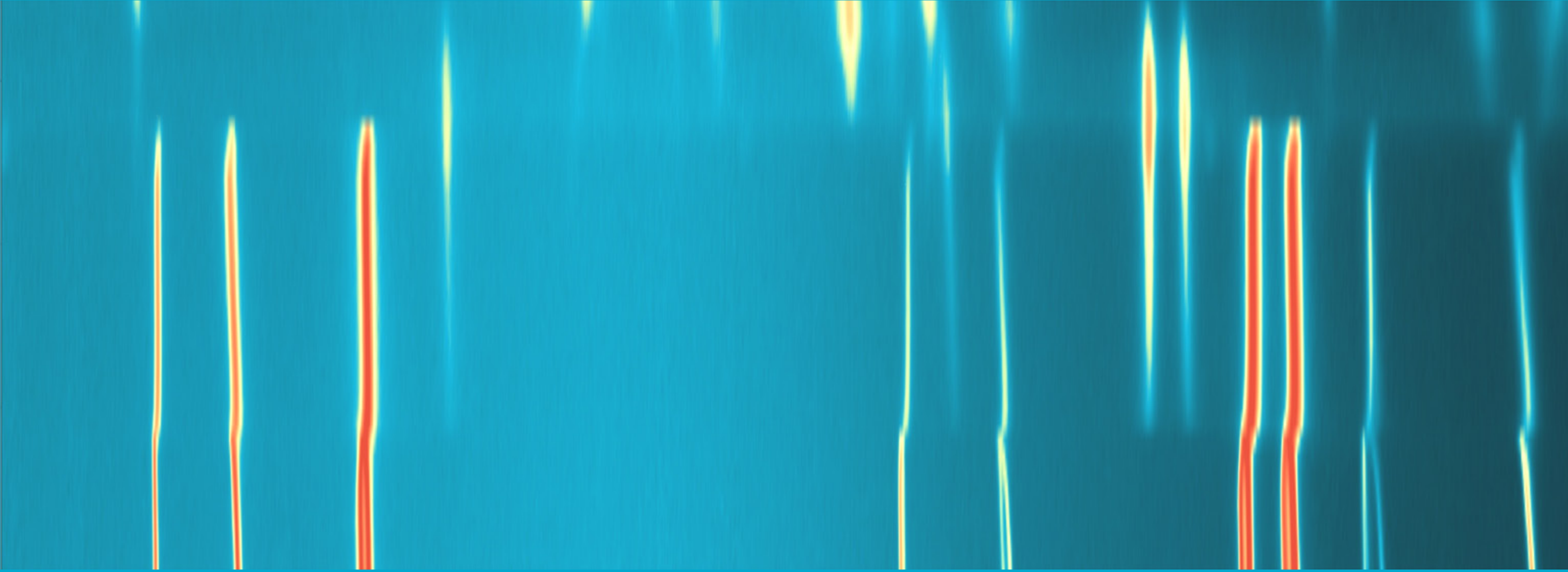

Dehydration of natrojarosite

Quantitative Phase Analysis (QPA)

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APD-IV | April 2013
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*"The uncertainty of the quantitative determination of phase composition by X-ray diffraction is seldom less than several percent absolute"**

Is this still true?

*Andre Guinier ("Theorie et Technique de la Radiocristallographie," Dunod, Paris 1956)

QPA via XRD

QPA via diffraction is not new

- Relation of peak intensity to abundance
  - Single peak methods from circa. 1919
  - Formalised in: Alexander, L.E. and H.P. Klug, X-ray diffraction analysis of crystalline dusts. Analytical Chemistry, 1948. 20: p. 886-894.

$$\boxed{I_x = \frac{CV}{\mu}}$$

I_x = measured intensity of diffraction line
V = volume fraction of phase
μ = linear absorption coefficient of specimen
C = constant for a given line

- Measurement of pure or known standards allowed determination of “absolute” abundances

Application of Rietveld method to QPA

- Whole pattern (Rietveld) methodology extended to QPA in ‘80s
  - D. L. Bish and S. A. Howard, (1988) J. Appl. Cryst. 21, 86-91 (Rec‘d 30/03/1987)
  - O‘Connor & Raven (1988) Powder Diffraction, 3(1), 2-6 (Rec‘d 31/03/1987)
  - R. J. Hill and C. J. Howard, (1987) J. Appl. Cryst. 20, 467-474 (Rec‘d 02/04/1987)
- Standardless method based on assumption that entire sample is crystalline and included in Rietveld model

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

W_α = weight fraction of phase, α, in an n component mixture
S = Rietveld scale factor
ZMV = mass and volume of unit cell

Advantages of QPA via XRD

- Direct phase measurement
  - Based on *structure* not *chemistry*
    - Polymorphs
- Additional (bonus) information available
  - Crystallite size/strain
  - Solid solution chemistry
  - Thermal expansion
- Whole pattern (Rietveld) analysis
  - Standardless
  - Can be high precision

Disadvantages of QPA via XRD

- Single peak methods
  - Strongly affected by any aberrations in data originating from sample preparation, data collection regime or the sample itself
    - Non-representative peak heights/areas
- Whole pattern – Rietveld
  - Generally returns *relative* abundances
  - Generally limited to well-defined crystalline species
  - Accuracy difficult to determine
    - Semi-quantitative???

Disadvantages of QPA via XRD

- Single peak methods
  - Strongly affected by any aberrations in data deriving either instrumentation or sample related
    - Non-representative peak heights/areas
- Whole pattern – Rietveld
  - Generally returns relative abundances
  - ***Generally limited to well-defined crystalline species??***
    - Not necessarily

Determination of Amorphous Content

Or: “What’s that funny shape in my background?”

What is an Amorphous Solid ?

- Pecharsky & Zavalij (2009):
  - *"Crystalline materials are frequently characterized as solids with fixed volume, fixed shape, and long-range order bringing about structural anisotropy, producing sharp diffraction peaks"*
  - *"Amorphous (or non-crystalline) materials are thus solids with fixed volume, fixed shape, characterized by short-range order, which, however, may also have loose long-range order"*
    - This definition embraces disordered materials possessing only one- or two-dimensional, or lesser, degrees of order

- Klug & Alexander (1974):
  - *"The term, amorphous solid, must be reserved for substances that show no crystalline nature whatsoever by any of the means available for detecting it"*

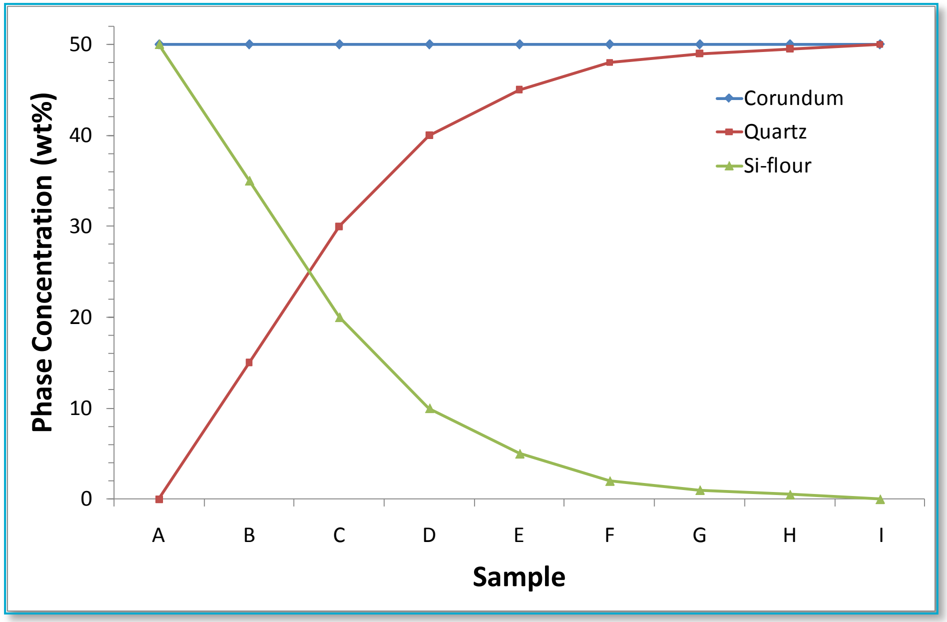
Quantifying Amorphous Phases

- There is no clear dividing line between crystalline and amorphous materials
  - "short" and "long" range order are arbitrary terms
- The ability to detect and characterize ordering is dependent upon the principles of the analytical method and models being used
- Conventional X-ray diffraction loses its power for crystalline material structures on the nano-scale, diffraction patterns become broad and features are less defined
  - Resulting ambiguities are paraphrased in literature by the term "X-ray amorphous" to highlight the limitations of X-ray diffraction

Accuracy of different analytical methods

- Prepare a set of synthetic mixtures inc. amorphous
  - Collect lab-based XRD data
- Data analysis methods used
  - <u>Indirect</u> – analyse crystalline components – put on absolute scale – calculate amorphous content by difference
  - <u>Direct</u> – estimate amorphous contribution to pattern
    - Calibrate using known standards, or
    - Include in whole sample analysis

- Samples have constant chemistry → constant μ_m
  - Possible to apply simple linear calibration models



Madsen, I.C., Scarlett, N.V.Y. and Kern, A. (2011) Z. Kristallogr., **226**, 944-955

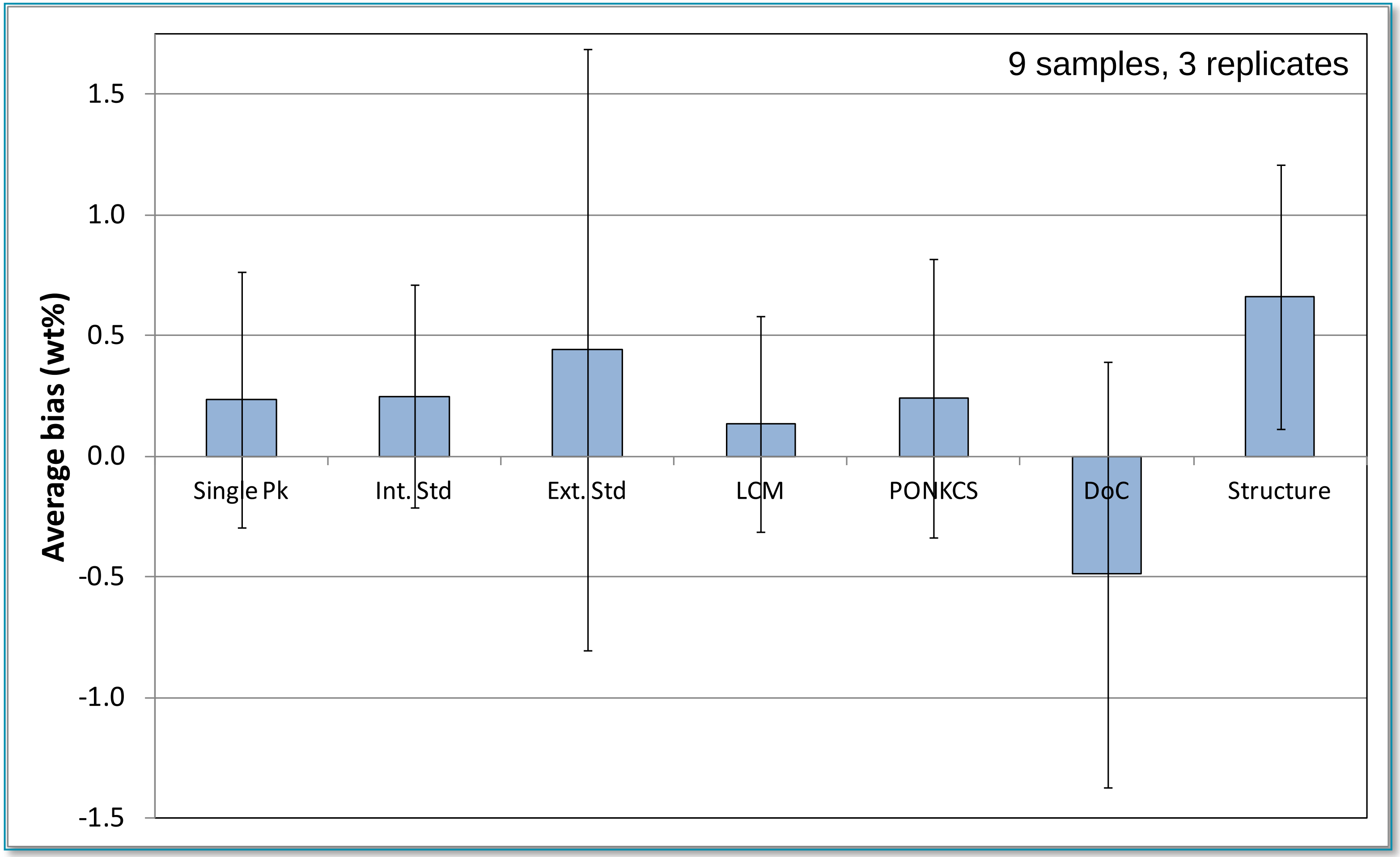
Indirect methods

- Internal standard
  - Requires addition of standard of known crystallinity to each sample
- External standard
  - Requires measurement of standard of known crystallinity under identical conditions to unknowns

