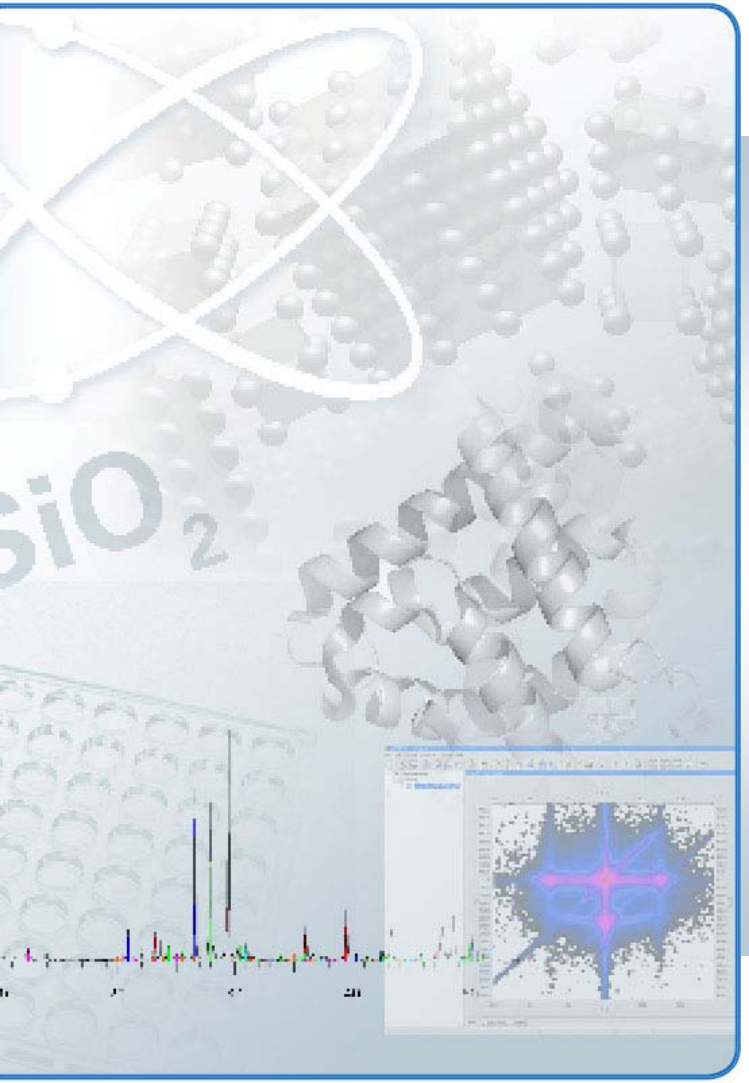


PONKCS

a method for the quantification of phases with **P**artial **O**r **N**o **K**nown **C**rystal **S**tructures

Bruker AXS, Karlsruhe, Germany

This document was presented at PPXRD - Pharmaceutical Powder X-ray Diffraction Symposium

Sponsored by The International Centre for Diffraction Data

This presentation is provided by the International Centre for Diffraction Data in cooperation with the authors and presenters of the PPXRD symposia for the express purpose of educating the scientific community.

All copyrights for the presentation are retained by the original authors.

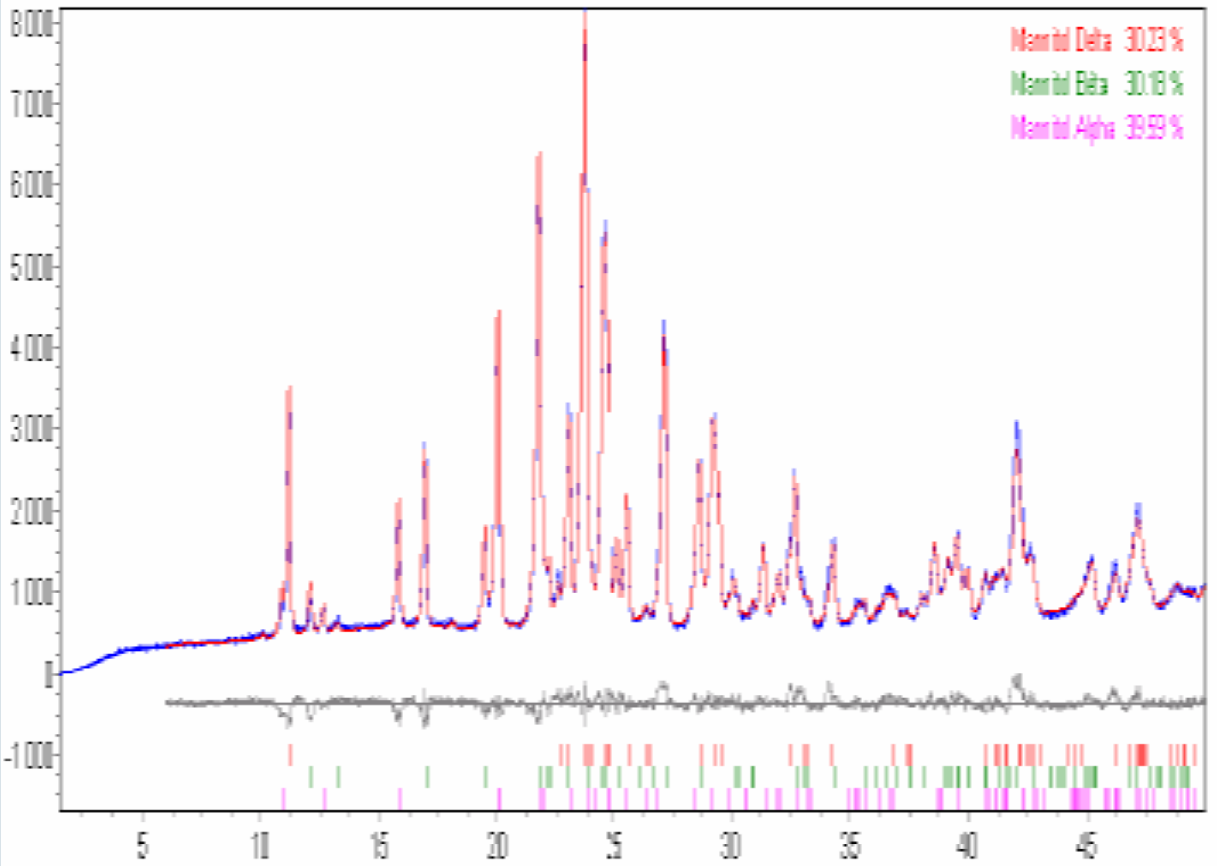
The ICDD has received permission from the authors to post this material on our website and make the material available for viewing. Usage is restricted for the purposes of education and scientific research.

PPXRD Website – www.icdd.com/ppxrd

ICDD Website - www.icdd.com

Classic Rietveld method

Quantification of Mannitol polymorphs



Courtesy of Dr. Clénet, Sanofi-Aventis

Classic Rietveld method

IF

- All phases in the mixture are known
- All phases are crystalline
- All crystal structures are known

THEN

- ‘ZMV algorithm’ [1] can be used to relate the Rietveld scale factor to the phase concentration

(1) Hill R.J. and Howard C.J. (1987) J. Appl. Crys. Vol 20, 467-474.

