



TOPAS

Quantitative phase analysis of phases with Partial Or No Known Crystal Structure: **PONKCS**



PONKCS (Scarlett & Madsen, 2006) is a method that relies upon the replacement of the traditional crystal structure in the Rietveld model with a set of peaks that may be scaled as a single entity. As a consequence, materials with partial or no known crystal structure can now be quantified with the same accuracy and precision as crystalline phases in a classical Rietveld analysis.

Together with TOPAS's superb modelling of anisotropic line broadening, PONKCS opens the door to accurate quantitative analysis of many industrially significant phases in the context of materials science and mineral processing.

Accurate quantitative phase analysis of

- Phases with no known crystal structure
- Phases with partially known structure
- Disordered materials
- Amorphous materials
- ...

Industrial application areas of PONKCS:

- Minerals and mining industry: Clay analysis
- Pharmaceutical industry: Amorphous materials and new polymorphs
- Cement industry: Slag additions and control of Gypsum dehydration
- ...

PONKCS

Example 1: Disordered materials

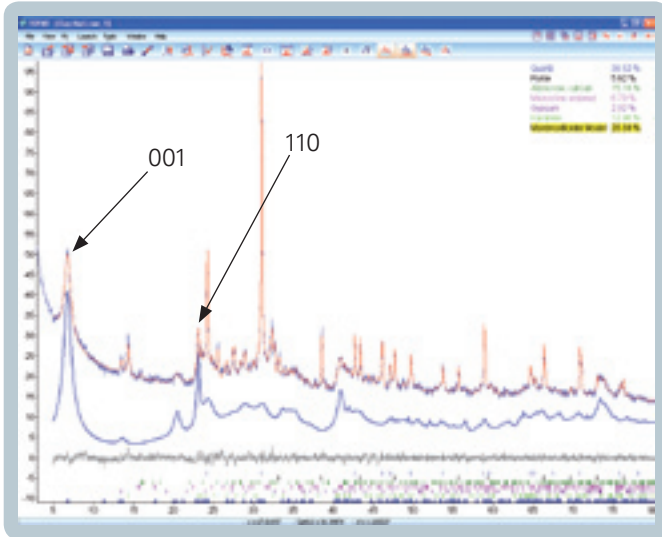


Figure 1: Composite from an andesite unit with argillic alteration. Note the extreme anisotropic line broadening of the Montmorillonite 001 and 110 reflections. Data in squareroot intensity representation to highlight details. Courtesy of M. Raudsepp, Vancouver, CA.

The PONKCS method is particularly suited for the quantification of materials with partially known crystal structures, such as disordered materials. Critical to its success is TOPAS's superb anisotropic line broadening modelling capabilities. TOPAS and PONKCS now enable XRD based quantitative analysis in mineral processing environments by non-specialists, something previously considered beyond reach. Typical applications include

- acid leaching processes
- ore flotation processes
- prediction / control of the acid neutralization / producing potential
- environmental mineralogy - CO₂ sequestration

Example 2: Unknown polymorphs

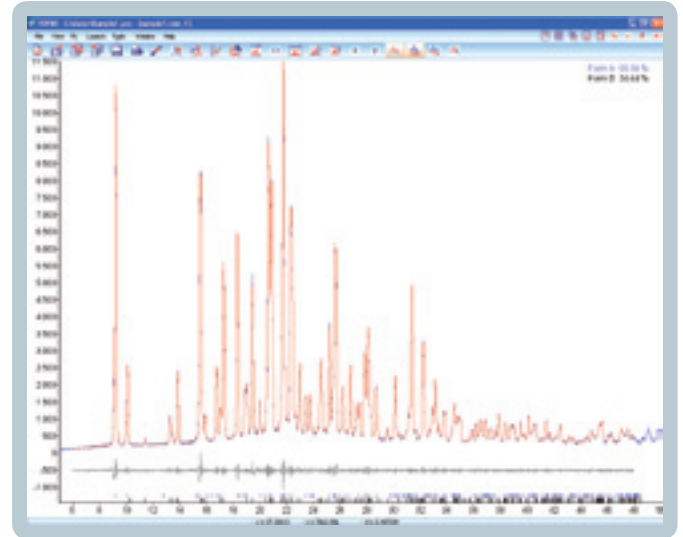


Figure 2: Quantitative analysis of 2 polymorphs of an undisclosed pharmaceutical compound. The crystal structure of Form B is unknown.

