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Quantification of amorphous phases - theory

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Slides from Wikipedia, Chiu Tang (I11, Diamond) and other web sources are used in this lecture

What is an "amorphous" form

"In condensed matter physics and materials science, an amorphous (from the Greek *a*, without, *morphé*, shape, form) or non-crystalline solid is a solid that lacks the long-range order characteristic of a crystal".



Material Classifications (forms)



Courtesy of Chiu Tang (I11, Diamond)

Quantification of amorphous phases by XRD Selected recent reviews

- Madsen, I.C. and Scarlett, N.V.Y. (2008) *Quantitative Phase Analysis* Chapter 11 in Powder Diffraction: Theory and Practice Editors: Dinnebier, R. & Billinge, S. RSC, 582 pages
- 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

Quantification of amorphous phases by XRD Methods

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

Quantification of amorphous phases by XRD Classification

Indirect measurement

- 1. Analyse crystalline phases
- 2. Put on absolute scale
- 3. Calculate amorphous content by difference
- <u>Direct measurement</u> 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

- 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 resulting in an increased peak overlap problem
 - Discrimination of peak tail / amorphous band / background intensities



Can we easily discriminate between peak and background intensity?









Quantification of amorphous phases by XRD Practical part (for afternoon lecture)

Sample	Corundum	Quartz	Silica Flour
A1, A2, A3	50.01	0.00	49.99
B1, B2, B3	49.98	15.03	34.99
C1, C2, C3	49.99	30.00	20.00
D1, D2, D3	50.00	40.00	10.00
E1, E2, E3	50.00	45.00	5.00
F1, F2, F3	50.01	48.00	1.99
G1, G2, G3	50.00	49.00	1.00
H1, H2, H3	50.02	49.48	0.50
1, 2, 3	49.87	50.13	0.00

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











Quantification of amorphous phases by XRD Methodology

Single Peak method

Traditional Rietveld method Internal Standard method External Standard method PONKCS method Linear Calibration Model Degree of Crystallinity Quantification of amorphous phases by XRD Single Peak Method

General procedure:

- 1. Prepare a series of standards containing the crystalline or amorphous phase of interest at known concentrations
- 2. Obtain a measure of the crystalline or amorphous phase'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 crystalline or amorphous phase and I_{α} is the measure of the intensity of the crystalline or amorphous phase

Single Peak Method



Example: Telmisartan form beta in form alpha

Single Peak Method

<u>Benefits</u>

- 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 wont go through the origin
- More than one amorphous phase could be analyzed (this will usually require profile fitting)

<u>Limitations</u>

- 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, preferred orientation, ...)
 - Needs redetermination to compensate for tube ageing and any instrument configuration changes
- Direct method for determination of amorphous content 22

Quantification of amorphous phases by XRD Methodology

> Single Peak method **Traditional Rietveld method** Internal Standard method External Standard method **PONKCS** method Linear Calibration Model **Degree of Crystallinity**

The Rietveld method: Properties

- 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 standardless¹ method and thus does not require any standards or calibration

¹⁾ Note:

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.

The Rietveld method



The famous two papers:

H. M. Rietveld

Acta Cryst. (1967). 22, 151-152, Line profiles of neutron powder-diffraction peaks for structure refinement

Appl. Cryst. (1969). 2, 65-71, A profile refinement method for nuclear and magnetic structures



First application on X-ray data: J. Appl. Cryst. (1977). 10, 7-11 Least-squares structure refinement based on profile analysis of powder film intensity data measured on an automatic microdensitometer, G. Malmros and J. O. Thomas

The Rietveld method: The overlap problem



The degree of overlap of individual reflection correlates with the uncertainty of their integrated intensities.