Classic Rietveld method

ZMV calibration constant

$$W_\alpha = \frac{S_\alpha (ZMV)_\alpha}{\sum_{k=1}^{n} S_k (ZMV)_k}$$

W = weight %
S = Rietveld scale factor
Z = No. of formula units in unit cell
M = molecular mass of formula unit
V = unit cell volume

- ZMV is a calibration constant which eliminates the need to measure:
  - instrument calibration constant
  - sample mass absorption
- If the crystal structure of a phase is not known, then the ZMV calibration constant is unknown

Classic Rietveld method

internal standard

A possible solution is to add an **internal standard** (spiking)

However, if there is more than one phase with an unknown or only partially known structure, these phases will be considered as a single group = **no information about the individual phases**

Quantification of phases with Partial Or No Crystal Structures (PONKCS)

An **individual** unknown or partially unknown crystalline phase can be quantified through PONKCS method, if:

- the phase is available as pure specimen
(or major phase in specimen → known impurities that can be quantified with the internal standard method)
- a synthetic mixture can be prepared in which the amounts of unknown and an internal standard are known
- the unknown phase in the ‚experimental‘ mixture does not vary too much from the pure specimen, used to derive the intensities

PONKCS method

- Crystalline (and even amorphous) phases can be fitted through:
  - **(hkl) phase** if the phase can be indexed (Pawley/Le Bail fit)
  - **peak phase** if the phase cannot be indexed

→ Result: list of peaks described by peak position and intensity

- This replaces structure information in Rietveld refinement
  - peak position and intensity **fixed**
  - group of peaks scaled as a single entity within Rietveld refinement

- ZMV constant is unknown and has to be provided through calibration

PONKCS method

- Calibration through the preparation of a mixture containing **known** amounts of unknown (α) and standard material (s)

$$\frac{W_\alpha}{W_s} = \frac{S_\alpha \left(ZMV\right)_\alpha}{S_s \left(ZMV\right)_s}$$

or

$$\left(ZMV\right)_\alpha = \frac{W_\alpha}{W_s} \cdot \frac{S_s}{S_\alpha} \cdot \left(ZMV\right)_s$$

all known

- $(ZMV)_\alpha$ has **NO** physical meaning

PONKCS method

TOPAS input file

```
xo_Is
phase_name Fluorite_pks
MVW( 394.583, 1.0000, 52.404 )
CS_L(csflu,     260.92396)
peak_type       fp
scale @ 0.9927054493

      xo        !pos1     28.27558263
      I         !int1     265.680902
      xo        !pos2     32.76196554
      I         !int2     1.270499308
      xo        !pos3     42.23070081
      I         !int3     1.017909015
      xo        !pos4     47.00863
      I         !int4     912.6184579
      etc
```

ZMV, through calibration

Refinable scale factor

Fixed intensities and positions, from fitting the pure ‚unknown' phase

PONKCS method

- Allows the quantification of compounds, where the classic Rietveld method fails.
  Amorphous phases, disordered phases, or phases with unknown crystal structures can be quantified with the same accuracy and precision as crystalline phases

- Important application areas:
  Quantification of
  - Phases with unknown structure, e.g. new polymorphs
  - Phases with partially known structure, e.g. C3S (!)
  - Disordered materials, e.g. clay minerals
  - Amorphous materials

PONKCS method

Quantification of phases with partial or no known crystal structures

Nicola V. Y. Scarlett and Ian C. Madsen
CSIRO Minerals, Box 312, Clayton South, Victoria, 3169, Australia

(Received 6 June 2006; accepted 18 September 2006)

Quantification of mixtures via the Rietveld method is generally restricted to crystalline phases for which structures are well known. Phases that have not been identified or fully characterized may be easily quantified as a group, along with any amorphous material in the sample, by the addition of an internal standard to the mixture. However, quantification of individual phases that have only partial or unknown structures is carried out less routinely. This paper presents methodology for quantification of such phases. It outlines the procedure for calibration of the method and gives detailed examples from both synthetic and mineralogical systems. While the method should, in principle, be generally applicable, its implementation in the TOPAS program from Bruker AXS is demonstrated here. © *2006 International Centre for Diffraction Data.* [DOI: 10.1154/1.2362855]

Key words: powder diffraction, Rietveld, quantitative phase analysis

I. INTRODUCTION

The Rietveld method (Rietveld, 1969) is one of the most commonly used means for the quantification of powdered mixtures using diffraction data (Madsen *et al.*, 2001). It has the ability to deal with a wide range of sample-related effects through use of the diffraction pattern as a whole. Nevertheless, in its simplest form it is reliant upon all phases within a given mixture being crystalline and their crystal structures being known. The so-called "*ZMV* algorithm" (Hill and Howard, 1987), used to relate the Rietveld scale factor to concentration, calculates relative, rather than absolute, phase abundances based upon a model constructed from the crystal structures of component phases. Any phases, crystalline or amorphous, that are not included in the model will not be considered in this calculation. However, the method will always return the sum of analysed phases as 100% regardless of the presence of nonanalysed phases. In many naturally occurring or synthetic systems, poorly ordered phases may be present that are not accurately modeled by published structure information. The addition of a known amount of an internal standard material allows the quantification of any material in the mixture that has not been included in the model, i.e., any amorphous material and/or phases that are unidentified or of unknown or only partially known crystal structure. Such a method of quantification considers these phases as a group and makes no distinction between them. This means that, for example, a clearly crystalline but uncharacterized phase will be included in the "amorphous/unknown" analysis.

There are a number of distinct possibilities for the modeling of phases present in natural and process materials. They include the following:

(1) *Complete structure information available*. In this case a conventional Rietveld analysis approach can be applied. The peak positions are defined by the space group, unit cell dimensions, and wavelength used to collect the data. The peak intensities are generated from the structure factors and multiplicities for each reflection, which are modified by experimental effects such as Lorentz-polarisation factors and sample absorption.
(2) *Partial structure information available* (*space group and unit cell dimensions*). As above, the space group, unit cell dimensions, and wavelength are used to define the peak positions, but the lack of atom type and coordinates means that peak intensities cannot be calculated. In this case, empirical "structure factors" can be derived by measuring peak intensities from a diffraction pattern of the pure material (or at least a sample where the phase of interest is a major component). Such a group of peaks is defined in TOPAS (Bruker AXS, 2003) jargon (and hereafter in this paper) as an "*hkl* phase."
(3) *No structure information available*. In this case, the phase can be represented by a set of individual peaks that can be scaled as a group. The positions and relative intensities of the peaks can be derived by measuring peak intensities from a diffraction pattern of the pure material (or at least a sample where the phase of interest is a major component). Alternatively, the peaks can be derived from a database such as the Powder Diffraction File (PDF) (ICDD, 1999). This type of peak group is denoted by TOPAS and in this paper as a "peaks phase."

In all cases, quantification relies on the derivation of an appropriate calibration factor for each phase. For the case where full structure information is available, calibration can be derived from the mass (*ZM*) and volume (*V*) of the unit cell (Hill and Howard, 1987).

For the partial structure case, refinement of the unit cell dimensions provides a value for *V*, but a value for *ZM* needs to be derived by preparing a mixture of the phase of interest with a known, well characterised standard. In this case the *ZM* does not represent the true unit cell mass, but does relate the empirical "structure factors," derived from measured peak intensities, to the phase concentration.

For the no structure case, neither *ZM* nor *V* are available, so an empirical value for *ZMV* must be derived by preparing a mixture of the phase of interest with a known, well characterised standard. Once again, the *ZMV* does not have physical significance, but serves to relate the phase "scale factor" to the phase concentration.

