Preparation of powder specimen for quantitative XRD

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References


Impact of crystallite statistics on the diffraction signal depends on:

- sample volume contributing to diffraction (limited by the primary slit system, sample holder, absorption)
- section of the diffraction rings seen by the detector (limited by Soller slits, receiving slit, detector area)
- number of particles per volume unit (limited by particle size)

- only the particle size may be optimized by sample preparation
- ideal case: “infinite number of crystallites” = continuous cones of diffraction
Crystallite statistics 2

Practical consideration: How many particles do contribute to our diffraction signal?

Exemplary calculation at: http://epswww.unm.edu/xrd/xrdclass/07-Errors-Sample-Prep.pdf

Quartz in different particle diameter in a conventional Bragg-Brentano diffractometer

<table>
<thead>
<tr>
<th>Particle diameter</th>
<th>40 µm</th>
<th>10 µm</th>
<th>1 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffracting particles</td>
<td>12</td>
<td>760</td>
<td>38 000</td>
</tr>
</tbody>
</table>

To achieve a standard uncertainty of < 1%, > 52900 particles would be needed!


Quartz in different particle diameter in a conventional Bragg-Brentano diffractometer

<table>
<thead>
<tr>
<th>Particle size fraction /microns</th>
<th>15-50</th>
<th>5-50</th>
<th>5-15</th>
<th>&lt;5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard deviation of I quartz_{101}/%</td>
<td>18.2</td>
<td>10.1</td>
<td>2.1</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Conclusions:

- If we want to measure single peak intensities of minerals correctly, we should try to mill any rock samples to < 5 µm.
- This is necessary to get reliable results of Rietveld structure analysis, too.
Microabsorption causes **loss of intensity** inside a particle. If this loss is different between two phases, the beam is interacting with different phase volumina! Thus, the QPA results will be falsified.

**High absorption**

**Lower absorption**
The theory of BRINDLEY (1945):

- depends on grain diameter $d$ and linear attenuation coefficient $\mu$

- intensity loss / correction factor can not be determined from the powder data!

- can be ignored if the product $\mu d$ is equal for all phases

- intensity resp. scale factor can be corrected if $\mu d < \sim 0.5$, and if both values are known for each phase!

Approximated BRINDLEY correction in the BGMN structure file:

GOAL: forsterite = GEWICHT * exp(my*d*3/4)

| GEWICHT | Rietveld scale factor, mass weighted |
| my      | linear attenuation coefficient in 1/µm, provided by BGMN |
| d       | estimated particle diameter in µm, to be set by the user in structure or control file |
Microabsorption 3

When does microabsorption occur in practice?

Example: QPA of sulphide bearing rocks

Absorption contrast between quartz and pyrite

coarseness according to BRINDLEY (1945)

<table>
<thead>
<tr>
<th>phase</th>
<th>grain size/µm</th>
<th>µd Cu Kα</th>
<th>µd Co Kα</th>
</tr>
</thead>
<tbody>
<tr>
<td>quartz</td>
<td>10</td>
<td>0.093 medium</td>
<td>0.146 coarse</td>
</tr>
<tr>
<td>pyrite</td>
<td>10</td>
<td>1.012 very coarse</td>
<td>0.516 coarse</td>
</tr>
</tbody>
</table>

Conclusions:

- No problem for fine clay fractions and silicate minerals having similar (low) µ.
- But, if we want to quantify rock samples containing high absorbing materials, we should try to mill the samples to < 5 µm.
For example, sedimentary rocks:

- large crystals (>mm, e.g. quartz), together with fine grained material (clay)
- hard and soft phases together
- differences in density may occur (pyrite, hematite, rutile, silicates…)
- mechanically or thermally sensitive phases (e.g. clay minerals, zeolites, sulphates)

What we want to get

- mean particle size below 5 µm, optimum 1-3 µm
- narrow particle size distribution, no amorphization, no “rocks-in-the-dust”
- no additional disorder (e.g. by shifting of layers)
- no contamination (e.g. by grinding elements)
- no loss of material (e.g. by dusting or dissolution)
- no phase transformation (e.g. by dissolution-precipitation, hydration-dehydration…)
- no phase separation (e.g. by hardness, density, primary particle size, electrostatic…)
Golden rules for milling

General principles:

- If a sample is not homogenous or not representative, any further efforts (for phase quantification in general) are unnecessary.

- The maximum grinding energy has to be adapted to the most sensitive phase.

- Some overmuch large grains are better than any destroyed phase(s).

- Working in closed containers to avoid loss of material by dusting, checking for losses by sedimentation, dissolution, electrostatic adhesion...

- Quick working for minimum contact with dissolution agents and air to avoid any phase alteration.