Direct methods

- Single peak & linear calibration method (LCM)
  - Requires calibration suite
  - Requires amorphous contribution to be “visible” within background
- PONKCS (Partial or No Known Crystal Structure) phase
  - Requires empirical determination of *ZMV* constant for amorphous component. *(Note method also applicable to crystalline materials)*
    - Requires a single calibration sample incorporating standard of known crystallinity
- DoC (degree of crystallinity)
  - Requires estimation of total intensity contributed by crystalline and amorphous components
- Structure
  - Requires a crystal structure which models peak positions and intensities of amorphous component

Average bias (measured-weighed)



Vertical lines represent the standard deviation of the mean

Quantifying Amorphous Phases

- All methods capable of determining amorphous material in mixtures in similar fashion to crystalline phases
  - Calibration methods most accurate
  - Amorphous “structure” least accurate
- Possibility of amorphous content frequently ignored in Rietveld analysis
  - If amorphous and/or unidentified phases not mentioned assume relative phase abundances
  - Intensity contributions of amorphous phases not always evident, especially at low concentrations

A cautionary tale…

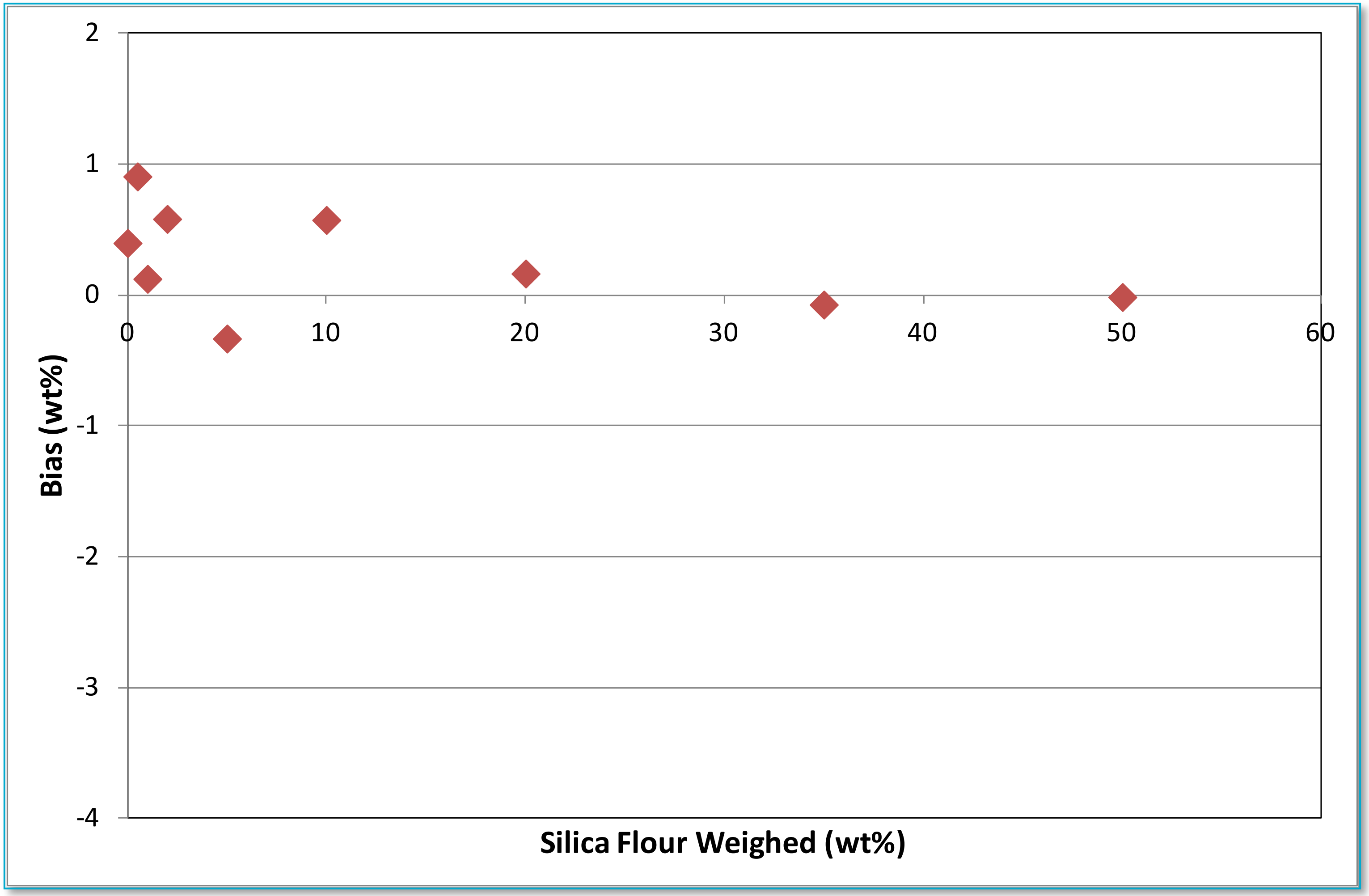
- During the amorphous study crystal structure refinements were undertaken on data from the pure crystalline phases of quartz and corundum
  - Refined atomic displacement parameters (ADPs) for corundum were within 1-2 SD of literature values
  - ADPs for quartz significantly higher
    - 0.83 Å^2 for Si (~0.4 Å^2 reported)
    - 1.24 Å^2 for O (~0.4 Å^2 reported)
- Refined ADPs improved fit of model
  - R_{wp} from 9.54 to 7.79%
  - R_{Bragg} from 6.32 to 3.83

A cautionary tale…

- Any factor which correlates with the Rietveld scale factor can have an impact on accuracy
  - ADPs correlate strongly with the Rietveld scale factor
    - ADP values used will impact on QPA
- All data reanalysed using refined ADP values for quartz and literature values for corundum
  - Internal standard method shown

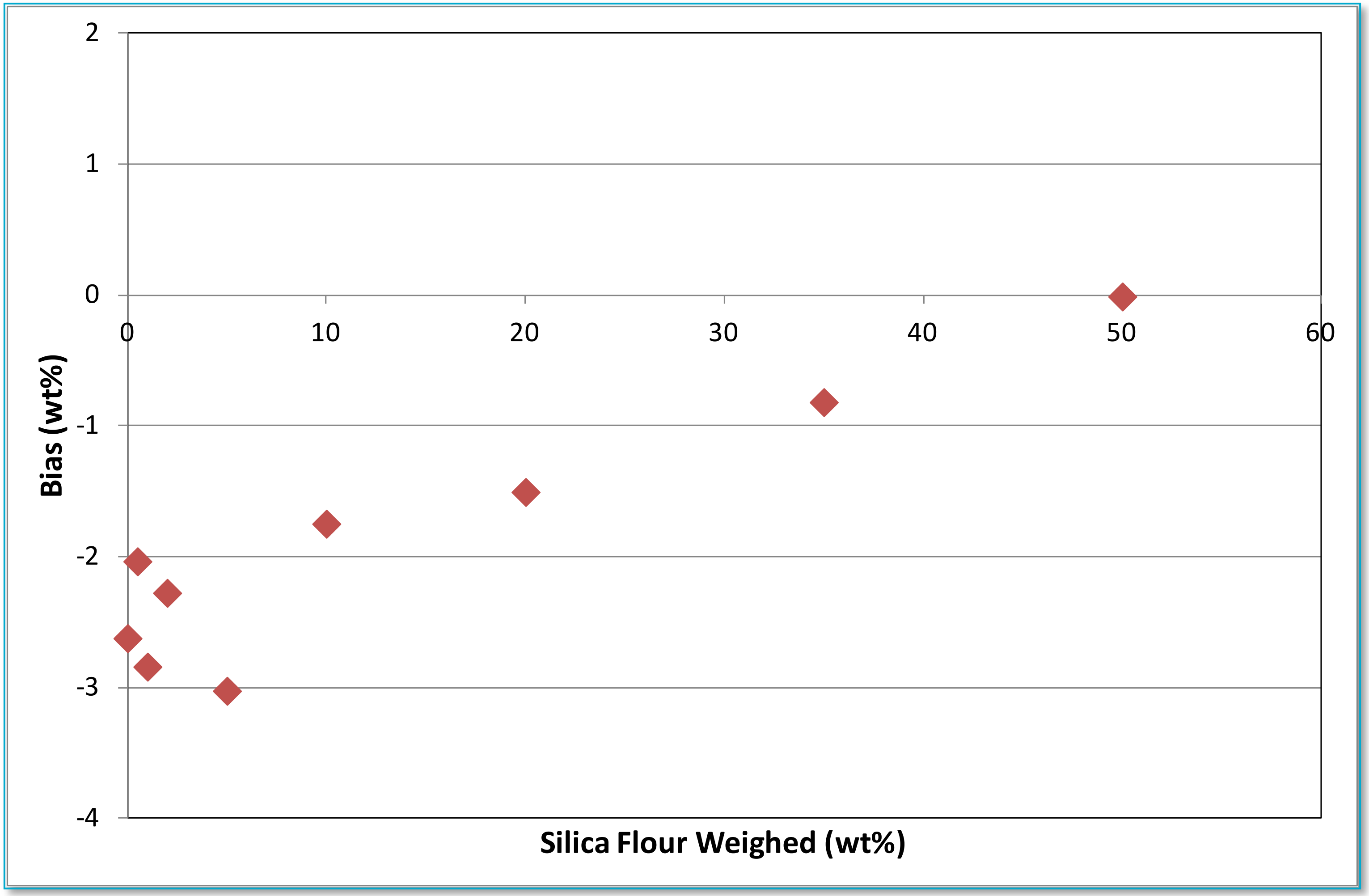
Bias *vs* Amorphous Content

Quartz ADP’s Set to Single Crystal Values



Bias *vs* Amorphous Content

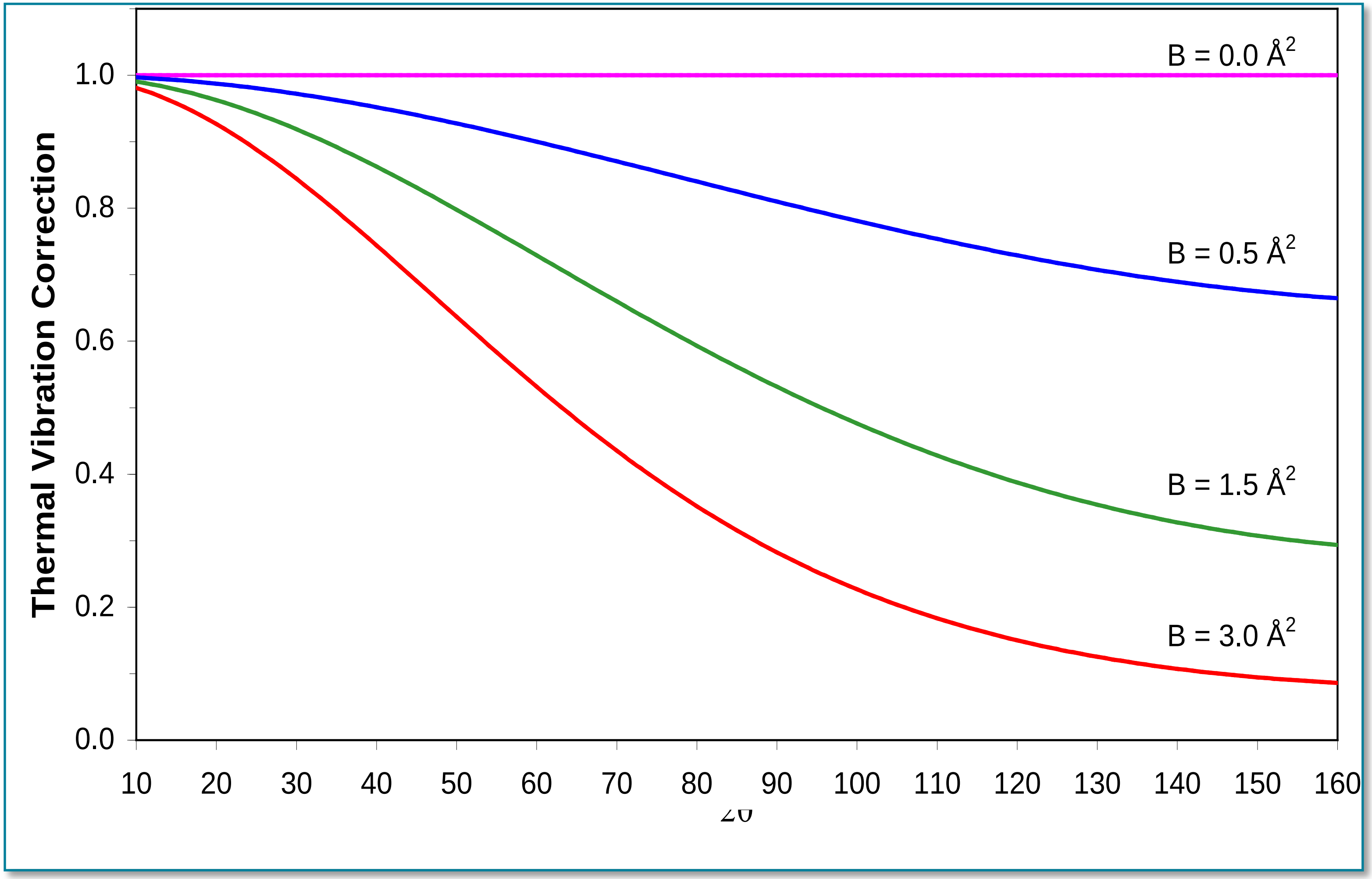
Quartz ADP's Set to Refined Values



What has happened?

