
Quantitative phase analysis

Crystal Structure Analysis
Materials Science & Engineering, Seoul National University
CHAN PARK

Jenkins & Snyder Chap 13
Cullity Chap 12
Bish & Post Chap 5
Klug & Alexander Chap 7
Krawitz Chap 8

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QPA - reference

- Madsen, I.C. and Scarlett, N.V.Y. (2008) Quantitative Phase Analysis In "Powder Diffraction: Theory and Practice." Dinnebier, R.E. and Billinge, S.J.L., Editors. The Royal Society of Chemistry: Cambridge, UK
- Madsen, I.C. and Scarlett, N.V.Y., Riley, D.P. and Raven, M.D. (2012) Quantitative Phase Analysis using the Rietveld Method In "Modern Diffraction Methods", Mittemeijer, E.J. and Welzel, U., Editors. Wiley-VCH
- 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
- Madsen, I.C., Scarlett, N.V.Y. and Webster, N.A.S. (2012) *Quantitative phase analysis.* Uniting Electron Crystallography and Powder Diffraction. Editors: Kolb, U., Shankland, K., Meshi, L., Avilov, A. & David, W. Springer

Presentation of Arnt Kern, DXC 2014 Workshop, "QUANTIFYING CRYSTALLINE AND AMORPHOUS PHASES"

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QPA - reference (continued)

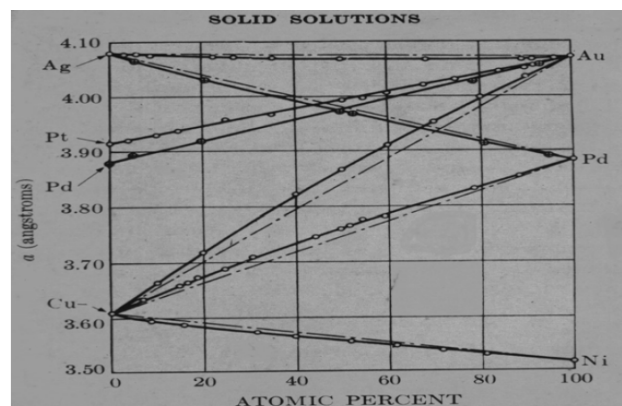
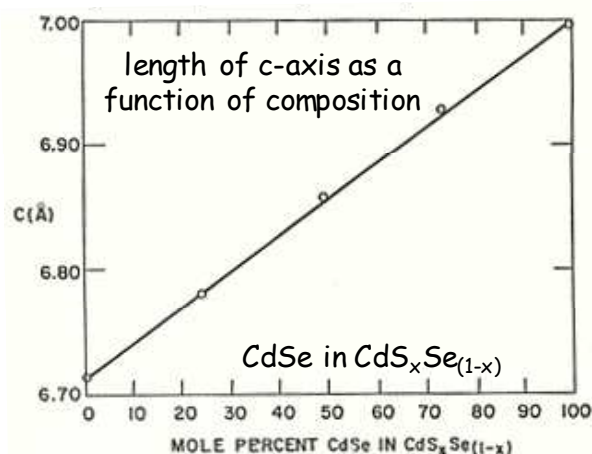
- Rietveld Refinement Round Robin (<http://www.iucr.org/iucr-top/comm/cpd/>)
 - ✓ Hill, R.J. (1992): "Rietveld Refinement Round Robin. I. Analysis of Standard X-ray and Neutron Data for PbSO₄". J. Appl. Cryst., 25, 589-610
 - ✓ Hill, R.J. & Cranswick, L.M.D (1994): "Rietveld Refinement Round Robin. II. Analysis of Monoclinic ZrO₂". J. Appl. Cryst., 27, 802-844

 - QPA Round Robin (<http://www.iucr.org/iucr-top/comm/cpd/>)
 - ✓ Madsen, I.C. et al. (2001): "Outcomes of the International Union of Crystallography Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis: samples 1a to 1h". J. Appl. Cryst., 34, 409-426
 - ✓ Scarlett, N.V.Y. et al. (2002): "Outcomes of the International Union of Crystallography Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis: samples 2, 3, 4, synthetic bauxite, natural granodiorite and pharmaceuticals". J. Appl. Cryst., 35, 383-400

 - Biannual "Reynold's Cup" series (<http://www.clays.org/Reynolds.html>) (Clay Minerals Society)

 - Quantitative Rietveld Phase Analysis of Pharmaceuticals"
 - ✓ Fawcett T.G., Needham, F., Faber, J.N. & Crowder, C.E. (2010): "International Centre for Diffraction Data Round Robin on Quantitative Rietveld Phase Analysis of Pharmaceuticals". Powder Diffraction, 25 (1), 1-8
- Presentation of Arnt Kern, DXC 2014 Workshop "QUANTIFYING CRYSTALLINE AND AMORPHOUS PHASES"
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Vegard's law



Deviations from Vegard's law

- Volume of a unit cell in a **substitutional solid solution** is linearly proportional to the fraction of sites substituted
- Can use measurement of lattice parameter of a substitutional solid solution in determining composition of material
- The **only** application of diffraction for quantitative analysis that **does not rely on intensity**

Quantitative phase analyses using line intensities

- First done by L. Navias (GE) in 1925 on sillimanite and mullite
- Typical accuracy worse than 10%
- Best RIR analysis ~3%
- Best multi-line Copland-Bragg analysis ~1%
- Routine Rietveld analysis ~1%

