Quantitative Phase Analysis Using a New Rietveld Algorithm - Assisted by Improved Stability and Convergence Behavior

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Abstract

A new Rietveld program called BGMN was developed recently. Improved convergence behavior was obtained by using an extended peak shape model. In addition, a redesigned mathematical refinement algorithm enabling fixed limits for each parameter was introduced. Most of the advantageous properties of modern Rietveld programs were included, for instance the texture description in positive definite spherical harmonics, the refining of molecules and the calculation of parameter errors.

The main advantage of the program for quantitative phase analysis is the excellent stability of refinement, even if minor phases are present.

During the investigation of rock specimens, no noticeable difficulties occurred in spite of the well known problem of strong preferred orientation and although a conventional BRAGG-BRENTANO diffractometer was used.

Introduction

Quantitative phase analysis using the Rietveld method is not yet common in the X-ray laboratory practice, although the power of this method is well known /2, 4, 6/ and a large number of Rietveld programs exist. One reason for this phenomenon is the difficult processing with the existing programs which require extensive experience with Rietveld analysis, and are often combined with frustrating bad convergence and run time errors.

A lot of work was done in quantitative phase analysis by various authors to achieve practicable solutions for particular systems of phases. The "refinement strategy" is manually done or programmed as a batch of iterations with an increasing number of free parameters.

There is an extensive discussion in the literature about refinement strategies and peak shape models in Rietveld programs. We feel, there is a strong interaction between both questions. Often the Rietveld program crashes, especially caused by wrong peak shape parameters u, v, w or a correlation of them with other parameters (e.g. for background).

Therefore, in 1993 we started the development of a new Rietveld software called BGMN, which employed a better peak shape model and a more stable algorithm /1/.

The main properties of the new program and some applications in phase analysis will be presented below.

Features of the program

A redesigned mathematical algorithm is essential for the improved convergence behavior. The new algorithm enables the definition of fixed lower and upper limits for each parameter /7, 8/. Moreover, built-in physical meaningful limits exist for common parameters like peak shape and texture parameters or Debye-Waller factors. These limits avoid wrong minima during refinement.

It is the essential advantage that the new program always finds a solution for the parameter set. There is no need for processing intermediate models ("refinement strategy"). That has the consequence that no extra inputs are necessary during the refinement. Therefore, the program is an ideal tool for fully automatic serial analysis. The calculation time needed depends on the complexity of the model used and on the quality of the data measured. A formula interpreter is available for enhancing the built-in functions.
Other advantageous features are:

- description of the preferred orientation (further briefly mentioned as texture) in positive definite spherical harmonics
- anisotropic real structure parameters individually calculated for size and strain broadening
- anisotropic Debye-Waller factors
- refinement of site occupancies
- refining of molecules as rigid bodies, which can be shifted or rotated.

Calculations of parameter errors allow the recognition of errors in the starting model. It is possible to identify abnormal high parameter errors after the refinement. If a parameter is shifted to a fixed limit or an error has the magnitude of the parameter value or a texture parameter is abnormally high, it is necessary to check the model, to choose other limits or texture functions and to start again.

Additional to the new refinement algorithm the program applies an "exact" peak shape model (Fig. 1). This peak shape model separates the influences of the instrument on the measured diagram similar to /5/, consequently the refinement is carried out on a fully corrected "sample diagram". The parameters of the wavelength distribution and the instrumental function are predefined. Therefore, correlation between profile and structure parameters is eliminated.

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**Exact peak shape model**

\[ \Lambda * G * P \]

***Wavelength distribution***

\[ \Lambda(1/\lambda) \]

determination

experimental intensity data

(thin Si sample, nearly ideal geometry)

result

wavelength distribution

\[ L_1 = \frac{1}{\pi} \frac{b}{b^2 + (x + x_0)^2} \]

***Instrumental function***

\[ G(\theta - \theta_0) \]

determination

experimental, theoretical

by deconvolution, by ray tracing

result

set of discrete 2D-dependent profiles described as sum of squared Lorentzian functions \( L_2 \)

\[ L_2 = \frac{2}{\pi} \frac{b'}{b^2 + (x - x_0)^2} \]

***Sample function***

\[ P(1/d) \]

broadening due to real structure parameters:

- crystallite size
- micro strain

modelled by

- \( L_1 \) (const. width for all hkl orders)
- \( L_2 \) with

\[ b' = \frac{b}{1 + d^2} \]

\[ L_{12} = L_1 * L_2 \]

\[ P = \sum L_{12} \]

---

Measured diagram is three fold sum:

\[ \sum_L \sum_G \sum_p L_{1L} * L_{2G} * P_{lp} \]

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Fig. 1. The profile modeling in the program BGMN.

