Quantification of Phases with Partial Or No Known Crystal Structure: PONKCS

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Quantification of Phases with Partial or No Known Crystal Structure (PONKCS!)

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Introduction

- Traditional Rietveld refinement requires all phases to be crystalline and their crystal structures included in the refinement model.
- Amorphous or unknown (or unidentified) phases can be taken care of as a group by the inclusion of an internal standard.
  ⇒ Spiking

Is it possible to quantify individual "unknown" phases separately?
PONKCS

Introduction

- TOPAS allows substituting of the structure factors of a phase by values derived from measurement of its peak intensities
  - If a phase is or can be indexed: Pawley or Le Bail fitting
  - If a phase cannot be indexed: Single line fitting
- Materials with partial or no known crystal structure can be quantified with the same accuracy and precision as crystalline phases
- Important application areas:
  - Quantification of
    - Phases with no known structures, e.g. new polymorphs
    - Phases with partially known structure, e.g. C3S (!)
    - Disordered materials, e.g. clay minerals
    - Amorphous materials
- PONKCS has opened the door to accurate quantitative phase analysis in materials science where PXRD is currently not in use!
Rietveld method requires the calculation of the ZMV “calibration constant” for quantification

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

Where:
- \( W = \text{wt\%} \)
- \( S = \text{Rietveld scale factor} \)
- \( Z = \text{No. formula units in unit cell} \)
- \( M = \text{molecular mass of formula unit} \)
- \( V = \text{unit cell volume} \)

Fitting an unknown with either a “peaks” phase or a Le Bail extraction does not provide this due to the lack of crystal structure information.
Derivation of ZMV

Calibration may be achieved via a mixture in which there are known amounts of the unknown ($\alpha$) and a standard material ($s$).

In such a mixture $W_\alpha$ and $W_s$ are known, as are the scale factors ($S_\alpha$ and $S_s$) and the unit cell mass and volume of the standard material ($ZMV_s$).
Derivation of ZMV

In this mixture, the ratio of the known weight fractions is given by:

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

A value for the ZMV of the unknown can be calculated by rearranging thus:

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

- all known
Diffraction Pattern for Si Flour
Modelled with 4x Pseudo-Voigt Peaks
PONKCS
Procedure

- Perform a best "envelope fit" to the peaks of the unknown structure or the amorphous halo
  - If a phase is or can be indexed: Pawley or Le Bail fitting
  - If a phase cannot be indexed: Single line fitting
  - The number of peaks as well as their positions and intensity is arbitrary and has little or no physical meaning; use whatever is required to obtain a best fit. This fit will yield a scale factor to calculate the ZMV calibration factor.

- Fix the relative intensities. A "PONKCS phase" can then be scaled as a single entity within a Rietveld refinement

- Lattice parameters or peak positions can be refined to account for peaks shifts

- For indexed phases, preferred orientation can be dealt with!
Use of peaks phase in place of structure

A “peaks” or “hkl” phase can then be scaled as a single entity within a Rietveld refinement

Peaks phase replaces traditional “str”:

```
xo_is
phase_name Fluorite_pks
MVW( 0.000, 0.0000, 0.000 )
CS_L(ccflu, 260.92396)
peak_type fp
scale @ 0.9927054493
```

```
xo !pos1 28.27558263I !int1 265.680902
l !int2 1.270499308
xo !pos2 32.76196554
l !int2 1.270499308
xo !pos3 42.23070081I !int3 1.017909015
l !int3 1.017909015
xo !pos4 47.00863
l !int4 912.6184579
etc
```

Note that at this stage we have no values for ZM and V, and therefore no answer for W!
This can then be substituted into the peaks phase and the value of $W$ will be calculated upon refinement.

Note that this ZM value has no physical meaning and $V$ is assigned a value of unity.
Nontronite
#2: Literature

Diffraction pattern of nontronite (Co Kα)
#2: Refinement of standard mixture

- Corundum: 49.78%
- Nontronite_hkl: 50.22%
The resultant phase model has been applied to a series of mixtures of known composition.

![Graph showing bias versus weighed composition]
Cement
Example: Quantitative Analysis of Cement

- Nishi & Takeuchi (1985) C3S structure - misfits due to structural deficiencies
- Only a "cosmetic" issue for Clinker quantification

```
C3S monoclinic (NISHI) 70.69 %
C2S beta (MUMME) 8.02 %
C3ANa orthorhombic 5.02 %
C3A cubic 2.76 %
C4AF Colville 10.20 %
Periclase 0.63 %
Lime 12.4 %
Arcanite K2SO4 1.44 %
```
Nishi & Takeuchi (1985) C3S structural deficiencies (intensity misfit) adversely affects Bassanite (CaSO₄ · ½H₂O) quantification due to inevitable peak overlap. Degree of overlap depends on Alite chemical composition.
Substitution of calculated intensities

```
phase_name C3S_hkl_Phase
scale @ 0.1
MVW( 0, 4331.778506, 0)
space_group 8
CS_L(cs_c3smoni, 1000 min =50; max =1000；)
a a_c3smoni 33.18748
b b_c3smoni 7.05051
c c_c3smoni 18.56319
be be_c3smoni 94.22338
r_bragg  0.006728277788

hkl_is
```

#### Classic Rietveld Refinement using the Nishi & Takeuchi (1985) C3S structure

#### PONKCS refinement
PONKCS
Quantitative Analysis of Bassanite

- Classic Rietveld Refinement using the Nishi & Takeuchi (1985) C3S structure
- PONKCS refinement
  - Bassanite: Estimated accuracy ~0.2%
  - Estimated precision <0.1%
Slag in Cement
BFSlag can be described via Pawley / Le Bail or single peak fitting.
PONKCS
Quantitative Analysis of BFSlag