RIR ; reference intensity ratio

Factors affecting line intensities in XRPD

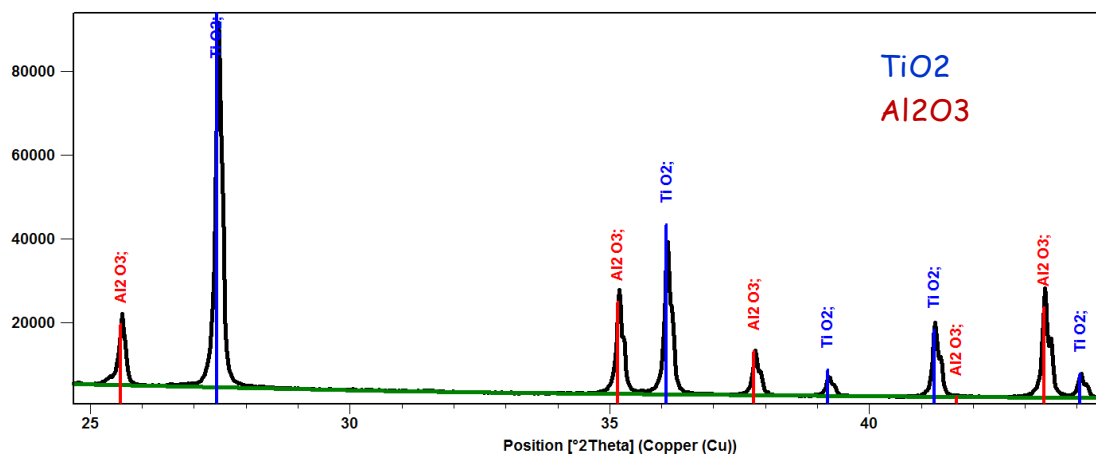
factor	parameter	factor	parameter
Structure-sensitive	Atomic scattering factor	Sample sensitive	Microabsorption
	Structure factor		Crystallite size
	Polarization		Degree of crystallinity
	Multiplicity		Residual stress
	Temperature		Degree of peak overlap
Instrument-sensitive (Absolute intensity)	Source intensity	Measurement-sensitive	Preferred orientation
	Diffractometer efficiency		Method of peak area measurement
	Voltage drift		Degree of peak overlap
	Takeoff angle of tube		Method of background subtraction
	Receiving slit width		Ka ₂ stripping or not
	Axial divergence allowed		Degree of data smoothing used
Instrument-sensitive (Relative intensity)	Divergence slit aperture		
	Detector dead time		

Sample sensitive parameters

- Preferred orientation - most serious effect, present to some degree in most specimen mounts
- Absorption - same at all angles in Bragg-Brentano diffractometer
- Microabsorption - can distort I's of all the lines, can be minimized by grinding powder to < 10um size
- Crystallite statistics
- Extinction
- Degree of crystallinity

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Intensity vs. phase quantity



- A mixture of equal amounts of TiO₂ and Al₂O₃
- The TiO₂ pattern is more intense because TiO₂ diffracts X-rays more efficiently
- With proper calibration, the amount of each phase present in the sample can be calculated

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Scott A. Speakman

Variation in RIR as a function of scan width

50:50 mixture of Si and Al_2O_3

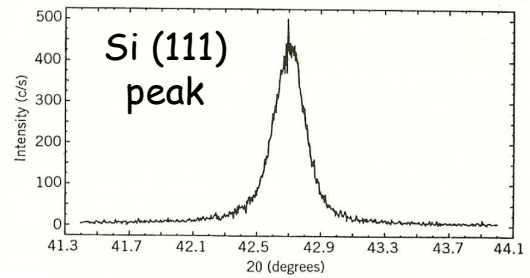
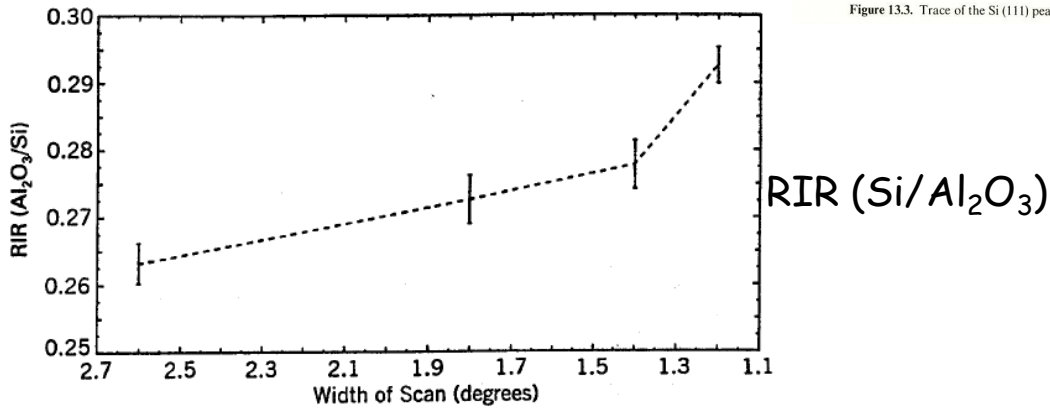
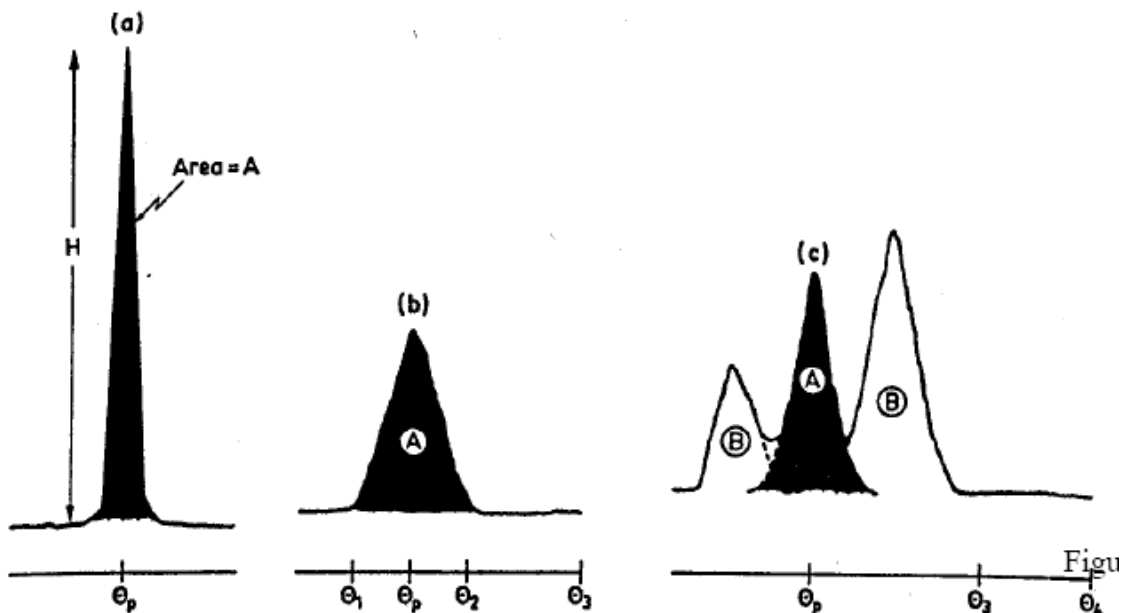