References to wavelength distribution e.g. /3/

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Application of the program in phase analysis

Experimental

Diffraction data were acquired using the following conventional BRAGG BRENTANO diffractometers:

<table>
<thead>
<tr>
<th>XRD-7</th>
<th>Rich. Seifert &amp; Co. Freiberger Präzisionsmechanik GmbH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu-anode, curved graphite diffracted-beam monochromator, sample rotation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>URD-6</th>
<th>Freiberger Präzisionsmechanik GmbH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co-anode, Fe-filtered radiation, fixed sample</td>
</tr>
</tbody>
</table>

step interval: 0.02 °2Θ, in some cases 0.05 °2Θ
counting time: max. 10 s/step
sample preparation: powder < 20 µm, stepwise ground and sieved, in a front-filled holder.
Preferred orientation was accepted to test the texture description by spherical harmonics.

The above mentioned experimental conditions were selected

- to test a procedure, which can be handled in any X-ray laboratory and
- to use data measured from the routine work in a mineralogical institute.

Silicon Nitride Ceramics

This simple system (α-Si₃N₄, β-Si₃N₄ and Si) was the first test of the program for phase analysis. Samples were prepared mixtures of synthesized silicon nitride and silicon powders.

conditions: XRD-7, 10-120 °2Θ, step 0.02 °, 10 s/step
refined parameters: lattice parameters; peak broadening by crystallite size, crystallite size distribution and residual stress of all phases; isotropic temperature factors

Crystallite size distribution and residual stress broadening parameters were refined to zero for all phases. Crystallite size broadening (Lorentz 1) gives small values for silicon (prepared from a single crystal), the values for the nitrides are four times larger.

Table 1. Quantitative results from reference mixtures

<table>
<thead>
<tr>
<th>phase</th>
<th>sample A conc./wt%</th>
<th>sample B conc./wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nominal Rietveld</td>
<td>nominal Rietveld</td>
</tr>
<tr>
<td>α-Si₃N₄</td>
<td>47.5 47.3</td>
<td>95.0 95.4</td>
</tr>
<tr>
<td>β-Si₃N₄</td>
<td>2.5 3.0</td>
<td>5.0 4.6</td>
</tr>
<tr>
<td>Si</td>
<td>50.0 49.7</td>
<td>- -</td>
</tr>
</tbody>
</table>

Ancient Mortars and Plasters

The purpose of the analysis of calcareous cement and gypsum in ancient mortars and plasters is the reconstruction of historical buildings. Mineral mixtures were prepared to test structure models and parameter sets. The procedure is now used as standard method in our laboratory.

Analytical problems are caused by the often low concentrations of gypsum, multiple preferred orientation in case of coarse-grained gypsum and different crystallite size broadening for calcite or gypsum.
Lattice parameters and size broadening were refined for all phases (upper limits only for feldspars). Moreover, complex texture models were used for gypsum and calcite. Control determinations on test mixtures consisting of quartz, calcite and gypsum show correct results down to 1 weight-% gypsum and 4 % calcite with relative errors < 10 %, for larger concentrations 2-5 %. The mineral mixtures, prepared from powdered crystals, could be refined only with strong preferred orientation (texture factor up to 1.8 for gypsum 020 and up to 1.5 for calcite 104 reflection).

A mortar from the Meissen Cathedral (Saxony) is shown as an example. It contains quartz, feldspars, calcite and gypsum. The quantitative Rietveld results are compared with concentrations calculated from chemical analyses (Table 2.) The texture correction of this real sample was not as high as in the case of the mineral mixtures.