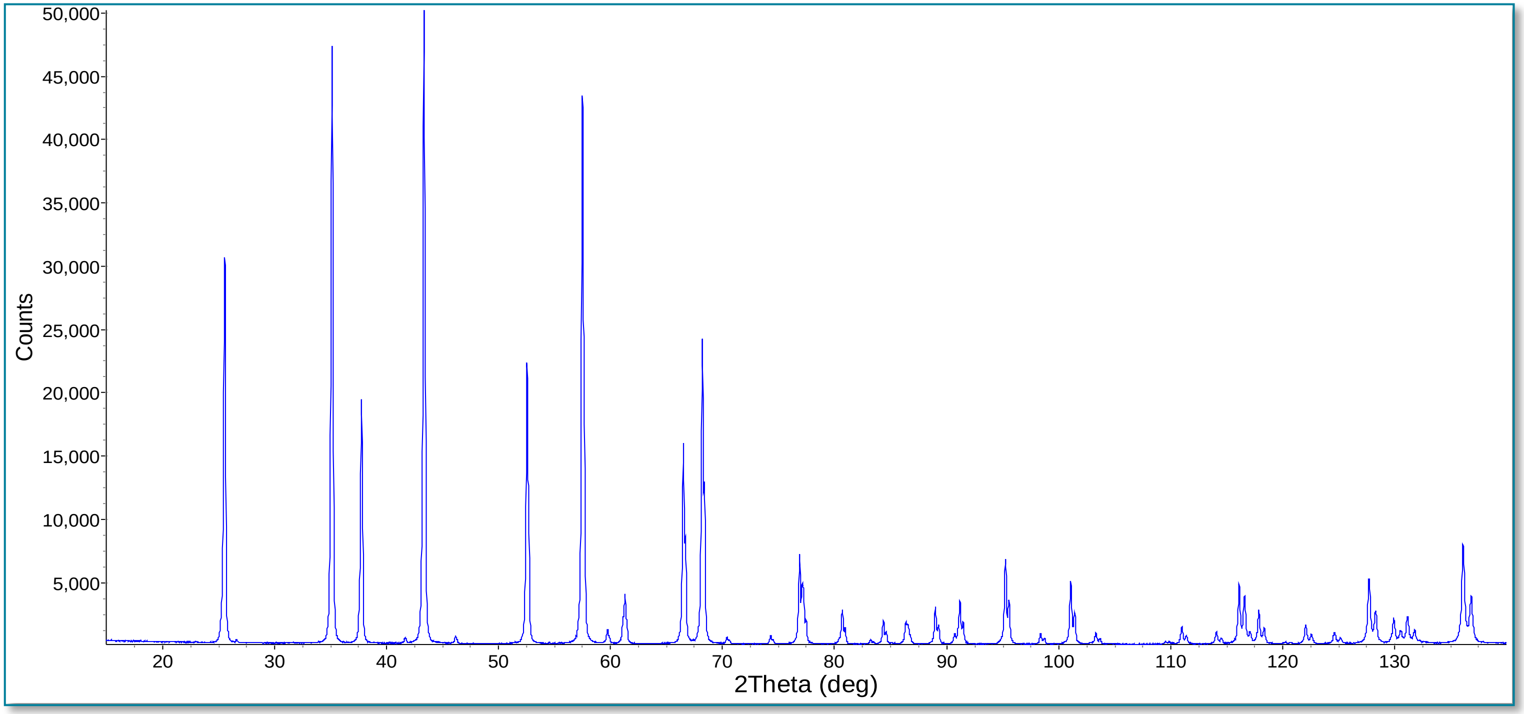
- Quartz scale factor has increased to compensate for “loss” of calculated intensity due to higher ADPs
  - Increase in weight fraction quartz analysed
  - Decrease in amorphous content determined by difference
- Why are the refined ADPs so much higher than the literature values as they are apparently incorrect?

Intensity Variation with ADPs



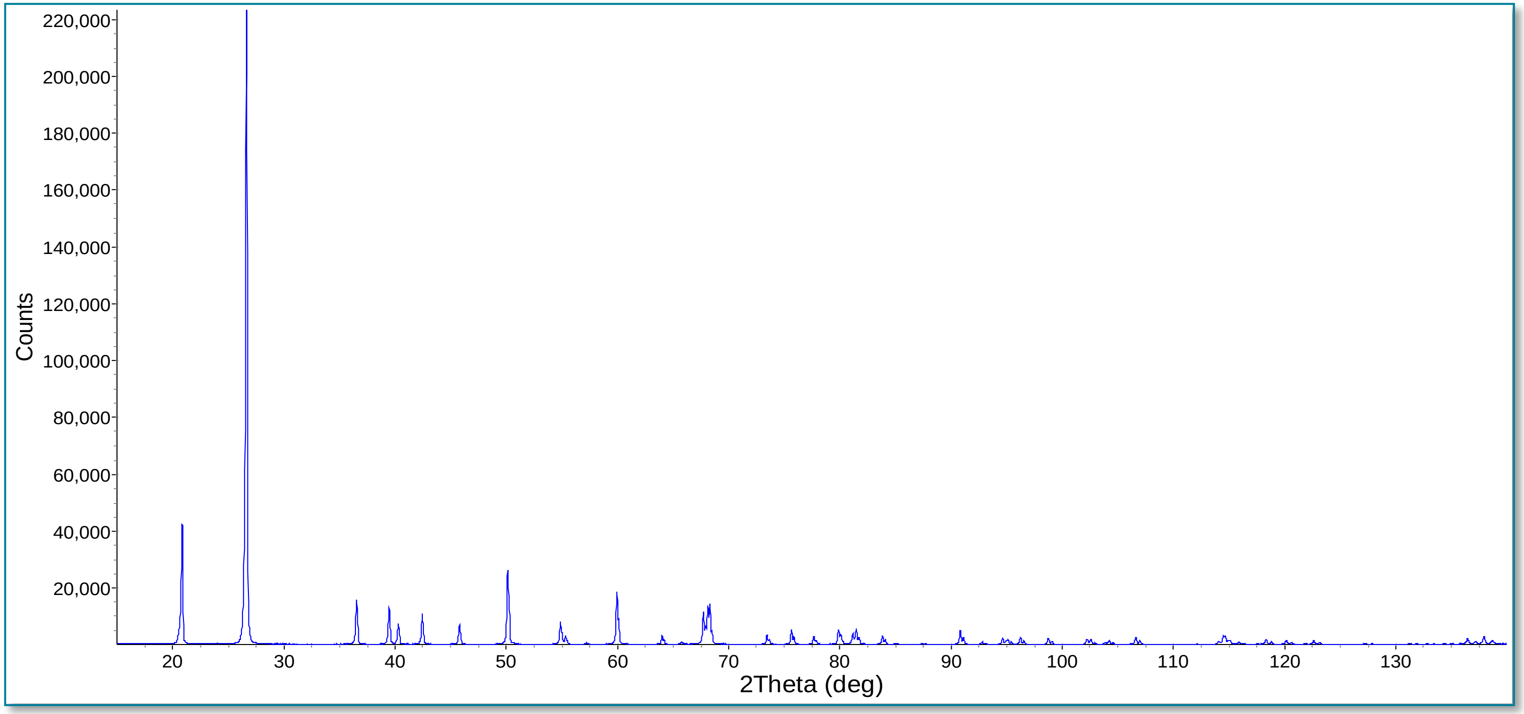
XRD Data (Cu Kα) for Corundum

- Fairly uniform distribution of intensity as a function of 2θ
  - Strong observed intensity at high angles to stabilise refinement of parameters with high angular dependence (i.e., ADPs)



XRD Data (Cu Kα) for Quartz

- A few low angle peaks dominate the intensity distribution
  - Parameters which vary as a function of 2θ will be sensitive to small changes in intensity of low angle peaks



Very real problem

- Many database structures do not include ADPs or they are set to arbitrary values (say 0.5 or 1.0 Å^2)
  - Conversion of *CIF* file to structure file in TOPAS assigns unity to ADPs if they are missing
- Incorrect values of ADPs has significant impact on QPA using these structures
  - Verification of database or refined values necessary to obtain highest accuracy of QPA

★ Non-trivial task ★

Issues in Precision and Accuracy

Estimating Errors in QPA

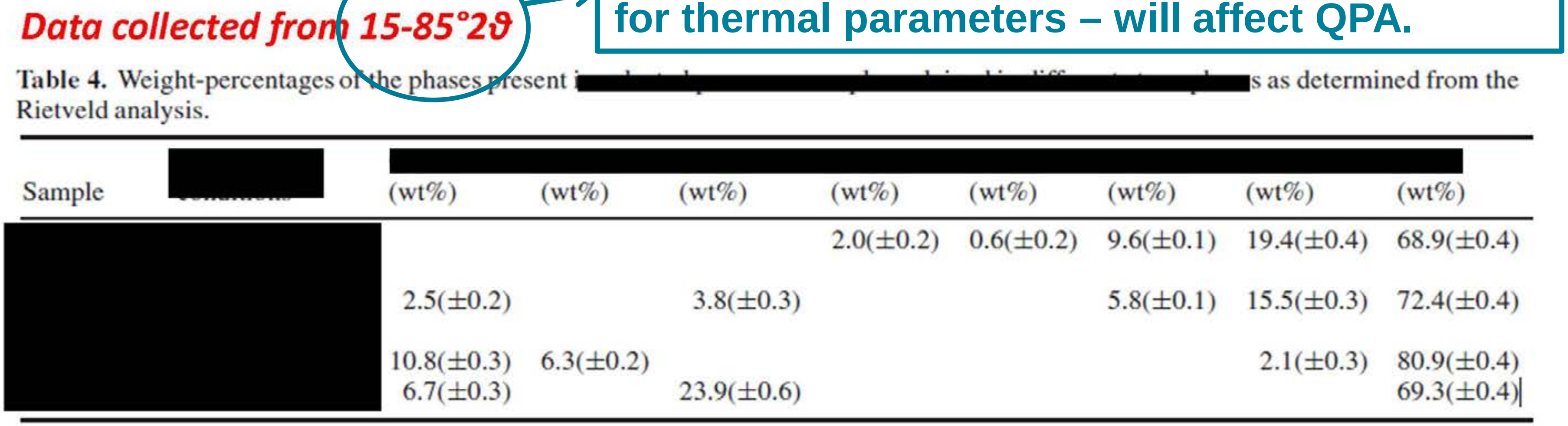
Precision, Accuracy & the Calculation of Error

- The issue of precision and accuracy in QPA via XRD is a difficult one
- How are errors actually determined?
- What, if any, errors are reported?
  - Research
  - Industry
- Determination of actual accuracy is not simple
  - Needs recourse to some other measure of the sample

Precision, Accuracy & the Calculation of Error

- Literature commonly reports errors on QPA with no mention of how they have been obtained
  - Example: A. Analyst and A.N. Other; *J. Irrepr. Results*. (2010)*

What is being refined?? Eg, inadequate range for thermal parameters – will affect QPA.



Data collected from 15-85°2θ

Table 4. Weight-percentages of the phases present i[redacted]s as determined from the Rietveld analysis.