- Samples should not be exposed any enhanced temperature.

- Note (or keep in mind) what treatments and changes your sample was exposed between sampling and XRD measurement.
Grinding methods useful for clay-bearing rocks 1

Hand grinding in agate mortar

- easy, but strenuous
- allows a stepwise sieving of < 20 µm, very mild
- resulting powder is mostly too coarse for high absorbing materials
- danger of loss by dusting

Foto: Detlev Müller
Grinding methods useful for clay-bearing rocks 2

McCrone micronising mill

- wet grinding (in water or alcohol) produces optimum grain distribution
- crushing the starting material < 0.4 mm is necessary
- danger of contamination by grinding elements (corundum, quartz, ZrO₂)
- dissolution and/or alteration by the grinding liquid (water, ethanol, hexane…)
- filtering or drying of the slurry and additional homogenisation is necessary

![Particle size distribution of McCrone milled quartz, from Hillier (2003)](image)
Homogenisation

- is necessary for admixing of any standards as well as to overcome the (unavoidable) separation processes during grinding, sieving, and sedimentation
- should be applied with minimum energy
- can also used for destroying of aggregates
- should be done immediately before filling the sample

Useful methods:
- admixing of standards by *grinding together* (to get similar grain size and intimate mixing)
- larger amounts of easily flowing powders by *overhead-shaking*
- small amounts by *manual stirring*
- homogenisation and destroying of aggregates by swirling the powder with small steel balls („Ardenne vibrating mill“ or Fritsch mini-mill “pulverisette 23“)
Making the powder mount for Bragg-Brentano XRD 1
are an old matter of debate, and sometimes treated like religion…

Possible pre-treatment of powder before filling:

- No pre-treatment (filling the milled and homogenised powder “as is”)
- Forming irregular shaped aggregates
  - by freeze-drying
  - by spray-freeze-drying
  - by admixing glass powder, plastics or organics, e.g. cork powder
- Forming spherical aggregates
  - by spray-drying with binder (cellulose-acetate, polystyrene, polyvinyl-alcohol)
  - by spray-drying without binder, application of heat
  - by mechanical aggregation in a shaking/sieving procedure (“sieving in”)

Aspects for decision: time consumption, material consumption, stability and density of the samples, loss of intensity by dilution, sample transparency, alteration of minerals, reproducibility, labour protection…
Making the powder mount for Bragg-Brentano XRD 2

Simple tricks may make the difference…

Front-loading (standard holders, very popular)

- powder pressed using a glass slide: very easy, but extreme PO
- powder roughened by emery paper: not so much PO, but badly reproducible and depending of the properties of the powder
- surface roughened by a razor blade: as above, plus high roughness
- sprinkling/sieving some powder on the surface: good randomness, but errors in sample height, high roughness, sometimes phase separation
- possible to do with any kind of aggregates, perfect randomness possible
Making the powder mount for Bragg-Brentano XRD 3

Back-loading (special Philips/Panalytical equipment)

- easy to do, but extreme PO
- no chance to use for unstable aggregates like freeze-dried clays
Making the powder mount for Bragg-Brentano XRD 4

Side-loading (with special side-opened holders, but also for standard holders)

- with normal powder: relatively easy, reproducible, acceptable PO
- with irregular aggregates: perfect randomness possible
- general problems are density, homogeneity, and stability, e.g. for rotated samples
Errors in sample preparation 1

Influence of overmuch large grains on the powder pattern

topaz bearing granite, samples ball-milled < 63 µm and hand-ground < 20 µm
Errors in sample preparation 2

Phase separation and loss of material during powder preparation

**Mineral mixtures**, ground by hand/dry sieving < 20 µm and McCrone milling/ethanol, filtered slurry

- **Errors in sample preparation 2**
  - Milling
  - Filling
  - Examples

**Problems**

- **Milling**
- **Filling**

**Examples**

- **Mica + quartz lost by dusting during dry sieving**

**Comparison of 2 Scans**

- **Mix3handco10.NJC; Scan 2**
- **Mix3McCroneco10.NJC; Scan 2**

- **Halite dissolved in ethanol**

**Mineral mixtures**
- ground by hand/dry sieving < 20 µm and McCrone milling/ethanol, filtered slurry
Errors in sample preparation 3

Sample contamination by abrasion from grinding elements

Kaolin Spergau reference sample, McCrone ground using corundum grinding elements and using agate grinding elements
Errors in sample preparation 4

Preferred orientation of grains/aggregates dependent on filling technique
Errors in sample preparation 5

Preferred orientation of grains/aggregates dependent on filling technique

Mixture quartz/dickite/muscovite 40:30:30, McCrone milled, different filling techniques (from Kleeberg et al., 2008)