Lesson 8
Publishing XRD Results

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…totally irrelevant to the rest of the world
- Quality of Rietveld refinement results
- Graphs
- «Experimental» section
Quality: Accurate + Precise

- High Precision, High Accuracy
- Low Precision, High Accuracy
- High Precision, Low Accuracy
- Low Precision, Low Accuracy

https://phidgets.wordpress.com
Quality of Rietveld Refined Data

XRD / Rietveld refinements are very difficult to validate:

- Often no complementary analytical technique available
- Hardly any reference materials available
- Refinement: Highly operator dependent

One option: Participate in round robins
→ Compare your results with other labs

Round robin on CaP phase quantification organized by RMS Foundation / Nicola Döbelin in 2012/2013
Accuracy of Rietveld Refined Data

Round Robin Reference Sample:
- Simple 2 phase system: HA + β-TCP
- Very homogeneous distribution
- No texture
- No micro-absorption
- Highly crystalline
- Mean crystal size ~200 nm

→ Nearly «Best Case» Scenario
Accuracy of Rietveld Refined Data

Round Robin

12 Labs with 26 different instruments / configurations analyzed the same powder

n=5

Results returned from one lab/instrument:

<table>
<thead>
<tr>
<th>Sample</th>
<th>β-TCP [wt-%]</th>
<th>HA [wt-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.01</td>
<td>71.99</td>
</tr>
<tr>
<td>2</td>
<td>28.22</td>
<td>71.78</td>
</tr>
<tr>
<td>3</td>
<td>28.49</td>
<td>71.51</td>
</tr>
<tr>
<td>4</td>
<td>28.29</td>
<td>71.71</td>
</tr>
<tr>
<td>5</td>
<td>28.20</td>
<td>71.80</td>
</tr>
<tr>
<td>Mean (Std. Dev)</td>
<td><strong>28.24 (0.17)</strong></td>
<td><strong>71.76 (0.17)</strong></td>
</tr>
</tbody>
</table>
Accuracy of Rietveld Refined Data

* p < 0.05
** p < 0.01


Precise Results ≠ Accurate Results
Uncertainty of Measurement

- Random Errors → Precision
  Determine $\sigma$ from $N$ measurements:

  \[ \sigma = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (x_i - \bar{x})^2} \]

- Systematic Errors → Accuracy
  Determine $\Delta$ with reference samples

  \[ \Delta = |\bar{x} - x_{\text{reference}}| \]

- Combined Uncertainty of Measurement

  \[ u(c) = \sqrt{\sigma^2 + \Delta^2} \]

- Expanded Uncertainty of Measurement ($k=2$)

  \[ U_{k=2} = 2 \cdot u(c) \]
Validation of $\beta$-TCP + HAp Quantification at RMS

Reference mixtures
Hydroxyapatite + $\beta$-TCP (Whitlockite)

Measured and refined 20x
Validation of $\beta$-TCP + HAp Quantification at RMS

$\Delta =$ refined - nominal (wt-%)

Accuracy (systematic error)

Precision (random error)

$\beta$-TCP signal drowns in counting noise = systematic error

Validation of $\beta$-TCP + HAp Quantification at RMS

Accuracy (systematic error)

Precision (random error)

$\beta$-TCP signal drowns in counting noise = systematic error

March 01 – 02, 2016, Freiberg, Germany
Validation of β-TCP + HAp Quantification at RMS

Validated uncertainties of measurement compliant with ISO 17025 accreditation

Quality of Rietveld Refined Data

BGMN error propagation = very realistic estimate of $\sigma$

- Standard Deviation
- Mean BGMN ESD

HAp Nominal (wt-%)

Standard Deviation (wt-%)

n=20

March 01 – 02, 2016, Freiberg, Germany
Detection Limits

Possible Definition of Quantification Limit (LOQ):

\[ \text{Phase Quantity} < 4 \cdot \sigma \]

Possible Definition of Detection Limit (LOD):

\[ \text{Phase Quantity} < 2 \cdot \sigma \]
Remember: BGMN ESDs are very realistic!
Guidelines for Reporting Phase Quantities

- For error bars use $3 \cdot \text{ESD}$ or $2.77 \cdot \text{ESD}$
  - $3 \cdot \text{ESD} = 99.7\%$ repeatability limit, normal distribution
  - $2.77 \cdot \text{ESD} = 95\%$ repeatability limit, t distribution [1]

- Report Values < LOQ as «$< 4 \cdot \text{ESD}$»
  - Report $0.76 \pm 0.23$ as «$< 0.92$»

- Report Values < LOD as «not detected»
  - Report $0.21 \pm 0.11$ as «not detected»

Graphs: XRD / Rietveld are «visual» methods

Methods
… phase quantities were calculated from XRD data…

Is the data good enough?

Your friendly reviewer

10 15 20 25 30 35 40 45 50 55
Intensity (a.u.)

Diffraction Angle (°2θ)

REJECTED

ACCEPTED

10 15 20 25 30 35 40 45 50 55
Intensity (a.u.)