Sample	[redacted]	[redacted]							
		(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)
[redacted]	[redacted]				2.0(±0.2)	0.6(±0.2)	9.6(±0.1)	19.4(±0.4)	68.9(±0.4)
		2.5(±0.2)		3.8(±0.3)			5.8(±0.1)	15.5(±0.3)	72.4(±0.4)
		10.8(±0.3)	6.3(±0.2)					2.1(±0.3)	80.9(±0.4)
		6.7(±0.3)		23.9(±0.6)					69.3(±0.4)

** Names changed to protect the guilty*

Precision, Accuracy & the Calculation of Error

Another cautionary tale…

- Consider Sample 4 from the IUCr CPD round robin*
- Mass absorption coefficients for commonly used wavelengths

	CoKa	CuKa	MoKa
Al_2O_3	48	32	0.1
Fe_3O_4	44	230	26
$ZrSiO_4$	117	82	9

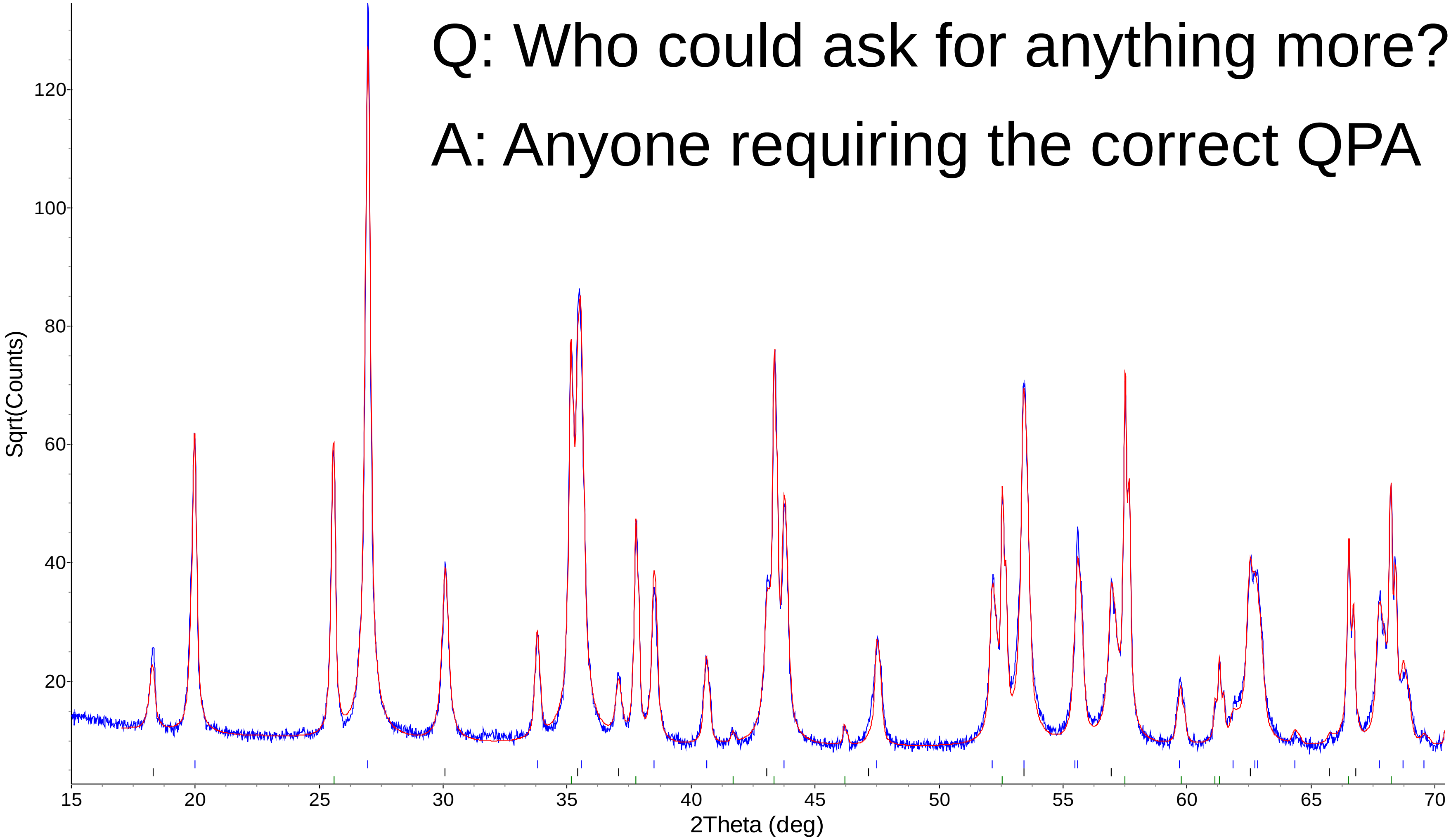
- All wavelengths produce some degree of absorption contrast
    - Microabsorption problem

**Discussed in more detail later*

Precision, Accuracy & the Calculation of Error

- Analysed using CuKα radiation
- 3 replicates measured
  - Repacked, data recollected
- Good fit between observed and calculated patterns
  - Low R-factors
    - Rwp 10.7 %
    - RBragg
      - Corundum 2.5 %
      - Magnetite 2.2 %
      - Zircon 4.1 %

Precision, Accuracy & the Calculation of Error



Q: Who could ask for anything more?

A: Anyone requiring the correct QPA

Precision, Accuracy & the Calculation of Error

3 replicates of IUCr CPD Round Robin Sample 4

	Al_2O_3	Fe_3O_4	$ZrSiO_4$
Mean Analysed wt% (n=3)	56.52	17.06	26.42
Mean Rietveld error	**0.15**	**0.11**	**0.11**

- Results often quoted as Rietveld wt% ± Rietveld error
  - Corundum 56.5(**2**) Magnetite 17.1(**1**) Zircon 26.4(**1**)
- Rietveld errors only indicate ***how well the model is fitting*** the observed diffraction pattern

Precision, Accuracy & the Calculation of Error

3 replicates of IUCr CPD Round Robin Sample 4

	Al_2O_3	Fe_3O_4	$ZrSiO_4$
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**

- If replicates are done (rare) results may be quoted as Rietveld wt% ± SD of mean
    - Corundum 56.5(**6**) Magnetite 17.1(**4**) Zircon 26.4(**4**)
- Replication errors only indicate the ***precision*** of the measurement

Precision, Accuracy & the Calculation of Error

3 replicates of IUCr CPD Round Robin Sample 4

	Al_2O_3	Fe_3O_4	$ZrSiO_4$
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 (measured – weighed)	**6.06**	**-2.58**	**-3.48**

- True errors only available if answer already known
  - Corundum 56(**6**) Magnetite 17(**3**) Zircon 26(**3**)

Community Assessment

International round robins

International round robins

- Quantitative phase analysis of α- and β-silicon nitrides. II. Round robins
  - *H. Toraya, S. Hayashia and T. Nakayasu; J. Appl. Cryst. (1999), 32, 716-729*
- International Union of Crystallography Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis
  - *Madsen et al; J. Appl. Cryst. (2001). 34, 409-426*
  - *Scarlett, N. V. Y et al. J. Appl. Cryst. (2002), 35, 383–400.*
- Reynolds Cup
  - Clay mineralogy
- Round robin on Rietveld quantitative phase analysis of Portland cements
  - *L. León-Reina et al; J. Appl. Cryst. (2009), 42, 906–916*
- International Centre for Diffraction Data round robin on quantitative Rietveld phase analysis of pharmaceuticals
  - *T. G. Fawcett, F. Needham, J. Faber, and C. E. Crowder; Powder Diffraction, (2010) 25 (1), 60-67.*

International round robins

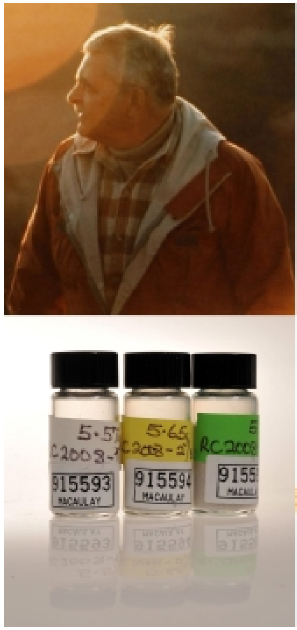
- Quantitative phase analysis of α- and β-silicon nitrides. II. Round robins
  - 42 selected participants
    - Second round robin subset of initial group of participants
  - Comparison of prescribed analytical methods to determine accuracy and precision for use as Japanese Industrial Standard (JIS) method
    - Mean normalised intensity using:
      - Peak height (MNI-P)
      - Integrated intensity (MNI-I)
    - Rietveld methods
  - Participant collected data

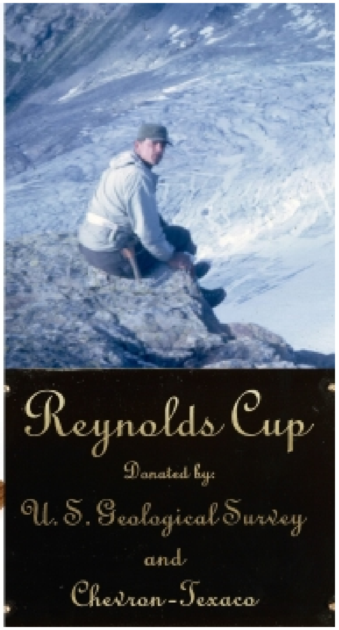
International round robins

- International Union of Crystallography Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis
  - 80 participants
  - 7 samples
    - 6 synthetic
    - 1 natural
  - CPD-supplied data
  - Participant collected data
  - Analysis methods to be determined by participants

International round robins

- Reynolds Cup
  - Biennial
  - Synthetic clay samples
  - Detailed presentation from Mark Raven following in this session





Reynolds Cup

Donated by:

U. S. Geological Survey

and

Chevron-Texaco

International round robins

- Round robin on Rietveld quantitative phase analysis of Portland cements
  - 2 Synthetic samples
    - Accuracy and precision
  - 3 commercial samples
    - Precision
  - 9 participants
  - Analysis methods to be determined by participants

International round robins

- International Centre for Diffraction Data round robin on quantitative Rietveld phase analysis of pharmaceuticals
  - 11 participants
  - Participant collected data
  - Analysis methods to be determined by participants

Factors affecting accuracy

How well are they being addressed?

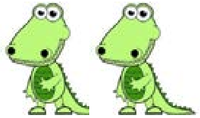
State of the art

- Last APD meeting (2001) detailed the “International Union of Crystallography (IUCr) Commission on Powder Diffraction (CPD) round robin on the determination of quantitative phase abundance from diffraction data”
- Overarching aims:
  - To survey methods and strategies employed
    - Data collection
    - Analysis
  - To assess levels of accuracy, precision and lower limits of detection achieved

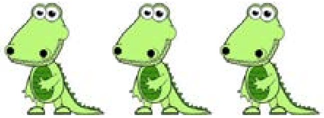
State of the art

- Two levels of investigation
  - Ability to analyse data provided by the CPD
  - Ability to collect and analyse own data
- Range of sample types covering typical XRD/QPA problems
  - Sample 1 – simple
    - 8 composition mixes of corundum (Al_2O_3), fluorite (CaF_2 and zincite (ZnO)

