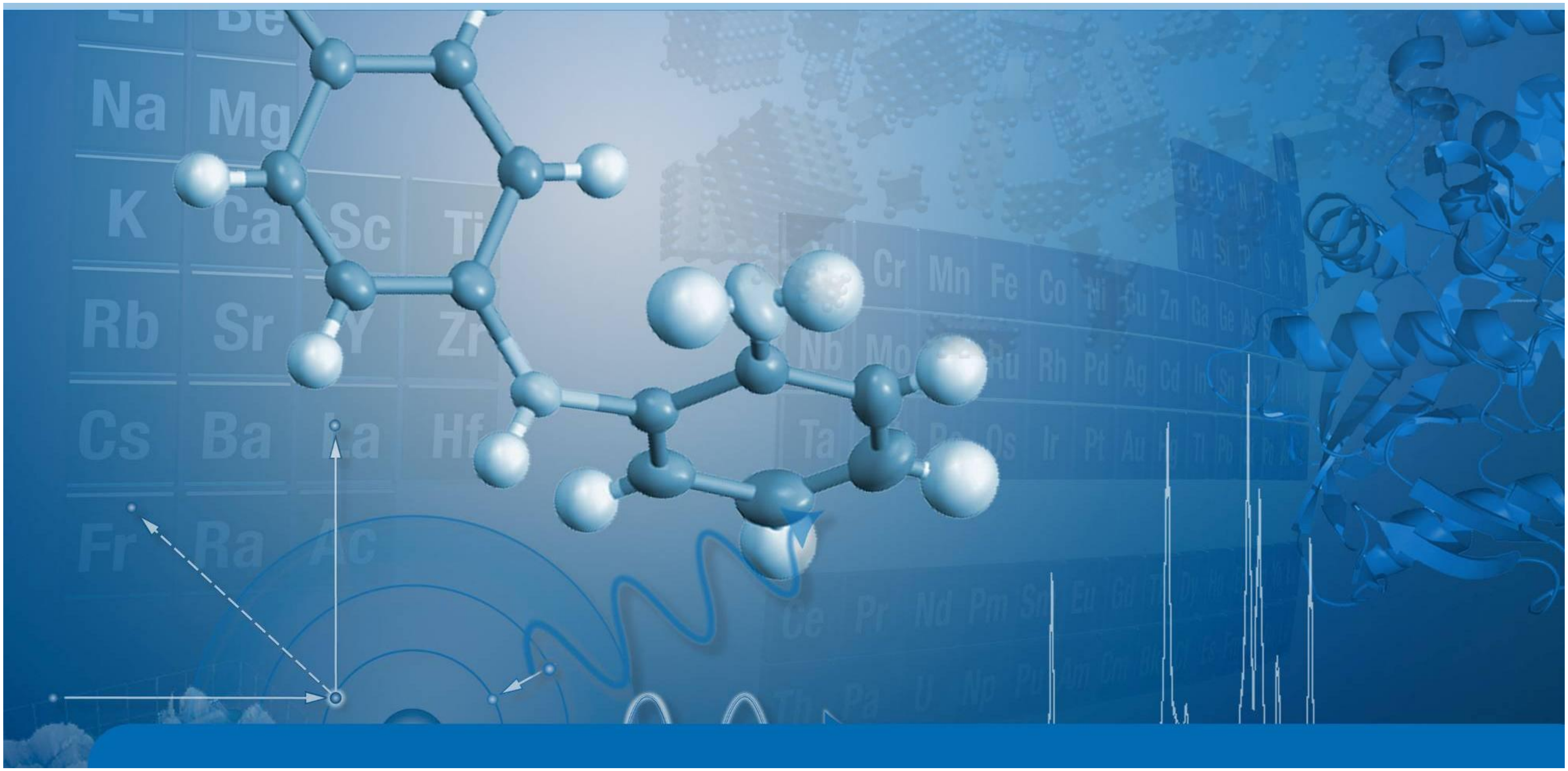
Quantifying Amorphous Phases

Kern, A., Madsen, I.C. and Scarlett, N.V.Y.



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

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Recent Papers

- Madsen, I.C., Scarlett, N.V.Y. and Kern, A. (2011)
  Description and survey of methodologies for the determination of amorphous content via X-ray powder diffraction.
  Z. Krist., 226, 944-955
- Kern, A., Madsen, I.C. and Scarlett, N.V.Y. (2012)
  Quantifying amorphous phases.
  Uniting Electron Crystallography and Powder Diffraction.
  Editors: Kolb, U., Shankland, K., Meshi, L., Avilov, A. & David, W.
  Springer. 434 pages. ISBN: 978-94-007-5585-7

Topics

- Introduction
- Selected Methods for Quantifying Amorphous Content
- Practical Assessment of Merits of Methods
- Summary

Introduction

Quantifying Amorphous Phases
Introduction

Motivation

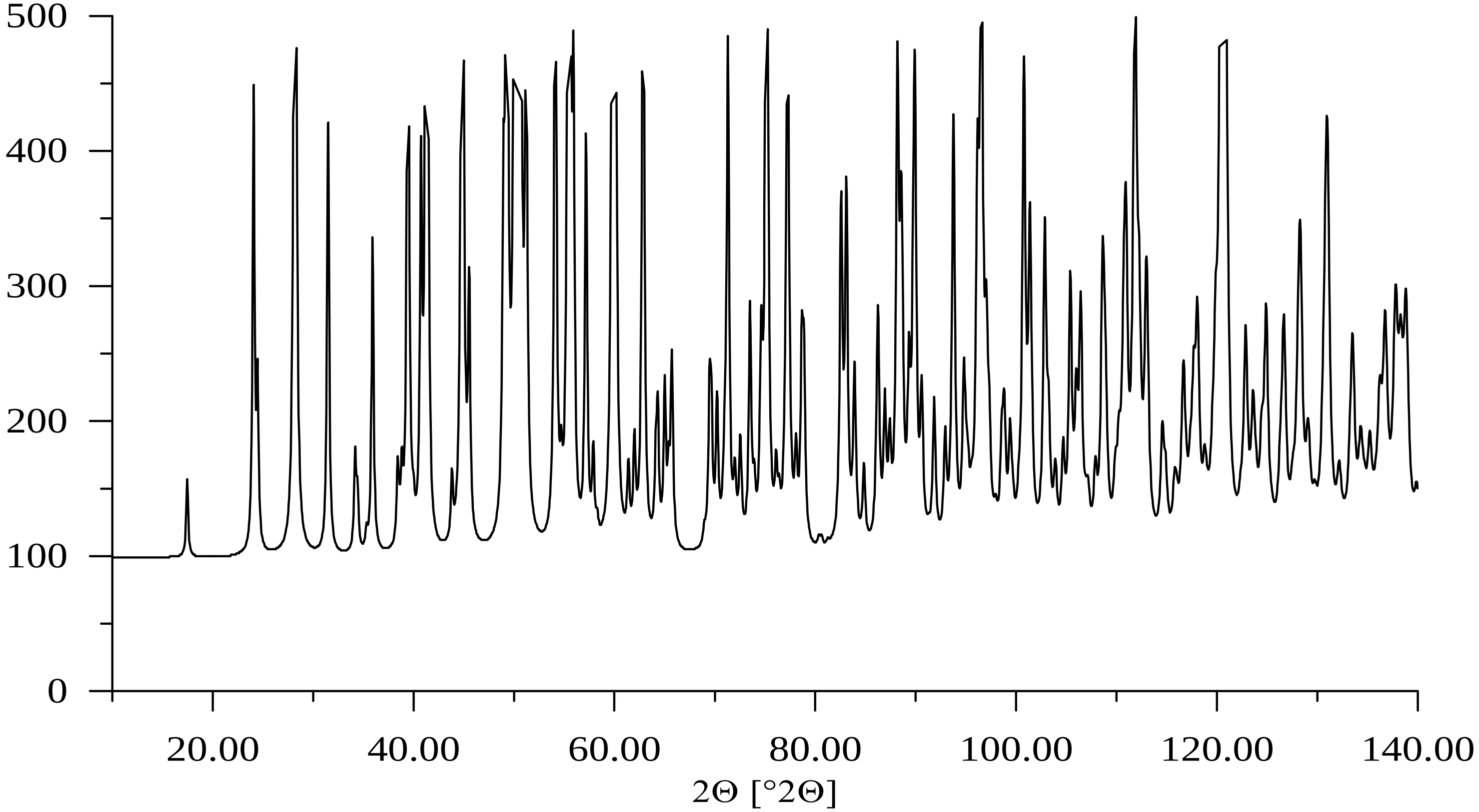
- Knowledge of absolute phase amounts and amorphous content is critical for the usefulness of an increasing number of materials
  - Cement
  - Minerals & Mining (disordered clays)
  - Polymers, geopolymers
  - Pharmaceuticals
  - ...
- Mathematical basis of quantitative phase analysis (QPA) is well established. Methods for QPA
  - are mature, extensively covered in literature, and enabled in many software packages
  - are basically the same for QPA of crystalline and amorphous content