Diffraction Angle (°2θ)
Graphs: XRD / Rietveld are «visual» methods

Methods
… XRD data was analyzed by Rietveld refinement…

How good was the refinement?

March 01 – 02, 2016, Freiberg, Germany
Graphs: XRD / Rietveld are «visual» methods

Recommendation:
- Show all your raw data (documents your data quality)
- Show 1 full refinement (documents your refinement quality)

- All the information is in the raw data
- Only additional information in refinement plots (Icalc, Idiff, Bkgr):
  «The refinement was done right»
Graphs: XRD / Rietveld are «visual» methods

Combine your raw patterns

Show more graphs if the manuscript improves
Match the level of detail to the relevance of XRD for the study

**Used for phase identification**

- Basic instrument parameters:
  - Instrument / Manufacturer
  - Scan range (start, end, step size)
- References to PDF / ICDD / COD phase entries
Influence of water content on hardening and handling of a premixed calcium phosphate cement
Johanna Engstrand *, Jonas Aberg, Håkan Engqvist

2. Method

2.7. X-ray diffraction (XRD)

The resulting phase composition of the cements after setting was analyzed using XRD (diffractometer, Siemens). Diffraction angles (2θ) 20–40 were analyzed at 0.45°/min. The set samples were crushed using a mortar prior to analysis.

3. Results

3.6. XRD

In Fig. 6 the spectra for the composition extremes, 0 and 6.8 wt.% water content, are shown. However, all cement formulations, regardless of water content, formed monetite after setting.

Fig. 6. XRD of cements containing 0 and 6.8 wt.% water after setting. Monetite reference pattern from PDF #00-009-0080.
Used for phase quantification

- Detailed instrument parameters:
  - Instrument / manufacturer
  - Scan range (start, end, step size [°2θ])
  - Radiation, filter / monochromator, divergence slit
- References to sources of crystal structures
- Rietveld software (program name, version, reference)
Growth kinetics of hexagonal sub-micrometric ϒ-tricalcium phosphate particles in ethylene glycol

Laetitia Galea, Marc Bohner, Juerg Thuering, Nicola Doebelein, Terry A. Ring, Christos G. Aneziris, Thomas Graule

The crystalline composition was analyzed by XRD measurements. For this, a concentrated ethanol suspension was dried on a glass plate, scratched off and spread on a silicon single crystal sample holder to minimize preferred orientation. XRD data were collected in reflective geometry on an X-Pert diffractometer (X’Pert Pro MPD, Panalytical, Almelo, The Netherlands). Ni-filtered Cu Kα radiation and a step size of 0.016° were used to measure from 4.01° to 59.99° 2θ. Due to the limited amount of sample material available, sample transparency, texture and variable irradiated volume limited the quality of the diffraction patterns. Therefore only semi-quantitative phase analyses could be done by Rietveld refinement using the FullProf.2k software (version 5.00) [23] and a previously determined instrument resolution function. Crystalline models for ϒ-TCP, monetite (DCP) and chloroapatite (Cl-HA) were taken from Schroeder et al. [24], Dickens et al. [25] and Hughes et al. [26].

Fig. 3. Representative XRD diffractogram of particles synthesized at 90 °C, 16 mM for 24 h showing the presence of highly crystalline ϒ-TCP and DCP phases. Observed, calculated, differences and background intensities are displayed, as well as the hkl line positions for ϒ-TCP (top), DCP (middle) and Cl-Ap (bottom).
«Materials and Methods» Section

Used for advanced refinements
(structural parameters, amorphous fractions, crystallite size analysis, texture analysis etc.)

- Detailed instrument parameters:
  - Instrument / manufacturer
  - Scan range (start, end, step size [°2θ])
  - Radiation, filter / monochromator, divergence slit
  - … (detector, masks, ASS, Soller slits, generator settings…)
- References to sources of crystal structures
- Rietveld software (program name, version, reference)
- Refinement strategy
- Any non-standard calculations, sample preparations, measurement conditions, etc…
Synthesis and Structure Refinement of Zinc-Doped \( \beta \)-Tricalcium Phosphate Powders

Sanjeevi Kannan, Friedlinde Goetz-Neunhoeffer, Jürgen Neubauer, and Jose M.F. Ferreira

