diffraction methodology and Rietveld-based software

Issues in Precision and Accuracy

Estimating Errors in QPA

Precision, Accuracy & the Calculation of Error



- The issue of precision and accuracy in QPA via XRD is a difficult one
- Analysts most often report Rietveld errors calculated during refinement as the errors in the final quantification
 - These values numbers are related purely to the mathematical fit of the model
 - They do not represent either precision or accuracy of the QPA !
- Determination of actual accuracy is no trivial task
 - Needs recourse to some other measure of the sample

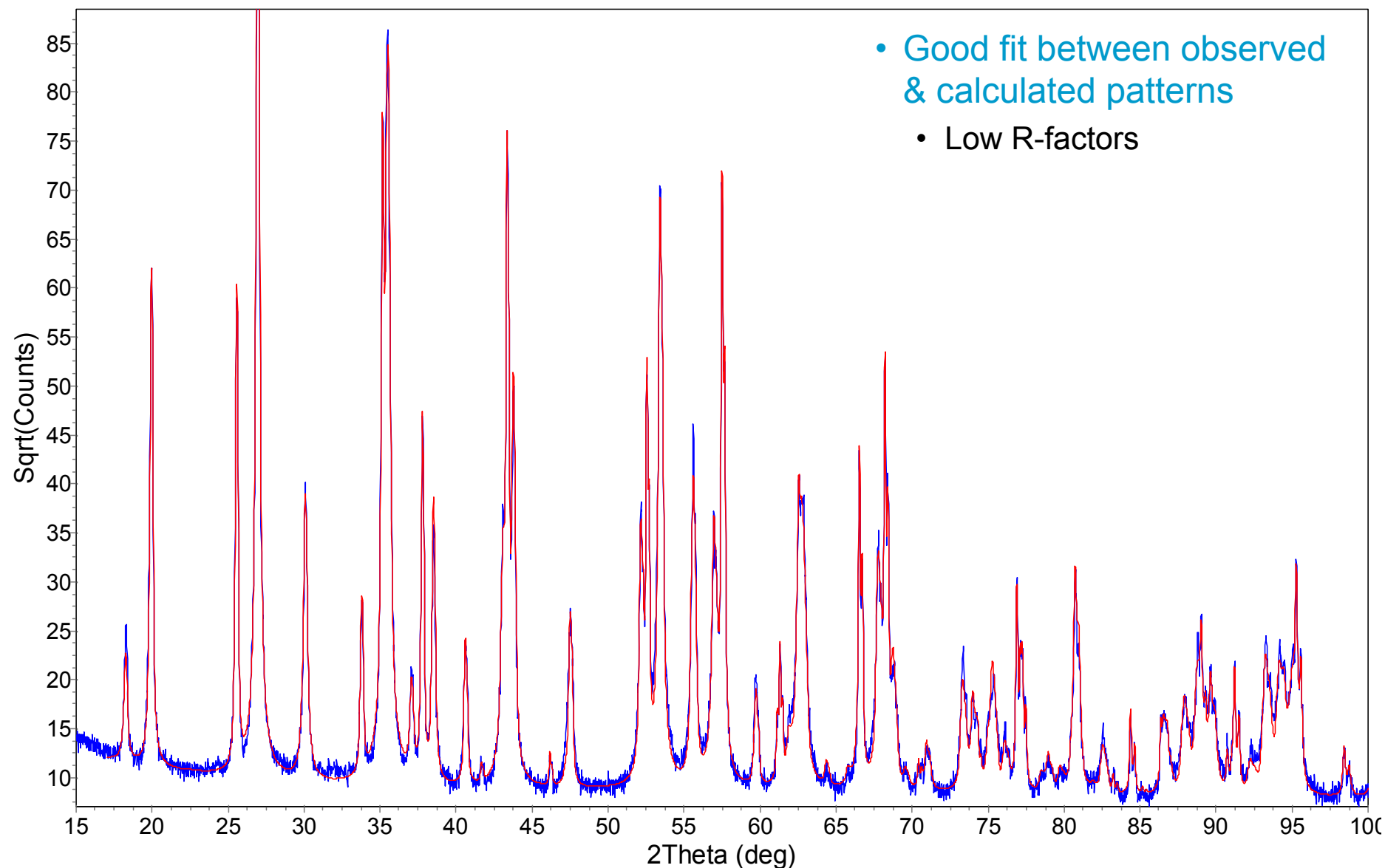
Precision, Accuracy & the Calculation of Error