Figure 13.3. Trace of the Si (111) peak using Cr radiation.



RIR; Ratio of the **background-corrected integrated intensities** of Si(111) peak to the 100% line of Al_2O_3

Types of line measured in quantitative analysis
peak height, peak area, overlapped peaks



$$I(hkl) = \left(\frac{I_0 A \lambda^3}{32\pi r} \right) \left[\left(\frac{\mu_0}{4\pi} \right)^2 \frac{e^4}{m^2} \right] \left(\frac{1}{v^2} \right) \left[|F(hkl)|^2 P \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \right] \left(\frac{e^{-2M}}{2\mu} \right)$$

- $I(hkl)$ = integrated intensity diffracted by a single phase powder specimen in a diffractometer
- I_0 = intensity of incident beam
- A = cross-sectional area of incident beam
- λ = wavelength of incident beam r = radius of diffractometer circle
- $\mu_0 = 4\pi \times 10^{-7} \text{ mkgC}^{-2}$ e = electron charge
- m = mass of electron v = volume of unit cell
- $F(hkl)$ = structure factor P = multiplicity factor
- θ = Bragg angle e^{-2M} = temperature factor
- μ = linear attenuation coefficient

Single phase
$$I(hkl) = \left(\frac{I_0 A \lambda^3}{32\pi r} \right) \left[\left(\frac{\mu_0}{4\pi} \right)^2 \frac{e^4}{m^2} \right] \left(\frac{1}{v^2} \right) \left[|F(hkl)|^2 P \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \right] \left(\frac{e^{-2M}}{2\mu} \right)$$

Mixture of phase α & β
$$I_\alpha(hkl) = I_\alpha = \frac{K_1 c_\alpha}{\mu_m}$$

c_α = volume fraction of alpha phase in the mixture
 μ_m = linear attenuation coefficient of the mixture

- c_α can be found from $I_\alpha/I(\text{reference})$
- Different methods depending on what is used as the reference line
 - ✓ External standard method - a line from pure α
 - ✓ Direct comparison method - a line from another phase in mixture
 - ✓ Internal standard method - a line from a foreign material mixed with the specimen
- $\mu_m = \mu_m(c_\alpha)$

- 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)

* Partial Or No Known Crystal Structures

-
- Powder XRD is ideal for crystalline mixture analysis
 - ✓ Each component produces characteristic pattern superimposed on those of other components
 - ✓ Intensity of lines in each component is proportional to the concentration of that component, disregarding the effects of absorption.
 - Absorption
 - ✓ When a mixture contains both a weak and strong absorber, lines of the weak-absorbing compound appear weaker (and those of the strong-absorbing compound stronger) than calculated from a linear relationship between pattern intensity and composition.

Nomenclature (Klug & Alexander)

- i, j, k, \dots lines in diffraction pattern
- I, J, K, \dots components of a mixture
- S subscript referring to component used as reference standard
- ρ_J density of components J
- f_J volume fraction of component J in a mixture
- x_J weight fraction of component J in a mixture
- μ_J linear absorption coefficient of component J for X-ray wavelength λ
- $\mu_J^* = \mu_J / \rho_J$ mass absorption coefficient of component J for X-ray wavelength λ
- μ linear absorption coefficient of sample with N components
- μ^* mass absorption coefficient of sample with N components $\mu^* = \sum x_J \mu_J^*$
- I_{iJ} intensity of i^{th} line of component J in mixture
- $(I_{iJ})_0$ intensity of i^{th} line of pure component J
- I/I_{cor} ratio of intensity of strongest peak of each component to a common standard, synthetic corundum, in a 1:1 mixture of sample and standard
- $RIR_{J,S}$ reference intensity ratio of phase J with respect to phase S

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Basic concepts

- $\mu =$ linear attenuation coefficient

- $\rho =$ density

- $\mu/\rho =$ mass attenuation coefficient; materials constant, $f(\lambda)$

$$\left(\frac{\mu}{\rho}\right)_s = \sum_j \left(\frac{\mu}{\rho}\right)_j X_j$$

- Integrated intensity proportional to analyte phase concentration
- Intensity functionally dependent on absorbing power of mixture for X-rays
- Dependence is generally non-linear and unknown
- Absorption

$$I_{iJ} = (K_{iJ} f_J) / \mu = (K_{iJ} x_J) / (\rho_J \mu^*)$$

- ✓ Density is constant for given phase

$$I_{iJ} = (K_{iJ} x_J) / \mu^* = (K_{iJ} x_J) / (\sum x_k \mu_k^*)$$

Can get x_J by

- ✓ Measuring intensity I_{iJ}
- ✓ Determining μ^* of sample
- ✓ Determining calibration constant K_{iJ}

