Quantitative phase analysis - amorphous content

Most slides in this ppt file is from the presentation of Arnt Kern of BRUKER @ DXC 2014 Workshop "QUANTIFYING CRYSTALLINE AND AMORPHOUS PHASES".

BRUKER

- 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

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QPA by XRD

Classification of methods described in this study with respect to quantification of amorphous content
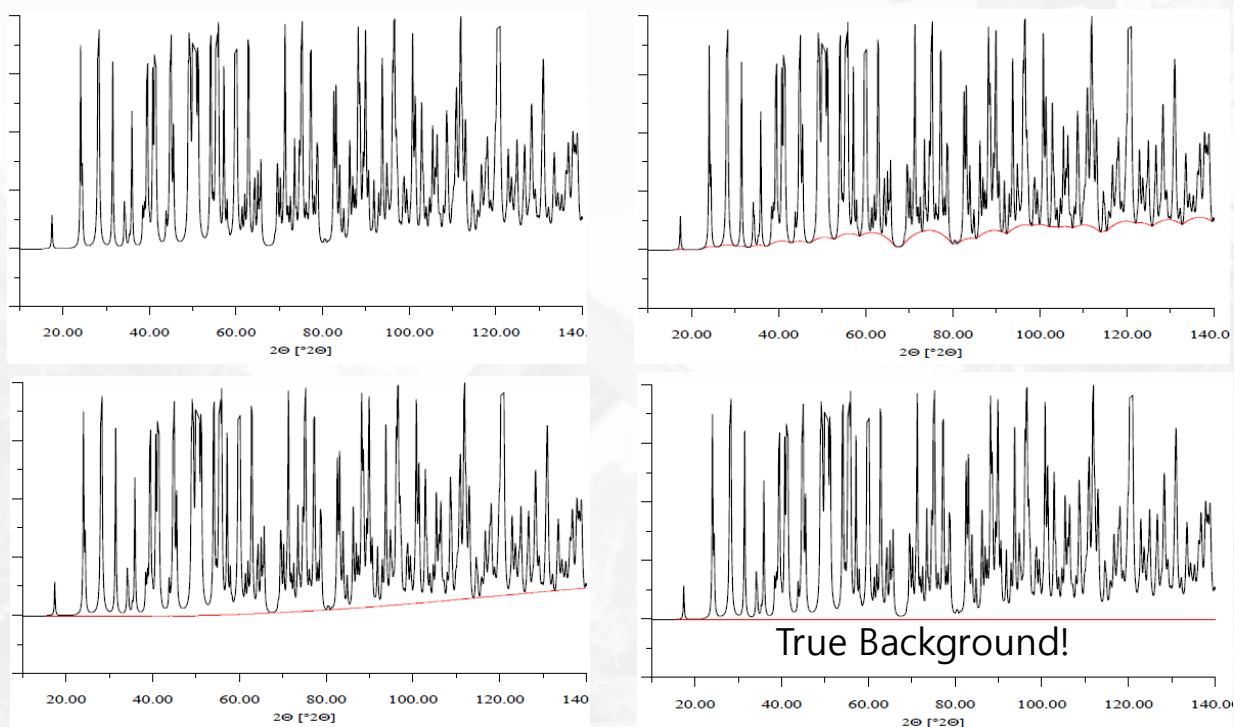
➢Indirect measurement

✓Analyse crystalline phases.

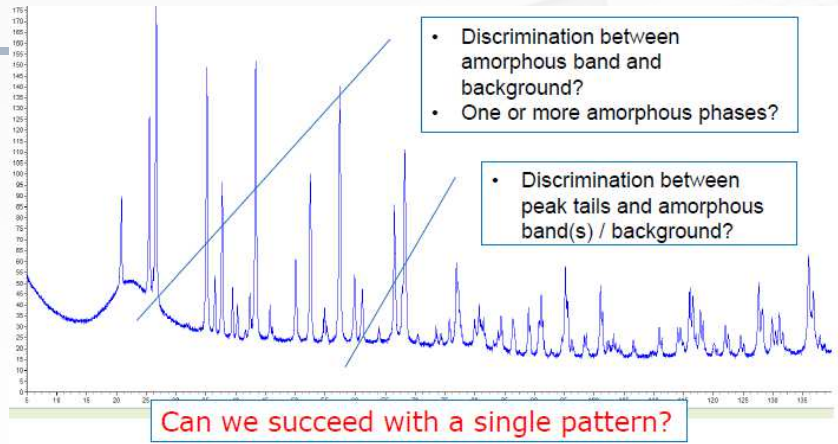✓Put on absolute scale.