- Consider Sample 4 from the IUCr CPD round robin
 - Components chosen to deliberately create a microabsorption problem
- Phases present
 - Corundum – Al_2O_3
 - Magnetite – Fe_3O_4
 - Zircon – ZrSiO_4

Precision, Accuracy & the Calculation of Error

IUCr CPD Round Robin Sample 4 - Cu K α radiation



Precision, Accuracy & the Calculation of Error

3 replicates of IUCr CPD Round Robin Sample 4



	Corundum	Magnetite	Zircon
Mean Analysed wt% (n=3)	56.52	17.06	26.42
Mean Rietveld error	0.15	0.11	0.11
S.D. of Analysed wt%	0.63	0.41	0.35
XRF	50.4(2)	19.6(1)	29.5(1)
Weighed	50.46	19.46	29.90
Mean of bias	6.06	-2.58	-3.48

- Results often quoted as Rietveld wt% $\pm$ Rietveld error
 - Corundum 56.5(2) Magnetite 17.1(1) Zircon 26.4(1)
- If replicates are done (rare) results quoted as Rietveld wt% $\pm$ SD of mean
 - Corundum 56.5(6) Magnetite 17.1(4) Zircon 26.4(4)
- 'Real' result – errors only available if answer already known
 - Corundum 56(6) Magnetite 17(3) Zircon 26(3)

Precision, Accuracy & the Calculation of Error



- Rietveld errors are not a measure of accuracy or precision
 - They only represent the 'goodness of fit' between calculated and observed patterns
- Standard deviation of replicates $\equiv$ precision of analysis, not accuracy
 - Many times larger than Rietveld errors
 - Low R-factors could lead the analyst to conclude that the mean value $\pm$ SD is an adequate measure of the phase abundance and error
- Rietveld errors and replication errors can be at least an order of magnitude smaller than the bias (measured – weighed)
 - In this case, bias is due to severe microabsorption
 - Represents the true accuracy which can be achieved if no further steps are taken to identify and eliminate the cause of the bias

What Alerts Us to the Potential for Error

- Rietveld R-factors & other measures of fit **X**
- Rietveld errors **X**
- Replication errors **X**
- Independent verification **Y**
 - Calculate expected chemistry and compare with measured chemistry
 - Use different X-ray wavelengths
 - Collect neutron diffraction data for selected samples
 - Not always possible with some sample types (e.g. minerals)

Issues in Precision and Accuracy

Microabsorption

Sample Related Factors Affecting Accuracy

Microabsorption



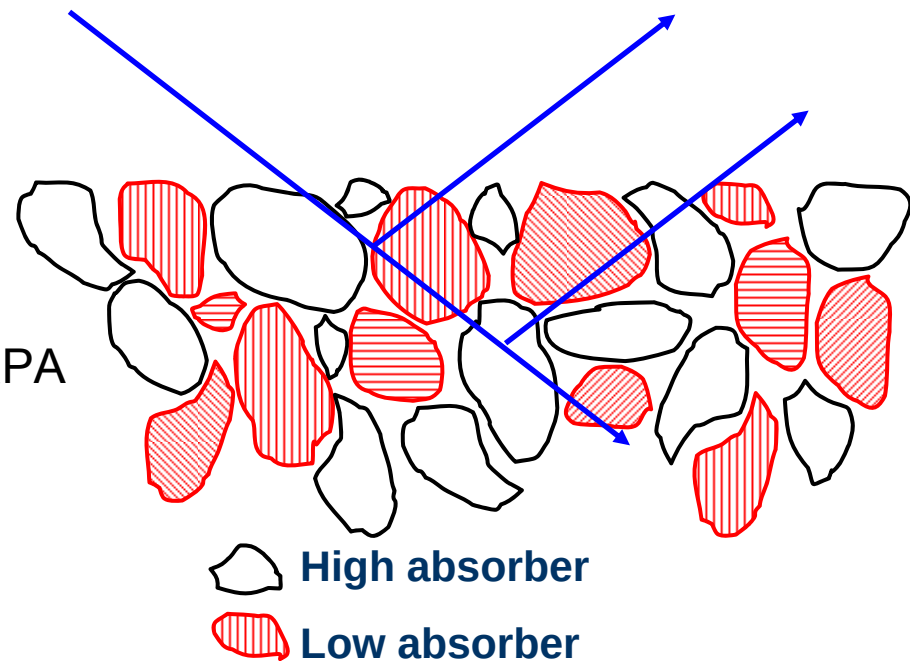
- Largest source of residual error in QPA by XRD due to microabsorption
- Occurs when sample contains a mix of low & highly absorbing phases
 - A disproportionate amount (more or less) of observed intensity comes from individual grains relative to what would be expected for the average absorption of the sample