This methodology may be used for the inclusion of a phase in a Rietveld model that (i) has a crystal structure that deviates to some extent from published data (e.g., clays), (ii)

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

Example*:

3-phase mixture

corundum

zincite

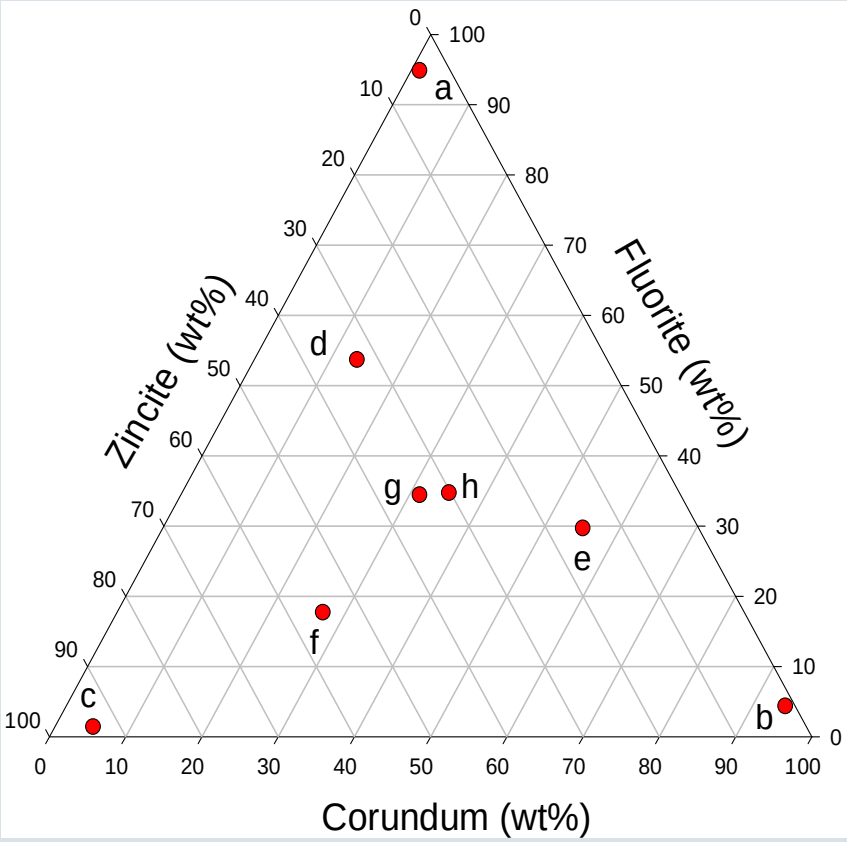
fluorite

* Nicola V.Y. Scarlett & Ian C. Madsen, CSIRO Minerals

PONKCS

3-phase mixture – round robin

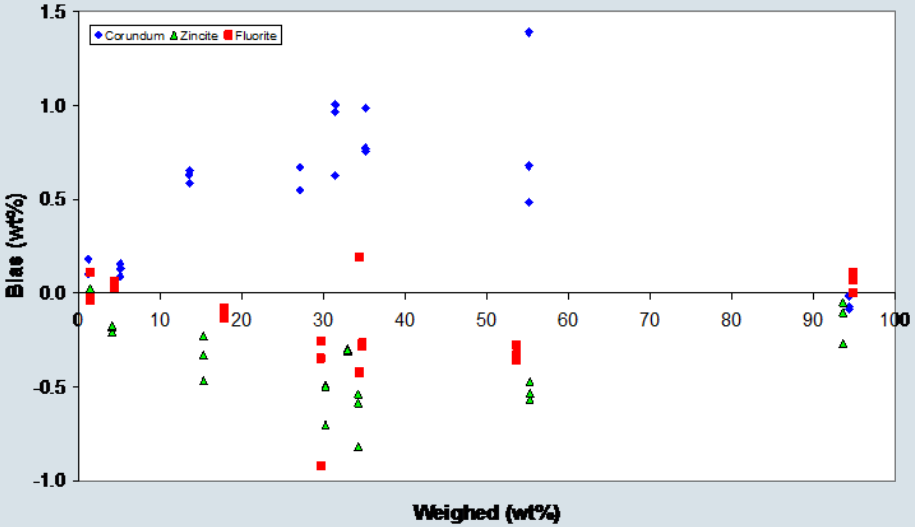
- IUCr CPD Round Robin on quantitative phase analysis
- Data available from: http://www.iucr.org/iucr-top/comm/cpd/QARR/index.html
- Madsen I.C., Scarlett N.V.Y., Cranswick L.M.D. and Lwin T. (2001) “Outcomes of the IUCR CPD Round Robin on Quantitative Phase Analysis: Samples 1a to 1h”, J.Appl. Cryst, 34, 409-426.
- For corundum, no crystal structure information was used



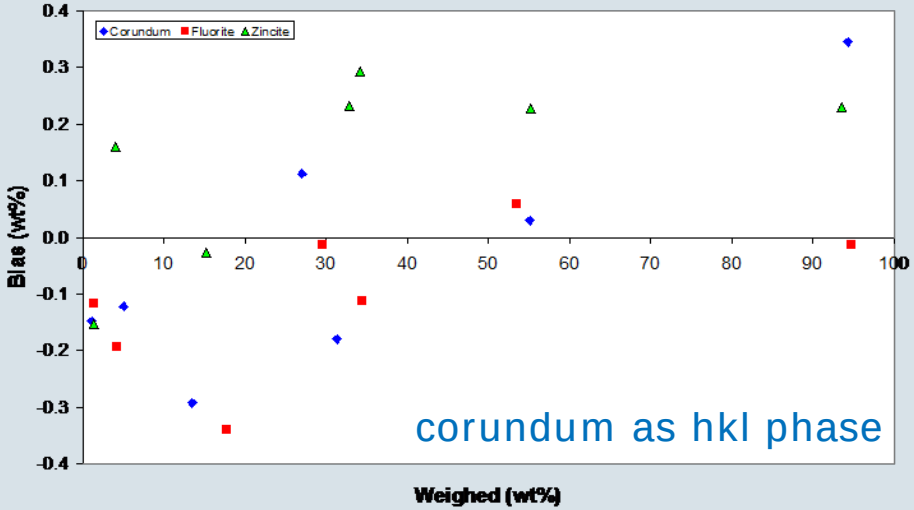
PONKCS

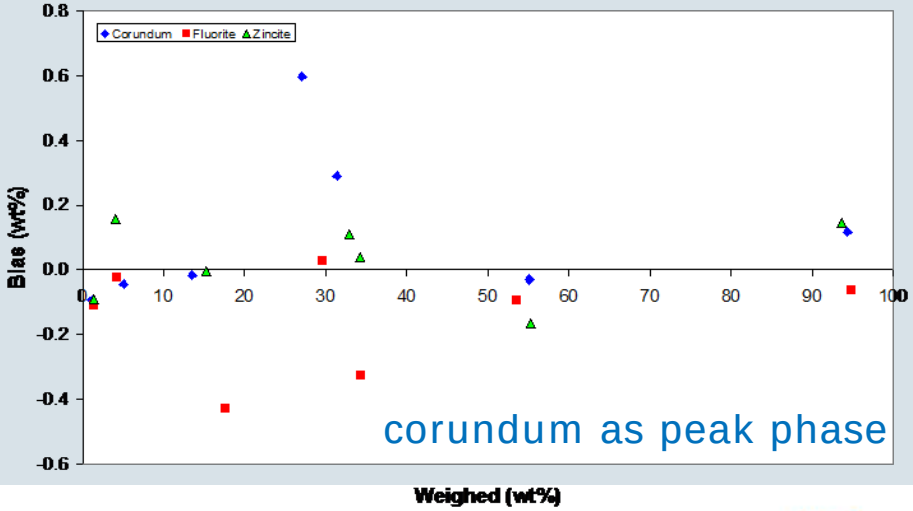
3-phase mixture – round robin

‚classic' Rietveld



PONKCS





Bias = difference between weighed and measured values

Example*:

Nontronite

Anisotropic line broadening

* Nicola V.Y. Scarlett & Ian C. Madsen, CSIRO Minerals

PONKCS

Nontronite

- Nontronite

  Component of nickel laterite

  Important source of nickel which substitutes for iron in its structure

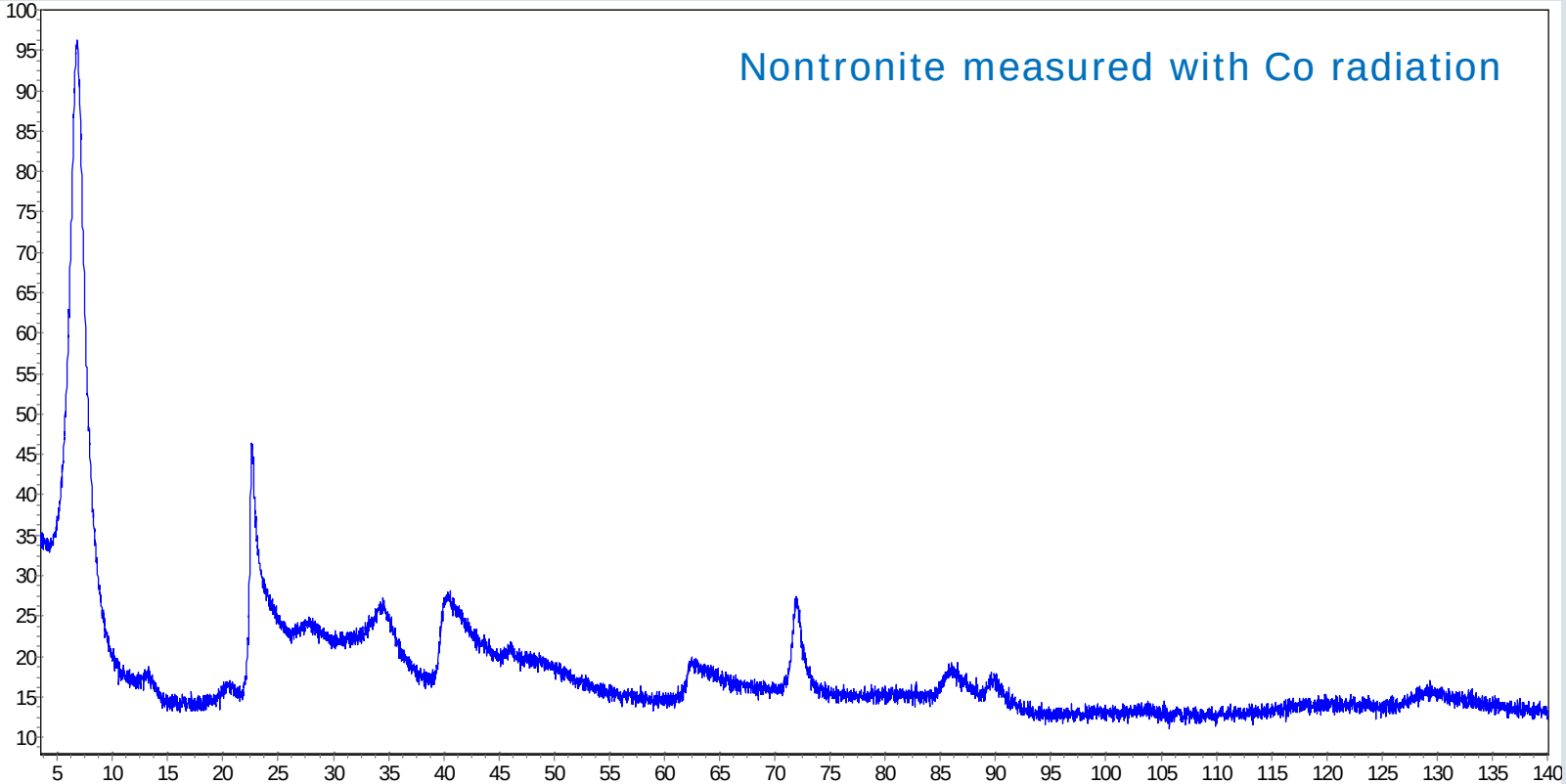
  $Na_{0.3}Fe_2(Si,Al)_4O_{10}(OH)_2.nH_2O$