✓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.
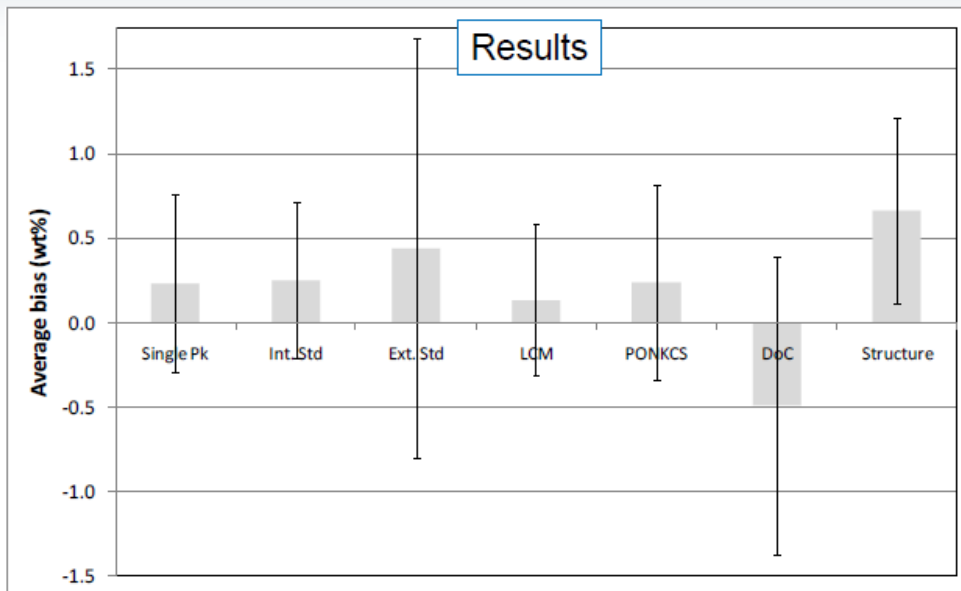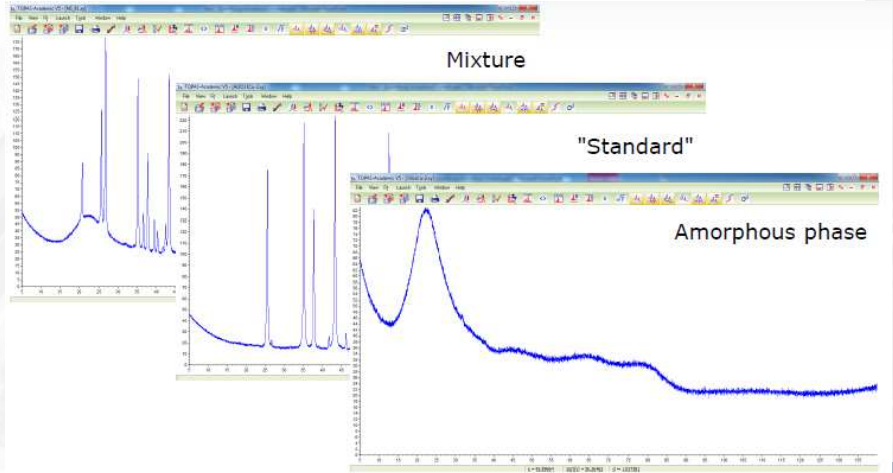
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➤ Mathematical basis of quantitative phase analysis (QPA) is well established.

➤ Methods for QPA

✓ are mature, extensively covered in literature, and enabled in many software packages.

✓ are the same for QPA of crystalline and amorphous content.

➤ Amorphous content can be difficult to quantify

✓ Intensity contribution to diffraction patterns is not always evident, especially at low concentrations.

✓ Broad diffraction halos result in an increased peak overlap problem.

✓ Discrimination of peak tail / amorphous band / background intensities

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➤ Can we easily discriminate between peak and background intensity?

True Background!

- 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?