E.g. Pawley fit strategy:
- Chose arbitrary space group and lattice parameters to allow for a couple of peaks
- Allow for extreme line broadening

Refined PONKCS model for BFSlag
## Preliminary results

### Vorläufige Ergebnisse

<table>
<thead>
<tr>
<th>Material</th>
<th>Untersuchtes Merkmal</th>
<th>Mittelwert</th>
<th>Vergleichs-σ</th>
<th>Wiederhol-σ</th>
<th>Ref.-Methode / Mischwert</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material 1 (CEM II/B-S)</td>
<td>XRD / Untergrund</td>
<td>24,61</td>
<td>1,91</td>
<td>1,49</td>
<td>25,15 / 25,00</td>
</tr>
<tr>
<td>Material 1 (CEM II/B-S)</td>
<td>XRD / Spike</td>
<td>23,84</td>
<td>1,13</td>
<td>1,90</td>
<td></td>
</tr>
<tr>
<td>Material 1 (CEM II/B-S)</td>
<td>Sonstige</td>
<td>24,49</td>
<td>2,18</td>
<td>0,22</td>
<td></td>
</tr>
<tr>
<td>Material 2 (CEM III/B 32,5 N-NW/H2S/NA)</td>
<td>XRD / Untergrund</td>
<td>69,24</td>
<td>2,35</td>
<td>1,06</td>
<td>67,01</td>
</tr>
<tr>
<td>Material 2 (CEM III/B 32,5 N-NW/H2S/NA)</td>
<td>XRD / Spike</td>
<td>67,21</td>
<td>1,40</td>
<td>1,26</td>
<td></td>
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<tr>
<td>Material 2 (CEM III/B 32,5 N-NW/H2S/NA)</td>
<td>Sonstige</td>
<td>69,33</td>
<td>2,13</td>
<td>0,19</td>
<td></td>
</tr>
<tr>
<td>Material 3 (CEM III/B 42,5 N-NW/H2S/NA)</td>
<td>XRD / Untergrund</td>
<td>71,42</td>
<td>1,15</td>
<td>0,99</td>
<td>72,03</td>
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<tr>
<td>Material 3 (CEM III/B 42,5 N-NW/H2S/NA)</td>
<td>XRD / Spike</td>
<td>72,32</td>
<td>1,01</td>
<td>0,74</td>
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<tr>
<td>Material 3 (CEM III/B 42,5 N-NW/H2S/NA)</td>
<td>Sonstige</td>
<td>72,28</td>
<td>1,71</td>
<td>0,49</td>
<td></td>
</tr>
</tbody>
</table>

PONKCS: (5 repeated analyses)

- 25.1 (2)
- 67.2 (2)
- 71.7 (2)

Wiederhol-Standardabweichung: 
- bis 5 % (Untergrund-Methode)
- bis 3 % (Spike-Methode)
Round Robin VDZ 2006/7
Quantitative Analysis of BFSlag

Accuracy and Precision (values in wt. %, SD in brackets/1σ)

- Every sample measured 5 times (D4 ENDEAVOR, LynxEye Detector)
- Reference values:
  - sample 1: 25,0 wt.%
  - sample 2: 67,0 wt.%
  - sample 3: 72,0 wt.%

<table>
<thead>
<tr>
<th>Measurement</th>
<th>BFSlag Sample 1</th>
<th>BFSlag Sample 2</th>
<th>BFSlag Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement 1</td>
<td>25,0</td>
<td>67,2</td>
<td>71,7</td>
</tr>
<tr>
<td>Measurement 2</td>
<td>25,1</td>
<td>67,3</td>
<td>71,9</td>
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<tr>
<td>Measurement 3</td>
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<td>67,0</td>
<td>71,6</td>
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<tr>
<td>Measurement 4</td>
<td>25,1</td>
<td>67,3</td>
<td>71,9</td>
</tr>
<tr>
<td>Measurement 5</td>
<td>25,3</td>
<td>67,0</td>
<td>71,5</td>
</tr>
<tr>
<td>Mean</td>
<td>25,1</td>
<td>67,2</td>
<td>71,7</td>
</tr>
<tr>
<td>SD</td>
<td>0,2</td>
<td>0,2</td>
<td>0,2</td>
</tr>
</tbody>
</table>
Scarlett, N.V.Y. & Madsen, I.C. (2006) Quantification of phases with partial or no known crystal structure
Powder Diffraction, 21(4), 278-284

Note:
The paper includes an example walkthrough on a TOPAS keyword level.
Walk-throughs and Example Data

- Scarlett, N.V.Y. & Madsen, I.C.
  *Quantification of Phases with Partial or No Known Crystal Structure (PONKCS!)*
  - Presented at the 1st - 3rd TOPAS User's Meetings
  - Presentation includes an example walk-through
  - All example data and INP files made available for distribution

- Schmidt, R.
  *Solving structural problems in QPA of Cements: Structureless modelling of Alite*
  - Presentation includes an example walk-through

- Cordes, H.
  *Quantitative Rietveld analysis with missing or poorly ordered structures*
  - Kaolonite / Illite / Nontronite / Chlorite example data
  - Presentation includes an example walk-through
  - All example data and INP files made available for distribution
Conclusions

- PONKCS allows the quantification of compounds, where the classic Rietveld method fails.
- Materials with partial or no known crystal structure can be quantified with the same accuracy and precision as phases with crystal structure. Often even better, due to the calibration step.
  - Crystalline and amorphous phase amounts, accuracy and LLOD < 1%
- Preferred orientation can be dealt with (if sample is indexed).