Quantitative Phase Analysis (QPA)

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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

\[
I_x = \frac{CV}{\mu} 
\]

- \(I_x\) = measured intensity of diffraction line
- \(V\) = volume fraction of phase
- \(\mu\) = 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
  - O’Connor & Raven (1988) Powder Diffraction, 3(1), 2-6 (Rec’d 31/03/1987)

- Standardless method based on assumption that entire sample is crystalline and included in Rietveld model

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

- \( W_\alpha \) = weight fraction of phase, \( \alpha \), in an \( n \) component mixture
- \( S = \) Rietveld scale factor
- \( ZMV = \) mass and volume of unit cell
Advantages of QPA via XRD

• Direct phase measurement
  o Based on *structure* not *chemistry*
    – Polymorphs

• Additional (bonus) information available
  o Crystallite size/strain
  o Solid solution chemistry
  o Thermal expansion

• Whole pattern (Rietveld) analysis
  o Standardless
  o Can be high precision
Disadvantages of QPA via XRD

• Single peak methods
  o 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
  o Generally returns *relative* abundances
  o Generally limited to well-defined crystalline species
  o Accuracy difficult to determine
    – Semi-quantitative???
Disadvantages of QPA via XRD

• Single peak methods
  o Strongly affected by any aberrations in data deriving either instrumentation or sample related
    – Non-representative peak heights/areas

• Whole pattern – Rietveld
  o Generally returns relative abundances
  o *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):
  
  o "Crystalline materials are frequently characterized as solids with fixed volume, fixed shape, and long-range order bringing about structural anisotropy, producing sharp diffraction peaks"
  
  o "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):
  
  o "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

- Indirect – analyse crystalline components – put on absolute scale – calculate amorphous content by difference
- Direct – estimate amorphous contribution to pattern
  - Calibrate using known standards, or
  - Include in whole sample analysis

- Samples have constant chemistry $\rightarrow$ constant $\mu_m$
  - Possible to apply simple linear calibration models

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.

9 samples, 3 replicates
Quantifying Amorphous Phases

• All methods capable of determining amorphous material in mixtures in similar fashion to crystalline phases
  o Calibration methods most accurate
  o Amorphous “structure” least accurate

• Possibility of amorphous content frequently ignored in Rietveld analysis
  o If amorphous and/or unidentified phases not mentioned assume relative phase abundances
  o 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 Å² for Si (~0.4 Å² reported)
    - 1.24 Å² for O (~0.4 Å² 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

![Graph showing bias vs silica flour weighed (wt%)](image-url)
Bias vs Amorphous Content
Quartz ADP’s Set to Refined Values

![Graph showing the relationship between Bias (wt%) and Silica Flour Weighed (wt%)](image-url)
What has happened?

• Quartz scale factor has increased to compensate for “loss” of calculated intensity due to higher ADPs
  o Increase in weight fraction quartz analysed
  o 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

![Graph showing the variation of thermal vibration correction with 2θ for different ADPs (B = 0.0 Å², B = 0.5 Å², B = 1.5 Å², B = 3.0 Å²).]
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)
A few low angle peaks dominate the intensity distribution

- Parameters which vary as a function of $2\theta$ will be sensitive to small changes in intensity of low angle peaks

XRD Data (Cu Kα) for Quartz
Very real problem

- Many database structures do not include ADPs or they are set to arbitrary values (say 0.5 or 1.0 Å²)
  - 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?
  o Research
  o Industry

• Determination of actual accuracy is not simple
  o 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.

* Names changed to protect the guilty
Another cautionary tale...

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

<table>
<thead>
<tr>
<th></th>
<th>CoKa</th>
<th>CuKa</th>
<th>MoKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>48</td>
<td>32</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>44</td>
<td>230</td>
<td>26</td>
</tr>
<tr>
<td>ZrSiO₄</td>
<td>117</td>
<td>82</td>
<td>9</td>
</tr>
</tbody>
</table>

- 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

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃</th>
<th>Fe₃O₄</th>
<th>ZrSiO₄</th>
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<tbody>
<tr>
<td>Mean Analysed wt% (n=3)</td>
<td>56.52</td>
<td>17.06</td>
<td>26.42</td>
</tr>
<tr>
<td>Mean Rietveld error</td>
<td>0.15</td>
<td>0.11</td>
<td>0.11</td>
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- 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