Quantifying Amorphous Phases
Introduction

Motivation

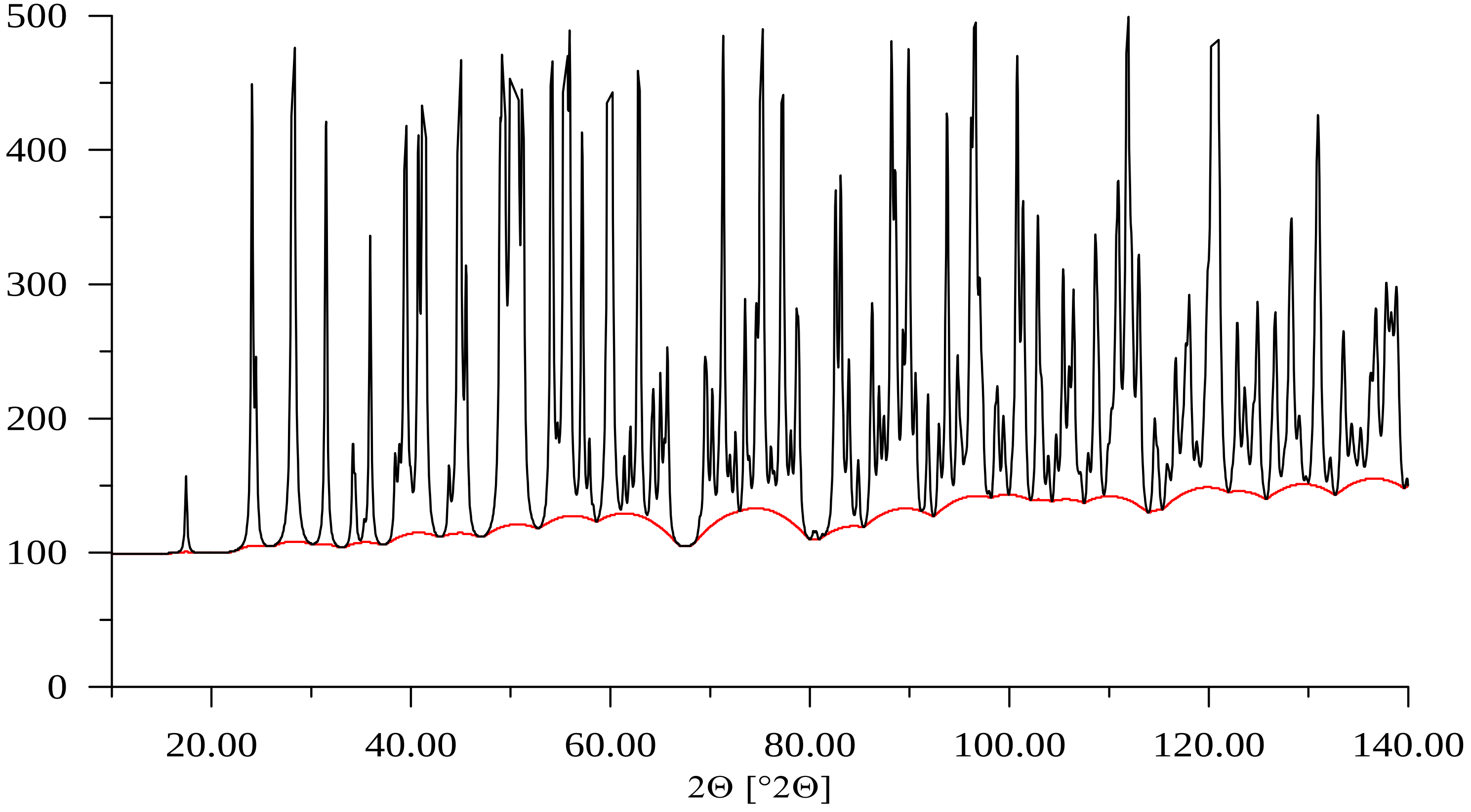
- Amorphous content can be difficult to quantify
  - Intensity contribution to diffraction patterns is not always evident, especially at low concentrations
  - Broad diffraction halos resulting in an increased peak overlap problem
  - Discrimination of peak tail / amorphous band / background intensities

Quantifying Amorphous Phases
Introduction

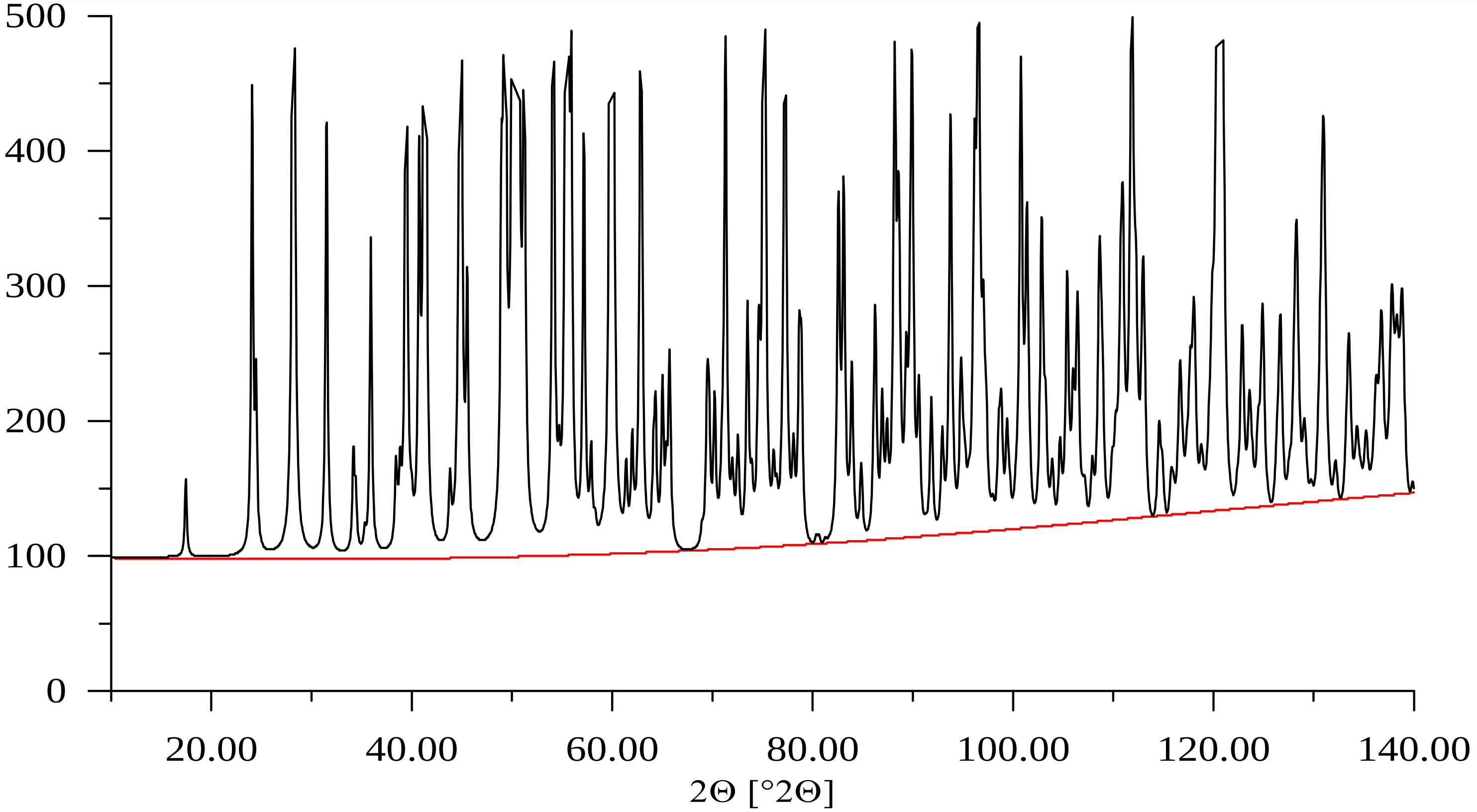


Can we easily discriminate between peak and background intensity?

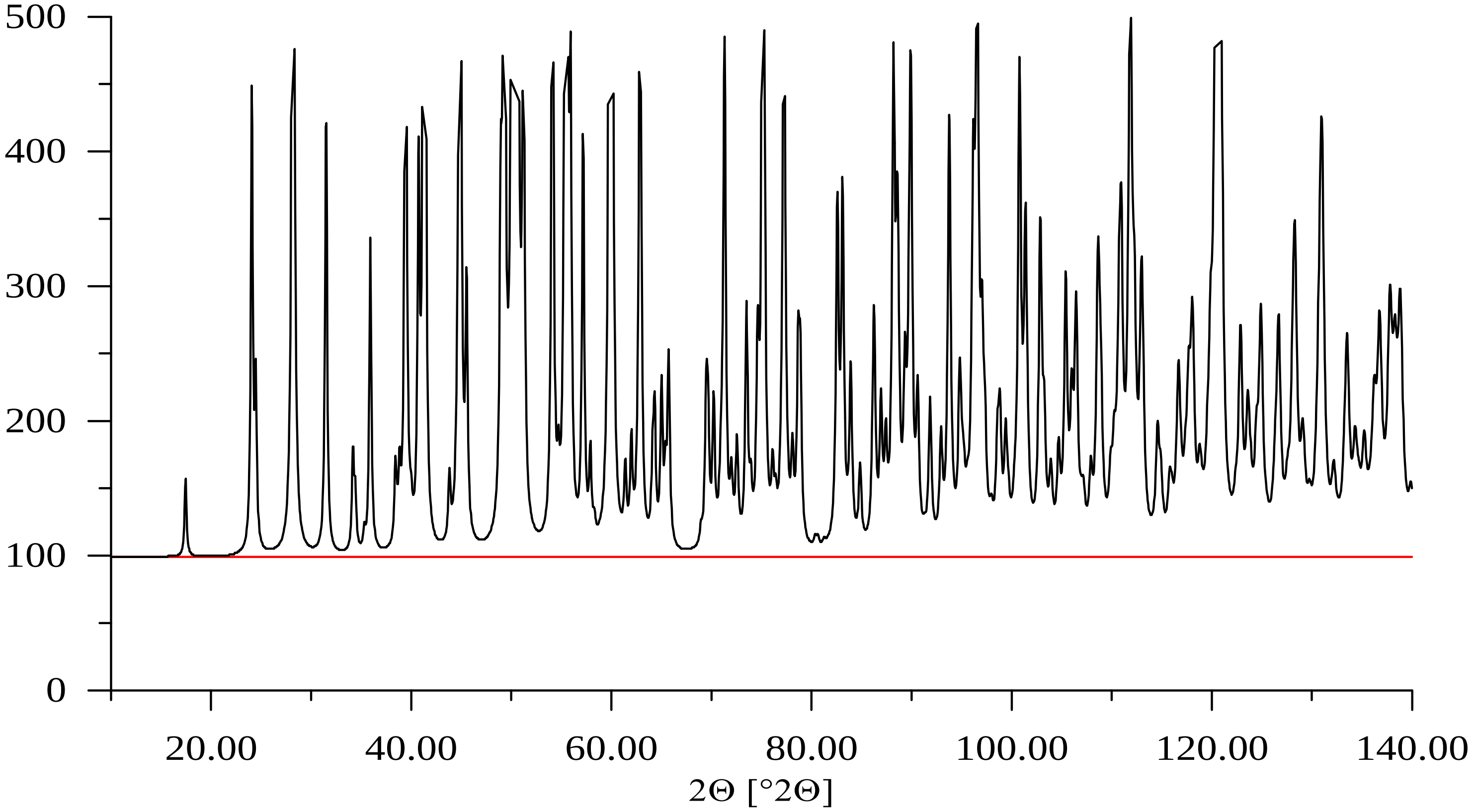
Quantifying Amorphous Phases
Introduction