- **High absorbers**

- Beam absorbed in surface of grain
 - Only a fraction of the grain diffracting
- Intensity under-estimated – low QPA

- **Low absorbers**

- Beam penetrates further into grain
 - Greater likelihood of 'volume diffraction' occurring
- Intensity over-estimated – high QPA



Sample Related Factors Affecting Accuracy

Microabsorption (cont'd)



- For the analyst encountering a new sample, it is difficult to determine whether a correction for microabsorption is required without first obtaining additional information
- The Brindley model is most frequently applied correction
 - Requires knowledge of absorption contrast and particle sizes
 - The latter is not easily achieved in 'real' samples
- The Brindley model assumes spherical particles of uniform size
 - Assumption is unrealistic in real samples
 - Even when particle size is measured by e.g. laser-sizing or SEM, the best form of correction can still be unclear

Sample Related Factors Affecting Accuracy

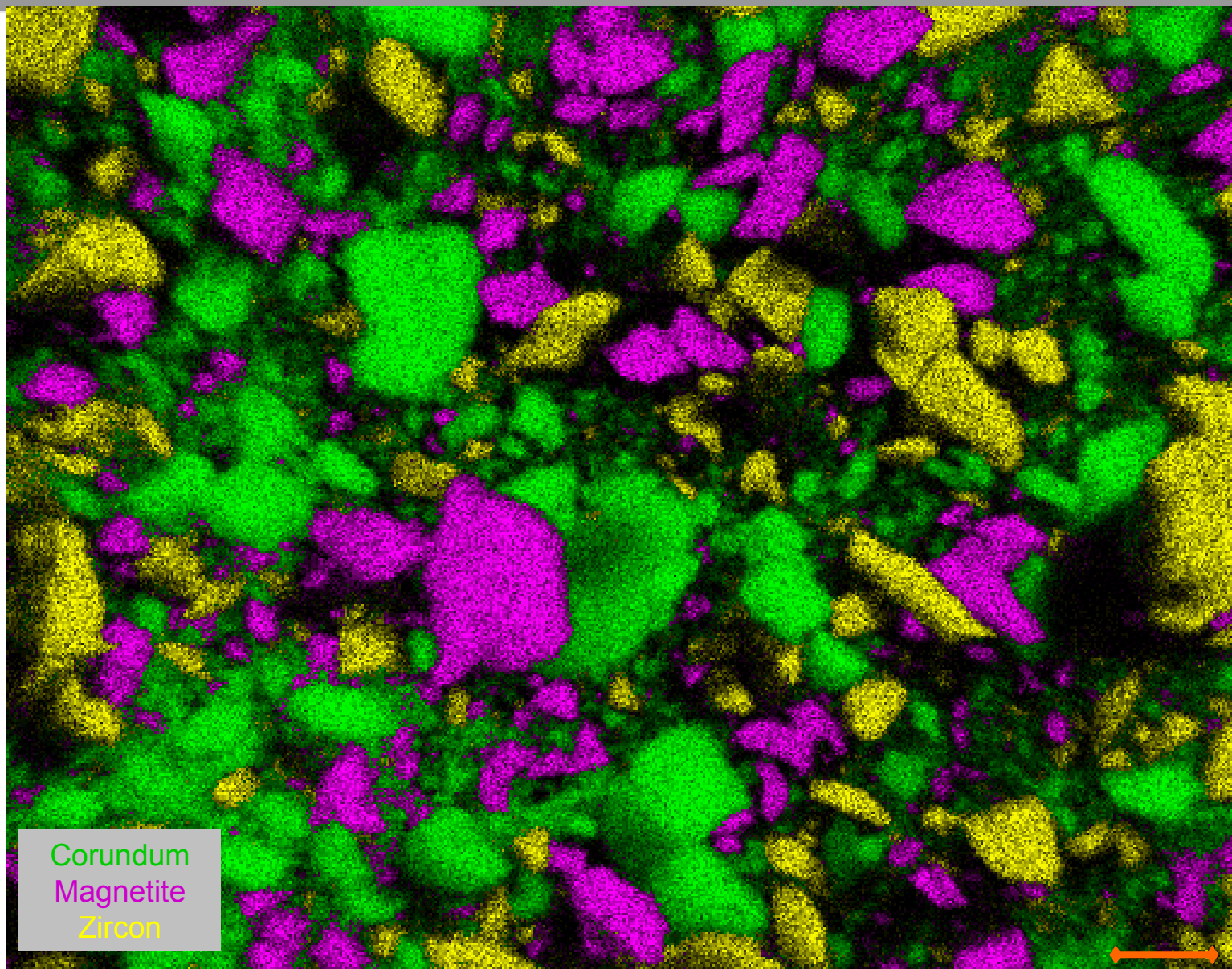
Microabsorption (cont'd)