<table>
<thead>
<tr>
<th></th>
<th>$\text{Al}_2\text{O}_3$</th>
<th>$\text{Fe}_3\text{O}_4$</th>
<th>$\text{ZrSiO}_4$</th>
</tr>
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<td>56.52</td>
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</tr>
<tr>
<td>S.D. of Analysed wt%</td>
<td>0.63</td>
<td>0.41</td>
<td>0.35</td>
</tr>
</tbody>
</table>

- 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

<table>
<thead>
<tr>
<th></th>
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<th>ZrSiO$_4$</th>
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</tr>
<tr>
<td>XRF</td>
<td>50.4(2)</td>
<td>19.6(1)</td>
<td>29.5(1)</td>
</tr>
<tr>
<td>Weighed</td>
<td>50.46</td>
<td>19.46</td>
<td>29.90</td>
</tr>
<tr>
<td>Mean of bias (measured – weighed)</td>
<td><strong>6.06</strong></td>
<td><strong>-2.58</strong></td>
<td><strong>-3.48</strong></td>
</tr>
</tbody>
</table>

• 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 $\alpha$- and $\beta$-silicon nitrides. II. Round robins

• International Union of Crystallography Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis

• 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
International round robins

• Quantitative phase analysis of α- and β-silicon nitrides. II. Round robins
  o 42 selected participants
    – Second round robin subset of initial group of participants
  o 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
  o 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
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 (Al₂O₃), fluorite (CaF₂) and zincite (ZnO)
  - Sample 2 – preferred orientation
  - Sample 3 – amorphous content
  - Sample 4 – microabsorption
  - Complex mineral suites
    - Synthetic
    - Natural
  - Pharmaceutical
State of the art

Majority of returns dealt with X-ray data (75% via the Rietveld method)
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
  - $\text{Al}_2\text{O}_3$ (the weakest scatterer) occurs at 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

\[
\text{Bias} = \frac{100 \times (\text{Meas}_i - \text{Meas}_{best})}{\text{Meas}_{best}}
\]

- 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

\[ \Delta 2\theta = 0.13^\circ \]
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
  o 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
• 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
• Large spread of values
• CPD-supplied data worse as sample agglomerated
  • Gibbsite particles “coated” with other phases and consequently underestimated
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

<table>
<thead>
<tr>
<th></th>
<th>C3S</th>
<th>C2S</th>
<th>C3A</th>
<th>C4AF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical conc. (%)</td>
<td>60-70</td>
<td>14-20</td>
<td>8-10</td>
<td>8-10</td>
</tr>
<tr>
<td>% Uncertainty (95% conf. lim.)</td>
<td>4.1-6.5</td>
<td>2.8-5.5</td>
<td>0.9-2.5</td>
<td>1.3-2.4</td>
</tr>
<tr>
<td>% Reproducibility r.s.d. = 100(s.d./mean)</td>
<td>3.2-5.4</td>
<td>8.8-28.8</td>
<td>10.3-26.9</td>
<td>9.6-17.5</td>
</tr>
</tbody>
</table>
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 Radiocrystallographie," Dunod, Paris 1956)
Community assessment over 10+ years

<table>
<thead>
<tr>
<th>Approx. conc. Level (%)</th>
<th>CPD-supplied data RR1</th>
<th>Cement</th>
<th>Pharmaceutical</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2-0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.7-1</td>
<td>0.1-2</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>3-6</td>
<td>10-30</td>
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<td>20</td>
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<td>50</td>
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<td>2-3</td>
<td>20-40</td>
</tr>
<tr>
<td>70</td>
<td></td>
<td>0.4-7</td>
<td></td>
</tr>
<tr>
<td>85</td>
<td></td>
<td></td>
<td>9-20</td>
</tr>
<tr>
<td>95</td>
<td>1-2</td>
<td></td>
<td></td>
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</table>

Absolute Bias = \( \text{Abs}((\text{mean} \pm 1\text{SD}) - \text{weighed}) \)
How do we make this better?

• Same problems as identified in IUCr CPD round robin 10+ years ago
  o Continued education required
    – Best practices
    – Awareness of limitations

• Pharmaceutical round robin shows 4 out of 11 labs obtained high accuracy and precision
  o *It can be done*

• Independent analysis of IUCr CPD round robin samples show high accuracy and precision can be obtained
  o *It can be done*

• Development of standard, system-specific procedures
  o Prescriptive round robins like SiN method development study to determine and test Japanese Industrial Standard (JIS) method
  o Standard methods in place in some automated industrial labs
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