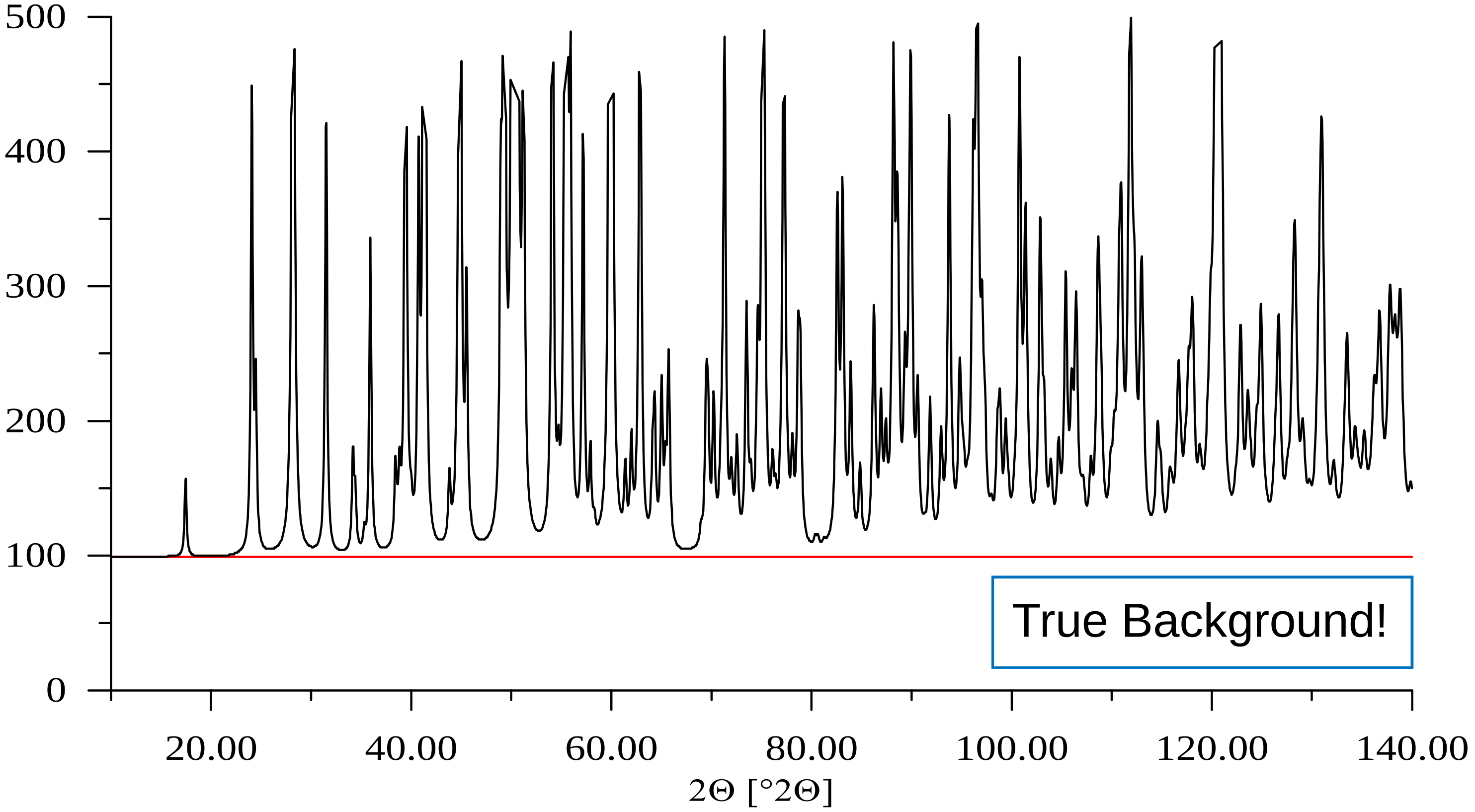
Quantifying Amorphous Phases
Introduction



Quantifying Amorphous Phases
Introduction

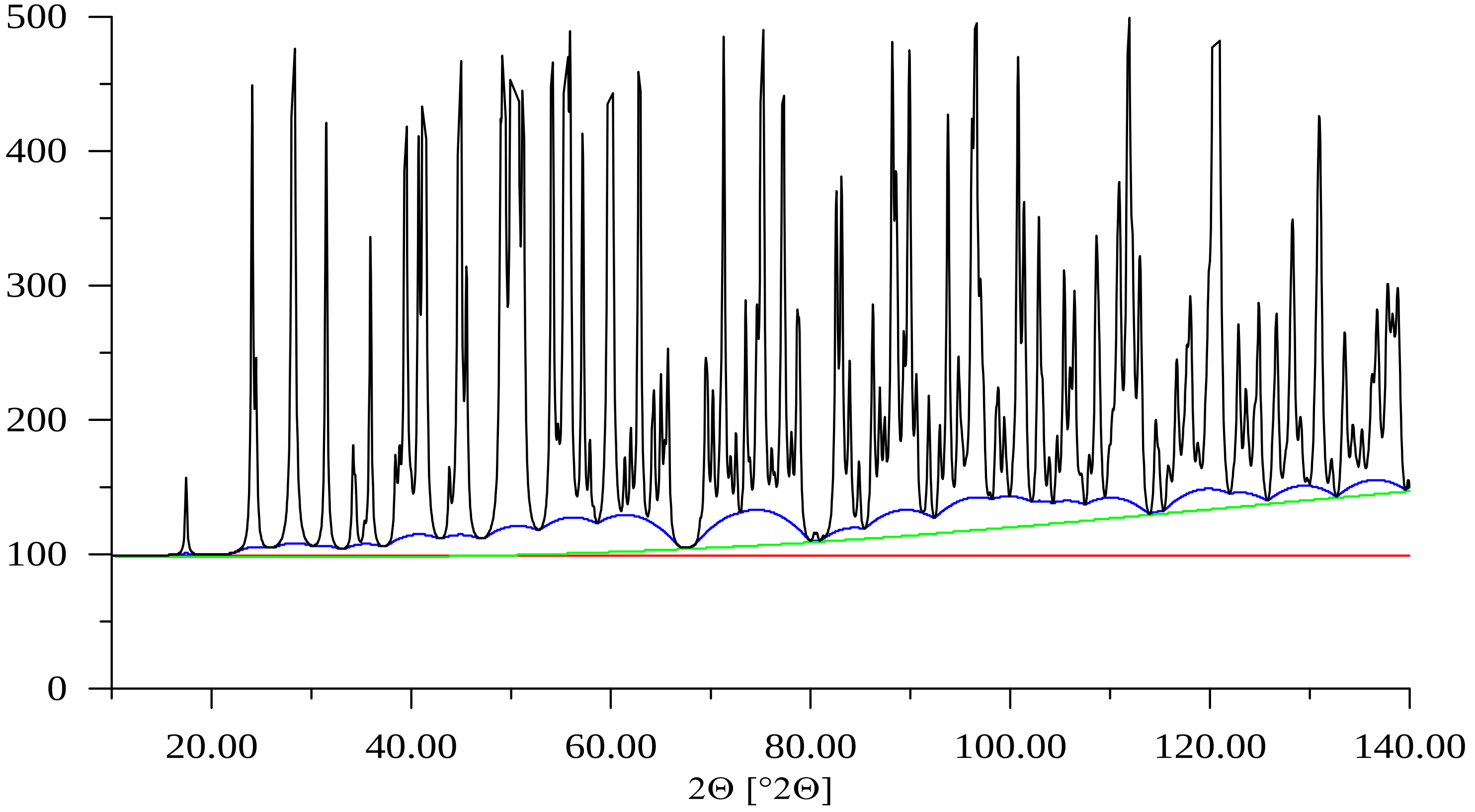


Quantifying Amorphous Phases
Introduction



True Background!

Quantifying Amorphous Phases
Introduction



Quantifying Amorphous Phases
Introduction

Motivation

- Amorphous content can be difficult to quantify
  - Intensity contribution to diffraction patterns is not always evident, especially at low concentrations
  - Broad diffraction halos resulting in an increased peak overlap problem
  - Discrimination of peak tail / amorphous band / background intensities
- In many cases, the presence of amorphous or poorly crystalline phases is undetected or simply ignored
  - Information about amorphous phase amounts is frequently not sought-after
  - Preferred / indiscriminate use of the Rietveld method

What is an amorphous solid?

