Problems of quantitative XRD mineral analyses and their solutions by non-Rietveld methods

Jan Środoń
Institute of Geological Sciences PAN
Senacka 1, 31-002 Kraków, Poland
ndsrodon@cyf-kr.edu.pl
## Artificial rock composition

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mudstone, RC-AR1 (%)</th>
<th>Siltstone, RC-AR2 (%)</th>
<th>Calcareous Mudstone, RC-AR3 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz (821-382, Columbia)</td>
<td>20</td>
<td>40</td>
<td>15</td>
</tr>
<tr>
<td>K-Feldspar (821-386, Microcline)</td>
<td>8</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Plagioclase (821-001, Albite)</td>
<td>8</td>
<td>10</td>
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</tr>
<tr>
<td>Calcite (821-383, Iceland Spar)</td>
<td>5</td>
<td>3</td>
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<td>Dolomite (821-392, Montana)</td>
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</tr>
<tr>
<td>Gypsum (821-389, Selenite)</td>
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<td>5</td>
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<tr>
<td><strong>Total Non-clay</strong></td>
<td><strong>54</strong></td>
<td><strong>74</strong></td>
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<td>Kaolinite (821-307, Kaofine90)</td>
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Total 100 100 100
Reynolds Cup 2002

AR-1
“Mudstone” Bias

AR-2
“Siltstone” Bias

AR-3
“Calc-mudstone” Bias

Contestant No.

Cumulative Error (differences from actual)
Problems of quantitative XRD

- Sample representative for the rock
- Homogenous sample
- Internal standard
- Grinding and mixing for quantitative XRD
- Orientation
- Sample density
- XRD pattern recording
- Non-Rietveld quantitative analysis of XRD patterns
Sample representative for the rock

• Statistic methods of sampling in order to make the mineralogical sample representative for the investigated geological object (techniques widely used for the evaluation of mineral deposits)
Homogenous sample

• How to make small samples needed for different analyses representative for a bulk piece of solid rock?
• Coarse grinding to pass ca. 0.4 mm sieve
• Splitting
Internal standard

- Absent from the investigated samples
- Isometric sub-micron grains (no need for grinding, no orientation)
- Possibly small number of reflections and minimum coincidences
- Possibly big scattering power (strong reflections=less standard needed=less dilution of the sample)
- 20% Al$_2$O$_3$ widely used (RIR)
- 10% ZnO selected by Środoń et al. (CCM, 2001)
Grinding and mixing for quantitative XRD

- Wet-grinding to avoid amorphisation
- Non-water grinding to avoid destroying clay aggregates
- Limited time to avoid peak broadening related to crystal-size reduction
- Normal distribution instead of lognormal to avoid „tail” of coarse grains
- Enough sample to minimize contamination by the mill material
- Solution: 5 min grinding of 3g sample in 4 ml methanol or hexane in McCrone mill. Mixing with ZnO by the same technique. Drying on magnetic stirrer to avoid segregation.
- Longer grinding of some pure standards
Particle Size Distribution, McCrone and Tema Mills (O’Connor & Chang, 1986)

The graph shows the frequency of particle sizes for different milling methods: Micronizing Mill (Wet), Micronizing Mill (Dry), and Tema Mill (Dry). The x-axis represents the particle size in micrometers (µm), ranging from 0.5 to 20. The y-axis represents the frequency (W/W%) ranging from 0 to 40. The milling time is indicated on the right side of the graph, with values of 1, 2, 5, and 10 minutes.
Grinding - special cases

- Pyrite will oxidize soon: ground samples cannot be preserved for longer times
- Gypsum may dehydrate partially to bassanite
- If dissolution-recrystallization possible (halite, gypsum etc.) better to use hexane
Orientation

• Problem of platy particles (layer silicates, gypsum, feldspars) present in the sample as individual grains
• Very strong effect on relative intensities
• Partial remedy: screening+side-loading
• Perfect remedy: spray-drying
Orientation Test: Kaolinite + Quartz

![Graph showing intensity vs. weight % Kaolinite with three different markers for Kaolinite 001, 020, and 060.](image-url)
= Pure Chlorite Ground in Hexane
= Chlorite 40%, Qtz 40%, ZnO 20%
Sample density

- Sample density controls the depth of penetration of X rays, i.e. the degree of departure from ideal focussing geometry
- Result: sample density affects peak shape and position
- Partial remedy: standardize sample prep. as much as possible
Reproducibility of XRD pattern

RC-AR1a-pe/ Reynolds Cup Artificial Rock 1a/ 3g-hex-5min/ 1
Reproducibility of XRD pattern

RC-AR2a-pe/ Reynolds Cup Artificial Rock 2a/ 3g-hex-5min/ 1
Reproducibility Test: 5 splits from same shale sample
Spray-dried clay: photo of S. Hillier
Spray-dried clay: photo of S. Hillier
Spray-dried clay: photo of S. Hillier
Spray-dried vs. side-loaded artificial rock
Spray-dried vs. side-loaded albite
XRD pattern recording

- 2Θ range which includes diagnostic peaks for all mineral components
- Sufficiently fine recording step to reproduce peak profiles well
- Sufficient recording time to assure high intensities and small counting error
- Maximum slits assuring pure quartz 3.34Å peak intensity within the linear range of the counter
- Possibly high peak/background ratio
- Our solution: 2-65°2Θ, step 0.02°/2min (105 min/sample), THERMO X’TRA with solid-state detector, slits: 0.9/1.6/1.6/0.3 receiving
Wt.% of mineral $X$ ($\%X$) in a mixture $m$ is proportional to the intensity of a reflection of mineral $X$ ($I_x$)

$$\% X = \frac{I_x \mu_m^*}{K_x}$$

Standard: $\% X = \frac{I_x \mu_m^*}{K_x}$

Spike: $\% S = \frac{I_S \mu_m^*}{K_S}$

$\mu_m^*$ = mass absorption coefficient of the mixture
$K_x$ = constant for a chosen reflection of mineral $X$
$I_x$ = intensity of a chosen reflection of mineral $X$
$\% S$ = Wt.% of an internal standard (spike)

$$MIF = \frac{K_x}{K_S} = \frac{I_x \cdot \% S}{I_S \cdot \% X}$$

$MIF_x$ ($= RIR_x$) does not depend on: Recording conditions, $\mu_m^*$ of mixture, or the type and content of other phases in the mixture.
Therefore:

\[ \%X = \frac{(I_X \cdot M_S \cdot 100)}{(I_S \cdot \text{MIF} \cdot M)} \]

\(M_s\) = mass of internal standard (spike)
\(M\) = mass of investigated sample
\(I_X\) = intensity of mineral X reflection used in MIF
\(I_S\) = intensity of internal standard (spike) reflection used in MIF
\(\%X\) = percent of mineral X in mass M (in investigated sample)
Non-Rietveld quantitative analysis of the XRD pattern: practice

- Recording standards and measuring MIFs
- Precise mineral identification
- Selections of standards appropriate for the identified minerals
- Measurement of peak intensities used by MIFs
- Calculation of mineral composition of the sample
- Verification of the result