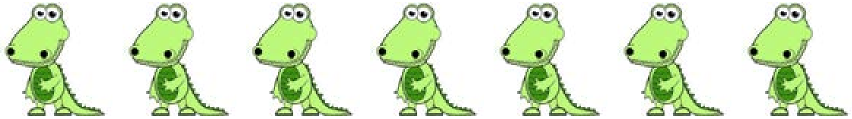
  - Sample 2 – preferred orientation



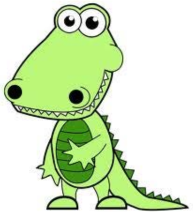
  - Sample 3 – amorphous content



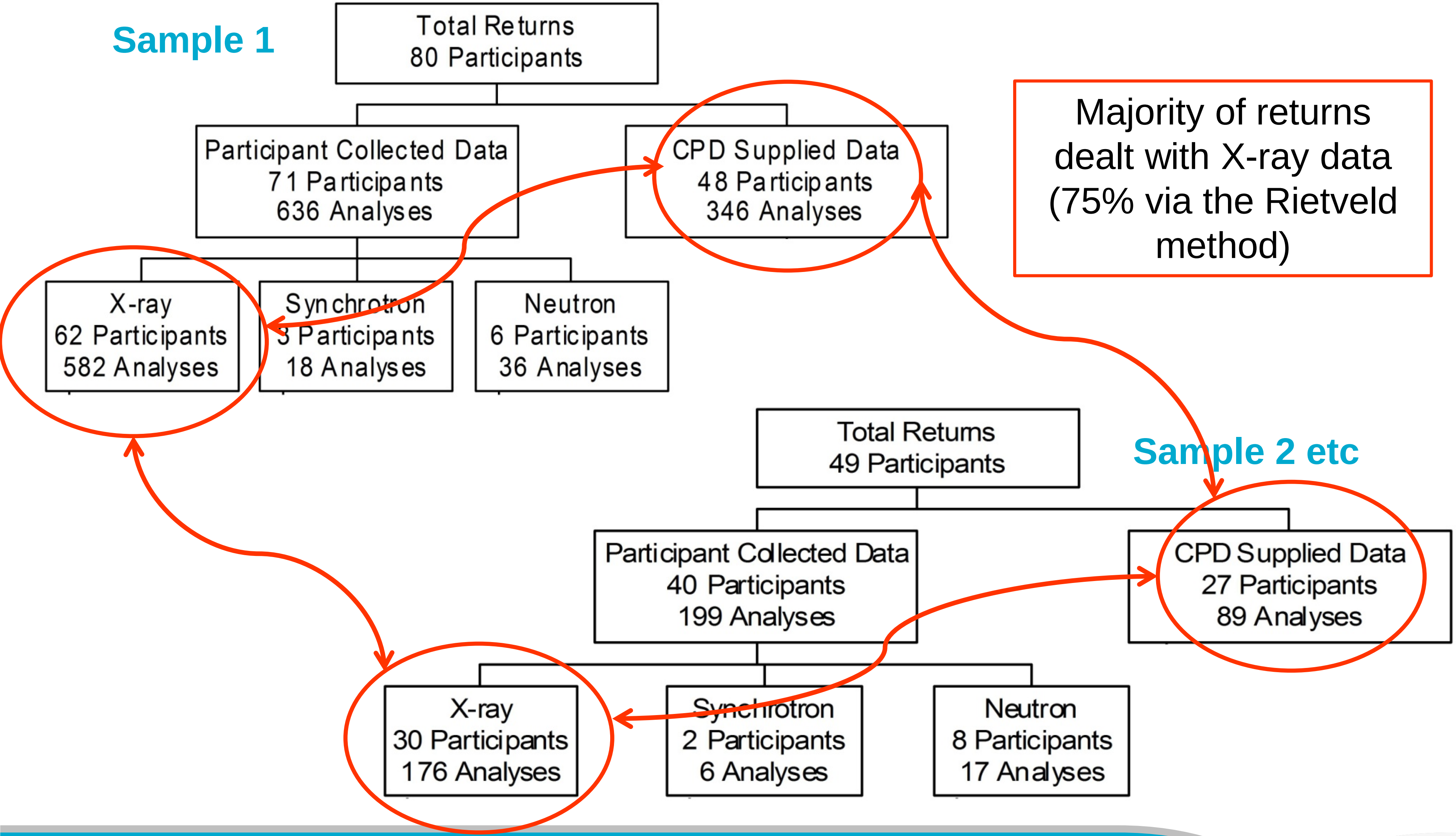
  - Sample 4 – microabsorption



  - Complex mineral suites
    - Synthetic
    - Natural
  - Pharmaceutical



State of the art



Sample 1

Total Returns
80 Participants

Participant Collected Data
71 Participants
636 Analyses

CPD Supplied Data
48 Participants
346 Analyses

X-ray
62 Participants
582 Analyses

Synchrotron
3 Participants
18 Analyses

Neutron
6 Participants
36 Analyses

Majority of returns dealt with X-ray data (75% via the Rietveld method)

Sample 2 etc

Total Returns
49 Participants

Participant Collected Data
40 Participants
199 Analyses

CPD Supplied Data
27 Participants
89 Analyses

X-ray
30 Participants
176 Analyses

Synchrotron
2 Participants
6 Analyses

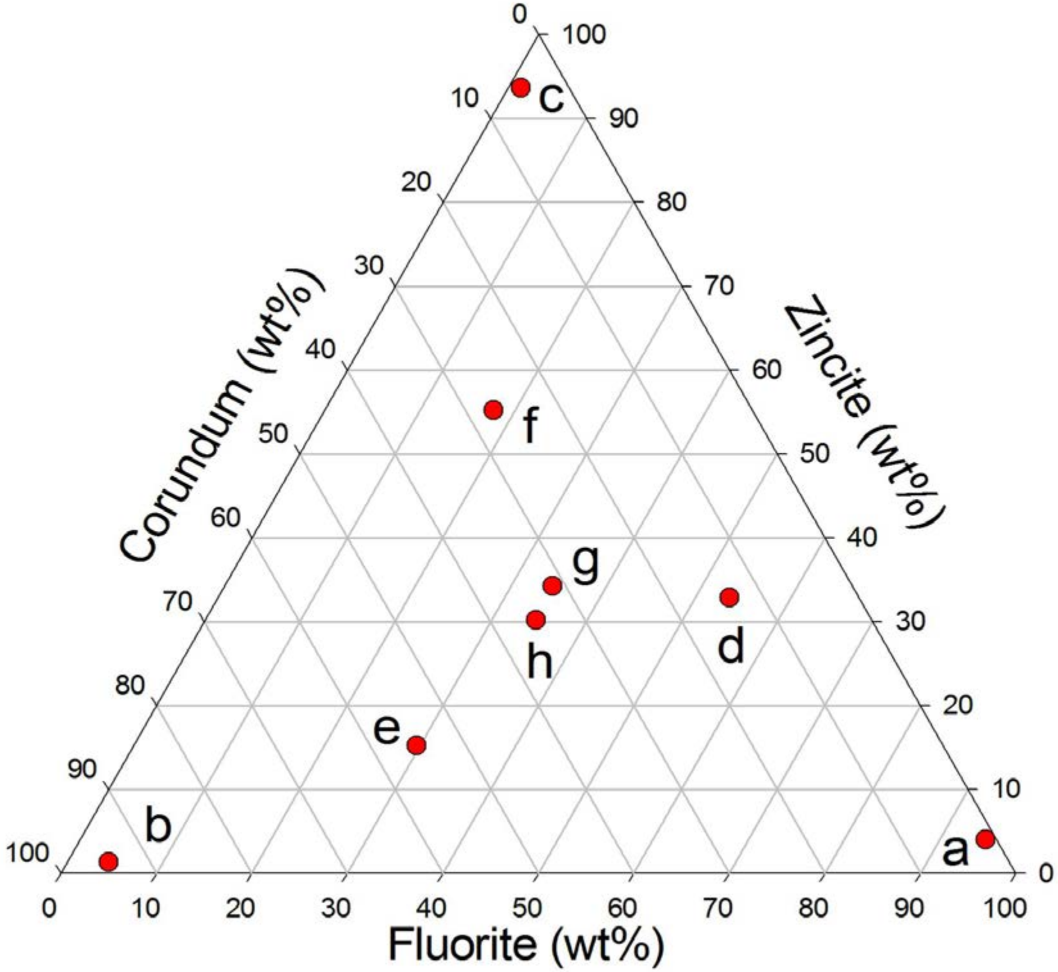
Neutron
8 Participants
17 Analyses

Factors affecting accuracy

- Basic case
  - Simple mixture or crystalline materials
  - Relatively free from sample related issues
    - Preferred orientation
    - Amorphous Content
    - Microabsorption
- Ideal case for benchmarking technique
  - Data collection
  - Data analysis

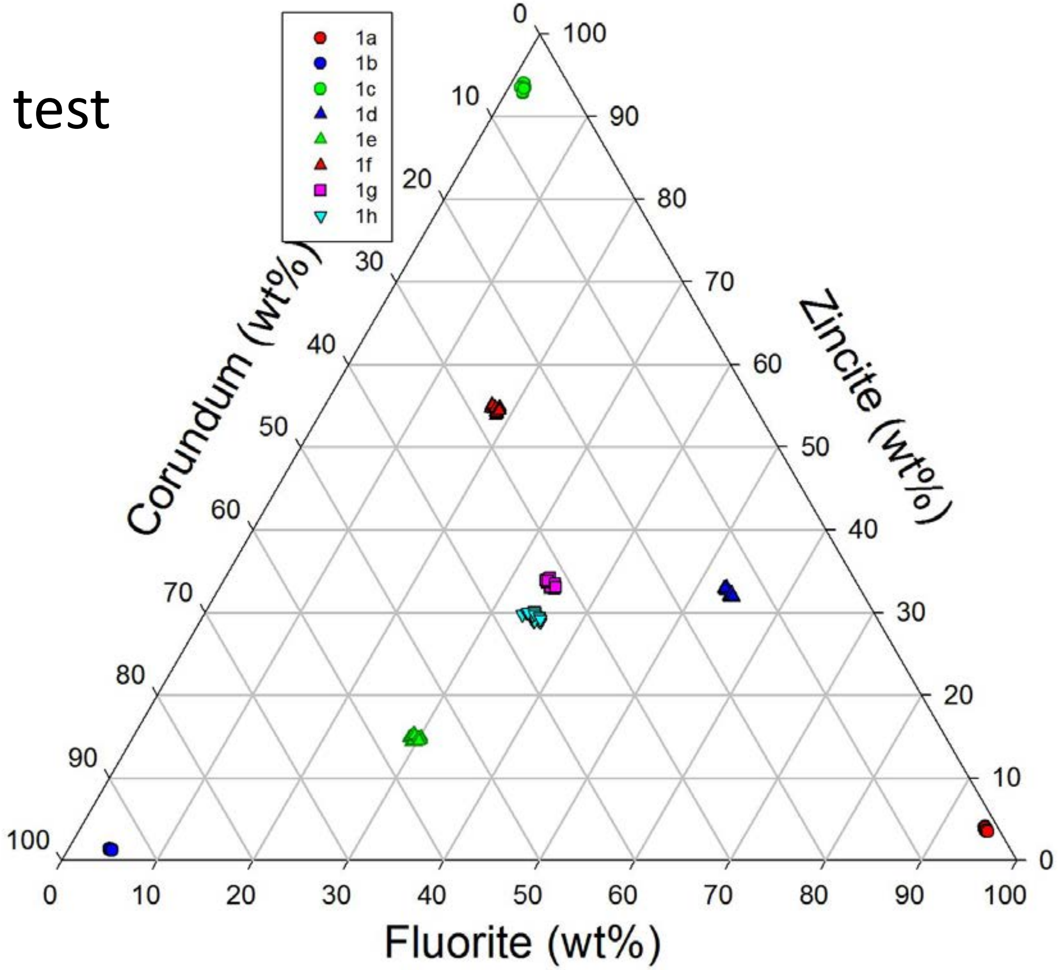
Basic case

- IUCr-CPD RR Sample 1
  - Ternary design
  - Crystalline phases
    - Corundum
    - Fluorite
    - Zincite
  - Chemically distinct phases
    - QPA may be achieved via analysis of bulk chemistry



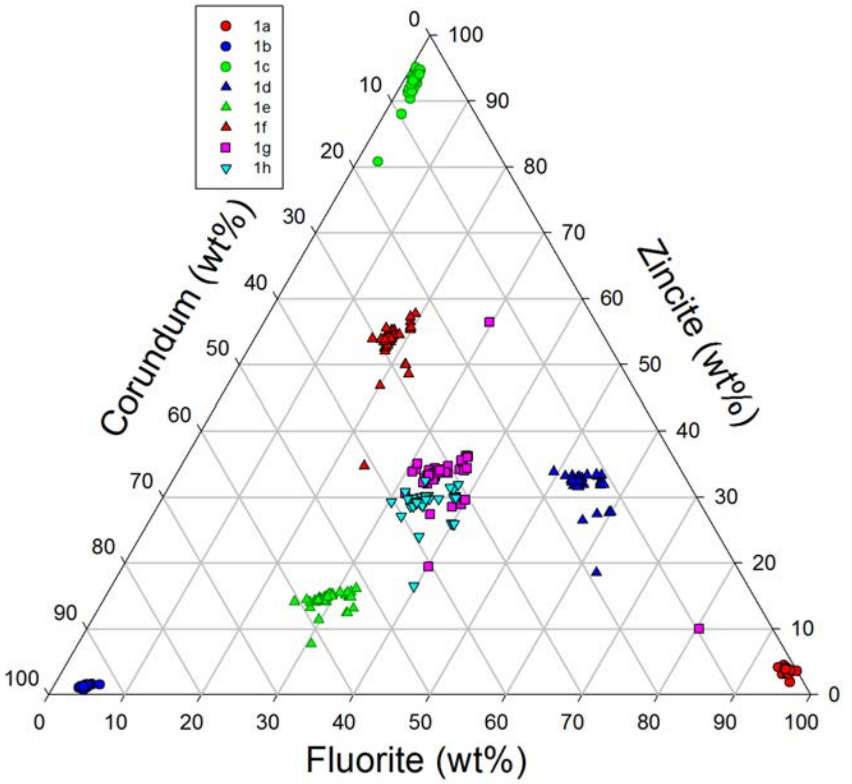
Basic case

- Verification
  - Results of assorted QPA test methods
    - Diffraction
      - Single peak
      - Whole pattern
    - XRF
  - Note that each group represents 24 separate analyses
    - 8 analytical methods
    - 3 replicates of each