Quantifying Amorphous Phases
Introduction

Pecharsky & Zavalij (2009):

- *"Crystalline materials are frequently characterized as solids with fixed volume, fixed shape, and long-range order bringing about structural anisotropy, producing sharp diffraction peaks"*
- *"Amorphous (or non-crystalline) materials are thus solids with fixed volume, fixed shape, characterized by short-range order, which, however, may also have loose long-range order"*
  - ⇨ This definition embraces disordered materials possessing only one- or two-dimensional, or lesser, degrees of order

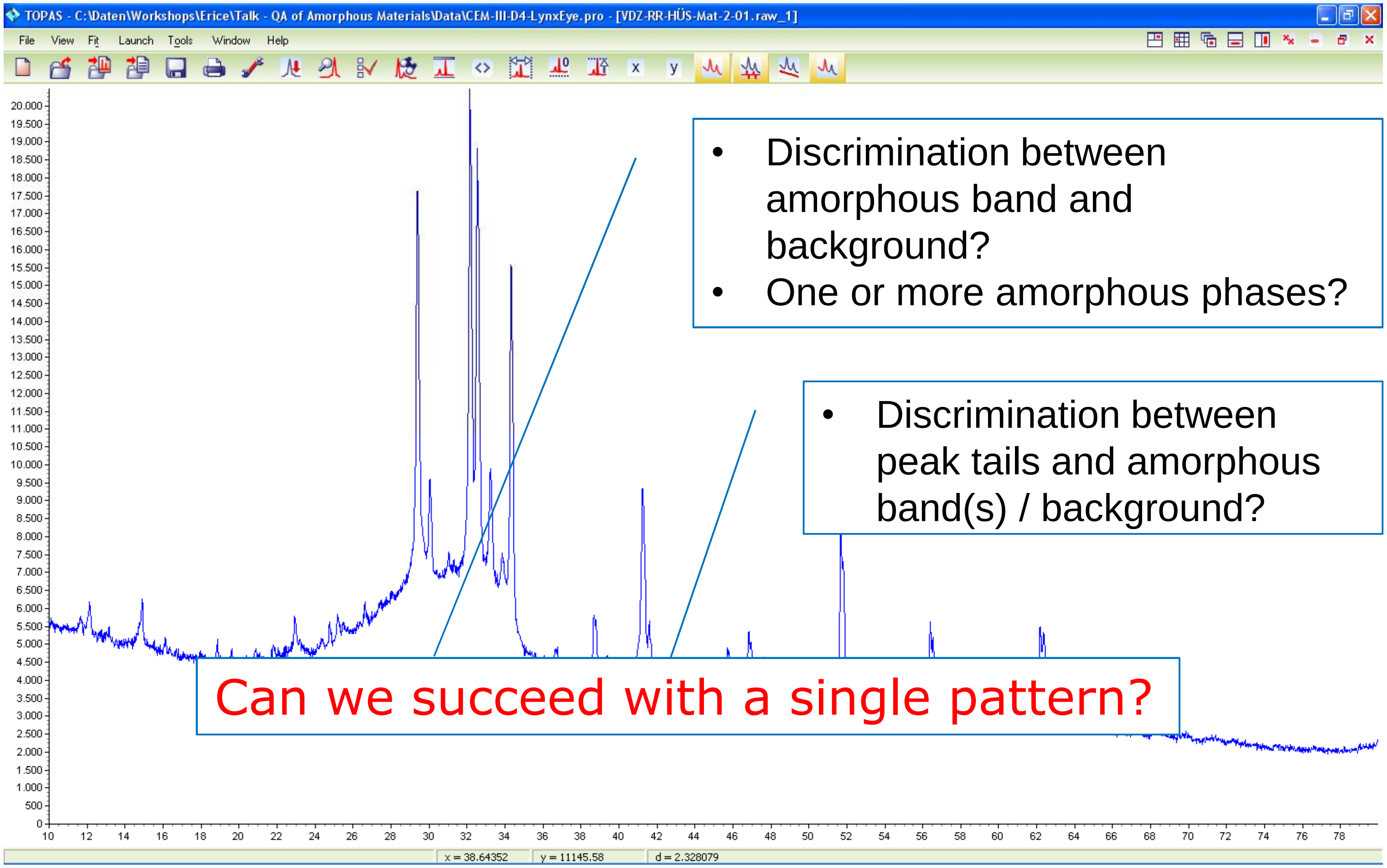
Klug & Alexander (1974):

- "*The term, amorphous solid, must be reserved for substances that show no crystalline nature whatsoever by any of the means available for detecting it*"

Quantifying Amorphous Phases
Introduction

- There is no sharp dividing line between crystalline and amorphous materials
  - "short" and "long" range order are arbitrary terms
- The ability to detect and characterize ordering is dependent upon the principles of the analytical method and models being used
- Conventional X-ray diffraction loses its power for crystalline material structures on the nano-scale, diffraction patterns become broad and features are less defined
  - Resulting ambiguities are paraphrased in literature by the term "X-ray amorphous" to highlight the limitations of X-ray diffraction

Quantifying Amorphous Phases
Introduction

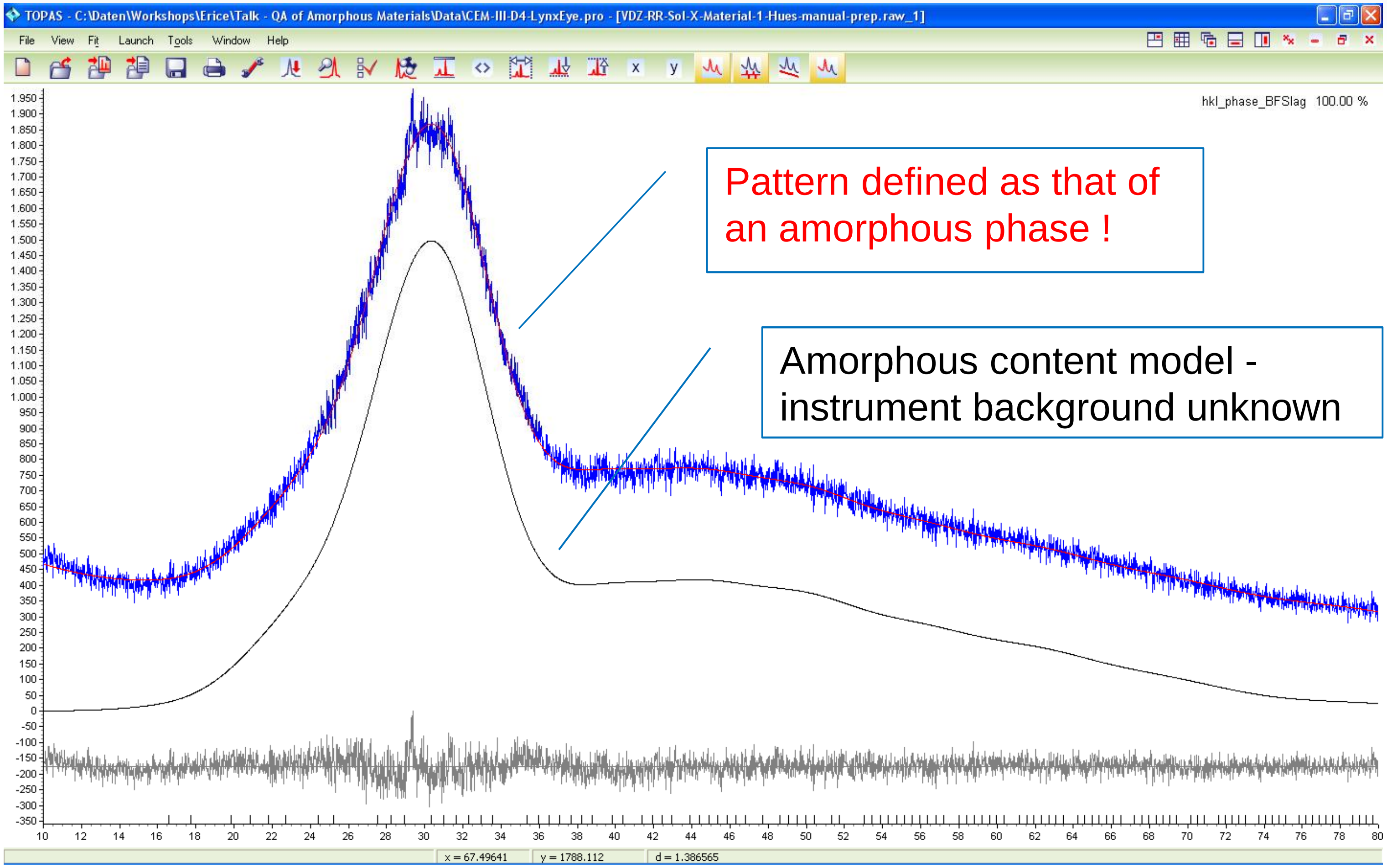


- Discrimination between amorphous band and background?
- One or more amorphous phases?

- Discrimination between peak tails and amorphous band(s) / background?

Can we succeed with a single pattern?

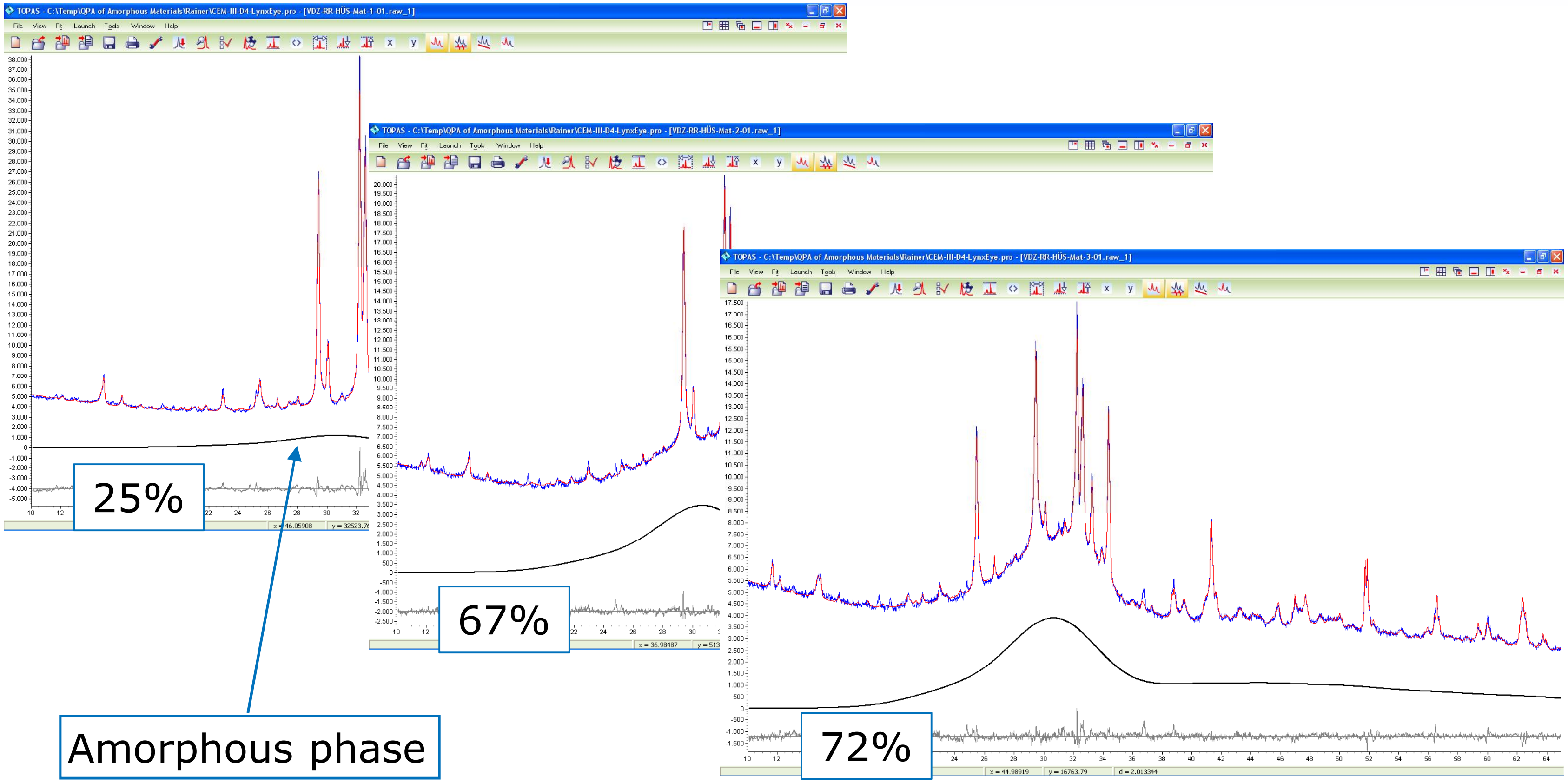
Quantifying Amorphous Phases
Introduction