  Smectite (swelling) clay

- Smectite (= paracrystalline mineral), exhibiting turbostratic stacking

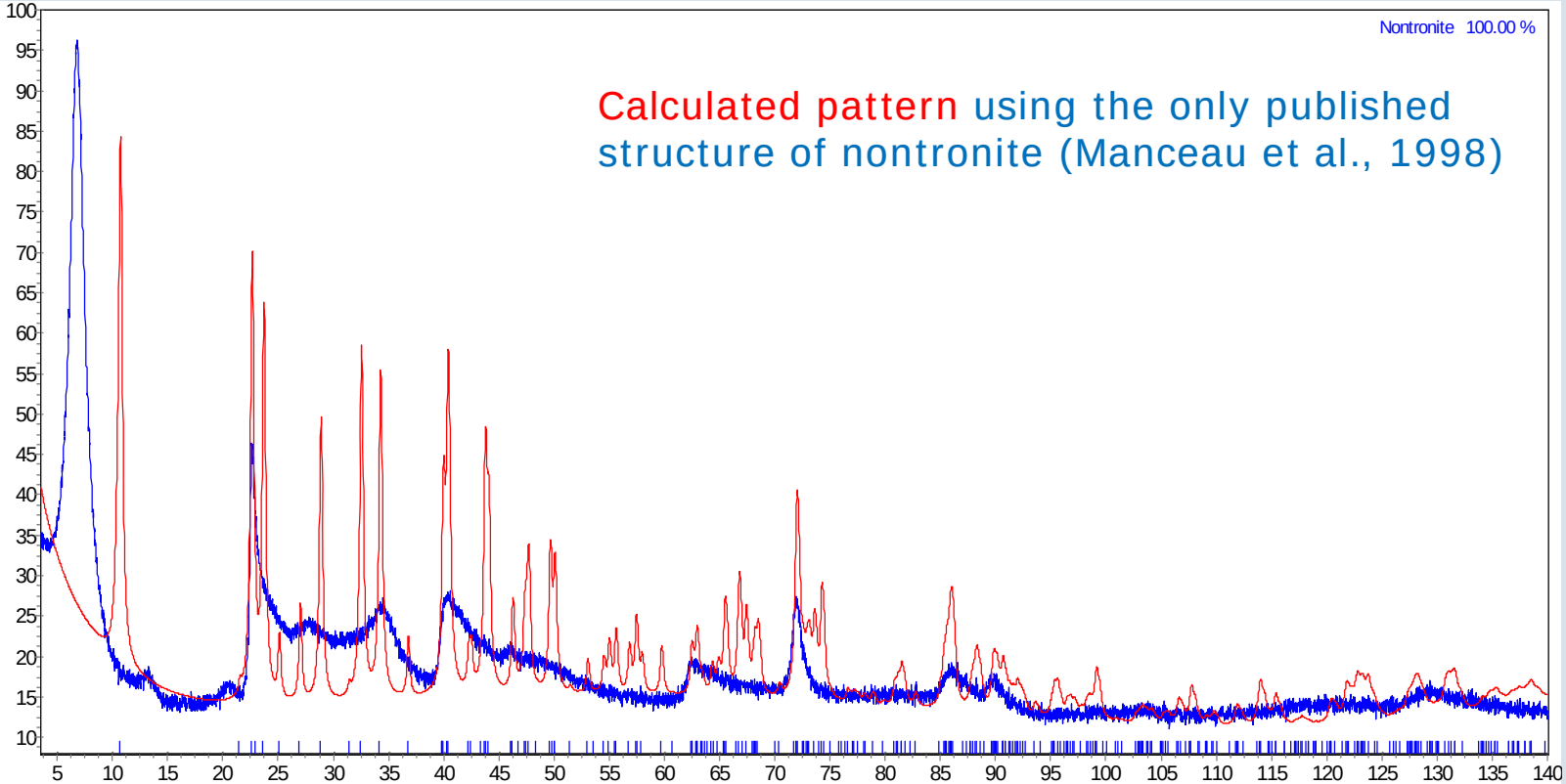
PONKCS

Nontronite



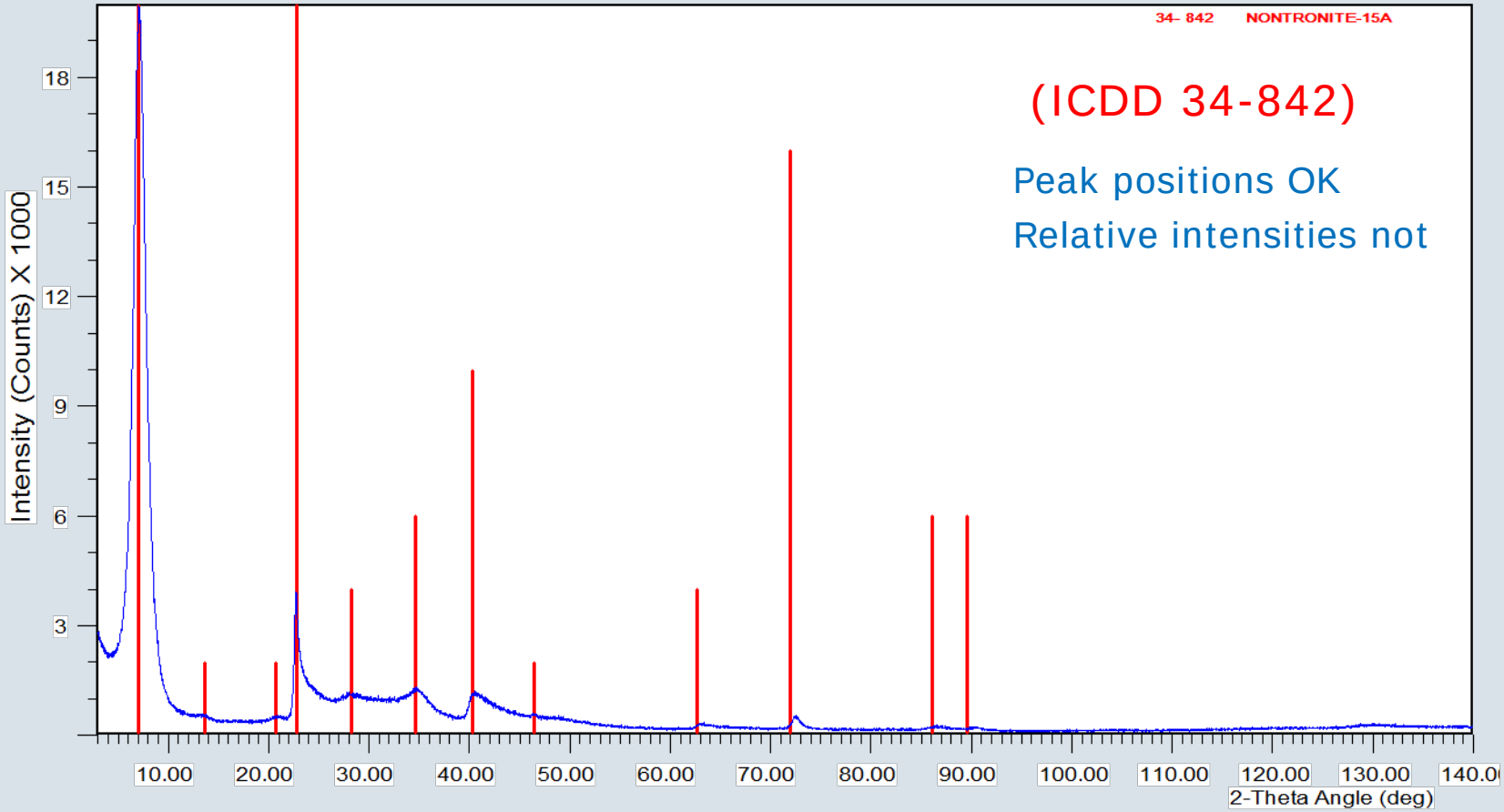
PONKCS

Nontronite



PONKCS

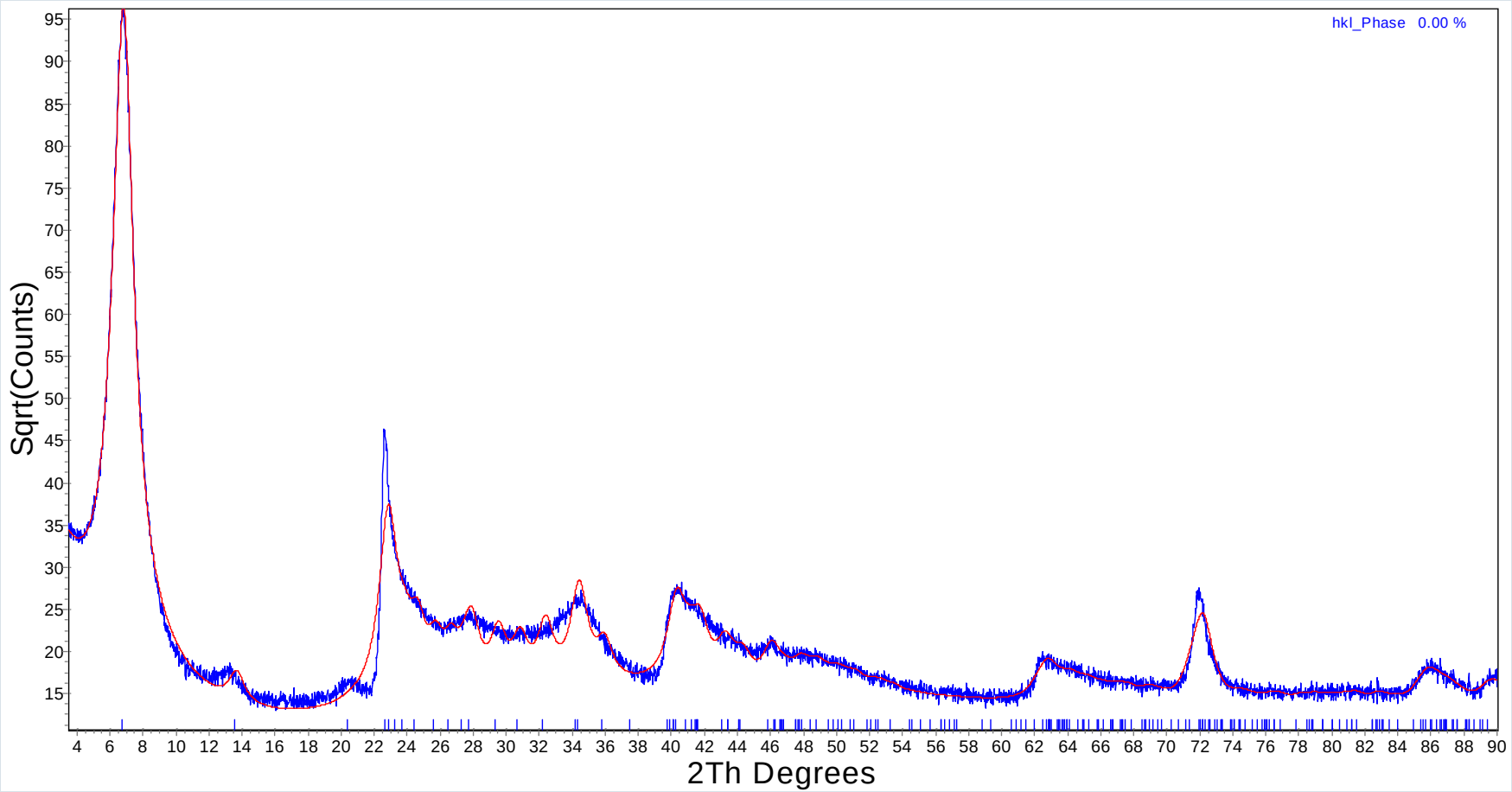