Intensity Discrimination

Mixture

"Standard"

Amorphous phase

Plot of the average bias (analysed – weighed) for the 27 determinations (9 samples x 3 replicates) for each method. The vertical lines represent the standard deviation of the mean.

PONCKS - Partial Or No Known Crystal Structures

LCM - Linear Calibration Model

DoC - Degree of Crystallinity

➤Single Peak Method

➤Whole pattern method

✓Traditional Rietveld method

✓Internal Standard method

✓External Standard method

✓PONKCS* method

✓Linear Calibration Model

✓Degree of Crystallinity

* Partial Or No Known Crystal Structures

Single Peak Method

➤General procedure

✓Prepare a series of standards containing the crystalline or amorphous phase of interest at known concentrations.

✓Obtain a measure of the crystalline or amorphous phase's intensity which is related to its concentration.

✓Generate a calibration curve, e.g.

$$W|_a = A * I_a + B$$

W_a ; the fraction of the crystalline or amorphous phase and

I_a ; the measure of the intensity of the crystalline or amorphous phase

Single Peak Method

> Benefits
> - ✓ Highly accurate, specifically for phases close to the detection limit
> - ✓ There is no need to characterize all phases in the mixture.
> - ✓ No need to determine the background. Note: If so, the calibration curve won't go through the origin.
> - ✓ More than one amorphous phase can be analyzed (this will usually require profile fitting).

> Limitations
> - ✓ 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
> - ✓ Sample properties must not change (chemistry, texture, ---).
> - ✓ Needs redetermination to compensate for tube ageing and any instrument configuration changes.
> - ✓ Direct method for determination of amorphous content

Traditional Rietveld Method

> The basic principle of the Rietveld method is the description of all data points of a powder pattern using an appropriate refinement model.

> The parameters of this model, consisting of crystal structure, sample, instrument and background parameters, are refined simultaneously using least squares methods.

> Minimize the differences between the calculated and measured powder diffraction pattern.

> Rietveld analysis is a "standardless" method and thus does not require any standards or calibration.

"standardless" : Instead of standards, accurate crystal structure are required for each crystalline phase in the sample. The impact of poor or wrong crystal structures on QPA results is widely underestimated.

Traditional Rietveld Method

➢ Benefits
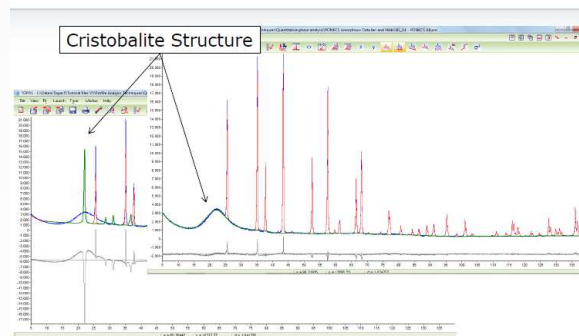
  ✓ Requires no standards or calibration.

➢ Limitations

  ✓ The Rietveld method <u>assumes that all phases are crystalline</u> and included in the analysis.

    ▪ Accurate crystal structure required for all phases

    ▪ Amorphous components cannot be considered

  ✓ Produces only relative phase abundances.

    ▪ The relative weight fractions of the crystalline phases are normalized to 100%.

    ▪ Crystalline phases may be overestimated if non-identified and/or amorphous phases are present.

Traditional Rietveld Method > Quantifying Amorphous Phases

➢ 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).

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Sample 1A
Madsen et a. (2011), Kern et al. (2012)

Cristobalite Structure
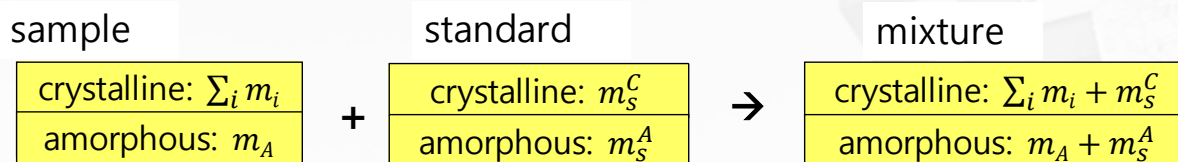
➢ Benefits

✓ Requires no standards or calibration.

✓ More than one amorphous phase can be analyzed.

➢ Limitations

✓ Direct method for determination of amorphous content

✓ 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).