Pattern defined as that of an amorphous phase !

Amorphous content model - instrument background unknown

Quantifying Amorphous Phases
Introduction



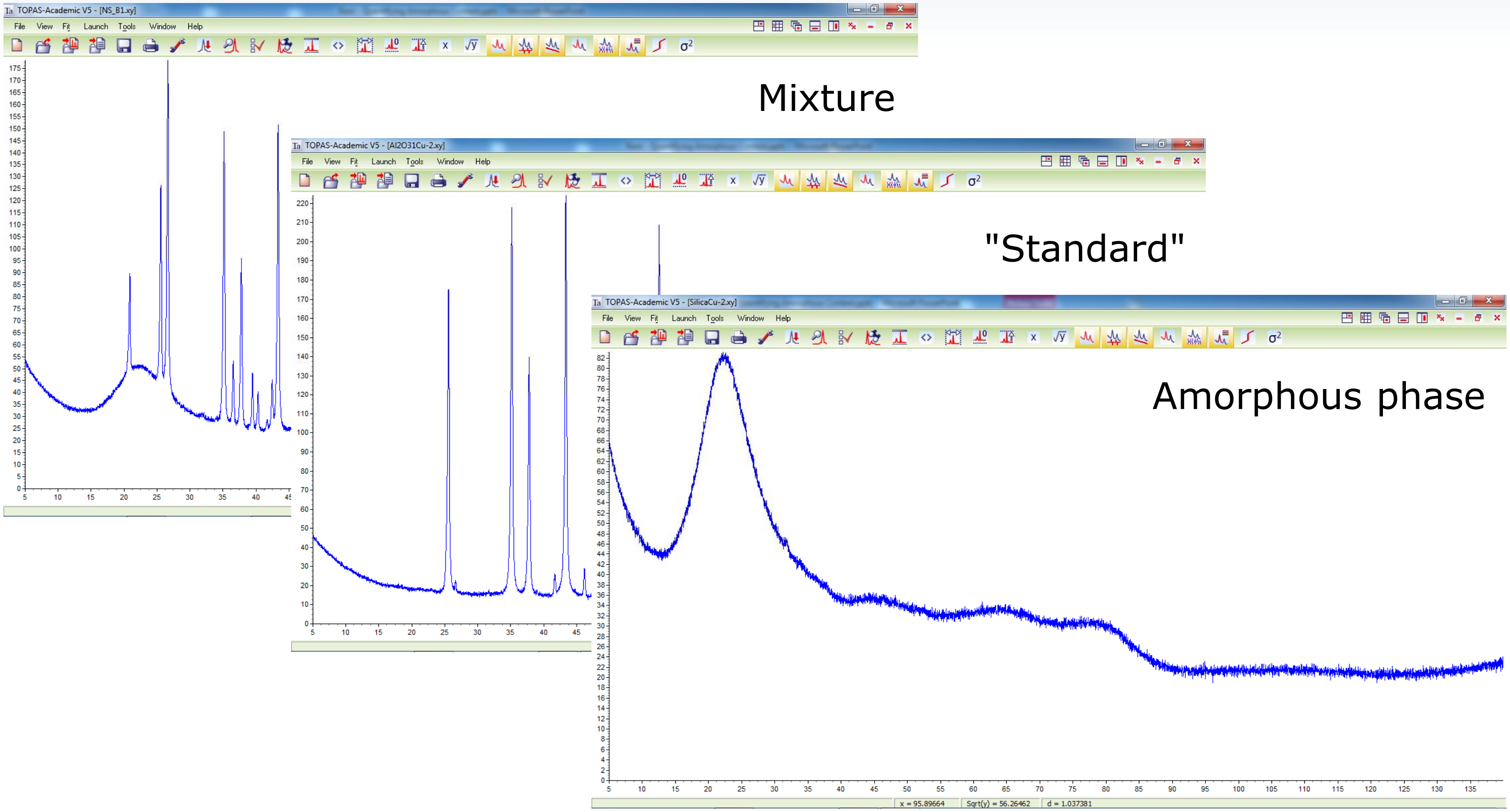
25%

67%

72%

Amorphous phase

Quantifying Amorphous Phases
Introduction

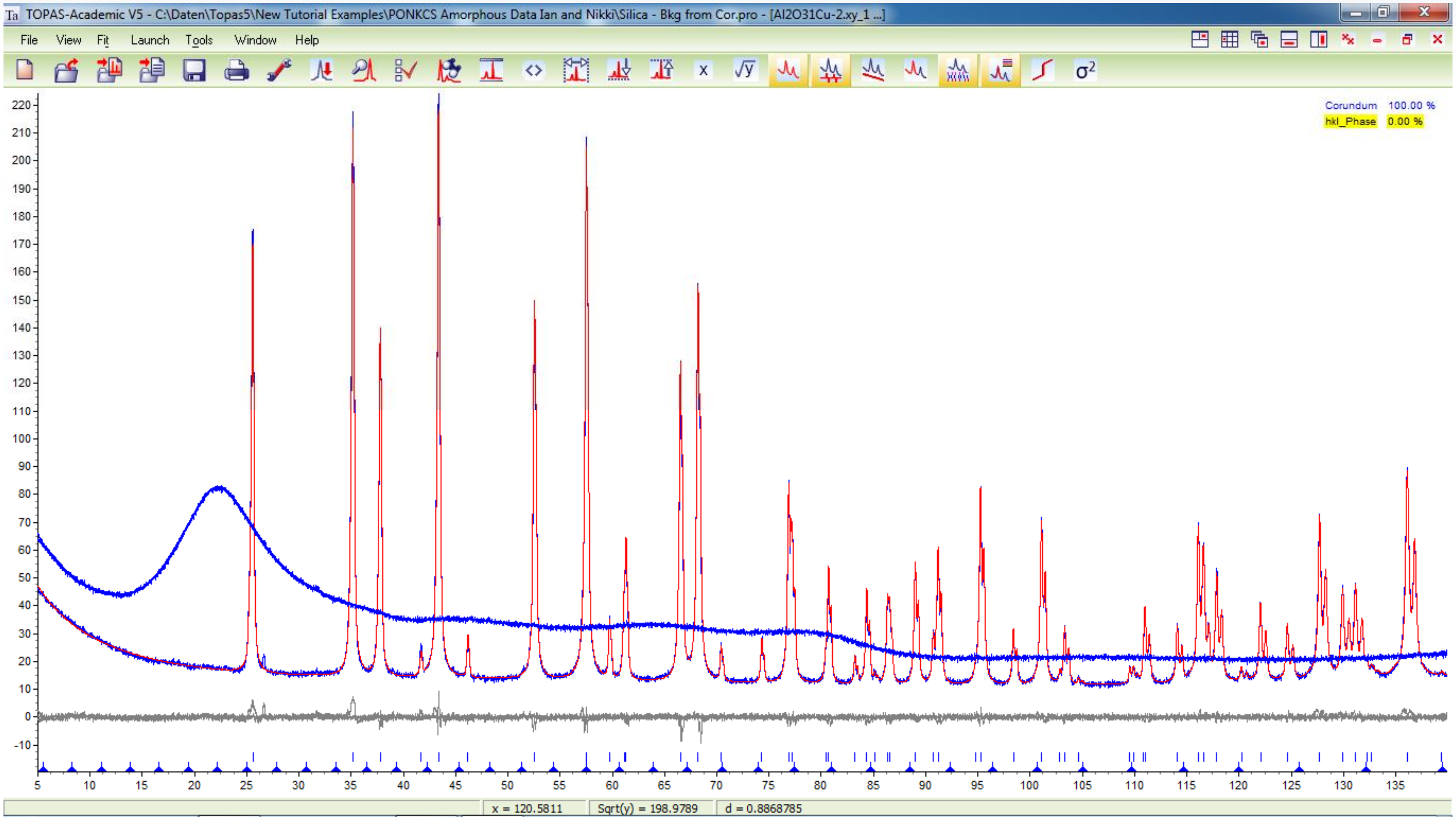


Mixture

"Standard"