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Multi-phase mixtures

- Absolute technique
 - ✓ When intensity of the peak in the pure analyte $(I_{ij})_0$ is involved in the equations to solve for x_j
 - ✓ Depend on experimental conditions (instrument type, setting, etc) so it is difficult to compare results from different labs
 - Relative technique (Ratio technique)
 - ✓ When ratios, not absolute intensities, are used (e.g. internal & external standard techniques)
 - ✓ Independent of experimental conditions
-
- Absorption-diffraction method (external standard method)
 - ✓ Compare the experimental line intensity from the mixture to a line from a pure phase
 - ✓ Known mass absorption coefficient for mixture
 - Internal standard method
 - ✓ Compare the experimental line intensity from the mixture to a line from foreign material mixed with the sample
 - ✓ Sample doped with reference
 - Direct comparison method
 - ✓ Compare the experimental line intensity from the mixture to a line from another phase in the mixture
 - Standard addition method (spiking method)
 - ✓ Sample spiked with analyte phase
 - Whole pattern profile matching/ Whole pattern fitting (Rietveld method)

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External standard method

Mixture of phase α & β

$$\left(\frac{\mu}{\rho}\right)_s = \sum_j \left(\frac{\mu}{\rho}\right)_j X_j \qquad \frac{\mu_m}{\rho_m} = w_\alpha \left(\frac{\mu_\alpha}{\rho_\alpha}\right) + w_\beta \left(\frac{\mu_\beta}{\rho_\beta}\right)$$

c_α = volume fraction of α in the mixture

w = weight fraction, ρ = density

in a unit volume of mixture,

weight of the mixture = ρ_m

weight of the α phase = $w_\alpha \rho_m$

volume of phase α = $c_\alpha = (w_\alpha \rho_m) / \rho_\alpha \rightarrow w_\alpha = (\rho_\alpha c_\alpha) / \rho_m$

μ_m = linear attenuation coefficient of the mixture

$$\mu_m = c_\alpha \mu_\alpha + c_\beta \mu_\beta = c_\alpha \mu_\alpha + (1 - c_\alpha) \mu_\beta$$

$$= c_\alpha (\mu_\alpha - \mu_\beta) + \mu_\beta;$$

$$I_{\alpha}(hkl) = I_{\alpha} = \frac{K_1 c_\alpha}{\mu_m} = \frac{K_1 c_\alpha}{c_\alpha (\mu_\alpha - \mu_\beta) + \mu_\beta}$$

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Cullity, page 350

External standard method

in a unit mass of mixture,
 volume of phase $\alpha = w_\alpha/\rho_\alpha$
 volume of phase $\beta = w_\beta/\rho_\beta$

$$c_\alpha = \frac{W_\alpha/\rho_\alpha}{W_\alpha/\rho_\alpha + W_\beta/\rho_\beta}$$

$$= \frac{W_\alpha/\rho_\alpha}{W_\alpha(1/\rho_\alpha - 1/\rho_\beta) + 1/\rho_\beta}$$

$$I_\alpha = \frac{K_1 c_\alpha}{\mu_m} = \frac{K_1 c_\alpha}{c_\alpha(\mu_\alpha - \mu_\beta) + \mu_\beta}$$

$$I_\alpha = \frac{K_1 w_\alpha}{\rho_\alpha \{w_\alpha[(\mu/\rho)_\alpha - (\mu/\rho)_\beta] + (\mu/\rho)_\beta\}} \quad (1)$$

For a pure phase α , $I_{\alpha p} = \frac{K_1}{\mu_\alpha}$; (2)

From (1) & (2), $\frac{I_\alpha}{I_{\alpha p}} = \frac{w_\alpha(\mu/\rho)_\alpha}{w_\alpha[(\mu/\rho)_\alpha - (\mu/\rho)_\beta] + (\mu/\rho)_\beta} = \frac{w_\alpha(\mu/\rho)_\alpha}{(\mu/\rho)_m}$

Can get w_α from $(\mu/\rho)_\alpha$, $(\mu/\rho)_m$, and $\frac{I_\alpha}{I_{\alpha p}}$

$$\frac{\mu_m}{\rho_m} = w_\alpha \left(\frac{\mu_\alpha}{\rho_\alpha} \right) + w_\beta \left(\frac{\mu_\beta}{\rho_\beta} \right)$$

External standard method

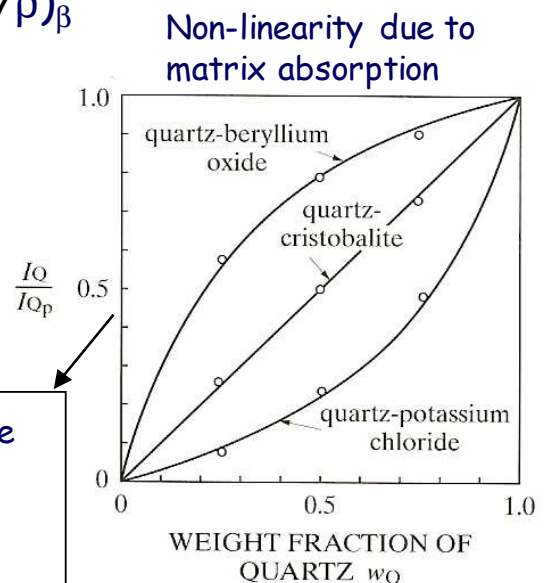
$$\frac{I_\alpha}{I_{\alpha p}} = \frac{w_\alpha(\mu/\rho)_\alpha}{w_\alpha[(\mu/\rho)_\alpha - (\mu/\rho)_\beta] + (\mu/\rho)_\beta}$$

can get w_α from $I_\alpha/I_{\alpha p}$, $(\mu/\rho)_\alpha$, & $(\mu/\rho)_\beta$

When μ/ρ of α & β are equal,

$$\frac{I_\alpha}{I_{\alpha p}} = w_\alpha$$

Shows how the I of a particular diffraction line from one phase depends on the absorption coefficient of the other phase



➤ Need to have a sample of pure phase of unknown

Direct comparison method

- The required reference line comes from another phase in the mixture → **do not need to have a sample of pure phase of unknown**
- The amount of retained austenite in hardened steel (austenite/martensite mixture) --- Cullity Chap 12-5
 - ✓ Composition of the mixture when two phases have the same composition but different crystal structure
 - ✓ External standard method cannot be used, because it is usually impossible to obtain a reference sample of pure austenite, or of known austenite content, of the same chemical composition as the austenite in the unknown