Internal Standard Method

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sample		standard		mixture
crystalline: $\sum_i m_i$		crystalline: m_s^C		crystalline: $\sum_i m_i + m_s^C$
amorphous: m_A	+	amorphous: m_s^A	→	amorphous: $m_A + m_s^A$

known weight fractions

standard in mixture: $w_s = \dfrac{m_s^C + m_s^A}{\sum_i m_i + m_s^C + mA + m_s^A}$

standard in mixture given by Rietveld method: $w_s^R = \dfrac{m_s^C}{\sum_i m_i + m_s^C}$

crystalline components in standard: $w_s^C = \dfrac{m_s^C}{m_s^C + m_s^A}$

to find

amorphous components in sample: $w_A = \dfrac{m_A}{\sum_i m_i + mA}$

Westphal, T. (2007). "Amorphous phase determination - theoretical approach and practical consequences."

$$w_A = \frac{m_A}{\sum_i m_i + m_A} = \frac{\dfrac{\sum_i m_i + m_S^C + mA + m_S^A - (\sum_i m_i + m_S^C + m_S^A)}{\sum_i m_i + m_S^C + mA + m_S^A}}{\dfrac{\sum_i m_i + m_S^C + mA + m_S^A - (m_S^C + m_S^A)}{\sum_i m_i + m_S^C + mA + m_S^A}}$$

$$= \frac{1 - \left(\dfrac{m_S^C}{\sum_i m_i + m_S^C + m_A + m_S^A}\dfrac{\sum_i m_i + m_S^C}{m_S^C} + \dfrac{m_S^A}{\sum_i m_i + m_S^C + m_A + m_S^A}\right)}{1 - \dfrac{m_S^C + m_S^A}{\sum_i m_i + m_S^C + m_A + m_S^A}}$$

$$= \frac{1}{1 - w_s}\left[1 - \frac{w_s w_S^C}{w_S^R} - w_s(1 - w_S^C)\right]$$

If standard consists of crystalline phase only (i.e., $w_s^C = 1$), $W_A = \dfrac{1}{1-ws}\left(1 - \dfrac{w_s}{w_S^R}\right)$

standard in mixture: $w_s = \dfrac{m_S^C + m_S^A}{\sum_i m_i + m_S^C + mA + m_S^A}$

standard in mixture given by Rietveld method: $w_s^R = \dfrac{m_S^C}{\sum_i m_i + m_S^C}$

crystalline components in standard: $w_s^C = \dfrac{m_S^C}{m_S^C + m_S^A}$

➢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:

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

✓ Corr (W_α) ; the corrected weight percent

✓ STD_{known} ; the weighed concentration of the standard in the sample

✓ $STD_{measured}$; the analyzed concentration

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

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

Sample = A + B + C + amorphous

Rietveld analysis　→　　Amount of A, B and C

　　　　　　　　　　　　50% + 30%　+ 20% = 100%

Sample 50% + standard(S) 50%

Rietveld analysis　　→　　Amount of A, B, C and S

　　　　　　　　　　　　20% + 12% + 8% + 60% = 100%

⬇

17.8% + 10% + 6.7% + 50%

⬇

35.6% + 20% +13.4% = 69% → 31% amorphous

　　　A　　　　B　　　　C

➢Benefits

✓Indirect method for determination of amorphous content

✓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 permanently contaminated.

✓The standard addition process is laborious (weighing, mixing), and not feasible in industrial, automated sample prep environments.

✓The method relies upon obtaining a standard of appropriate absorption contrast to prevent the introduction of a microabsorption problem.

External Standard

- 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 – $\mu_m{}^*$.

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

  - ✓ $\mu_m{}^*$ 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.
- 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

External Standard

- Benefits
  - ✓ Indirect method for determination of amorphous content
  - ✓ Uses an external standard, the sample is not contaminated.
- Limitations
  - ✓ Requires the mass absorption coefficient for the entire sample.
    - ▪ Cannot be used in transmission geometry; sample holder (capillary, foils, etc.) contribute to pattern!
  - ✓ 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.