Nontronite



PONKCS

Nontronite

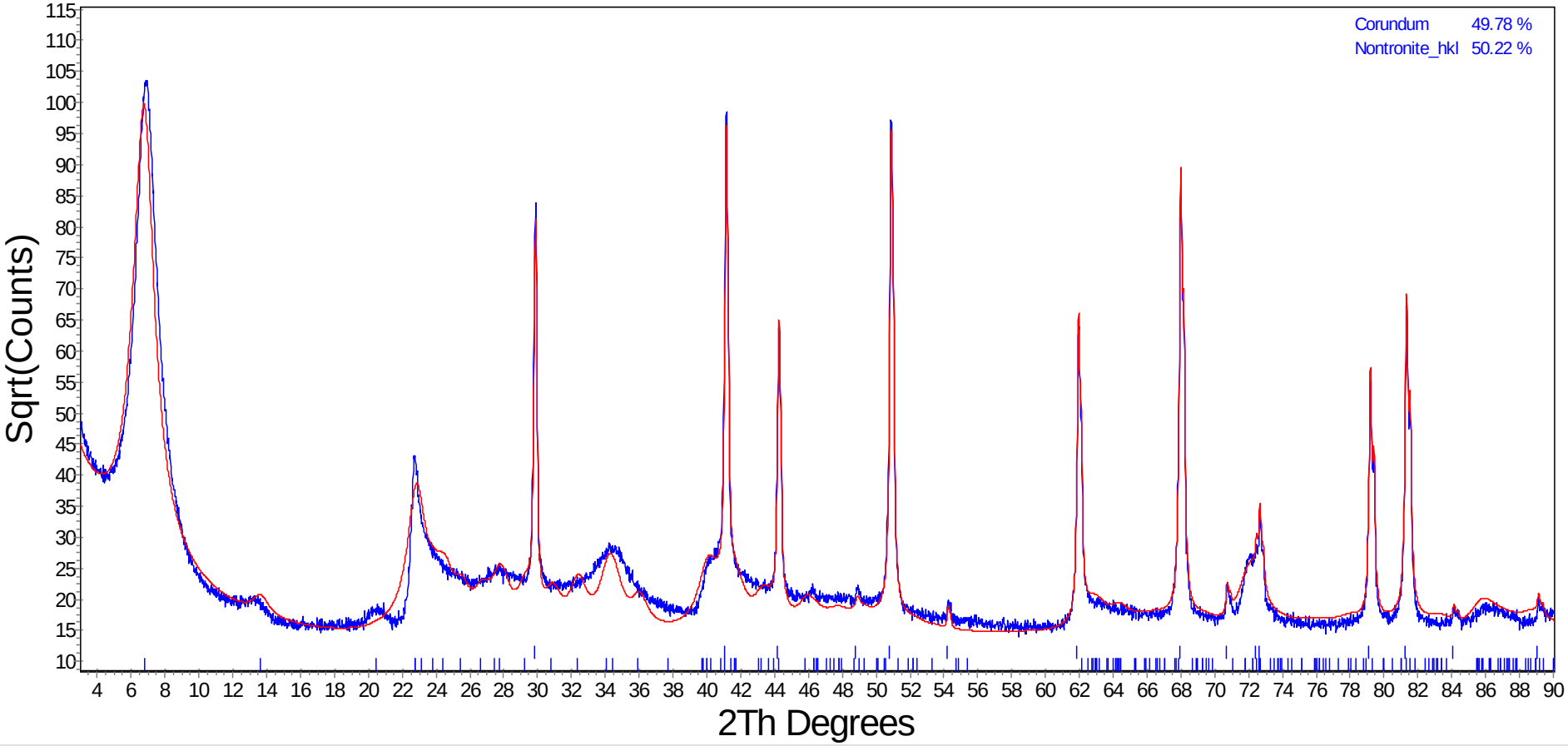
Pawley fit (isotropic) to get a list of peaks with relative intensities



PONKCS

Nontronite

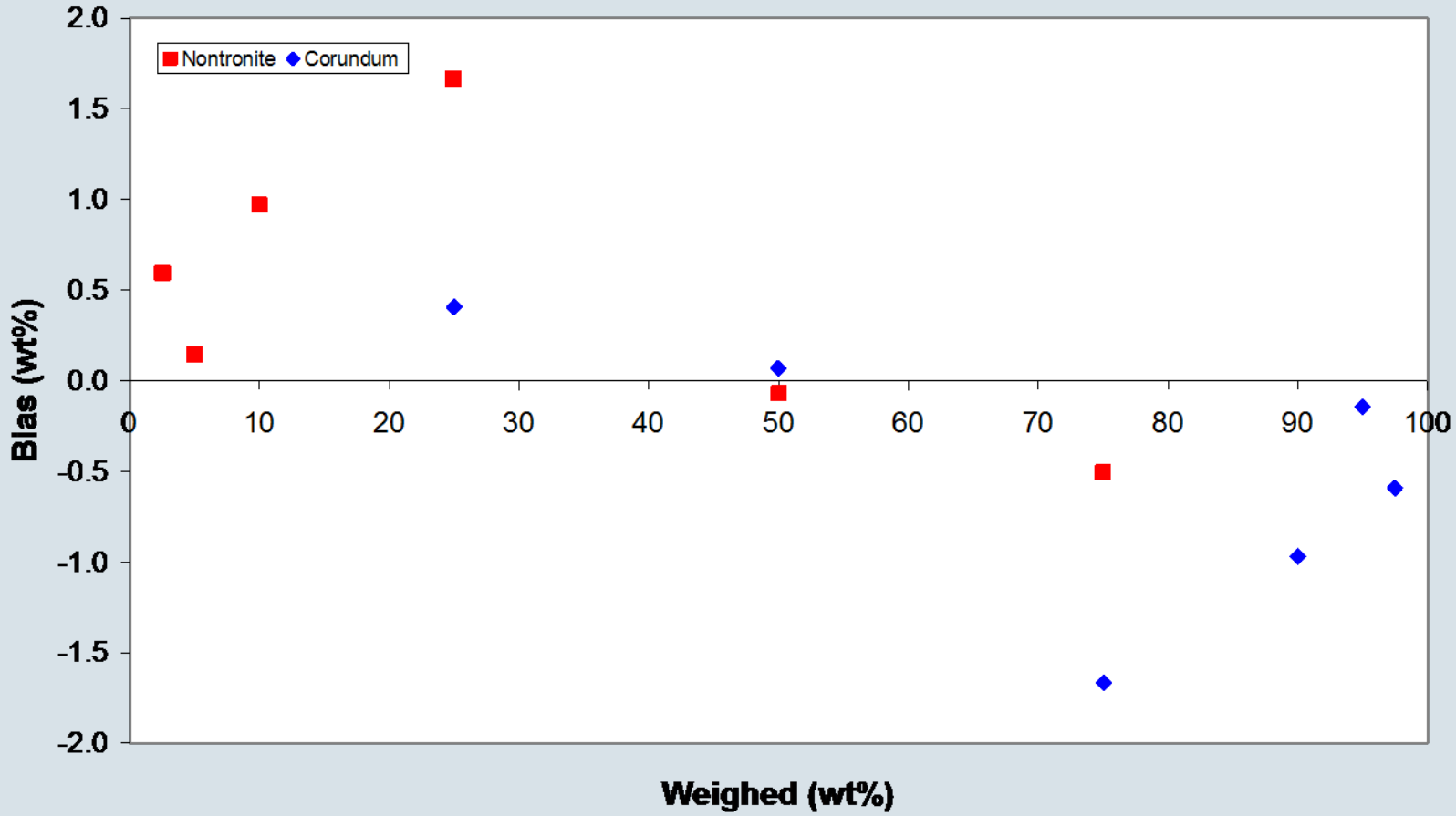
Mixture with corundum to determine calibration constant