- Many applications suffer from unnecessary and/or excessive correction
 - Minor microabsorption problem in Sample 1 suite in Round Robin
 - Largely overcorrected when addressed
- Better results achieved through care in sample preparation than in application of correction
- Microabsorption is virtually absent for neutrons
 - Neutron diffraction based results can act as a 'benchmark' for X-ray studies

SEM Image - Sample 4G

Corundum, Magnetite & Zircon - Micronised



Brindley Correction for Microabsorption

Effect of Arbitrarily Chosen Values of Particle Size



- Once alerted to the potential for micro-absorption, what value of particle size do we choose?

<u>Wt%</u>	<u>Corundum</u>	<u>Magnetite</u>	<u>Zircon</u>
Weighed	50.46	19.46	29.90
No correction			
Mean	56.52	17.06	26.42
Bias	6.06	-2.58	-3.48
Brindley model, $\varnothing = 1\mu\text{m}$			
Mean	55.76	17.81	26.43
Bias	5.30	-1.83	-3.47
Brindley model, $\varnothing = 5\mu\text{m}$			
Mean	52.49	21.18	26.33
Bias	2.03	1.54	-3.57
Brindley model, $\varnothing = 10\mu\text{m}$			
Mean	47.76	26.15	26.08
Bias	-2.70	6.51	-3.82

Factors Affecting Accuracy

Particle Statistics

Sample Related Factors Affecting Accuracy

Particle Statistics (PS)



- PS refers to the statistical variation in the number of particles (crystallites) contributing to the diffracted intensity for a given reflection
- Need to measure intensities such that they are reproducible within about $\pm 1\text{-}2\%$ relative
 - Ability to do this influenced by size of diffracting crystallites in the sample
 - Small changes to instrument & sample configurations can significantly improve the sample's particle statistics
- Define fractional particle statistics error, σ_{PS} in terms of number of crystallites diffracting N_{diff} §

$$\sigma_{PS} = \frac{\sqrt{N_{diff}}}{N_{diff}}$$

§ Elton & Salt (1996)

Sample Related Factors Affecting Accuracy

Particle Statistics (cont'd)



- Effect of particle size on number of crystallites diffracting[§]
 - Particle size comparisons for stationary quartz samples in Bragg-Brentano geometry

<u>Crystallite Diameter</u>	<u>40μm</u>	<u>10μm</u>	<u>1μm</u>
Crystallites/20mm ³	5.97 x 10 ⁵	3.82 x 10 ⁷	3.82 x 10 ¹⁰
Number Diffracting	12	760	38,000
σ_{PS}	0.289	0.036	0.005

[§] D. K. Smith (1992)