External Standard

sample

crystalline α: w_α
crystalline β: w_β
amorphous: $1 - (w_\alpha + w_\beta)$

standard

crystalline: w_s^c
amorphous: $1 - w_s^c$

➢ $w_\alpha \propto (SZMV)_\alpha \mu_m^*$

➢ $w_s^C \propto (SZMV)_s \mu_s^*$

⬇

➢ $w_\alpha = \dfrac{(SZMV)_\alpha \mu_m^*}{(SZMV)_s \mu_s^*} w_s^C$

➢ $w_A = 1 - \sum_i w_i$

S	Rietveld scale factor
Z	number of formula units in unit cell
M	molecular mass of formula unit
V	volume of unit cell
μ_m^*	mass absorption coefficient of sample
μ_s^*	mass absorption coefficient of standard
w_α	weight fraction of phase α in sample
w_s^c	w of crystalline components in standard
w_A	w of amorphous components in sample

Nicolich, J. (2012). "Amorphous Content Determination Using External Standards."

PONKCS (Partial Or No Known Crystal Structures)

➢Phases with <u>Partial Or No Known Crystal Structure</u> 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.

PONKCS

> Benefits

 ✓ Allows quantification of phases without known crystal structure.

 ✓ Crystalline and amorphous phases are included in the analysis model.

 ✓ More than one amorphous phase can be analyzed.

> Limitations

 ✓ Requires availability of a standard mixture to derive an empirical ZMV.

 ✓ Direct method for determination of amorphous content

Linear Calibration Model

> The intensity contribution of crystalline or an amorphous phase to the powder pattern is modeled via single line, Pawley or Le Bail fitting methods, but only a 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 crystalline or amorphous phase concentration, W_{phase},

$$W_{phase} = |A \cdot S - B$$

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

Linear Calibration Model

> Benefits

- ✓ Allows quantification of phases without known crystal structure.
- ✓ More than one amorphous phase can be analyzed.

> Limitations

- ✓ Direct method for determination of amorphous content
- ✓ 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.

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 $W_{amorph} = 1 - DOC$.

Degree of Crystallinity

➢Benefits

  ✓More than one amorphous phase can be analyzed.

  ✓The method is enabled in many software packages.

➢Limitations

  ✓Direct method for determination of amorphous content

  ✓The method only delivers accurate results, if the chemistry of the amorphous phase is identical to that of the whole sample.

  ✓If this is not the case, then an additional calibration step is required to obtain absolute phase amounts.

Summary 1

Method	Calculation of amorphous content	Requires calibration suite or standard	Can correct for microabsorption errors	Can deal with more than one amorphous phase	Singular samples
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	One-time calibration with single mixture	Partly	Yes	
LCM	Direct	Calibration suite	Yes	Yes	
DOC	Direct	Case dependent	No	Yes	+

Summary 2

➢ Lower limits of detection / accuracy / precision:

  ✓ Detection, identification and quantification of crystalline phases less than 0.1% possible

  ✓ Detection, identification and quantification of amorphous phases less than 1% possible

➢ Limitations are the same for quantitative analysis of crystalline as well as amorphous phases and are dictated by sample properties and the analytical technique used.

➢ For the determination of crystalline and / or amorphous material, the problem will dictate the methodology used.

Summary 3

➢ The traditional Rietveld method only delivers relative phase amounts by default; in the presence of amorphous and/or any amount of unidentified crystalline phases, the analyzed crystalline weight fractions may be significantly overestimated.

➢ Most phase abundances reported in literature, obtained via Rietveld analysis, are provided in a manner suggesting absolute values.

➢ Where no allowance of amorphous and/or unidentified phases has been made/reported, it is reasonable to assume relative phase abundances instead.

- Calibration based methods usually have the potential to achieve the highest accuracy, as most aberrations are included in the calibration function.
- Any calibration sample and standard will contain amorphous materials which, if not accounted for, will decrease accuracy.
  - ✓ Any material possesses a non-diffracting surface layer with some degree of disorder / inclusion of surface reaction products and adsorbed species.
  - ✓ Such a layer can easily account for a mass fraction of several % in a finely divided solid.

- Intensity contributions of amorphous phases to the diffraction pattern are not always evident, especially at low concentrations.
  - ✓ Indirect methods will usually perform better.
- Where intensity contributions of amorphous phases are evident, any method based on modeling amorphous bands provides improved accuracy (direct methods).
  - ✓ Usually a sample of pure amorphous material, or a sample where the amorphous content is high, is required to establish an accurate model.

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