«Materials and Methods» Section

(2) Structure Refinement

For refinement studies, all the powders were heat treated in a Thermodark furnace (Pt30%Rh/Pt6%Rh-thermocouple) with a heating rate of 5°/min to achieve a predetermined temperature of 1000°C, followed by a dwelling time of 2 h, and then cooled to room temperature at the rate of 5°/min. Although low crystalline \( \beta \)-Ca\(_3\)(PO\(_4\))\(_2\) forms at about 800°C, a higher heat treatment temperature of 1000°C was required to obtain the desired well-crystallized phase for Rietveld refinement. Collection of X-ray powder diffraction (XRPD) pattern data was performed with a Siemens D5000 (Karlsruhe, Germany) equipped with a diffracted beam graphite monochromator. The software TOPAS 3 (Bruker AXS, Karlsruhe, Germany) with the fundamental parameters approach was used for Rietveld refinements. All powders were prepared and measured three times independently. Rietveld refinement was performed using the structural model of ICSD card number of \# 6191\(^{23}\) for \( \beta \)-TCP. Refined parameters were scale factor, specimen displacement, background as Chebyshev polynomial of fifth grade, crystallite size, microstrain, lattice parameters, and occupancy factors. As the scattering factor for \( P^{3+} \) is not implemented in the TOPAS 3 Rietveld software, the \( P \) sites were refined with a combination of \( Si^{4+} \) and \( P \) for pure \( \beta \)-Ca\(_3\)(PO\(_4\))\(_2\) phase. This leads to an improved refinement of Ca\(^{2+}\) occupancy and of the zinc substitution at Ca\(^{2+}\) sites. Zinc content in the heat-treated powders was analyzed by the ICP technique.

Refinement strategy
In situ XRD data sets were collected using a powder diffractometer (X’Pert Pro MPD, PANalytical, Almelo, the Netherlands) in 0/2 configuration using Ni-filtered CuKα radiation and a fixed divergence slit of 1/8” opening. A heating chamber (HTK-1200, Anton Paar, Ostfildern, Germany) was attached to the goniometer. The samples were prepared in a ceramic sample holder spinning at approximately 1 rpm. Data sets were collected from 2°–65° 2θ with a step size of 0.01° 2θ and a counting time of 1 s per step at the following temperatures: 25°, 50°, 100°, 150°, 200°, 250°, 300°, 350°, 400°, 450°, 500°, 550°, and again at 25°C. The heating rate was set to 1°C/min for all heating sequences, which was slow enough to prevent overshooting within the accuracy of the furnace control unit (±1°C). During data collection, the temperature was held constant, and for the last data acquisition the sample was cooled from 1000° to 25°C at 60°C/min.

XRD patterns were analyzed by Rietveld refinement using the software FullProf2k.29 Starting models for the crystal structures were taken from Mathew et al.37 for α-TCP, Dickens et al.25 for β-TCP, and Sadarsanan and Young27 for hydroxyapatite (HA). No additional crystalline phases were observed in the diffraction patterns. The refinements were performed in three steps, starting with vertical sample displacement, scale factors for all phases, and sampled background points with linear interpolation until convergence was reached. In the second step, the cell parameters of all phases were released for refinement, and in the last step isotropic peak broadening of all phases and one common overall isotropic displacement parameter (Biso,overall) were optimized. The instrument resolution function and peak asymmetry were determined with an ‘NIST SRM 660a—Line Profile Lab’ standard before the refinement of the sample data sets. Peak shapes were modeled with a pseudo-Voigt function accounting for peak asymmetry due to axial divergence.40 Average crystallite sizes were calculated from isotropic Gaussian peak broadening using the Scherrer equation.

The most common method to determine X-ray amorphous fractions in a specimen is to add a known quantity of a crystalline internal standard. However, at temperatures up to 100°C, solid-state reactions of the specimen with the standard powder are to be expected. Relative weight fractions \( W_F \) of the crystalline phase \( F \), on the other hand, can be calculated from refined parameters and chemical information of all phases as follows:

\[
W_F = \frac{S_F(ZMV)_F}{\sum S_M(ZMV)_M}, \tag{1}
\]

where \( S \) is the Rietveld scale factor, \( Z \) the number of formula units per unit cell, \( M \) the molecular mass of the formula unit, \( V \) the unit cell volume, and \( \sum \) over all crystalline phases. The absolute mass \( m_0 \) of each crystalline component in the specimen is proportional to

\[
m_0 \propto S_F(ZMV)_F \tag{2}
\]

By making the reasonable assumptions that (i) the intensity of the primary beam and the detector configuration were identical for all data sets, (ii) the total amount of powder in the specimen remained constant during the experiment, and (iii) all phases involved, including the amorphous powder, have similar particle sizes and absorption coefficients, the dependency of \( \alpha \) could be reduced to the phase abundance and the overall atomic displacement parameter. The latter, as well as the unit cell volume, are temperature dependent. The value \( \alpha \) calculated from Eq. (2) for a constant amount of a phase \( F \) will thus show a slight linear decrease with the increasing temperature.

In order to determine the amount of X-ray amorphous material in the specimen, a 100% crystalline reference was needed. As the sum of \( m_F \) values of all crystalline phases remained constant between 800°C and 1000°C, except for a steady decrease caused by the temperature-dependent parameters, it was assumed that all amorphous material was crystallized below 800°C. A linear regression through the sums of \( m_F \) values between 800°C and 1000°C thus served as references for 100% crystallinity for the calculation of absolute phase quantities.
Summary: DOs and DON’Ts in Manuscripts

Do:
- Show your raw data (stacked plots)
- Show one full refinement
- Give details according to the relevance of XRD data for the manuscript

Don’t:
- Spam the manuscript with refinement plots
- Publish results from non-standard samples
- Publish results from poor refinements!!!