The decisive advantage of PONKCS is the capability to quantify individual phases within a mixture, of which the crystal structure is completely unknown. This explicitly includes phases, which cannot be indexed, thanks to the possibility to use single line fitting and to scale independent peak intensities as a group. The typical accuracy obtained of such quantification results is ~1% absolute. There is no necessity for time consuming spiking with an internal standard, and therefore no sample pollution.



Example 3: Amorphous phase amounts

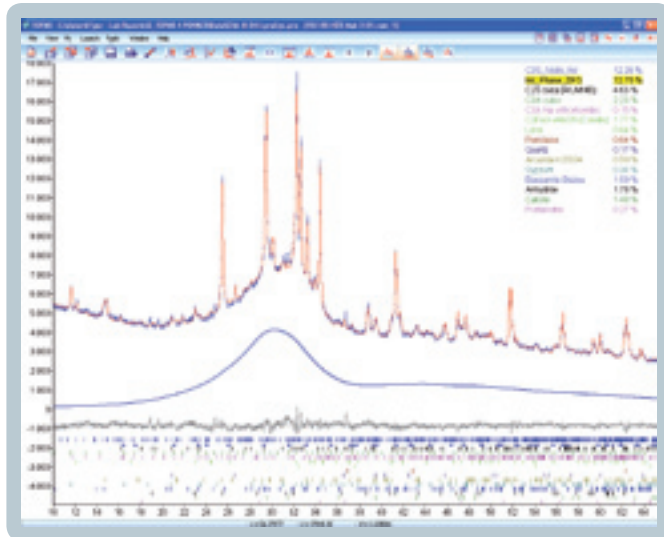


Figure 3: Blast furnace slag cement (CEM-III), the amorphous compound is shown by the bold blue line.

PONKCS can be applied to the quantification of amorphous phase amounts, here blast furnace slag in a CEM-III type cement. The blast furnace slag model has been obtained from measured intensities obtained from the pure material. The accuracy of the blast furnace slag determination is known to be significantly better than 1% absolute. This surpasses the accuracy obtainable by any method outlined in DIN ENV 196-4 und DIN 1164-1.

Example 4: Incorrect crystal structures: C3S

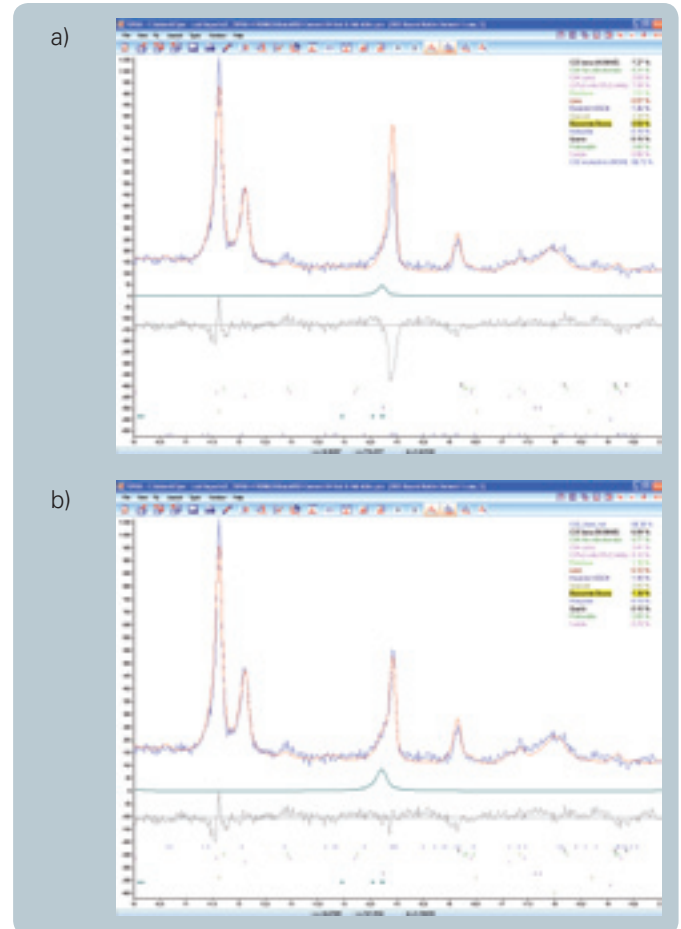
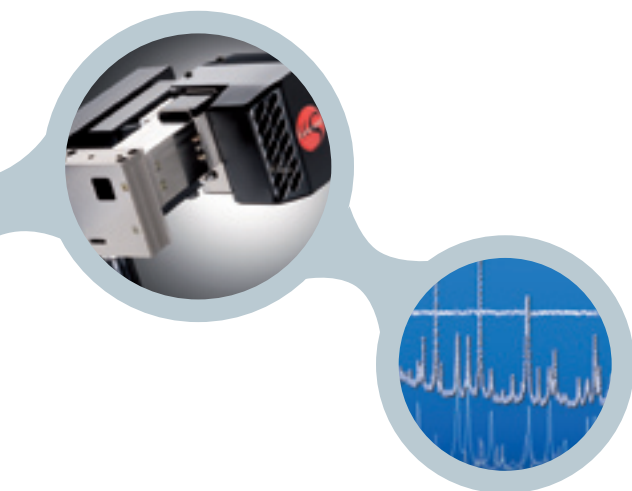