Table 2. Comparison of Rietveld and chemical analysis of a ancient mortar

<table>
<thead>
<tr>
<th>phase</th>
<th>wt%</th>
<th>chemical analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>calcite</td>
<td>20.4</td>
<td>23.1 from carbon</td>
</tr>
<tr>
<td>gypsum</td>
<td>10.6</td>
<td>10.1 from sulphur</td>
</tr>
<tr>
<td>quartz</td>
<td>57.1</td>
<td></td>
</tr>
<tr>
<td>albite</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>orthoclase</td>
<td>7.9</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 2. Observed and calculated patterns from a mortar (Meissen cathedral)](image)

Co Kα radiation, Fe-filtered
URD-6, 10-80 °2θ, step 0.05 °, 5 s/step (routine measurement)
Minor Phases in Silcrete

Silcretes, sedimentary quartz cemented rocks, contain TiO$_2$-phases. In the example there is also a trace of halite. There was no noticeable amount of amorphous silica or opal CT. Consequently, this natural rock could be used as a good test of the sensitivity of the program parameters for low concentrations.

Two TiO$_2$-modifications, anatase and rutile, are present in the samples. Their largest peaks are positioned near the 101 quartz peak. Quartz occurs in two genetic types:

- coarse-grained clastic quartz (sandy fraction)
- fine-grained chalcedony (cement).

For this reason, two quartz phases were refined simultaneously. Lattice parameters were free for all phases. The two quartz phases were refined with free crystallite size and strain parameters. To give a difference, the starting value of size broadening for quartz 2 was set different from 0. For the other phases, only size broadening was refined using an upper limit. Fixed atomic positions and temperature factors were used.

The quantitative results of this sample are compared with chemical analysis. Halite is calculated from Na$_2$O and Cl, the sum of anatase and rutile from TiO$_2$.

Table 3. Comparison of Rietveld and chemical analysis of a silcrete

<table>
<thead>
<tr>
<th>phase</th>
<th>wt% Rietveld</th>
<th>chemical analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>anatase</td>
<td>0.56(3)</td>
<td>-</td>
</tr>
<tr>
<td>rutile</td>
<td>0.48(3)</td>
<td>-</td>
</tr>
<tr>
<td>$\Sigma$ TiO$_2$</td>
<td>1.04</td>
<td>1.25 TiO$_2$</td>
</tr>
<tr>
<td>halite</td>
<td>0.55(3)</td>
<td>0.51 from Na$_2$O</td>
</tr>
</tbody>
</table>

Crystallite size broadening and strain broadening parameters for quartz 1 were refined to zero, that means that no size/strain broadening exists. The broadening parameters of quartz 2 were shifted to higher values. Because of the insufficient crystallite statistics for quartz (< 30 μm), the accuracy of real structure parameters and the ratio quartz1/quartz2 should not be overestimated.

![Fig. 3. Observed and calculated patterns of an Australian silcrete, Cu K$_\alpha$ radiation XRD-7, 15-120°2θ, step 0.02°, 10 s/step](image-url)
Mixtures of quartz, calcite and perthitic alkali feldspar

Mixtures of quartz, calcite, perthitic alkali feldspar (microcline and albite) and 1% opaque minerals, originally prepared for testing a microscopic method, were used as examples of complex patterns containing 1524 calculated reflections between 10 and 120°2Θ.

Multiple preferred orientation occurs for feldspars. In the case of low concentrations, meaningless high texture correction parameters were calculated using the most complex texture models. Consequently, it was necessary to use more simple models. The first calculation of sample 1 resulted in a value of albite content being too large combined with very high broadening parameters. After limiting the crystallite size broadening parameter, the refinement gives acceptable results (Table 4). The needed calculation time (WINDOWS NT Version 3.51, Pentium 133 processor, 32 MB RAM) is high and differs from sample to sample. Note, the given time is the complete computation time without any interaction of the user!