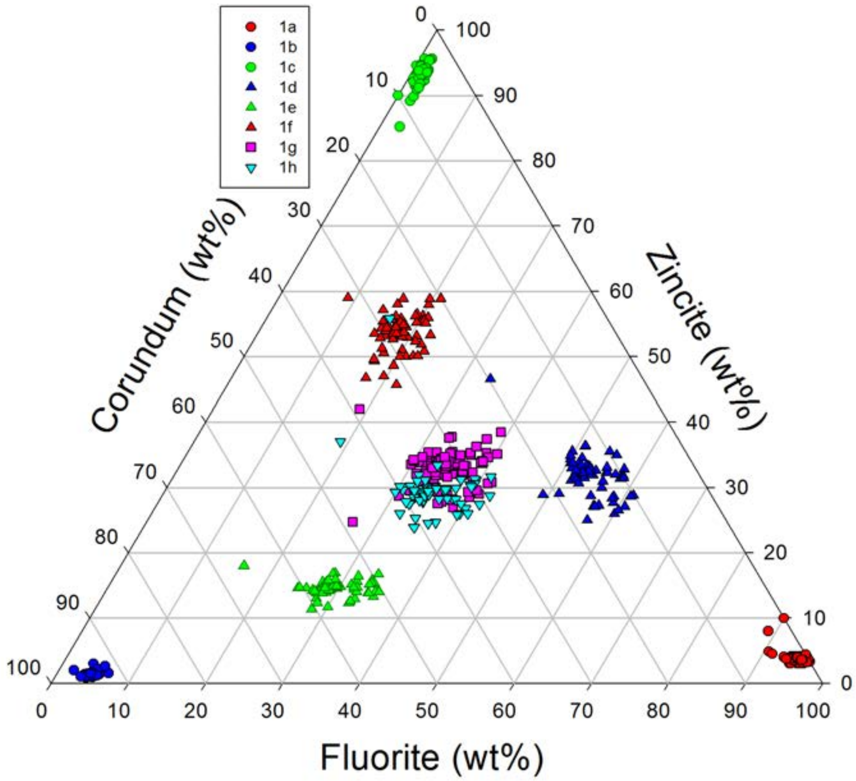


Basic case

- CPD-supplied data



- Participant-collected data



Issues with data collection

- Data collection regimes not prescribed
- Participant data collection conditions not fully known
- Effect of step size and data collection time on accuracy examined using CPD RR1

Effect of Step Width & Time on QPA

Estimating Errors in QPA

Data Collection Design

- CPD RR1 (8 compositions)

- Step width (°2θ)
  - 0.01
  - 0.05
  - 0.10
  - 0.15
  - 0.20
  - 0.25
  - 0.30

- Time per step (seconds)
  - 0.0125
  - 0.05
  - 0.2
  - 1
  - 4

- Time is varied by a factor of approx. four to give a two-fold variation in counting statistics

- Total of 280 datasets

Factors affecting refinement stability

- Sample absorption
  - Samples with high average MAC produce fewer counts/sec/wt%
- Scattering Factor
  - A phase of low average atomic number → fewer counts/sec/wt%
    - Analysis more unstable than a phase with higher average atomic number
- Phase Abundance
  - A phase present at low concentration will be more unstable with poor quality data than a high concentration phase

Data Stability Results

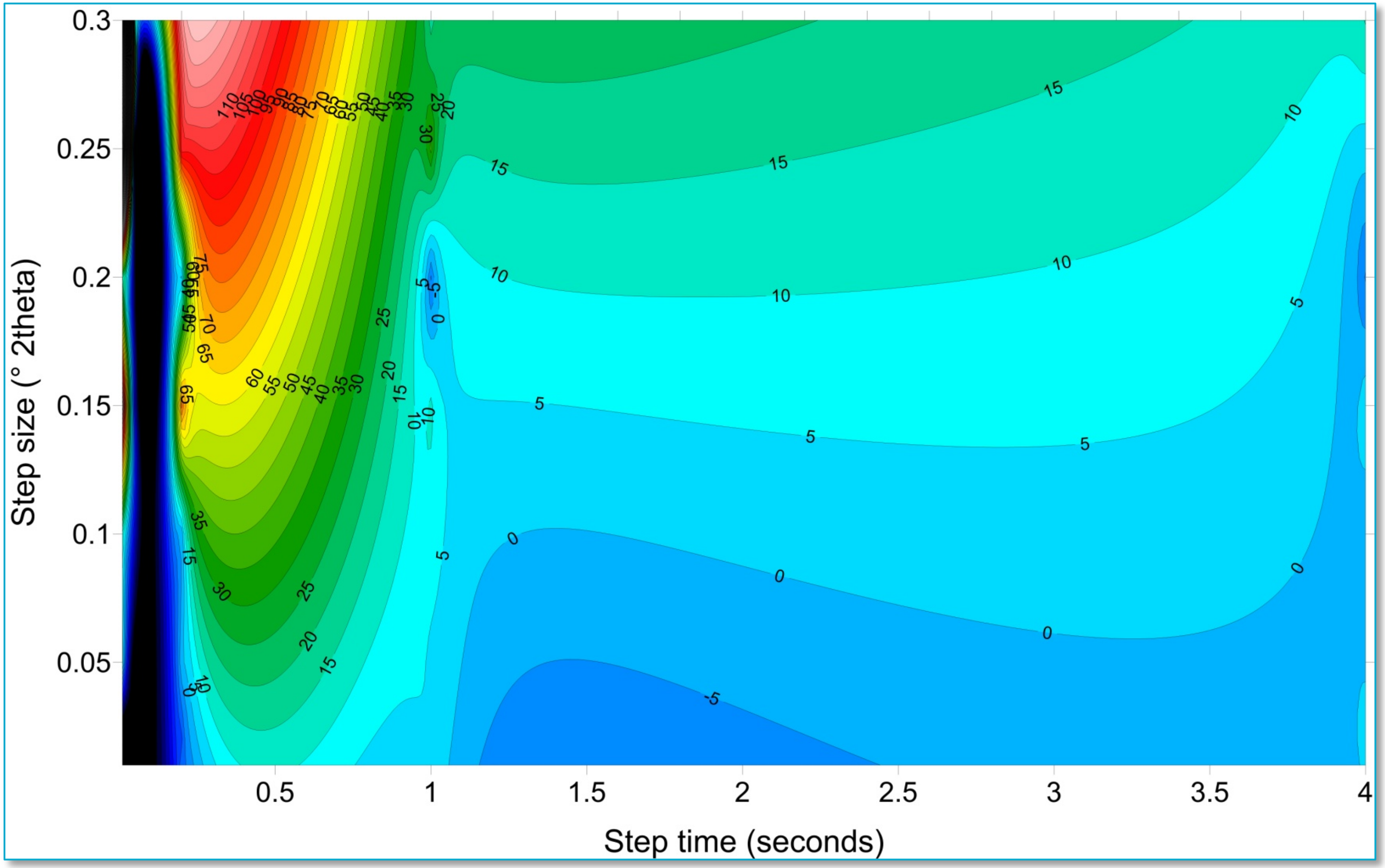
- The worst case to examine is Sample 1A
  - Al_2O_3 (the weakest scatterer) occurs its lowest level 1.2 wt% with 4.1 wt% ZnO and 94.1 wt% CaF_2 (strongest absorber)
    - Microabsorption issue here as well
- Bias calculated relative to the analysed wt% from the best data, i.e., 4 sec/step, 0.01°/step

$$Bias = \frac{100 * (Meas_i - Meas_{best})}{Meas_{best}}$$

- Replication error determined from repeat analysis
  - For corundum, the replication error is 0.07wt% = 5.2% relative
  - For 2 e.s.d.'s, a bias of approximately ±10% relative can be tolerated