Figure 4: Quantitative analysis of cement, the main bassanite peak is shown by the bold cyan line.

a) Classic Rietveld refinement using the Nishi & Takeuchi (1985) C3S structure. b) PONKCS refinement. In a classic Rietveld refinement bassanite is underdetermined as the calculated intensity for the overlapping C3S peak is too high. With PONKCS the bassanite quantity is correctly obtained.

Monitoring the gypsum to bassanite dehydration in cement mill operation is critical for product quality control and cost-effective milling. With classic Rietveld analysis, the accurate quantification of bassanite is unreliable due to the overlap of the main bassanite with C3S peaks. As the pattern of C3S is not adequately described due to deficiencies in the typically used Nishi & Takeuchi (1985) C3S structure model, the Bassanite quantification is adversely affected. This issue is completely solved by adjusting the C3S reflections using the PONKCS method. The perfect description of the C3S intensities now allows to reliably quantify the bassanite abundance with an impressive accuracy of 0.2% absolute. This not only ensures high product quality, but also allows significant electrical energy savings >>100.000 EUR per year due to optimized milling operation.



PONKCS?

Classically, quantitative phase analysis via the Rietveld method is generally restricted to crystalline phases with well known crystal structure. Unidentified, structurally uncharacterised, and amorphous materials may be quantified as a single group, by spiking the mixture with an internal standard. This, however, can only give the total abundance of all compounds without known crystal structure - individual phase amounts are not accessible.

The TOPAS implementation of PONKCS represents an extremely successful solution to this problem:

For phases with well known crystal structure a conventional Rietveld analysis approach can be applied, where peak intensities are generated from the structure factors.

For phases where complete structural information is incomplete or unavailable, TOPAS allows substituting of the structure factors of a phase by values derived from measurement of its peak intensities. There are 2 cases:

1) Partial crystal structure information available:

With a space group (guess) and lattice parameters „empirical structure factors“ can be obtained for a phase from measured intensities (Pawley or Le Bail fitting).

For a phase with a structure deviating to some extent from published data (e.g. disordered materials), the optimization can be limited to selected individual peaks only, with the remaining structure factors kept as calculated from the published structure.

2) No crystal structure information available:

In this case, a phase can be represented by a set of peak intensities obtained from single line fitting, that can be scaled as a group.

In both cases, quantification relies on an appropriate calibration factor for each phase, „ZMV“¹, which can be readily derived from a mixture with an internal standard, a process which only needs to be performed once for a given phase. The result is a structure factor file, which can be stored in a database along traditional crystal structure data and can be used in any refinement in place of crystal structure data.

¹ „ZM“ = the mass and „V“ = the volume of the unit cell

References:

Nishi, F. & Takeuchi, Y. (1985): „Tricalcium silicate Ca₃O[SiO₄]: The monoclinic superstructure.“ - Z. Krist., 172, 297-314.

Scarlett, N.V.Y. & Madsen, I.C. (2006): „Quantification of phases with partial or no known crystal structure.“ Powder Diffraction, 21(4), 278-284.

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