Sample Related Factors Affecting Accuracy

Ways to improve particle statistics



- Increase the instrument beam divergence
 - Use a broad focus rather than a fine focus tube
 - Use wider divergence and receiving slits
 - σ_{PS} improved by $\sim 2x$
 - Issue for synchrotron based work
 - Geometry serves to decrease divergence
- Rotate the sample
 - About the vertical to sample surface – flat plate sample
 - About the sample axis – capillary sample
 - σ_{PS} improved by ~ 5 to $6x$

Sample Related Factors Affecting Accuracy

Ways to improve particle statistics (cont'd)



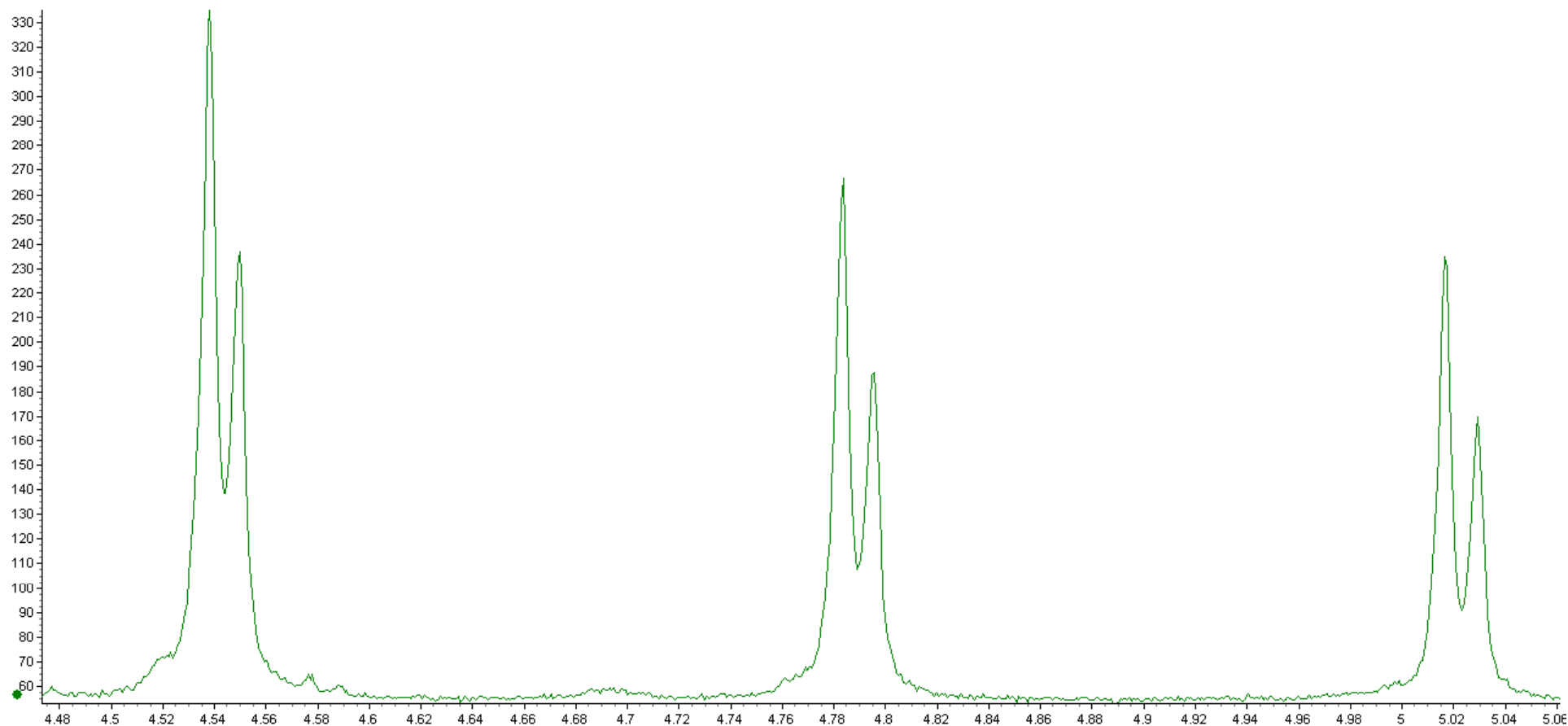
- Oscillate the sample about θ axis (flat plate geometry)
 - Destroys $\theta/2\theta$ relationship
 - Aberrations in peak intensities, positions & profile shapes
 - σ_{PS} improvement depends on the range of oscillation used
- Repack the sample, recollect and reanalyse the diffraction data
 - Averaging results produces more meaningful parameter values
 - Independent determination of parameter esd's
- Reduce mean crystallite size by mechanical comminution of the sample
 - The most effective method of increasing the number of crystallites examined
 - McCrone micronising mill reduces particle size to $\sim 10\mu\text{m}$ or less in 1-20 min.