Amorphous phase

Quantifying Amorphous Phases
Introduction

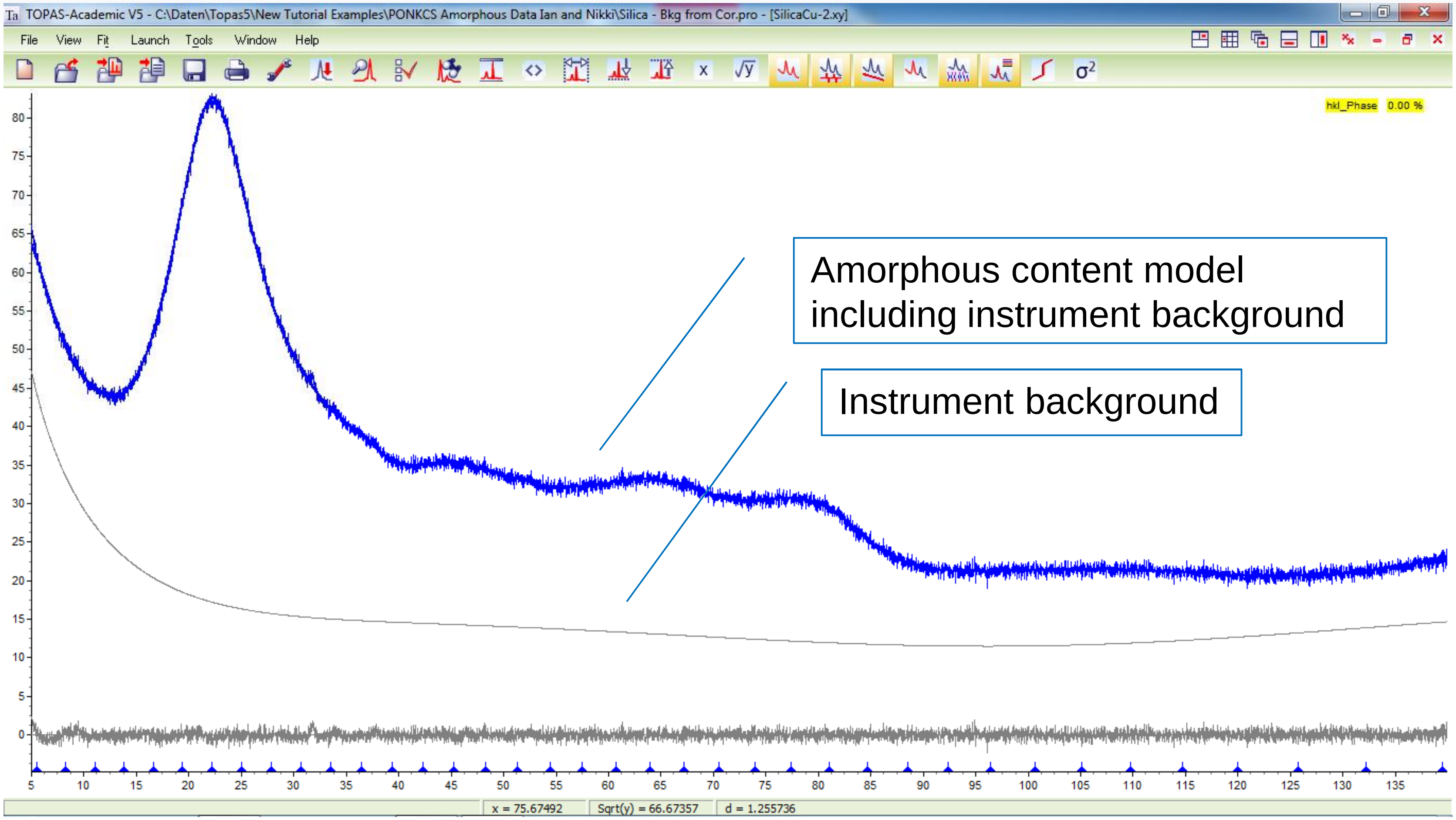


TOPAS-Academic V5 - C:\Daten\Topas5\New Tutorial Examples\PONKCS Amorphous Data Ian and Nikki\Silica - Bkg from Cor.pro - [Al2O31Cu-2.xy_1 ...]

Corundum 100.00 %
hkl_Phase 0.00 %

x = 120.5811 Sqrt(y) = 198.9789 d = 0.8868785

Quantifying Amorphous Phases
Introduction



TOPAS-Academic V5 - C:\Daten\Topas5\New Tutorial Examples\PONKCS Amorphous Data Ian and Nikki\Silica - Bkg from Cor.pro - [SilicaCu-2.xy]

hkl_Phase 0.00 %

x = 75.67492

Sqrt(y) = 66.67357

d = 1.255736

Amorphous content model including instrument background

Instrument background

Selected Methods for Quantifying Amorphous Phases

Quantifying Amorphous Phases

Classification of methods described in this study

- Single peak method
- Whole pattern methods
  - Traditional Rietveld method
  - Internal Standard method
  - External Standard method
  - PONKCS method
  - Linear Calibration Model (LCM)
  - Degree of Crystallinity (DOC)

Quantifying Amorphous Phases

Classification of methods described in this study

- Indirect measurement
  1. Analyse crystalline components
  2. Put on absolute scale
  3. Calculate amorphous content by difference
- Direct measurement – estimate amorphous contribution to pattern
  - Calibrate using known standards, or
  - Include in whole sample analysis via modeling
  - ➔ Relies on the ability to observe the intensity contribution of amorphous phases to the diffraction pattern

Practical Assessment of Merits of Methods

Single Peak Method

Quantifying Amorphous Phases
Single Peak Method

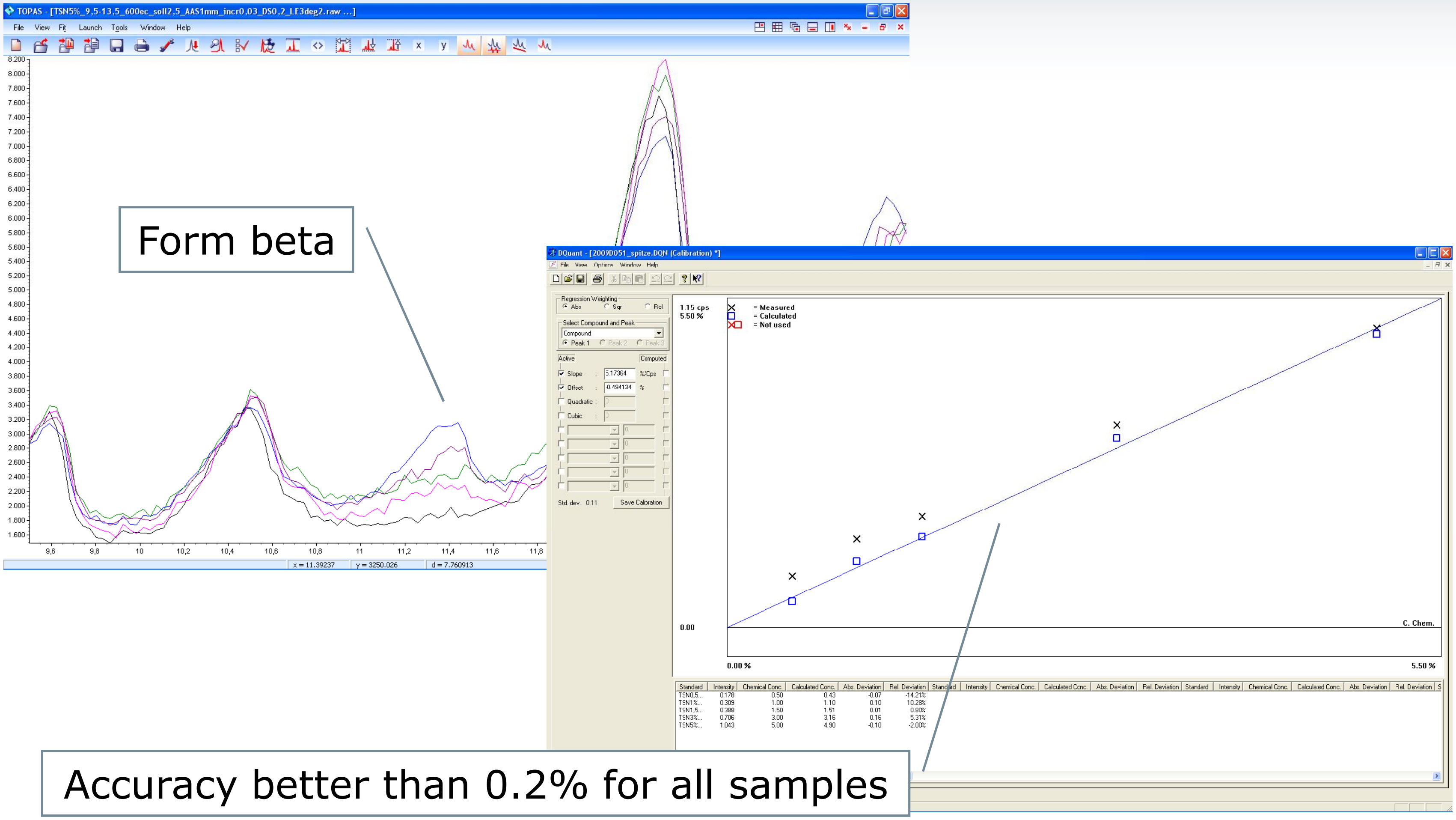
General procedure

1. Prepare a series of standards containing the amorphous phase at known concentrations
2. Obtain a measure of the amorphous component’s intensity which is related to its concentration
3. Generate a calibration curve, e.g.

$$W_a = A * I_a + B$$

where W_α is the fraction of the amorphous phases and I_α is the measure of the intensity of the amorphous phase

Sample 1 (051, Telmisartane) "Form Beta in Form Alpha"