Rietveld's idea:

Modelling of the entire powder pattern while minimizing the difference to the measured powder pattern by LSQ's techniques takes the peak overlap intrinsically into account²⁶

The Rietveld method: How to

The idea of least squares

$$Min = \sum_{i} \left(w_i \left(y_{calc} \left(2\theta_i \right) - y_{obs} \left(2\theta_i \right) \right)^2 \right)$$

$$\sum_{i=0}^{n-1} \left(w_i (Yobs_i - Ycalc_i (p_1 \dots p_m)) \frac{\partial Ycalc_i}{\partial p_j} \right) = 0$$

using Taylor series expansion



The Rietveld formula: 5 main contributions





The Rietveld formula: QPA

Integrated intensity I of a reflection *hkl* for phase α in a multi-phase mixture measured on a flat plate sample with *"*infinite thickness":

$$I_{(hkl)\alpha} = \left[\frac{I_0\lambda^3}{32\pi r}\frac{e^4}{m_e^2c^4}\right] \cdot \left[\frac{M_{hkl}}{2V_{\alpha}^2}\left|F_{(hkl)\alpha}\right|^2 \left(\frac{1+\cos^22\theta\cos^22\theta_m}{\sin^2\theta\cos\theta}\right)\right] \cdot \left[\frac{W_{\alpha}}{\rho_{\alpha}\mu_m^*}\right]$$

Which can be simplified using a constant for reflection hkl in a particular experimental setup

$$I_{(hkl)\alpha} = C_{(hkl)\alpha} \cdot \frac{1}{V_{\alpha}^{2}} \cdot \left[\frac{W_{\alpha}}{\rho_{\alpha}\mu_{m}^{*}}\right]$$

In Rietveld analysis, all reflection intensities of a phase α are proportional to the corresponding scale factor:

$$I_{(hkl)\alpha} \propto S_{\alpha}$$

This leads to an with a scaling factof K which depends exclusively on the instrumental conditions and not on the sample/phases. :

$$S_{\alpha} = \mathbf{K} \cdot \frac{1}{V_{\alpha}^2} \cdot \left[\frac{W_{\alpha}}{\rho_{\alpha}\mu_{\alpha}^*}\right]$$

The Rietveld formula: QPA

Using the X-ray density

$$\rho_{\alpha} = 1.6604 \cdot \frac{ZM_{\alpha}}{V_{\alpha}}$$

the scale factor of phase α can be rewritten as:

$$S_{\alpha} = \mathbf{K} \cdot \frac{1}{V_{\alpha}^{2}} \cdot \left[\frac{W_{\alpha}V_{\alpha}}{1.6604 \cdot ZM_{\alpha}\mu_{m}^{*}} \right]$$

from which the weight fraction of phase α can be calculated

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

assuming all phases to be crystalline, the following normalization relation can be used:

$$\sum_{\alpha} W_{\alpha} = 1$$

allowing to eliminate the instrument constant and the mass absorption coefficient of te sample:

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

Effects strongly influencing QPA Absorption correction



Effects strongly influencing QPA Transparancy effect



$$w_{\rm T}(x;\mu,T,R,2\theta) = \begin{cases} \frac{1}{\gamma_{\rm T}} \exp\left(\frac{x}{\gamma_{\rm T}}\right) & \text{for } -x_{\rm T} < x < 0, \\ 0 & \text{elsewhere} \end{cases}$$

where x is the deviation from the peak position, μ is the linear absorption coefficient of the specimen, T is the thickness of the specimen, R is the goinometer radius, 2θ is the diffraction angle, $\gamma_{\rm T} = \frac{\sin 2\theta}{2\mu R}, \ x_{\rm T} = \frac{2T\cos\theta}{R}.$

Effects strongly influencing QPA Preferred orientation



Alternatively symmetry adapted spherical harmonics of 2, 4, or 8th order

W. A. Dollase, J. Appl. Cryst. (1986). 19, 267-272. Correction of intensities for preferred orientation in powder diffractometry: application of the March model.

Effects strongly influencing QPA Displacement parameter



$$t_j(2\theta_{hkl}) = \exp\left(-B_j\frac{\sin^2\theta_{hkl}}{\lambda}\right)$$

$$B_j = 8\pi^2 \left(u^2\right)_j \quad \text{ in } [\text{\AA}^2]$$

$$B_{ij} = \begin{pmatrix} B_{11} & B_{12} & B_{13} \\ B_{21} & B_{22} & B_{23} \\ B_{31} & B_{32} & B_{33} \end{pmatrix}$$

The Rietveld method

Benefits

Requires no standards or calibration¹⁾

¹⁾ Note:

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

Limitations

- The Rietveld method assumes that all phases are crystalline 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 nonidentified and/or amorphous phases are present

The Rietveld method *for 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)

The Rietveld method *for amorphous phases*



Sample 1A from

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 38

The Rietveld method *for amorphous phases*

<u>Benefits</u>

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

<u>Limitations</u>

- 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).