Effect of Particle Size

XRD Data for SRM 660a LaB_6



- Laboratory XRD Instrument
 - $\text{Cu K}\alpha_{1,2}$
 - Stationary sample – beam divergence ensures good ‘powder average’

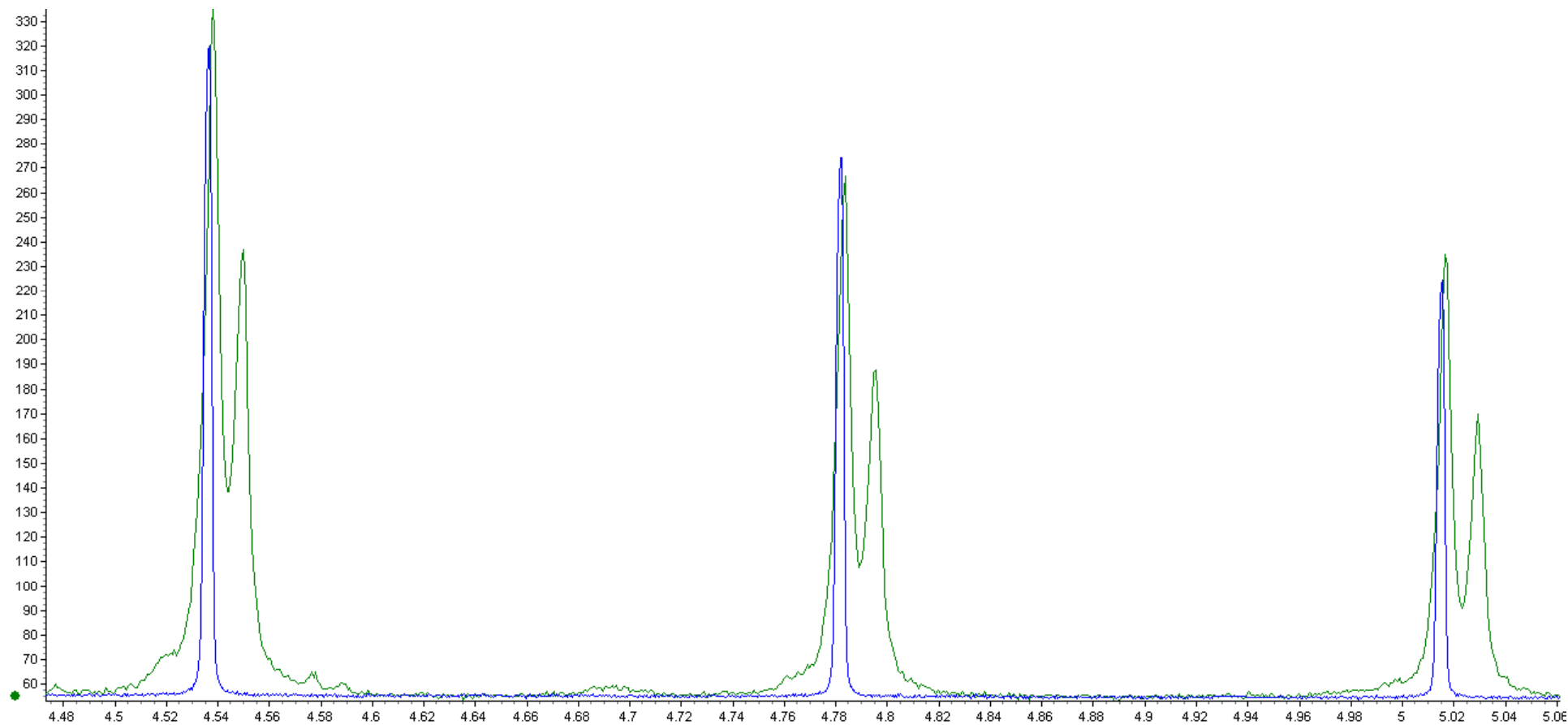


Effect of Particle Size

XRD Data for SRM 660a LaB_6



- Australian Synchrotron
 - 0.3mm capillary
 - Spinning sample – rotating sample ensures a good ‘powder average’