Direct comparison method

$$I(hkl) = \underbrace{\left(\frac{I_o A \lambda^3}{32\pi r}\right) \left[\left(\frac{\mu_o}{4\pi}\right)^2 \frac{e^4}{m^2}\right] \left(\frac{1}{v^2}\right)}_{K_2} \left[|F(hkl)|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}\right)\right] \left(\frac{e^{-2M}}{2\mu}\right)$$

$$R = \left(\frac{1}{v^2}\right) \left[|F|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}\right)\right] (e^{-2M})$$

$I = \frac{K_2 R}{2\mu}$ K_2 constant, independent of the kind & amount of the diffracting substance
 R depends on θ , hkl , and the kind of substance

<p>2 phase mixture α, γ</p> $I_\gamma = \frac{K_2 R_\gamma c_\gamma}{2\mu_m}$ $I_\alpha = \frac{K_2 R_\alpha c_\alpha}{2\mu_m}$ <p>can get c_γ/c_α</p> <p>can get c_γ and c_α from $c_\gamma + c_\alpha = 1$</p>	<p>3 phase mixture α, γ, c</p> $I_\gamma/I_\alpha = (R_\gamma/R_\alpha)(c_\gamma/c_\alpha)$ $I_\gamma/I_c = (R_\gamma/R_c)(c_\gamma/c_c)$ <p>can get c_γ/c_α and c_γ/c_c</p> <p>can get c's from $c_\gamma + c_\alpha + c_c = 1$</p>
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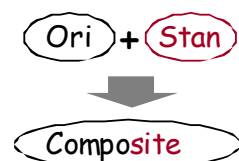
Internal standard method

- Can eliminate any effects due to variations in instrument or specimen
- Useful when there is little prior knowledge of the composition of samples
- Diffraction line from the unknown phase is compared with a line from a standard substance mixed with the sample in known proportions → can be used in powder samples only

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Internal standard method

- Need to get amount of phase A in a mixture of phases A, B, C, & others
- Mix known amount of original sample & known amount of standard substance (S)
- c_A = volume fraction of phase A in the original sample
- c'_A = volume fraction of phase A in the composite sample
- c_S = volume fraction of S in the composite sample



$$I = \frac{K_2 R}{2\mu} \quad \rightarrow \quad I_A = \frac{K_3 c'_A}{\mu_m}, \quad I_S = \frac{K_4 c_S}{\mu_m} \quad \rightarrow \quad \frac{I_A}{I_S} = \frac{K_3 c'_A}{K_4 c_S}$$

in composite sample

$$c_\alpha = \frac{W_\alpha / \rho_\alpha}{W_\alpha / \rho_\alpha + W_\beta / \rho_\beta}$$

mixture of phase α & β

$$c'_A = \frac{w'_A / \rho_A}{w'_A / \rho_A + w'_B / \rho_B + w'_C / \rho_C + \dots + w'_S / \rho_S}$$

mixture of phase A, B, C, others, S

Internal standard method

in composite sample

$$I = \frac{K_2 R}{2\mu} \rightarrow I_A = \frac{K_3 c'_A}{\mu_m}, \quad I_S = \frac{K_4 c'_S}{\mu_m} \rightarrow \frac{I_A}{I_S} = \frac{K_3 c'_A}{K_4 c'_S}$$

mixture of phase α & β

$$c_\alpha = \frac{W_\alpha/\rho_\alpha}{W_\alpha/\rho_\alpha + W_\beta/\rho_\beta}$$

mixture of phase A, B, C, others, S

$$c'_A = \frac{w'_A/\rho_A}{w'_A/\rho_A + w'_B/\rho_B + w'_C/\rho_C + \dots + w'_S/\rho_S}$$

$$\frac{c'_A}{c'_S} = \frac{w'_A \rho_S}{\rho_A w'_S}$$

$$\rightarrow \frac{I_A}{I_S} = K_5 w'_A$$

$$\frac{I_A}{I_S} = K_6 w_A$$

$$w'_A = w_A(1 - w_S)$$

w_S is kept constant in all composite samples

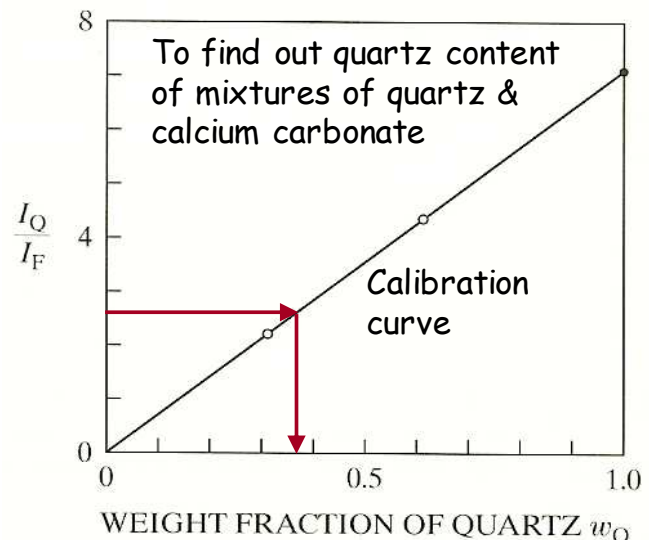
- Calibration curve (w_A vs. (I_A/I_S)) → w_A can be obtained from (I_A/I_S) for a composite with same w_S which was used in the calibration curve

