THE QUANTIFICATION OF DISORDERED CLAY MINERALS BY THE RIETVELD METHOD - SOME PRACTICAL ASPECTS

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Rietveld in QPA - outcomes of the 2\textsuperscript{nd} Reynolds Cup:

20 of 35 participants used Rietveld as primary quantification tool,
16 of them as the only method!
Despite of the presence of clays!

Participants reached very different results by using the same Rietveld program!

Why?

<table>
<thead>
<tr>
<th>Sum bias</th>
<th>XRD single line</th>
<th>XRD pattern summation</th>
<th>XRD Rietveld</th>
<th>XRD oriented samples</th>
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Parameters to be refined in practical Rietveld QPA?

\[ y_i = \sum_p S_p \sum_k \left[ L_k P_k H_k |F_k|^2 G(\Delta \Theta_{ik}) P_{O_k} \right] + y_{bi} \]

Structural as well as non-structural parameters!

- Lattice parameters
- Atomic positions
- Site occupation
- Temperature factors

- Profile shape parameters
- Preferred orientation
- Background contribution
- Zero point, sample height
The optimisation problem in Rietveld phase analysis, e.g. for a common 10-phase sample:

10 scale factors
+ 30 lattice parameters (1-6 per phase)
+ 8 background + zero point + sample displacement
+ 20 line broadening parameters (size and microstrain)
+ 10 occupation factors
+ 20 parameters of preferred orientation models (conservative estimation)

= 100 parameters must be refined

Complexity of the QPA problem is comparable to structure refinement.

Parameter correlations are unavoidable and heavily to predict.
Rietveld refinement is profile fitting!

\[ y_i = \sum_p \left[ S_p \sum_k \left[ L_k P_k H_k F_k \left\{ G(\Delta \Theta_{ik}) P_o_k \right\} \right] \right] + y_{bi} \]

Structural as well as non-structural parameters!

- Lattice parameters
- Atomic positions
- Site occupation
- Temperature factors
- Profile shape parameters
- Preferred orientation
- Background contribution
- Zero point, sample height
**Fundamental Parameter Approach profile model**

**Wavelength distribution**
\[ \Lambda(1/\lambda) \]
- Determination: Experimental + Literature data
- Thin Si sample, nearly ideal geometry
- Result: Wavelength distribution

**Instrumental function**
\[ G(\theta - \theta_0) \]
- Determination: Experimental + Theoretical
- By deconvolution + By raytracing
- Result: Set of discrete \( \theta \)-dependent profiles
- Described as sum of squared Lorentzian functions

**Sample function**
\[ P(1/d) \]
- Broadening due to real structure parameters:
  - Crystallite size
  - Micro strain
- Modelled by: \( L_1 \) (constant width for all hkl orders)
- \( b^2 = k_2 \cdot \frac{1}{d^2} \)
- \( L_{12} = L_1 \ast L_2 \)
- \[ P = \sum L_{12} \]

**Measured profile is three fold sum:**
\[ \sum \sum \sum L_{1\Lambda} * L_{2G} * L_{12P} \]
The ordered reciprocal lattice, isotropic size related broadening:
Part of the ordered reciprocal lattice, isotropic size and strain related broadening:

\[ h = 2 \]

\[ C^* \]

\[ l = 3 \]

\[ l = 2 \]

\[ l = 1 \]

\[ l = 0 \]

\[ a^* \]

\[ k = 3 \]

\[ k = 2 \]

\[ k = 1 \]

\[ k = 0 \]

\[ b^* \]

\[ h = 0 \]

\[ h = 1 \]

\[ h = 2 \]
Alternative model for calculation of a diffraction peak:
Integration in the reciprocal lattice along spheres of growing $1/d$

In practice, resulting peak shapes are approximated by Lorentzian functions.
Application of the isotropic line broadening model:

KGa1 pattern, fitted using the coordinates of Bish & VonDreele, standard isotropic size-strain broadening model

Some approaches for modelling of clay profiles by the Rietveld method:

Asymmetric line shape for selected peaks, “ideal” cell
   TOPAS, other programs?

Modified $F_{hkl}$ list, from ideal cell, based on experimental standard profiles
   SIROQUANT (Taylor & Matulis, 1994), QUANTO (?)

Very large supercells, based on previous DIFFAX modelling
   (Gualtieri et al. 2001)

$hkl$ dependent line broadening and shifting of multiple lines, mean cell
   (Bergmann & Kleeberg, 1997)

Single layer approach for turbostratically disordered structures
   (Ufer et al., 2004)
Only \( \frac{b}{3} \) translations:
Approximation of a $02\ell$ rod by splitting into two (or more) “peaks”:

“line shift” $\Delta 1/d,$
“line broadening”
both related to the length and to the orientation of the rod.
Both $b/3$ and $a/3$ translations:

Is this a „true model“?
Parameters for an empirical description of complex disorder by broadening/shifting of Bragg peaks:

- Isotropic line broadening due to microstrain
- Length of the rods of the $hkl$ with $k \neq 3n$
- Length of the rods of the $hkl$ with $h \neq 3n$
- Anisotropic line broadening due to thickness of the domains
- Ratio of ordered to disordered “phase”

Is this a „true model“?
Application of the model:

KGa1 pattern, fitted using the coordinates from Bish & VonDreele, combined with the 2-subphase broadening model

Not completely true, but better than nothing!
Application of the model to “more disordered“ phases:

\[ R_{wp} = 12.9\% \]
Testing the approaches for quantification of a real kaolin product

b) stacking fault model (platelets, size, micro strain)
QPA results for kaolin Hirschau using different broadening models for the main phase kaolinite

<table>
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<tr>
<th>model</th>
<th>size/strain isotropic</th>
<th>size ellipsoidal</th>
<th>stacking faults</th>
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<tbody>
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<td>kaolinite (wt-%)</td>
<td>76.2(20)</td>
<td>80.7(18)</td>
<td>85.0(14)</td>
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<tr>
<td>muscovite (wt-%)</td>
<td>11.2(17)</td>
<td>8.9(14)</td>
<td>3.6(13)</td>
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<tr>
<td>microcline (wt-%)</td>
<td>9.3(14)</td>
<td>7.8(14)</td>
<td>8.8(9)</td>
</tr>
<tr>
<td>quartz (wt-%)</td>
<td>1.6(6)</td>
<td>1.2(5)</td>
<td>1.6(4)</td>
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<tr>
<td>gorceixite (wt-%)</td>
<td>1.1(3)</td>
<td>1.4(2)</td>
<td>1.0(1)</td>
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<tr>
<td>parameters</td>
<td>50</td>
<td>55</td>
<td>62</td>
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<tr>
<td>$R_{wp}$ (%)</td>
<td>17.85</td>
<td>15.03</td>
<td>8.96</td>
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The use of very wrong profile models for kaolinite causes systematic errors of mass fractions of kaolinite and muscovite by correlation problems.
Turbostratic disorder (non-correlated stacking):
Turbostratic disorder modelling by the single layer approach
Positions of the Bragg peaks generated by the “single layer approach”
- dioctahedral smectite, cell elongated 10 times along c\(^+\) (c_0 = 125 Å)
- atomic positions of the 2:1 layer taken from Tsipursky & Drits (1984)
- interlayer cation Na\(^+\), one water layer
Application of “disordering” models to a mixture:

Phase | true | calculated
--- | --- | ---
broadening model muscovite: | easy | too complex
parameters | 59 | 66
quartz | 10 | 9.5 (6) | 9.5(4)
smectite | 30 | 30.8 (15) | 24.2(15)
kaolinite | 30 | 30.6(10) | 35.2(10)
muscovite | 30 | 29.1(9) | 31.1(10)
Halloysite as completely turbostratically disordered phase?

Fit of the Weillen halloysite by the full turbostratic model
Single layer approach, combined with modulations of certain rods
Halloysite as partially ordered phase?

Fit of the Weillen halloysite by the “modulated rods” model
Again the old “subphase” model to KGa2:

\[ R_{wp} = 12.9\% \]
FIGURE 5. Selected-area diffraction patterns from (a) dickite and (b) kaolinite, with the beam direction parallel to [100]. Note that no streak exists in (a) but 0kl reciprocal rows are heavily streaked in (b).
Application of the "modulated rods" model to KGa2:

\[ R_{wp} = 9.0 \% \]
halloysite + quartz 1:1

QPA: halloysite 49.4(6) % quartz 50.6(6) % $R_{wp}=8.87\%$
halloysite + muscovite 1:1, no PO modelling

QPA: halloysite 43.8(15) %  muscovite 56.2(15) %  $R_{wp} = 11.9\ %$
halloysite + muscovite 1:1, including PO modelling

QPA: halloysite 50.3(12) % muscovite 49.7(12) % R_{wp} = 8.5 %
halloysite + muscovite 1:1, including complex stacking fault model and occupation refinement for muscovite

QPA: halloysite 47.2(15) % muscovite 52.8(15) % $R_{wp} = 7.94$ %
Application of three “disordering” models to a mixture:
quartz 40 %, montmorillonite 20 %, kaolinite 20 %, illite 1Mt 20 %

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<td>17.8(15)</td>
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Limitation of all these approaches:
No tool for modelling non-rational 00l-series until now!

“Illite” Füzzerradvany, complex stacking faults model, anisotropic size
Using “compromise” models in the hard reality: RC 2/1

BGMN version 3.5.4, 2602 measured points, 2867 peaks, 191 parameters calculation time 17:22 min

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The Rietveld user should balance out:

- Stability of the refinement
  - data quality
  - constraints
  - known parameters

- Flexibility of the model
  - free parameters
  - parameter space
The Golden Rules
for getting reliable results in Rietveld QPA

Prepare a useful sample, run an adequate measurement

Restrain all parameters to meaningful ranges

Use adequate, physically based models

Avoid the use of redundant or correlated parameters