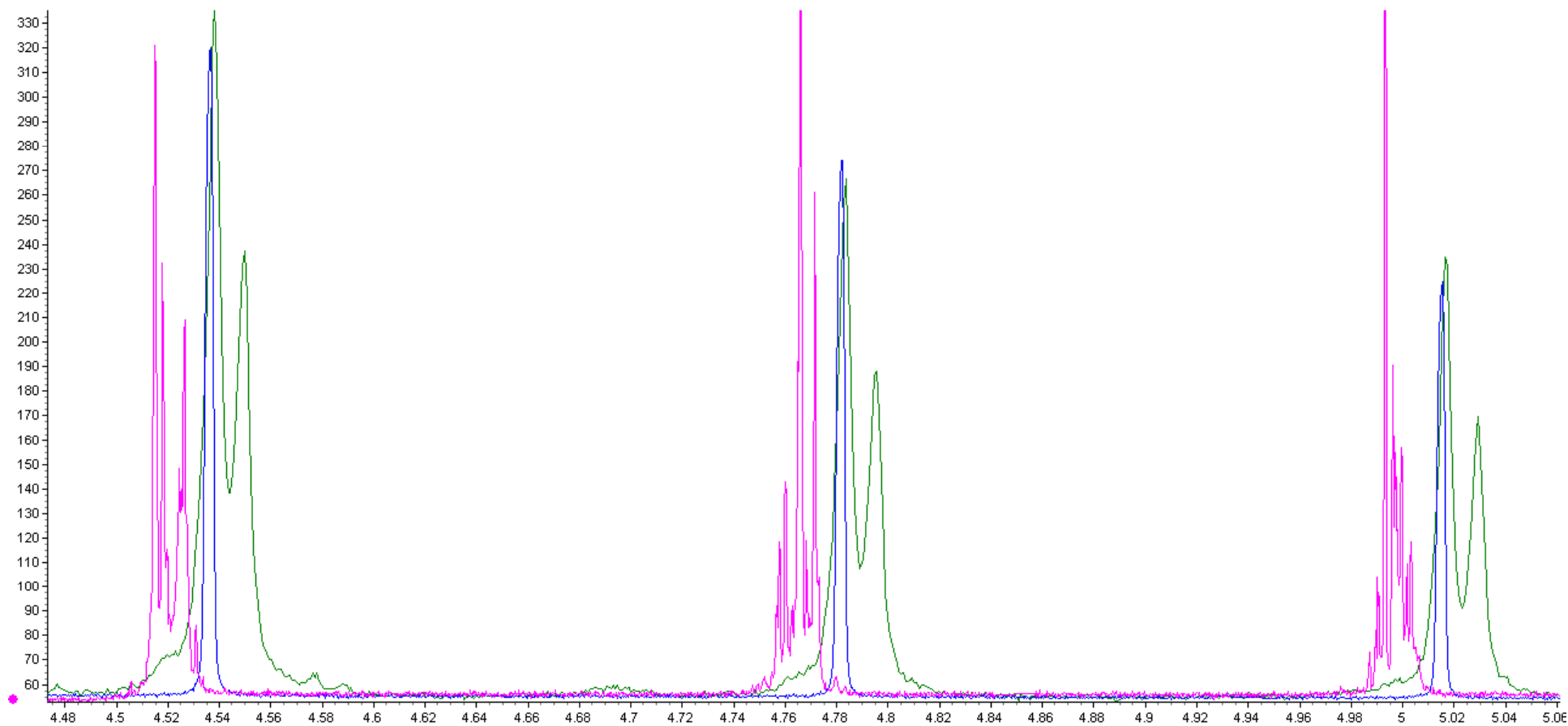


Effect of Particle Size

XRD Data for SRM 660a LaB_6



- Australian Synchrotron
 - Flat plate sample – high temperature stage
 - Sample rocking $\pm 2^\circ$ on omega axis