Form beta

x = 11.39237 y = 3250.026 d = 7.760913

Regression Weighting: ● Abs ○ Sqr ○ Rel

Select Compound and Peak: Compound ● Peak 1 ○ Peak 2 ○ Peak 3

☑ Slope : 5.17364 %/Cps

☑ Offset : -0.494134 %

☐ Quadratic : 0

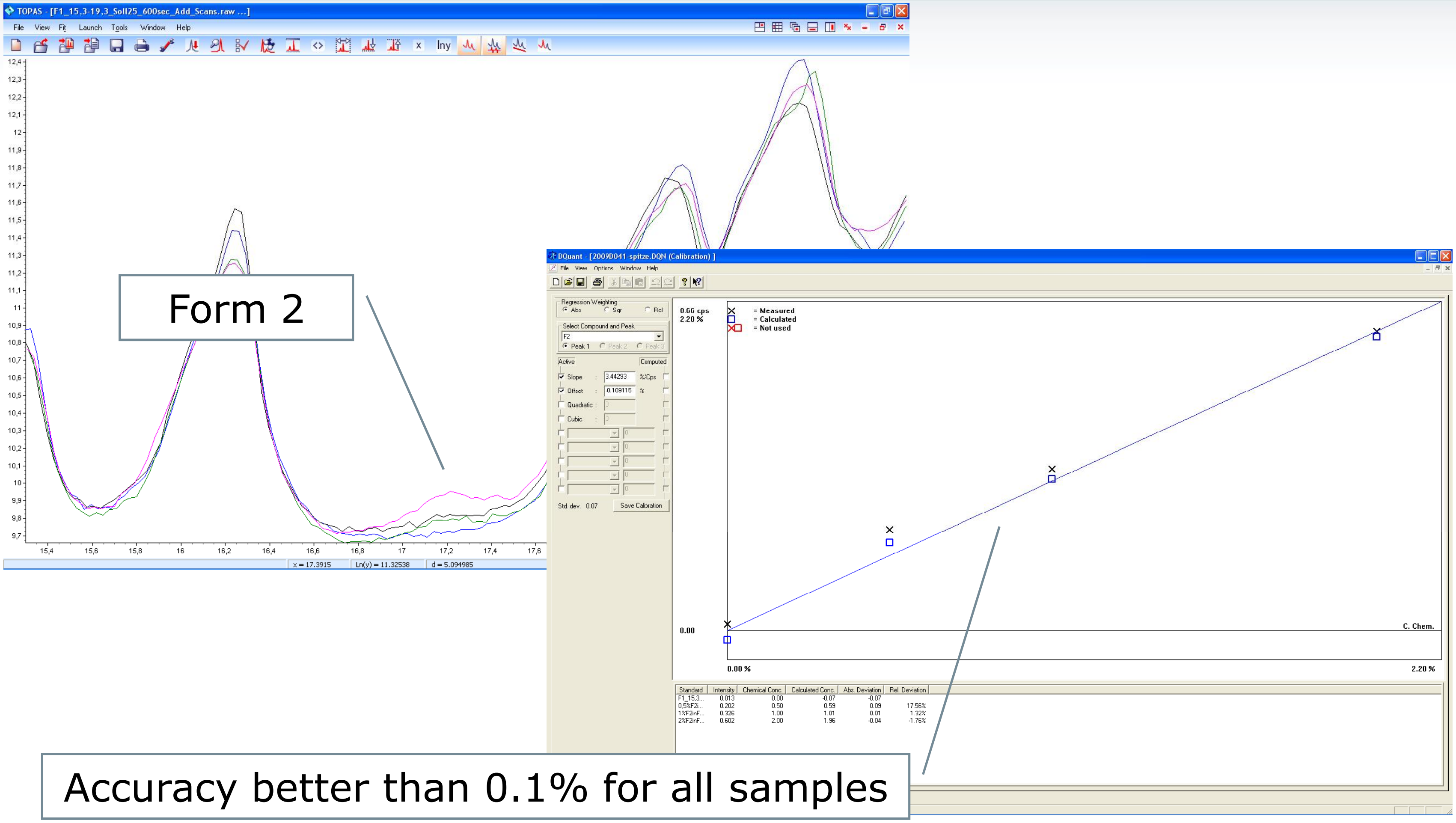
☐ Cubic : 0

Std dev. 0.11

Standard	Intensity	Chemical Conc.	Calculated Conc.	Abs. Deviation	Rel. Deviation
TSN0,5...	0.178	0.50	0.43	-0.07	-14.21%
TSN1%...	0.309	1.00	1.10	0.10	10.28%
TSN1,5...	0.388	1.50	1.51	0.01	0.80%
TSN3%...	0.706	3.00	3.16	0.16	5.31%
TSN5%...	1.043	5.00	4.90	-0.10	-2.00%

Accuracy better than 0.2% for all samples

Sample 2 (041, undisclosed)
"Form 2 in Form 1"



x = 17.3915
Ln(y) = 11.32538
d = 5.094985

Regression Weighting: ● Abs ○ Sqr ○ Rel

Select Compound and Peak: F2 ● Peak 1 ○ Peak 2 ○ Peak 3

Active / Computed

☑ Slope : 3.44293 %/Cps ☐

☑ Offset : -0.109115 % ☐

☐ Quadratic : 0 ☐

☐ Cubic : 0 ☐

Std dev. 0.07

× = Measured

☐ = Calculated

× ☐ = Not used

Standard	Intensity	Chemical Conc.	Calculated Conc.	Abs. Deviation	Rel. Deviation
F1_15,3...	0.013	0.00	-0.07	-0.07	
0,5%F2i...	0.202	0.50	0.59	0.09	17.56%
1%F2inF...	0.326	1.00	1.01	0.01	1.32%
2%F2inF...	0.602	2.00	1.96	-0.04	-1.76%

Form 2

Accuracy better than 0.1% for all samples

Quantifying Amorphous Phases
Single Peak Method

Benefits

- There is no need to characterize all phases in the mixture
- Potential to minimize errors related to microabsorption
- More than one amorphous phase can be analyzed (this will usually require profile fitting)
- No need to determine the background.
  Note: If so, the calibration curve wont go through the origin

Limitations

- Direct method
- Need access to region of pattern free from excessive peak overlap
- Requires access to materials for preparation of standards
- Method only applicable to mixtures similar to calibration suite
  - Needs redetermination to compensate for tube ageing and any instrument configuration changes

Practical Assessment of Merits of Methods

Traditional Rietveld method
Internal Standard method
External Standard method
PONKCS method
Linear Calibration Model
Degree of Crystallinity

Quantifying Amorphous Phases Traditional Rietveld Method

- Relies on finding a crystal structure which adequately models the positions and relative intensities of the observable bands of an amorphous component in a diffraction pattern
  - e.g. Le Bail, 1995; Lutterotti et al., 1998
- Allowance for extreme peak broadening provides peak widths and shapes which represent those of the amorphous bands in the observed data
- Since this approach treats all components as crystalline and includes them in the analysis, the amorphous phase abundance can be obtained using the traditional Rietveld methodology
(Hill and Howard, 1987):

Quantifying Amorphous Phases
Traditional Rietveld Method

Benefits

- Requires no standards or calibration
- More than one amorphous phase can be analyzed

Limitations

- Direct method
- Cannot correct for microabsorption errors
- Some amorphous material will not have a representative crystal structure
  - Available crystal structures (with long-range order) may not accurately represent material which only has short-range order (e.g. glasses).

Practical Assessment of Merits of Methods

Traditional Rietveld method
Internal Standard method
External Standard method
PONKCS method
Linear Calibration Model
Degree of Crystallinity

Quantifying Amorphous Phases
Internal Standard Method

- The sample is "spiked" with a known mass of standard material and the QPA normalized accordingly
- The weight fractions of the crystalline phases present in each sample are estimated using the Rietveld methodology
- Concentrations to be corrected proportionately according to:

$$Corr(W_\alpha) = W_\alpha \frac{STD_{known}}{STD_{measured}}$$

where $Corr(W_\alpha)$ is the corrected weight percent, STD_{known} the weighed concentration of the standard in the sample and $STD_{measured}$ the analyzed concentration

- The amount of amorphous material $W_{amorphous}$ can then be derived from:

$$W_{amorphous} = 1 - \sum_{j=1}^{n} Corr(W_j)$$

Quantifying Amorphous Phases
Internal Standard Method

Benefits

- Indirect method
- The Internal Standard Method is enabled in many Rietveld analysis packages

Limitations

- Only the sum of all amorphous and unidentified phases can be reported
- Cannot correct for microabsorption errors
- The sample is contaminated
- The standard addition process is laborious (weighing, mixing), and not feasible in industrial, automated sample preparation environments
- The method relies upon obtaining a standard of appropriate absorption contrast to prevent the introduction of a microabsorption problem

Practical Assessment of Merits of Methods

Traditional Rietveld method
Internal Standard method
External Standard method
PONKCS method
Linear Calibration Model
Degree of Crystallinity

Quantifying Amorphous Phases
External Standard Method

- An external standard is used to determine a "normalisation constant" *K* for the experimental setup
  - Independent of sample and phase related parameters
  - A single measurement is sufficient for analysis
  - Requires the mass absorption coefficient for the entire sample – $\mu_m{}^*$

$$W_{\alpha(abs)} = \frac{S_\alpha (ZMV)_\alpha \mu_m^*}{K}$$

- Amorphous content derived in same way as internal standard method
  - Puts the determined crystalline components on an absolute scale and derives the amorphous content by difference

O'Connor and Raven (1988), Powder Diffraction, 3(1), 2-6

Quantifying Amorphous Phases
External Standard Method

- μ_m^* can be calculated e.g. from the elemental composition of the sample, determined, for example, by X-ray fluorescence (XRF)
- K requires regular redetermination to compensate for tube ageing

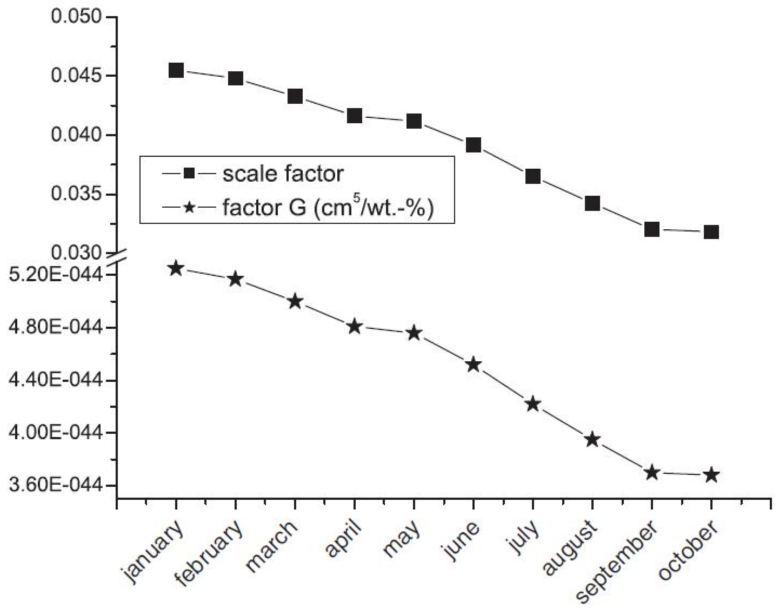


Fig. 1. Change in the scale factor and factor G over time (10 month).