Internal standard method

- Prepare a set of synthetic samples (known amount of A + constant amount of standard) → multiple measurements → calibration curve
- Calibration curve (w_A vs. (I_A/I_S)) → w_A can be obtained from (I_A/I_S) for a composite with same w_S which was used in the calibration curve

$$\frac{I_A}{I_S} = K_6 w_A$$

- Quartz + Calcium Carbonate
- Fluorite (standard)
- $w_S = 0.2$



Internal standard method

- Relative class
- Sample doped with known amount of reference material (internal standard)
 - ✓ x'_J weight fraction of the unknown phase J in the doped sample
 - ✓ x_J weight fraction of phase J in the un-doped sample
 - ✓ x_S weight fraction of internal standard
- $x'_J = x_J (1 - x_S)$
- $I_{iJ} = (K_{iJ} x_J) / \mu^*$ ---- (Q1)
- $I_{iJ} = K_{iJ} x_J (1 - x_S) / \mu_d^*$ (for phase J)
 - ✓ μ_d^* mass absorption coefficient of doped sample
- $I_{hS} = K_{hS} x_S / \mu_d^*$ (for internal standard)
- $I_{iJ} / I_{hS} = [K_{iJ} x_J (1 - x_S)] / [K_{hS} x_S]$
 - ✓ Ratio of intensity is independent of absorption
- $x_J = [K_{hS} x_S] / [K_{iJ} (1 - x_S)] \cdot [I_{iJ} / I_{hS}] = \text{constant} \cdot [I_{iJ} / I_{hS}]$
- Can be used to analyze any phase in a mixture without analyzing remaining phase.

www.ccp14.ac.uk/poster-talks/david-hay-quant-notes-axaa99/html/sld001.htm

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Quantitative analysis - Jenkins & Snyder

Intensity of line hkl of phase α

$$I_{(hkl)\alpha} = \underbrace{\left[\frac{I_0 \lambda^3}{64 \pi r^2} \left(\frac{e^2}{m_e c^2} \right)^2 \right]}_{K_e \text{ experiment}} \underbrace{\left[\frac{M_{(hkl)}}{V_\alpha^2} |F_{(hkl)\alpha}|^2 \left(\frac{1 + \cos^2 2\theta \cos^2 2\theta_m}{\sin^2 \theta \cos \theta} \right) \right]}_{K_{(hkl)\alpha} \text{ specimen}} \left[\frac{X_\alpha}{\rho_\alpha \left(\frac{\mu}{\rho} \right)_s} \right]$$

$$I_{(hkl)\alpha} = \frac{K_e K_{(hkl)\alpha} X_\alpha}{\rho_\alpha \left(\frac{\mu}{\rho} \right)_s}$$

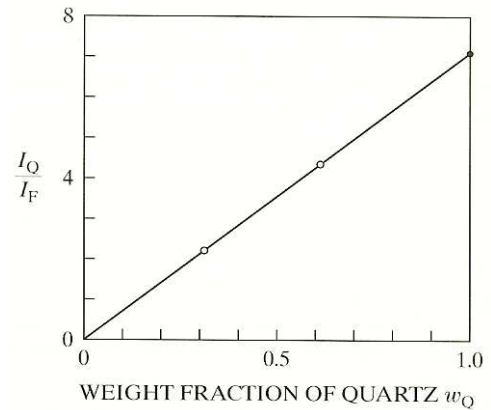
- X is not an independent variable
- All X_j must be known to compute the mass absorption coefficient

$$\left(\frac{\mu}{\rho} \right)_s = \sum_j \left(\frac{\mu}{\rho} \right)_j X_j$$

Internal standard method

$$I_{(hkl)\alpha} = \frac{K_e K_{(hkl)\alpha} X_\alpha}{\rho_\alpha \left(\frac{\mu}{\rho}\right)_s} \rightarrow \frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} = \left(\frac{K_{(hkl)\alpha}}{K_{(hkl)'\beta}}\right) \left(\frac{\rho_\beta}{\rho_\alpha}\right) \left(\frac{X_\alpha}{X_\beta}\right) \rightarrow \frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} = k \frac{X_\alpha}{X_\beta}$$

- The ratio of a line from phase α to a line from phase β in any specimen causes the mass absorption coefficient to cancel
- Adding a phase of known concentration to the specimen will permit the evaluation of k for a known and then the evaluation of the wt. fraction of alpha in any unknown



Absorption-diffraction method (external standard method)

- μ^* (mass absorption coeff of sample with N components, $\mu^* = \sum x_J \mu_J^*$) previously determined by
 - ✓ Calculation from known composition, summation of atomic absorption coefficients
 - ✓ Direct absorption measurement
 - ✓ Measurement of Compton scattering
 - ✓ Case with constant μ^* (include phase transitions where chemical composition remains unchanged during the transition)

Absorption-diffraction method

- Multiple phases, variable absorption coefficient
- Requires measurement of $(I_{iJ})_0$ for the pure phases in the mixture
- $I_{iJ} = (K_{iJ} x_J) / \mu^*$ → pure phase ($x_J = 1$) → $(I_{iJ})_0 = K_{iJ} / \mu_J^*$
- $x_J = (I_{iJ}) / (I_{iJ})_0 \cdot (\mu^* / \mu_J^*)$
- x_J can be obtained from (I_{iJ}) , $(I_{iJ})_0$, μ^* , and μ_J^*
- $\log x_J - \log[(I_{iJ}) / (I_{iJ})_0] = \log [\mu^* / \mu_J^*]$ → should be a straight line, but deviates (due to microabsorption)
 - $x_J = (I_{iJ}) / (I_{iJ})_0 \cdot (\mu^* / \mu_J^*)^\alpha$
- α is not constant, depends on grain size of analyte and the nature of the matrix of other phases
- Microabsorption effect can be severe when absorption properties and crystallite size distribution of the pure phase J and the multi-phase mixture are widely different

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Absorption - diffraction method

- Compare $I_{(hkl)\alpha}$ of a line in a mixture to its value in pure phase α

$$I_{(hkl)\alpha} = \frac{K_e K_{(hkl)\alpha} X_\alpha}{\rho_\alpha \left(\frac{\mu}{\rho} \right)_s}$$

$$\frac{I_{i\alpha}}{I_{i\alpha}^\circ} = \frac{\frac{K_e K_{i\alpha} X_\alpha}{\rho_\alpha \left(\frac{\mu}{\rho} \right)_m}}{\frac{K_e K_{i\alpha} 1.0}{\mu_\alpha^\circ}} \quad \rightarrow \quad \frac{I_{i\alpha}}{I_{i\alpha}^\circ} = \frac{\left(\frac{\mu}{\rho} \right)_\alpha X_\alpha}{\left(\frac{\mu}{\rho} \right)_m}$$