Table 4. Results of refinement of mineral mixtures

<table>
<thead>
<tr>
<th>No.</th>
<th>wt-%</th>
<th>calcite</th>
<th>microc.</th>
<th>albite</th>
<th>Σ feldspars</th>
<th>Rwp/</th>
<th>time/</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Rietveld</td>
<td>Rietveld</td>
<td>Rietveld</td>
<td>Rietveld</td>
<td>%</td>
<td>h</td>
</tr>
<tr>
<td>1</td>
<td>41.6(2)</td>
<td>45</td>
<td>51.3(2)</td>
<td>49</td>
<td>5.5(2)</td>
<td>1.4(3)</td>
<td>6.9</td>
</tr>
<tr>
<td>2</td>
<td>35.7(2)</td>
<td>35</td>
<td>31.3(2)</td>
<td>32</td>
<td>26.3(3)</td>
<td>6.3(2)</td>
<td>32.6</td>
</tr>
<tr>
<td>3</td>
<td>77.5(2)</td>
<td>79</td>
<td>10.7(1)</td>
<td>10</td>
<td>9.2(2)</td>
<td>2.4(1)</td>
<td>11.6</td>
</tr>
<tr>
<td>4</td>
<td>76.4(2)</td>
<td>79</td>
<td>10.9(1)</td>
<td>10</td>
<td>9.6(2)</td>
<td>2.9(1)</td>
<td>12.5</td>
</tr>
<tr>
<td>5</td>
<td>5.0(1)</td>
<td>5</td>
<td>48.9(2)</td>
<td>50</td>
<td>34.9(3)</td>
<td>11.1(2)</td>
<td>46.0</td>
</tr>
</tbody>
</table>

Mixture of quartz and muscovite

A binary 1:1 mixture of quartz and muscovite 2M1 was prepared for testing the reliability of the texture correction and the peak shape model. The well known problem of preferred orientation, here occurring in an extreme state, we tried to describe by a 6th order spherical harmonic model. In a first refinement, isotropic model of crystallite size and strain broadening for muscovite was used. A second refinement with anisotropic model of crystallite size and strain broadening for muscovite gives much better results (see below).

Results:

- isotropic peak shape modeling: \( R_{wp} = 12.7 \% \), quartz 55.1 wt%, muscovite 44.9 wt%
- anisotropic peak shape modeling: \( R_{wp} = 9.7 \% \), quartz 47.5 wt%, muscovite 52.5 wt-%

Note the extreme texture corrections for muscovite 002. In the first refinement, the unusual calculated crystallite size broadening parameter of 0 for muscovite may be caused by the shape of the 001 peaks, which are no "powder reflections" because of the extreme orientation. The "volcano-like" difference plots (Fig. 4.) of the hkl peaks reflect the insufficient peak shape modeling. Therefore, the anisotropic model was necessary. The dramatic decrease of \( R_{wp} \) is connected with a slightly higher refined muscovite content. The peak shapes do fit much better (Fig. 5). The poorly fitting intensity ratio 004/006 may be influenced by the unknown (and not refined) chemical composition of the muscovite or by polarization effects from the highly oriented mica crystallites.
Fig. 4. Rietveld refinement plot of 1:1 quartz/muscovite, isotropic modeling of muscovite peak broadening. Co Kα radiation, Fe filtered
URD-6, 15-100 °2Θ, step 0.02 °, 5 s/step

Fig. 5. Rietveld refinement plot of 50:50 quartz/muscovite, anisotropic modeling of muscovite peak broadening. Co Kα radiation, Fe filtered
URD-6, 15-100 °2Θ, step 0.02 °, 5 s/step
Table 5. Selected refined peak parameters of 1:1 quartz/muscovite mixture

<table>
<thead>
<tr>
<th>reflection</th>
<th>Lorentz 1 broadening</th>
<th>texture correction factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>isotropic modeling</td>
<td>anisotropic modeling</td>
</tr>
<tr>
<td>quartz 101</td>
<td>0.001</td>
<td>0.0009</td>
</tr>
<tr>
<td>muscovite 002</td>
<td>0</td>
<td>0.0016</td>
</tr>
<tr>
<td>muscovite 021</td>
<td>0</td>
<td>0.007</td>
</tr>
<tr>
<td>muscovite -112</td>
<td>0</td>
<td>0.003</td>
</tr>
<tr>
<td>muscovite 060</td>
<td>0</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Metashale reference sample

An Ordovician metashale from Böhlscheiben/Thuringia was investigated during the 60's in a round robin combining conventional X-ray diffraction and chemical methods /9/. This reference sample was investigated as natural example, containing high abundance of layer silicates. Muscovite (idealized formula) was modeled with 6th order spherical harmonics texture description and anisotropic crystallite size/strain broadening. For chlorite (rhipidolite) 1MIIb structure and albite 2nd order texture correction and isotropic broadening model was assumed. After the first refinement, low 0.324 nm reflection in difference plots indicate the presence of potassium feldspar. Microcline was included in final refinement (without texture correction, with limited crystallite size broadening). $R_{wp}=7.13\%$ (background corrected 17.4%) was reached. Better results may be calculated using additional chemical information about the layer silicates, but unfortunately only powdered samples are available.