Quantification of amorphous phases by XRD Methodology

> Single Peak method Traditional Rietveld method Internal Standard method External Standard method **PONKCS** method Linear Calibration Model Degree of Crystallinity

Internal Standard Method

Amorphous/unknown content can be determined by adding an internal standard s:

$$W_{\alpha(meas)} = W_{s(meas)} \cdot \frac{S_{\alpha(meas)} (ZMV)_{\alpha(meas)}}{S_{s(meas)} (ZMV)_{s(meas)}}$$

The absolute weight fractions of the known materials can then be can calculated by:

$$W_{\alpha(abs)} = W_{\alpha(meas)} \times \frac{W_{std(known)}}{W_{std(meas)}}$$

The weight fraction of the unknown material (e.g. amorphous content) follows directly by:

$$W_{(unk)} = 1.0 - \sum_{k=1}^{n} W_{k(abs)}$$

Internal Standard Method

<u>Benefits</u>

- 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 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

Quantification of amorphous phases by XRD Methodology

> Single Peak method Traditional Rietveld method Internal Standard method External Standard method PONKCS method Linear Calibration Model **Degree of Crystallinity**

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 μ_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

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



Jansen *et al.,* 2011

External Standard Method

Benefits

- Indirect method for determination of amorphous content
- Uses an external standard, the ۲ sample is not contaminated

Limitations

- Requires the mass absorption coefficient for the entire sample
 - \Rightarrow 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

Quantification of amorphous phases by XRD Methodology

> Single Peak method Traditional Rietveld method Internal Standard method External Standard method PONKCS method Linear Calibration Model **Degree of Crystallinity**

- 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

Determine a set of intensities (group of single peaks, Pawley or LeBail) with an overall fixed scale factor (=1.0) and apply a Lorenz-Polarisation correction:

$$I'_{meas} = \frac{I_{meas}}{Lp}$$

With help of an internal standard s, an artificial ZM can be calculated:

$$(ZM)_{\alpha} = \frac{W_{\alpha}}{W_s} \cdot \frac{s_s}{s_{\alpha}} \cdot \frac{(ZMV)_s}{V_{\alpha}}$$
 using $V_{\alpha} = 1$ for group of peaks

the "correct" ZM value requires knowledge of the density of the unknown material

$$(ZM)_{\alpha(true)} = \frac{\rho_{\alpha}V_{\alpha}}{1.6604}$$

Peak intensities can then be scaled by:

$$\frac{(ZM)_{\alpha(true)}}{(ZM)_{\alpha}}$$









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

<u>Limitations</u>

- Requires availability of a standard mixture to derive an empirical ZMV
- Direct method for determination of amorphous content

Quantification of amorphous phases by XRD Methodology

> Single Peak method Traditional Rietveld method Internal Standard method External Standard method **PONKCS** method Linear Calibration Model Degree of Crystallinity

Linear calibration model

- The intensity contribution of crystalline or an amorphous phase to the powder pattern is modeled via single line or 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



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

Quantification of amorphous phases by XRD Methodology

> Single Peak method Traditional Rietveld method Internal Standard method External Standard method **PONKCS** method Linear Calibration Model Degree of Crystallinity

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

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

Hint: The method can also be used in case of non-Bragg contributions (e.g. Warren type peaks) from disorder.

Degree of Crystallinity



Example: M2A

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

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	+

Results of the practical part



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.

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

- Lower limits of detection / accuracy / precision:
 - Detection, identification and quantification of <u>crystalline</u> phases less than 0.1% possible
 - Detection, identification and quantification of <u>amorphous</u> phases less than 1% possible
- Limitations are the same for quantitative analysis of crystalline and 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

- The traditional Rietveld method only delivers <u>relative</u> 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 percent in a finely divided solid

- Singular 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 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.