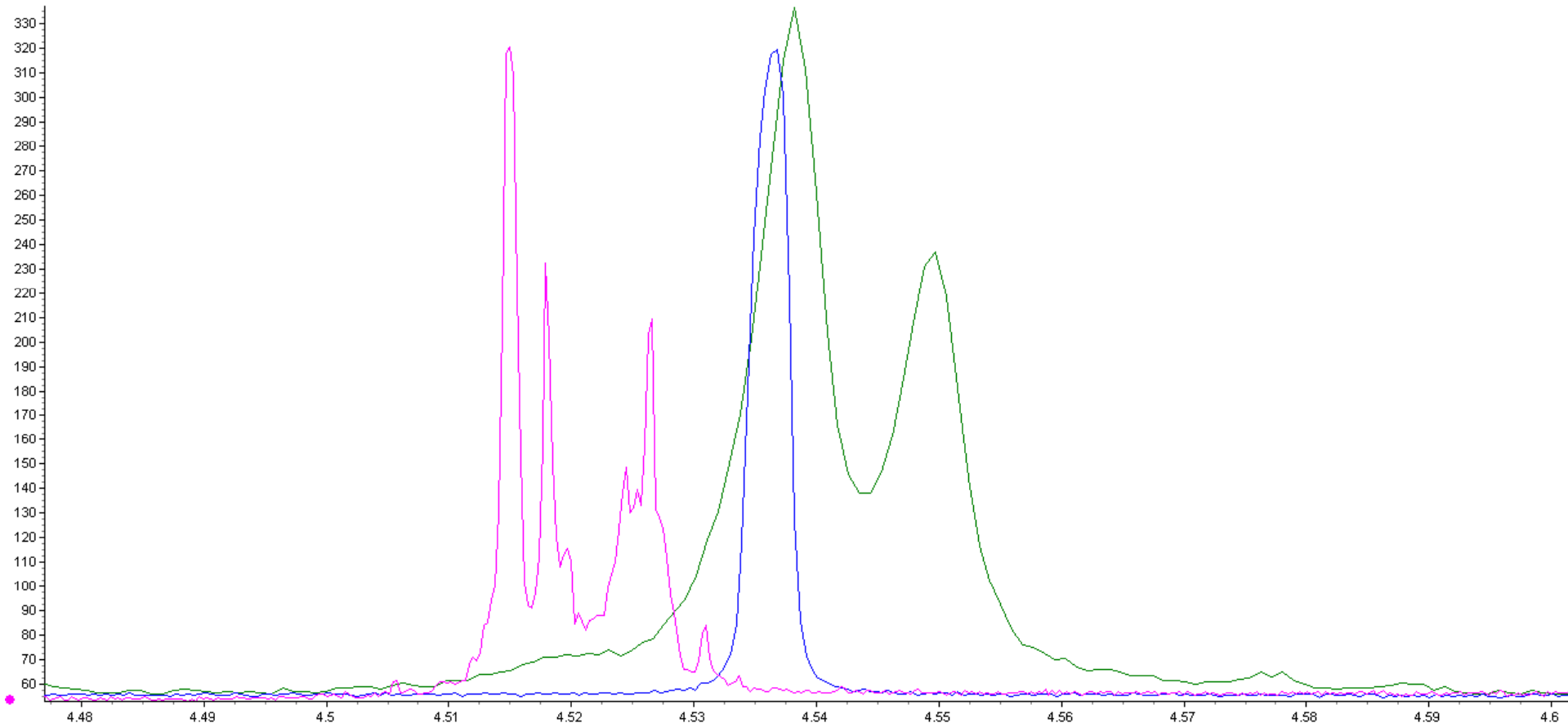
Effect of Particle Size

XRD Data for SRM 660a LaB_6



- Australian Synchrotron

- Flat plate sample – high temperature stage
- Sample rocking $\pm 2^\circ$ on omega axis – not sufficient for good ‘powder average’
 - Data is unusable !



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