In case of polymorph,

$$\frac{I_{i\alpha}}{I_{i\alpha}^\circ} = X_\alpha$$

Cristobalite in quartz and amorphous SiO₂ matrix

Cubic, tetragonal, & monoclinic forms of ZrO₂ in pure ZrO₂ body

Anatase in rutile (TiO₂)

Absorption - diffraction method

Use of Klug's equation for any two phase mixture

$$I_{(hkl)\alpha} = \frac{K_e K_{(hkl)\alpha} X_\alpha}{\rho_\alpha (\mu/\rho)_s} \quad \rightarrow \quad I_{(hkl)\alpha} = \frac{K_e K_{(hkl)\alpha} X_\alpha}{\rho_\alpha [X_\alpha (\mu/\rho)_\alpha + X_\beta (\mu/\rho)_\beta]}$$

$$I_{(hkl)\alpha}^0 = \frac{K_e K_{(hkl)\alpha}}{\rho_\alpha (\mu/\rho)_\alpha}$$

$$\frac{I_{(hkl)\alpha}}{I_{(hkl)\alpha}^0} = \frac{X_\alpha (\mu/\rho)_\alpha}{X_\alpha (\mu/\rho)_\alpha + X_\beta (\mu/\rho)_\beta} \quad \rightarrow \quad \frac{I_{(hkl)\alpha}}{I_{(hkl)\alpha}^0} = \frac{X_\alpha (\mu/\rho)_\alpha}{X_\alpha [(\mu/\rho)_\alpha - (\mu/\rho)_\beta] + (\mu/\rho)_\beta}$$

$X_\alpha + X_\beta = 1$

Klug's equation $X_\alpha = \frac{(I_{(hkl)\alpha}/I_{(hkl)\alpha}^0)(\mu/\rho)_\beta}{(\mu/\rho)_\alpha - (I_{(hkl)\alpha}/I_{(hkl)\alpha}^0)[(\mu/\rho)_\alpha - (\mu/\rho)_\beta]}$

Can determine the amount of a single phase in a binary mixture where values of both (μ/ρ) 's are known

Can use (μ/ρ) measured or derived from elemental chemical analysis data

Spiking method (method of standard addition)

$$\frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} = \left(\frac{K_{(hkl)\alpha}}{K_{(hkl)'\beta}} \right) \left(\frac{\rho_\beta}{\rho_\alpha} \right) \left(\frac{X_\alpha}{X_\beta} \right)$$

Add Y_α grams of phase alpha per gram of unknown

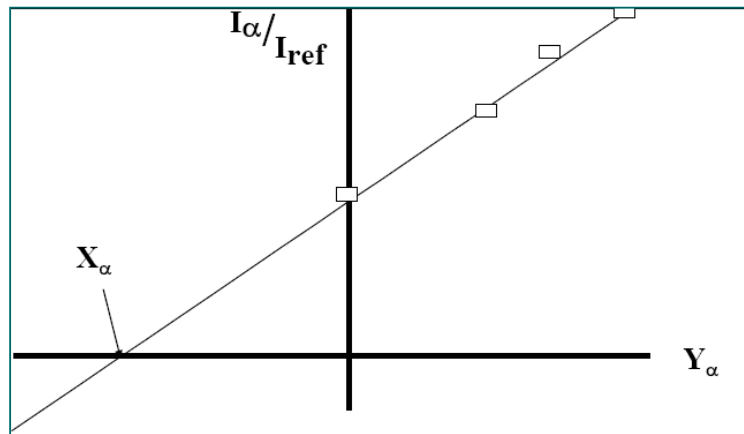
$$\frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} = \frac{K_{(hkl)\alpha} \rho_\beta (X_\alpha + Y_\alpha)}{K_{(hkl)'\beta} \rho_\alpha X_\beta}$$

$$\frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} = K(X_\alpha + Y_\alpha)$$

- X_α initial weight fraction of α
- X_β initial weight fraction of β
- Y_α # grams of phase alpha added per gram of original sample
- The ratio of a line from phase alpha to a line from phase beta in any specimen causes the mass absorption coefficient to cancel

Spiking method (method of standard addition)

$$\frac{I_{(hkl)\alpha}}{I_{(hkl)\beta}} = K(X_{\alpha} + Y_{\alpha});$$



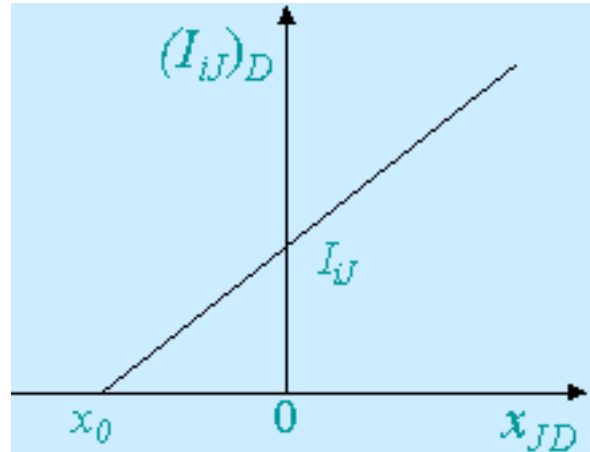
- X_{α} initial weight fraction of alpha
- X_{β} initial weight fraction of beta
- Y_{α} # grams of alpha added per gram of original sample