PONKCS

Nontronite

The resultant phase model has been applied to a series of 6 mixtures of known composition



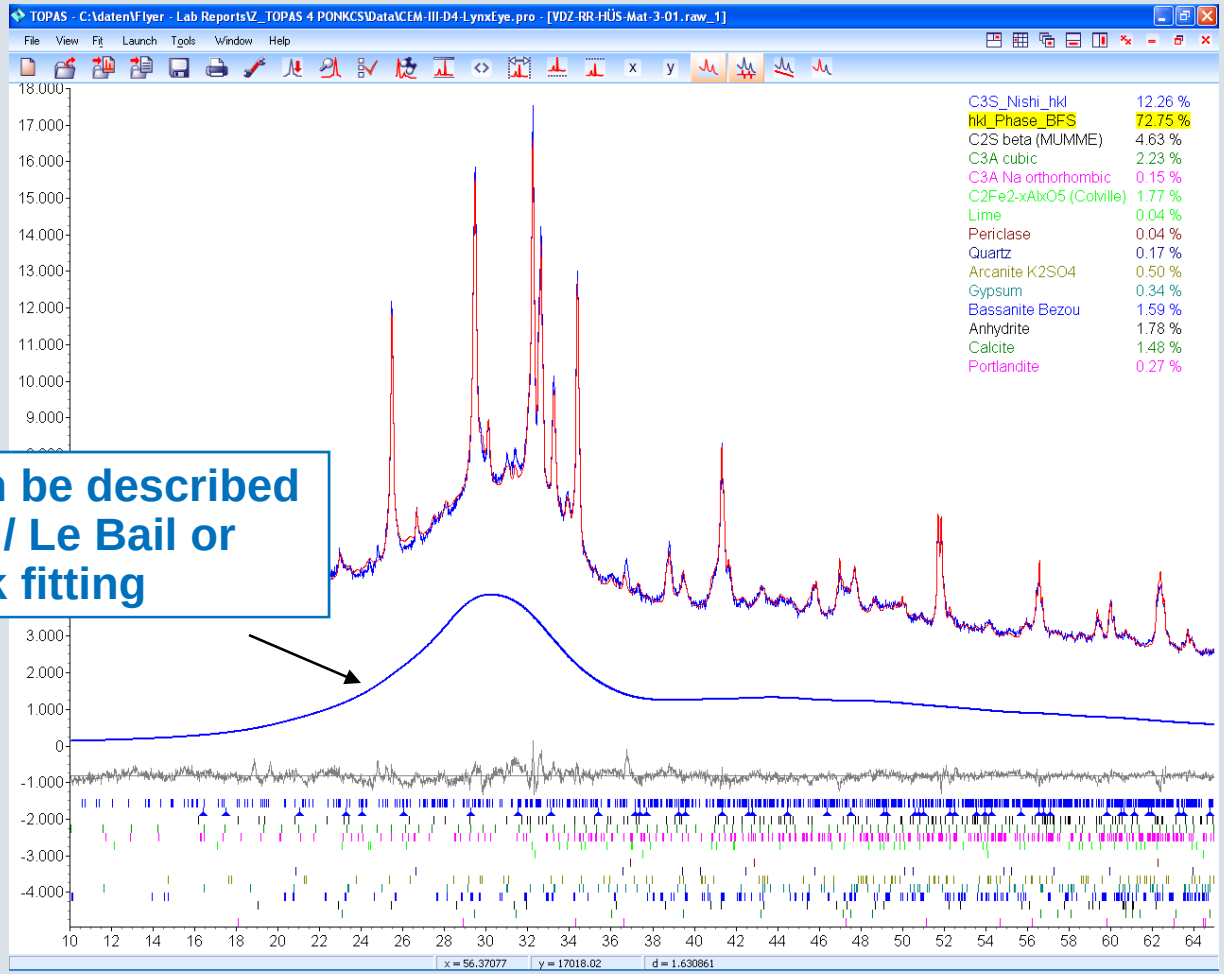
Example:

Slag in Cement

amorphous content

PONKCS

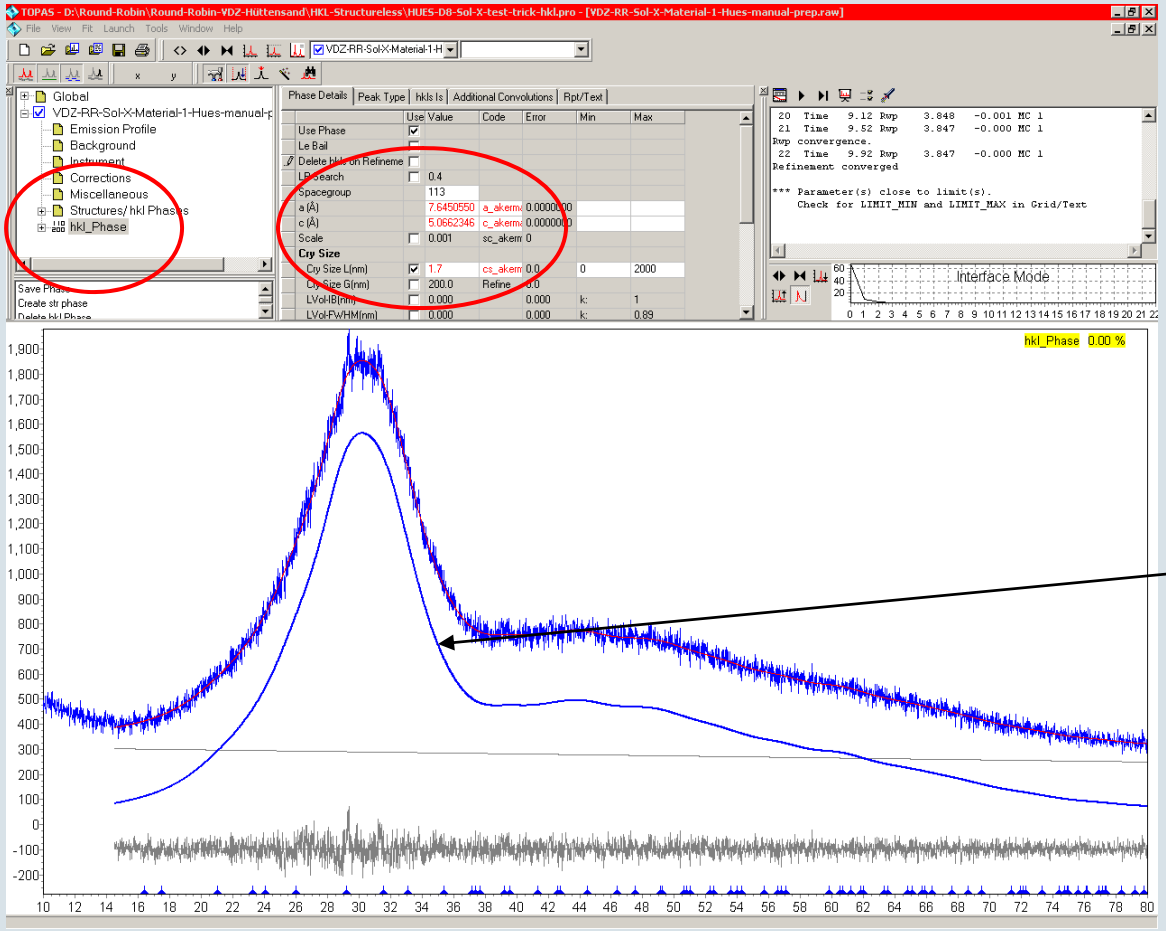
Quantitative Analysis of BFSlag



BFSlag can be described via Pawley / Le Bail or single peak fitting

PONKCS

Quantitative Analysis of BFSlag



E.g. Pawley fit strategy:

- Choose arbitrary space group and lattice parameters to allow for a couple of peaks
- Allow for extreme line broadening

Refined PONKCS model for BFSlag

Round Robin VDZ 2006/7

Quantitative Analysis of BFSlag

- Preliminary results

Vorläufige Ergebnisse

Material	Untersuchtes Merkmal	Mittel-wert	Vergleichs-σ	Wiederhol-σ	Ref.-Methode / Mischwert
Material 1 (CEM II/B-S)	XRD / Untergrund	24,61	1,91	1,49	25,15 / 25,00
	XRD / Spike	23,84	1,13	1,90	
	Sonstige	24,49	2,18	0,22	
Material 2 (CEM III/B 32,5 N-NW/HS/NA)	XRD / Untergrund	69,24	2,35	1,06	67,01
	XRD / Spike	(67,21)	(1,40)	(1,26)	
	Sonstige	69,33	2,13	0,19	
Material 3 (CEM III/B 42,5 N-NW/HS/NA)	XRD / Untergrund	74,26	4,15	0,99	72,03
	XRD / Spike	72,32	1,01	0,74	
	Sonstige	72,28	1,71	0,49	

Wiederhol-Standardabweichung: - bis 5 % (Untergrund-Methoden)
- bis 3 % (Spike-Methoden)

vdz.

PONKCS:
(5 repeated analyses)

25.1 (2)

67.2 (2)

71.7 (2)

Round Robin VDZ 2006/7

Quantitative Analysis of BFSlag

Accuracy and Precision (values in wt. %, SD in brackets/1σ)

- Every sample measured 5 times (D4 ENDEAVOR, LynxEye Detector)
- Reference values:
  - sample 1: 25,0 wt.%
  - sample 2: 67,0 wt.%
  - sample 3: 72,0 wt.%

	BFSlag Sample 1	BFSlag Sample 2	BFSlag Sample 3
Measurement 1	25,0	67,2	71,7
Measurement 2	25,1	67,3	71,9
Measurement 3	24,7	67,0	71,6
Measurement 4	25,1	67,3	71,9
Measurement 5	25,3	67,0	71,5
Mean	**25,1**	**67,2**	**71,7**
SD	**0,2**	**0,2**	**0,2**

Pharma example:

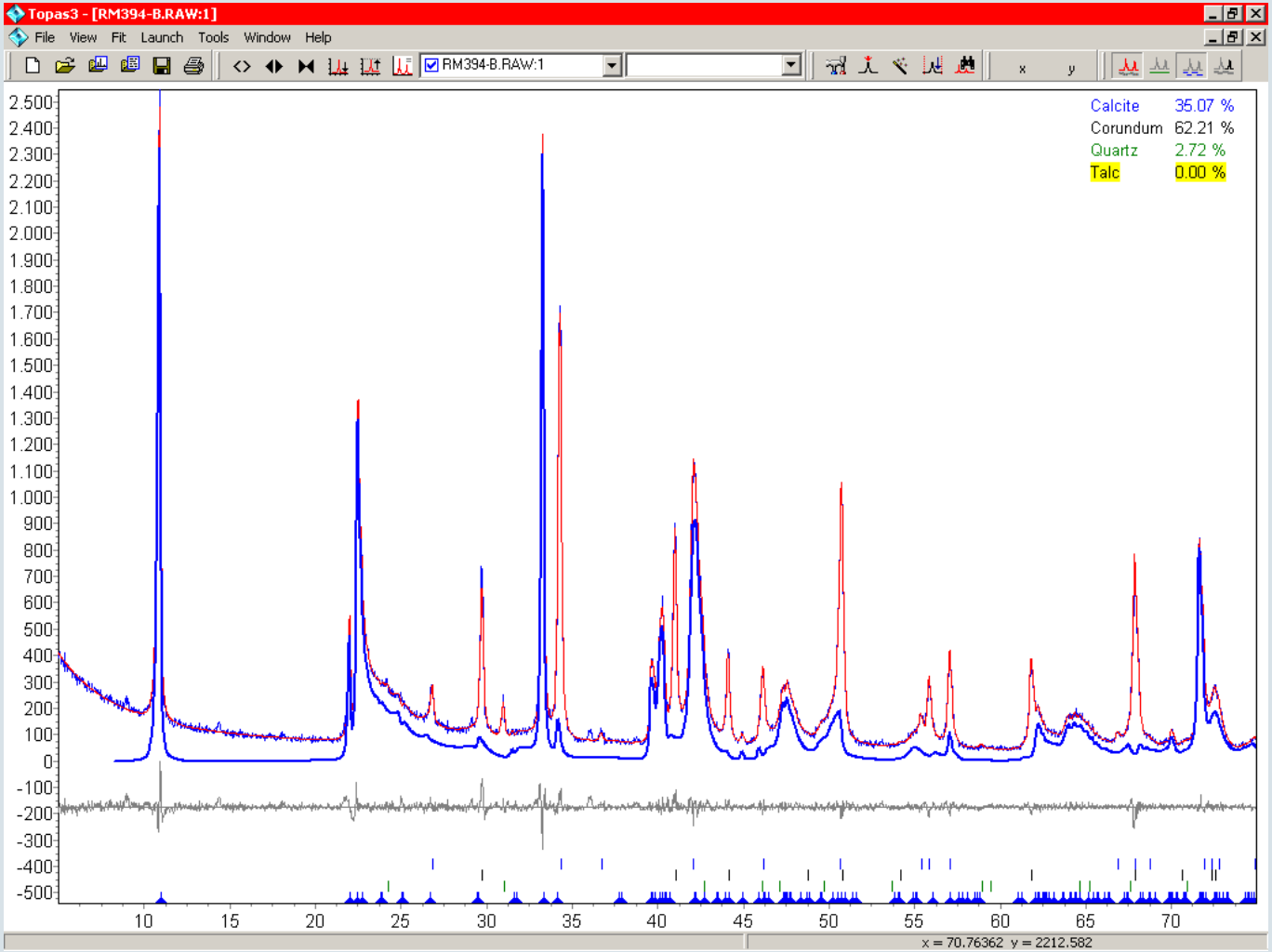
Isotibolone in tibolone

See poster:

„Quantitative phase analysis of isotibolone in tibolone raw material using the Scarlett-Madsen method“

Selma Gutierrez Antonio et al.

BRUKER

www.bruker-axs.com

Anisotropic line broadening