Fig. 6. Rietveld refinement plot of the Böhlscheiben metashale
Co Kα radiation, Fe filtered, URD-6, 10-100 °2Θ, step 0.02 °, 8 s/step
Table 6. Results from the Böhlscheiben metashale

<table>
<thead>
<tr>
<th>phase</th>
<th>wt%</th>
<th>STARKE (1969)</th>
<th>Rietveld</th>
</tr>
</thead>
<tbody>
<tr>
<td>quartz</td>
<td>30</td>
<td>32.9</td>
<td></td>
</tr>
<tr>
<td>muscovite</td>
<td>39</td>
<td>40.9</td>
<td>3.2 /002</td>
</tr>
<tr>
<td>chlorite</td>
<td>19</td>
<td>15.2</td>
<td>3.3 /002</td>
</tr>
<tr>
<td>albite</td>
<td>10</td>
<td>8.8</td>
<td>1.2 /020</td>
</tr>
<tr>
<td>microcline</td>
<td></td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>accessories</td>
<td>2</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Kaolins

Australian kaolins from a weathering profile have been investigated, containing relatively well-ordered kaolinite, quartz and traces of anatase and halite. Note, no other layer silicates and no opal CT are present. The complex texture model and anisotropic broadening parameters were refined for kaolinite. Isotropic peak broadening was assumed for anatase and halite.

The XRD results are similar to the kaolinite modes calculated from Al₂O₃ content. The differences in texture from sample to sample clearly show the problem of preparation, nevertheless, it was successfully compensated by the texture description.

Table 7. Quantitative results and refined texture factors for kaolinite

<table>
<thead>
<tr>
<th>sample</th>
<th>wt% kaolinite</th>
<th>texture 001</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rietveld</td>
<td>mode from Al₂O₃</td>
</tr>
<tr>
<td>A3513</td>
<td>52.2</td>
<td>54.9</td>
</tr>
<tr>
<td>A3519</td>
<td>32.7</td>
<td>31.9</td>
</tr>
<tr>
<td>A3522</td>
<td>45.2</td>
<td>42.5</td>
</tr>
</tbody>
</table>

Fig. 7. Rietveld refinement plot of a kaolin sample. Co Kα radiation, Fe filtered
URD-6, 10-80 °2Θ, step 0.05 °, 5 s/step (routine measurement)
Experiences and Conclusions

The program BGMN was successfully tested for quantitative phase analysis. It is easy to use and only the starting model is critical for successful refinement. However, the excellent stability of the algorithm may seduce the user into the creation of overcomplex models. To avoid systematic errors, some rules for the designing of a starting model are noteworthy:

Lattice parameters need good starting values. Fixed limits should be set in agreement with definition of the mineral in a solid solution (e.g. plagioclase, mica). Atomic positions should be fixed for phase analysis.

Scale, peak broadening, background polynomial parameters and temperature factors need no manual predetinition.

Site occupation and temperature factors may be refined for major phases and heavy elements; fixed upper limits are useful.

Peak broadening from crystallite size and/or strain may be refined, fixed upper limits are necessary for minor phases in complex diffractograms. In case of high concentrations of layer silicates, anisotropic broadening parameters should be used.

Complex texture models are suitable for minerals with multiple cleavage like feldspars, but may cause systematic errors in case of highly oriented phases occurring in low concentrations. In this case, we prefer the use of the simple ellipsoid model. The preferable way is, of course, to avoid texture e.g. by transmission geometry /4/.

In our opinion, the new program offers some new and powerful tools in phase analysis of complex composed samples.

Acknowledgements

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References