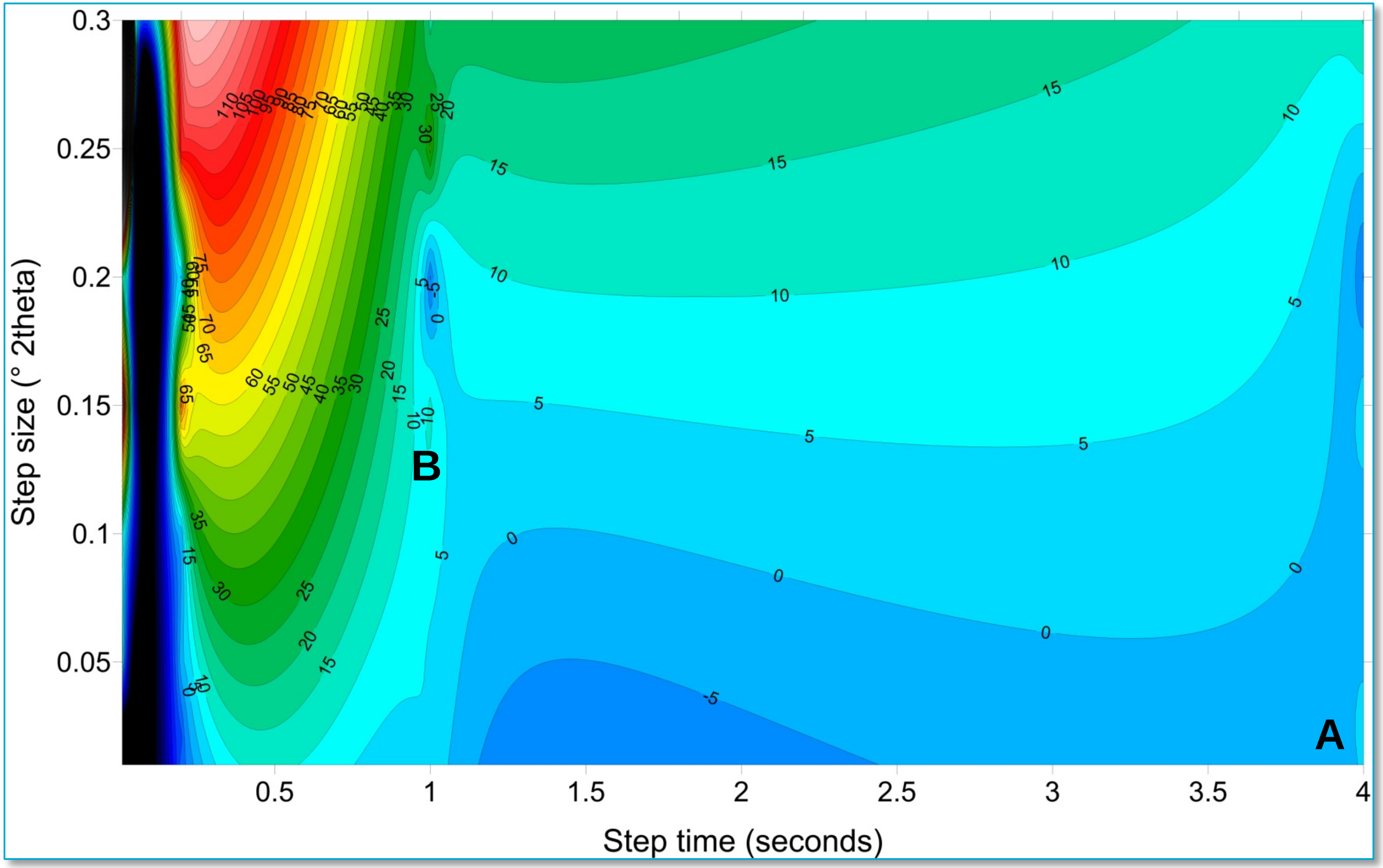
Corundum Bias

- Above ~1s/step, effect of step time not as significant as step width



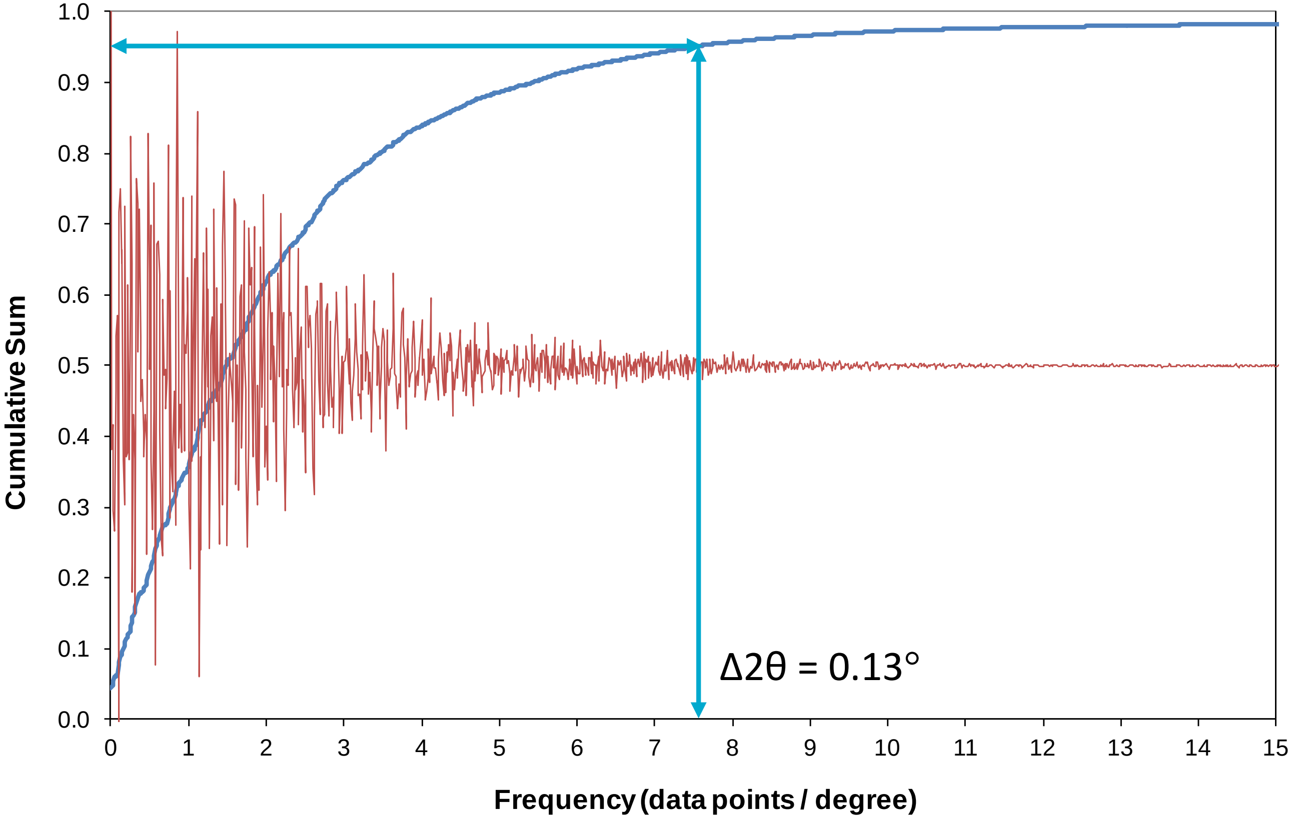
Corundum Bias

- A = 16 hours; B = 1 hour 14 minutes



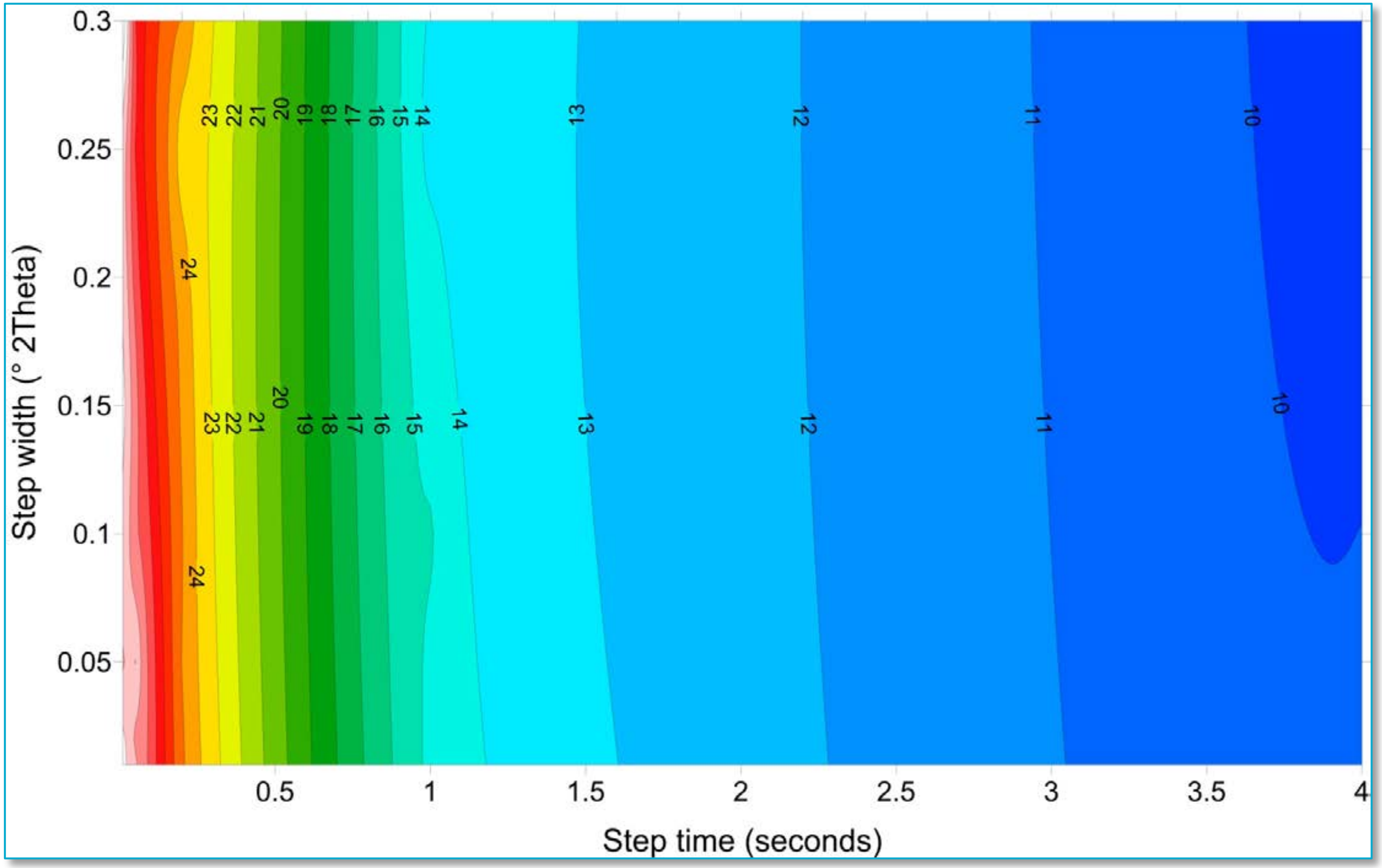
Fourier Analysis

- Cut-off defined (arbitrarily) for cumulative sum at 0.95
  - Little additional information to be gained by using smaller step width
  - Good agreement with previous plot



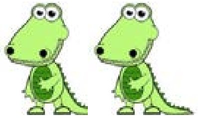
Trap for the unwary…

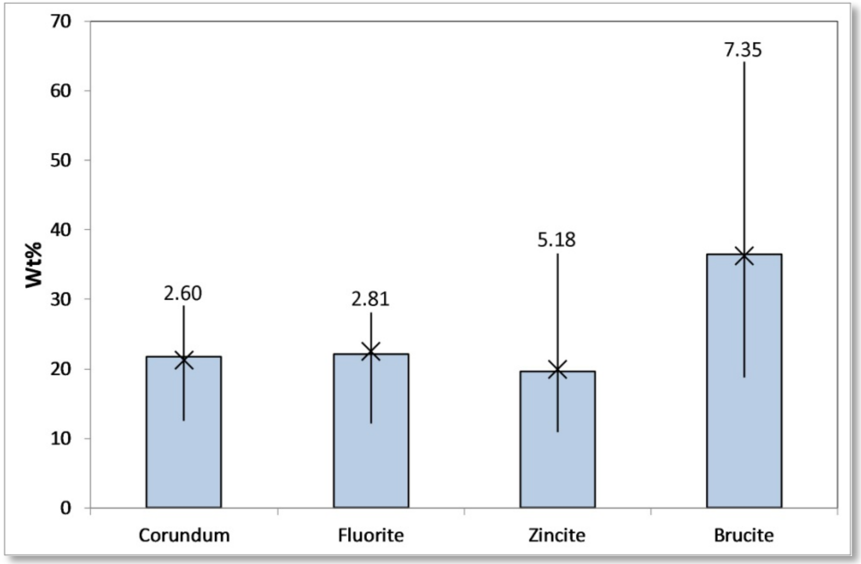
- R_{wp} is more dependent on step time than number of data points
  - Little indication of accuracy

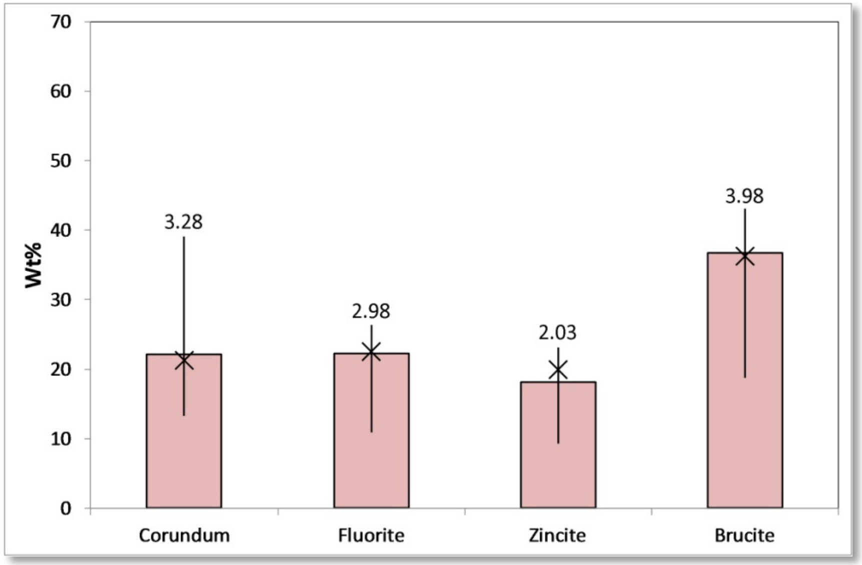


Step width and time summary

- Large areas of step time / width combinations exist where there is no significant improvement in QPA
- At very short step times, changes in step width have little effect on QPA
- At longer step times, step width dominates the effect on QPA
- Reliance upon Rwp as the sole measure of fit is dangerous
  - Reducing the number of data points has little effect on Rwp whilst the QPA can become unstable

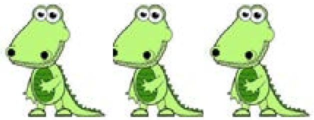
Sample 2 () – preferred orientation

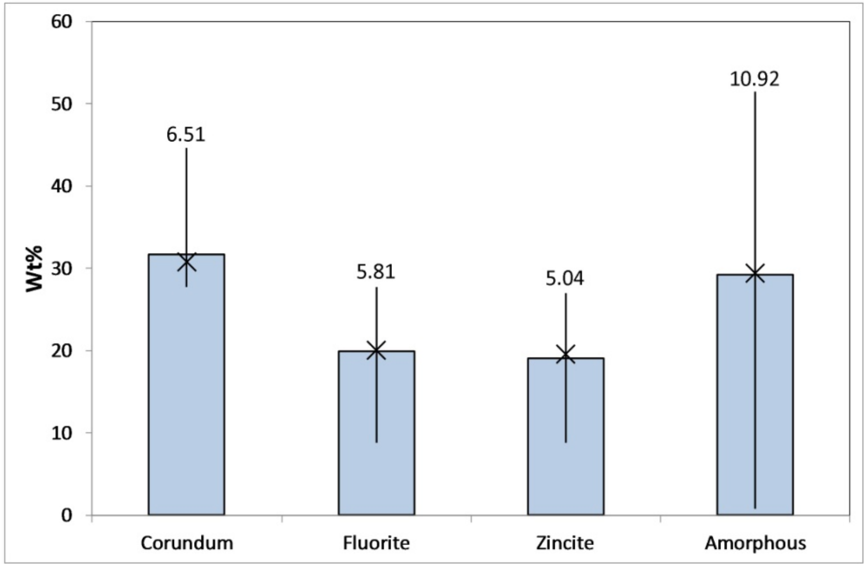


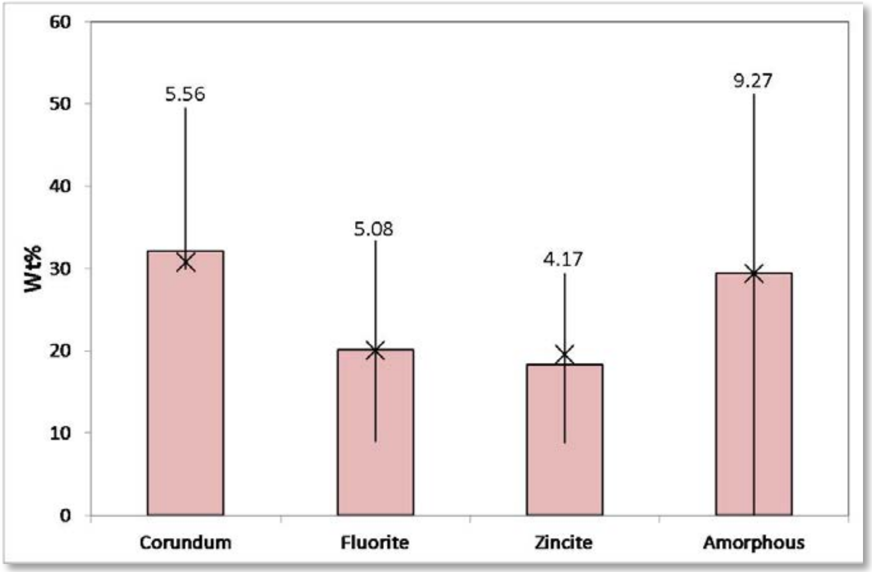


- Mean values close to weighed values
- Large spread of values
- PO Correction (March-Dollase, spherical harmonics) used