Jansen et al., 2011

Quantifying Amorphous Phases
External Standard Method

Benefits

- Indirect method
- Uses an external standard, the sample is not contaminated

Limitations

- Requires the mass absorption coefficient for the entire sample
- Only the sum of all amorphous and unidentified phases can be reported
- Cannot correct for microabsorption errors
- The normalization constant *K* is dependent on the instrumental conditions
  - Needs redetermination to compensate for tube ageing and any instrument configuration changes

Practical Assessment of Merits of Methods

Traditional Rietveld method
Internal Standard method
External Standard method
PONKCS method
Linear Calibration Model
Degree of Crystallinity

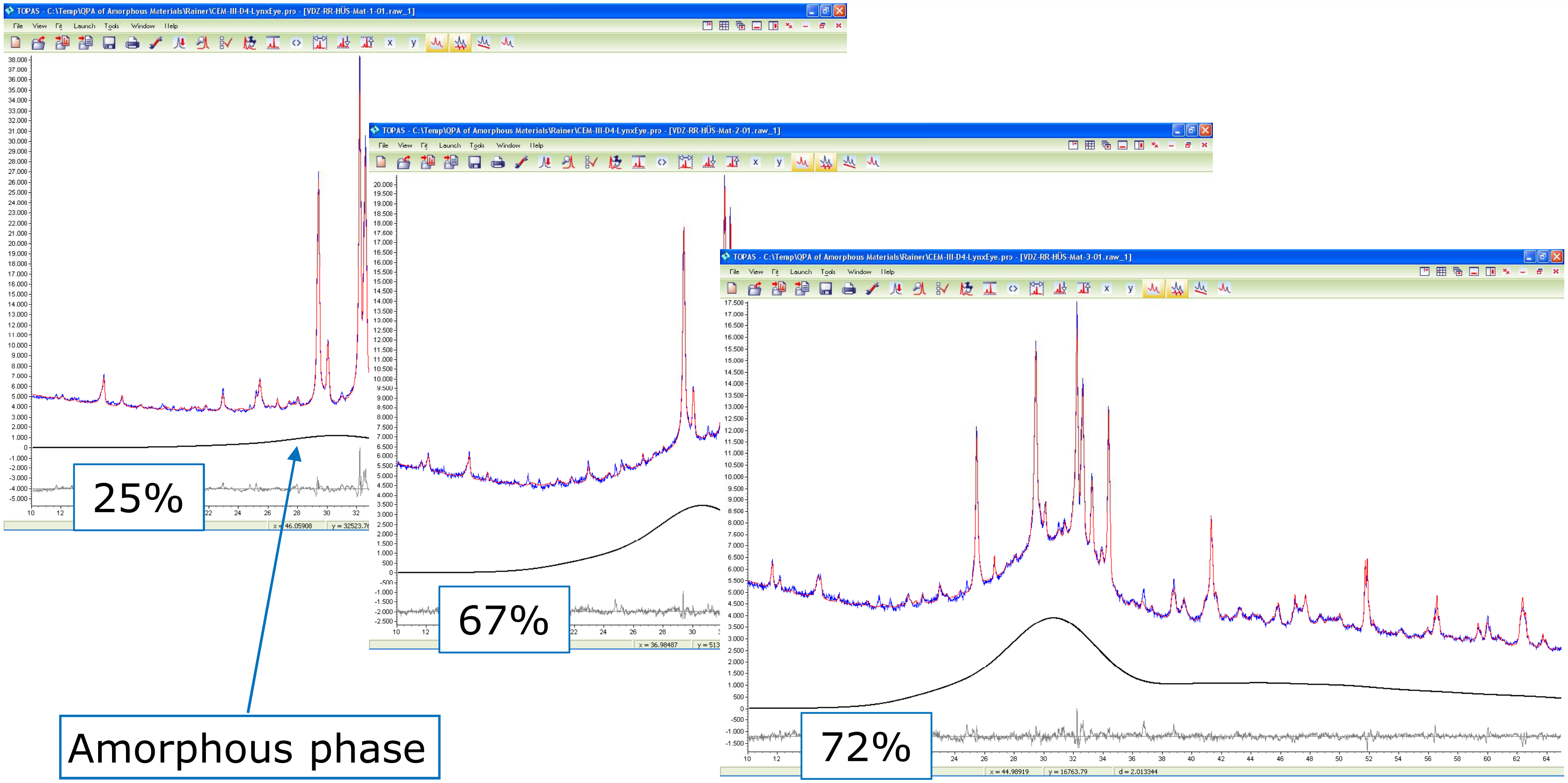
Quantifying Amorphous Phases
PONKCS Method

- Phases with Partial Or No Known Crystal Structure are characterized by measured rather than calculated structure factors
- Follows the same general form as that used in the Rietveld Method but now includes all crystalline and amorphous phases characterized by either calculated or empirical structure factors
- For all phases α using empirically derived structure factors ZMV "calibration constants" must be derived, e.g. via an internal standard *s*

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

- A one time calibration per phase with a single standard mixture is usually sufficient

Quantifying Amorphous Phases
Introduction



25%

67%

72%

Amorphous phase

Quantifying Amorphous Phases
PONKCS Method

Benefits

- The amorphous phase is included in the analysis model
- More than one amorphous phase can be analyzed
- Can deal with preferred orientation and microstructure broadening
- Potential to partially minimize errors related to microabsorption, when ZMVs have been calibrated for all phases
    - Consider to use the PONKCS methodology also for all crystalline phases with known crystal structures are known
    - Depends on calibration procedure and concentration range

Limitations

- Direct method
- Requires availability of a standard mixture to derive an empirical ZMV

Practical Assessment of Merits of Methods

Traditional Rietveld method
Internal Standard method
External Standard method
PONKCS method
Linear Calibration Model
Degree of Crystallinity

Quantifying Amorphous Phases
Linear Calibration Model

- Initially similar to previous methods, however, the information pertaining to the crystalline phases is discarded
- The intensity contribution of an amorphous phase to the powder pattern is modeled via single line or Pawley or Le Bail fitting methods, but only the refined scale factor is used in subsequent analysis
- A simple linear calibration model is derived from a suite of standard mixtures, which relates the refined scale factor, *S*, to the amorphous phase concentration, W_{amorph},

$$W_{amorph} = A \cdot S - B$$

where A and B are the slope and any residual offset of the calibration, respectively

Quantifying Amorphous Phases
Linear Calibration Model

Benefits

- More than one amorphous phase can be analyzed

Limitations

- Direct method
- Requires access to materials for preparation of standards
- Method only applicable to mixtures similar to calibration suite
  - Needs redetermination to compensate for tube ageing and any instrument configuration changes

Practical Assessment of Merits of Methods

Traditional Rietveld method
Internal Standard method
External Standard method
PONKCS method
Linear Calibration Model
Degree of Crystallinity

Quantifying Amorphous Phases
Degree of Crystallinity

- Based on the estimation of the total intensity or area contributed to the overall diffraction pattern by each component in the analysis
- The degree of crystallinity, *DOC*, is calculated from the total areas under the defined crystalline and amorphous components from

$$DOC = \frac{Crystalline\ Area}{Crystalline\ Area + Amorphous\ Area}$$

- The weight fraction of the amorphous material, W_{amorph}, can be calculated from

$$W_{amorph} = 1 - DOC$$

Quantifying Amorphous Phases
Degree of Crystallinity

Benefits

- More than one amorphous phase can be analyzed
- The method is enabled in many software packages

Limitations

- Direct method
- If the chemistry of the crystalline phase is different from the whole sample then an additional calibration step is required to obtain absolute phase amounts

Summary

Quantifying Amorphous Phases
Comparison of Methods

Method	Calculation of amorphous content	Requires calibration suite or standard	Can correct for microabsorption errors	Can deal with more than one amorphous phase
Single Peak	Direct	Calibration suite	Yes	Yes
Rietveld Method	Direct	No	No	Yes
Internal Standard	Indirect	Internal standard	No	No
External Standard	Indirect	External standard	No	No
PONKCS	Direct	Single mixture	Partly	Yes
LCM	Direct	Calibration suite	Yes	Yes
DOC	Direct	Case dependent	No	Yes

Summary

For the determination of amorphous material, the problem will dictate the method(s) used

- All methods discussed are principally capable of determining (*of what has been defined as*) amorphous material in mixtures with the same accuracy (and precision) as for crystalline phases, in ideal cases even down to 1% absolute or better
- Limitations are the same as for QPA of crystalline phases and are dictated by sample properties and the analytical techniques used

Summary

- Single samples do not afford the luxury of making a calibration suite
- Intensity contributions of amorphous phases to the diffraction pattern are not always evident, especially at low concentrations
  - Indirect methods (Internal or External Standard Method) will usually perform better.
- Where intensity contributions of amorphous phases are evident, any method based on modeling amorphous bands provides improved accuracy
  - Usually a sample of pure amorphous material, or a sample where the amorphous content is high, is required to establish an accurate model.
- Calibration based methods usually have the potential to achieve the highest accuracy, as many aberrations, most notably microabsorption, are included in the calibration function

Credits

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