🟦 Mean CPD-supplied data; 🟥 mean Participant-collected data; X = weighed, | = min; max, number = SD

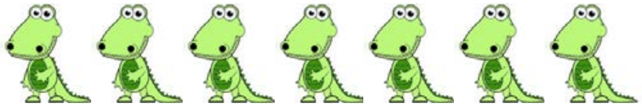
Sample 3 () – amorphous content

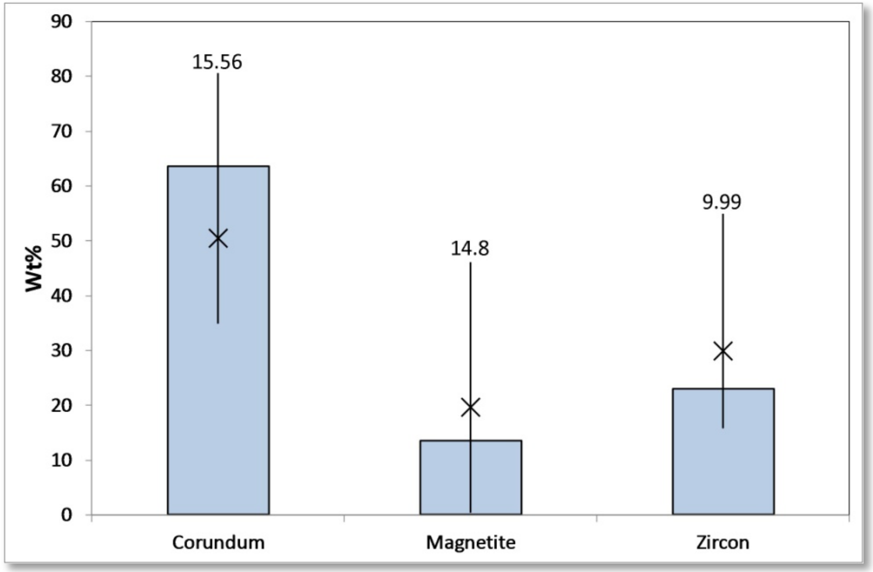


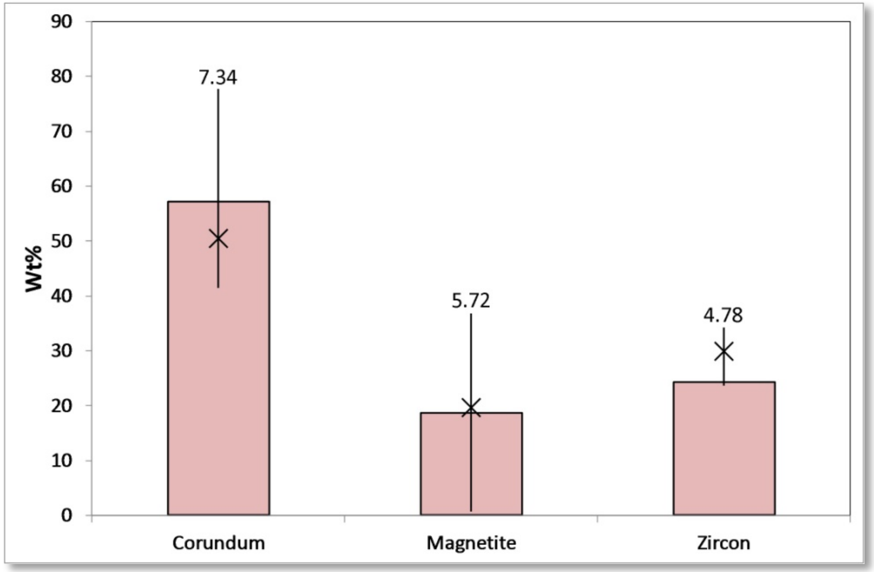


- Mean values close to weighed values
- Large spread of values
- Some participants failed to calculate amorphous content following analysis of crystalline component (corrected values presented)

🟦 Mean CPD-supplied data; 🟥 mean Participant-collected data; X = weighed, | = min; max, number = SD

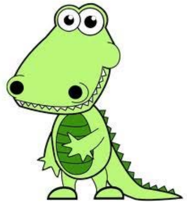
Sample 4 () - microabsorption

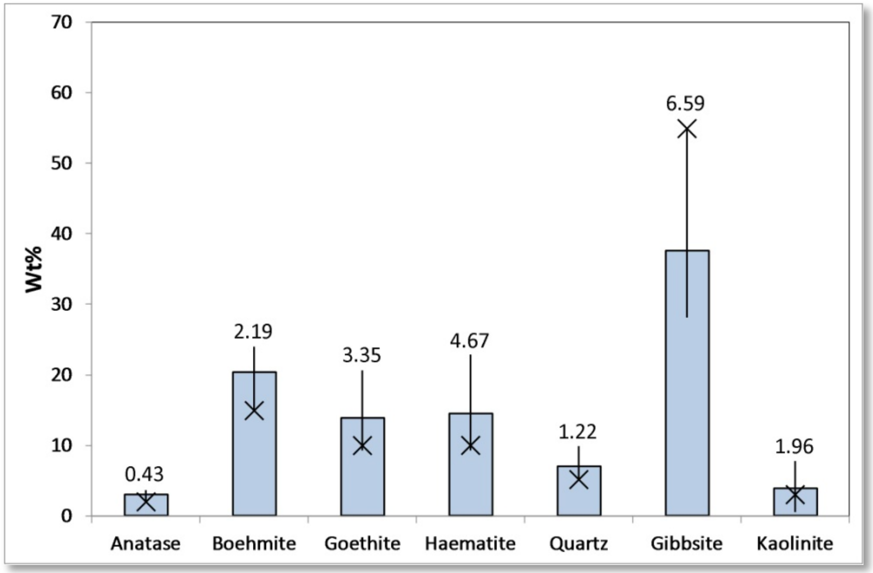


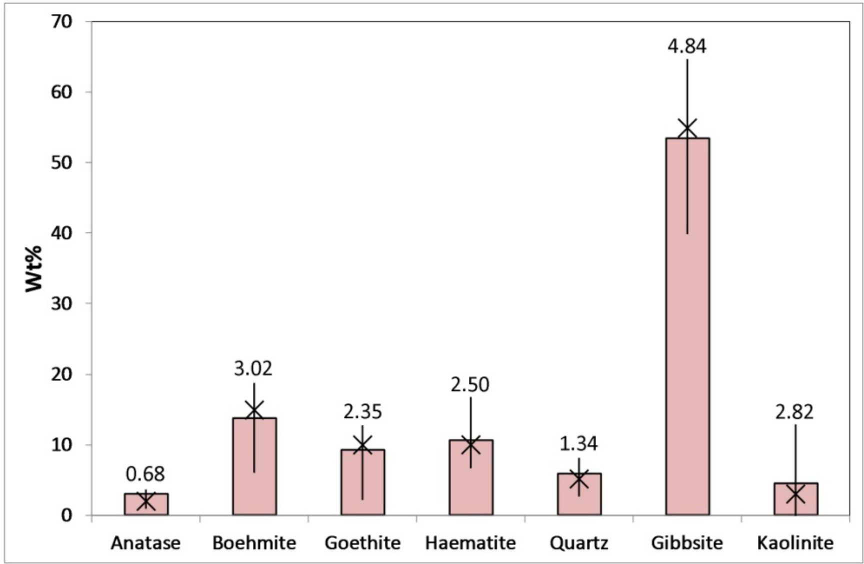


- Corundum (low absorber) overestimated
- Zircon & magnetite (high absorbers) underestimated
- Large spread of values
- CPD-supplied data worse as collected from coarse grained sample

🟦 Mean CPD-supplied data; 🟥 mean Participant-collected data; X = weighed, │ = min; max, number = SD

Synthetic bauxite () - complexity





- Large spread of values
- CPD-supplied data worse as sample agglomerated
  - Gibbsite particles “coated” with other phases and consequently underestimated

🟦 Mean CPD-supplied data; 🟥 mean Participant-collected data; X = weighed, │ = min; max, number = SD

What went wrong?

- Generally larger spread of results from participant collected data than from CPD-supplied*
  - Instrumental configuration
  - Data collection strategies
- Use of inappropriate RIR values in single peak methods
- Excessive correction for microabsorption when not necessary
- Lack of crystallographic expertise
- Lack of understanding of program operation and/or interpretation of the output

*Exceptions being Sample 4 and synthetic bauxite which required additional sample preparation

What went wrong?

- General operator error
  - Incorrect thermal parameters
    - Several participants set values of zero which were not refined
  - Incorrect atom coordinates
  - Incorrect space group
  - Omission of phases (despite being told what was in there…)
  - Misreporting values from Rietveld output!!!
  - Stopping refinement prior to convergence
  - Failure to refine or adequately restrain refinement of parameters
    - Acceptance of physically unrealistic refined values

And the other round robins?

- Portland cement (9 participants)
  - Statistical study to determine precision ranges and general uncertainties for accuracy

	C3S	C2S	C3A	C4AF
Typical conc. (%)	60-70	14-20	8-10	8-10
% Uncertainty (95% conf. lim.)	4.1-6.5	2.8-5.5	0.9-2.5	1.3-2.4
% Reproducibility r.s.d. = 100(s.d./mean)	3.2-5.4	8.8-28.8	10.3-26.9	9.6-17.5

And the other round robins?

- ICDD pharmaceutical (11 participants)
  - Nearly 10 years later, same issues as IUCr CPD round robin
    - Sample preparation
    - Data collection
    - Operator error
- However, there is hope!
  - 4 out the 11 participants achieved excellent results
    - *"Suggests that the technique is robust and standardized practices would be expected to yield reproducible accuracy and precision."*

Summary

Where to from here?

Overall

- Determination of accuracy not always possible
  - Especially for high throughput labs, one-off samples, etc
- Precision may be determined
  - Adequate time/money for replicates
- Awareness of limitations
  - Microabsorption may not be avoided but awareness of the effect gives indication of over/underestimated phases
- Best data collection and analytical practice can, however, maximise achievable accuracy
  - Still semi-quantitative without external confirmation
  - Calibration methods may help for multiple samples of similar concentration/composition

*"The uncertainty of the quantitative determination of phase composition by X-ray diffraction is seldom less than several percent absolute"**

Is this still true?

*Andre Guinier ("Theorie et Technique de la Radiocristallographie," Dunod, Paris 1956)

Community assessment over 10+ years

	Approx. spread in absolute bias (%)		
Approx. conc. Level (%)	CPD-supplied data RR1	Cement	Pharmaceutical
1	0.2-0.4		
5	0.7-1	0.1-2	
10		2-[illegible]	
15	1-2	3-6	10-30
20		4-8	
[illegible]0	2-3		
50	2-3		20-40
70		0.4-7	
85			9-20
95	1-2		

GUINIER WAS RIGHT!

Absolute Bias = Abs((mean±1SD)-weighed)

How do we make this better?

- Same problems as identified in IUCr CPD round robin 10+ years ago
  - Continued education required
    - Best practices
    - Awareness of limitations
- Pharmaceutical round robin shows 4 out of 11 labs obtained high accuracy and precision
  - ***It can be done***
- Independent analysis of IUCr CPD round robin samples show high accuracy and precision can be obtained
  - ***It can be done***
- Development of standard, system-specific procedures
  - Prescriptive round robins like SiN method development study to determine and test Japanese Industrial Standard (JIS) method
  - Standard methods in place in some automated industrial labs

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