Spiking method

- Absolute class
- Sample to be analysed is spiked with known amount of analyte phase J
 - ✓ M = mass of sample
 - ✓ $x_J M$ = mass of phase J in undoped sample
 - ✓ x_{JD} = weight fraction of dopant = $M_{JD} / (M + M_{JD})$
 - ✓ $(x_J)_D$ = weight fraction of phase J in spiked sample
- $(x_J)_D = (x_J M + M_{JD}) / (M + M_{JD}) = x_J(1 - x_{JD}) + x_{JD}$
- $\mu_D^* = \mu^* (1 - x_{JD}) + \mu_J^* x_{JD}$
- $I_{iJ} = (K_{iJ} x_J) / \mu^*$ ---- (Q1)
- $(I_{iJ})_D = [K_{iJ} (x_J)_D] / \mu_D^* = K_{iJ} [x_J (1 - x_{JD}) + x_{JD}] / [\mu^* (1 - x_{JD}) + \mu_J^* x_{JD}]$
 $= K_{iJ} [x_J (1 - x_{JD}) + x_{JD}] / [\mu^* \{1 + x_{JD}(\mu_J^* - \mu^*) / \mu^*\}]$ --- (Q4)
 - ✓ In case the dopant does not change the overall μ^* significantly, $\mu^* \approx \mu_D^*$
- $(I_{iJ})_D = K_{iJ} [x_J (1 - x_{JD}) + x_{JD}] / \mu^*$
- $(I_{iJ})_D = (K_{iJ} / \mu^*) x_J + (K_{iJ} / \mu^*) (1 - x_J) x_{JD} = I_{iJ} + (K_{iJ} / \mu^*) (1 - x_J) x_{JD}$

Spiking method

- $I_{iJ} = (K_{iJ} x_J) / \mu^*$ ---- (Q1)
- $(I_{iJ})_D = (K_{iJ} / \mu^*) x_J + (K_{iJ} / \mu^*) (1 - x_J) x_{JD}$
- $(I_{iJ})_D$ vs. x_{JD}
- @ x_0 , $(I_{iJ})_D = 0$, and $x_J = x_0 / (x_0 - 1)$



www.ccp14.ac.uk/poster-talks/david-hay-quant-notes-axaa99/html/sld001.htm

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Reference intensity ratio (RIR)

generalization of internal standard method

- Scale the peak intensities to a particular peak (of a reference phase) to bring them to common scale
- deWolff & Visser (1964) suggested the (113) peak of corundum (100% peak)
- RIR = ratio of strongest peak of phase J to that of corundum (113) in 1:1 (weight) mixture
- $RIR_{J,c} = I_{iJ} / I_{hc}$
- General case of α & β , $RIR_{\alpha,\beta} = I_{i\alpha} / I_{h\beta}$

- Integrated intensities have to be used
- Any number of constituents can be used
- Mixture can contain amorphous components
- Mass absorption coefficient of mixture need not be known in advance

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- The slope of the internal standard curve is a materials constant

$$\frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} = k \frac{X_{\alpha}}{X_{\beta}}$$

- Scale the peak intensities to a particular peak (of a reference phase) to bring them to common scale
- deWolff & Visser (1966) suggested that all materials be mixed 50:50 with corundum and the ratio of the 100% lines be published with reference patterns.
- ICDD has a great number in the current PDF

Reference intensity ratio (RIR)

$$\frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} = \left(\frac{K_{(hkl)\alpha}}{K_{(hkl)'\beta}} \right) \left(\frac{\rho_{\beta}}{\rho_{\alpha}} \right) \left(\frac{X_{\alpha}}{X_{\beta}} \right) \rightarrow \frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} = k \frac{X_{\alpha}}{X_{\beta}}$$

$X_{\beta} \frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}}$ vs. X_{α} ➔ straight line (slope = k)
 k; measure of inherent diffracted intensities of the two phases

$\beta = \text{corundum, 1;1 mixture, hkl's} = 100\% \text{ intensity lines}$

$$\rightarrow \left(\frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} \right) \left(\frac{X_{\beta}}{X_{\alpha}} \right) = \frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} = k = I/I_{\text{cor}}$$

$\beta = \text{any phase arbitrary concentration hkl's} = \text{any lines}$

$$\rightarrow \text{RIR}_{\alpha,\beta} = \left(\frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} \right) \left(\frac{I_{(hkl)'\beta}^{\text{rel}}}{I_{(hkl)\alpha}^{\text{rel}}} \right) \left(\frac{X_{\beta}}{X_{\alpha}} \right)$$

I_j^{rel} - relative intensity of line j scaled to 100% line

Reference intensity ratio (RIR)

$$\text{RIR}_{\alpha,\beta} = \left(\frac{I_{(hkl)\alpha}}{I_{(hkl)\beta}} \right) \left(\frac{I_{(hkl)\beta}^{\text{rel}}}{I_{(hkl)\alpha}^{\text{rel}}} \right) \left(\frac{X_{\beta}}{X_{\alpha}} \right) \rightarrow X_{\alpha} = \left(\frac{I_{(hkl)\alpha}}{I_{(hkl)\beta}} \right) \left(\frac{I_{(hkl)\beta}^{\text{rel}}}{I_{(hkl)\alpha}^{\text{rel}}} \right) \left(\frac{X_{\beta}}{\text{RIR}_{\alpha,\beta}} \right)$$

$$\text{RIR}_{\alpha,\beta} = \frac{\text{RIR}_{\alpha,\gamma}}{\text{RIR}_{\beta,\gamma}}, \quad \rightarrow \quad X_{\alpha} = \left(\frac{I_{(hkl)\alpha}}{I_{(hkl)\beta}} \right) \left(\frac{I_{(hkl)\beta}^{\text{rel}}}{I_{(hkl)\alpha}^{\text{rel}}} \right) \left(\frac{\text{RIR}_{\beta,c} X_{\beta}}{\text{RIR}_{\alpha,c}} \right)$$

$$\left(\frac{X_{\alpha}}{X_{\beta}} \right) = \left(\frac{I_{(hkl)\alpha}}{I_{(hkl)\beta}} \right) \left(\frac{I_{(hkl)\beta}^{\text{rel}}}{I_{(hkl)\alpha}^{\text{rel}}} \right) \left(\frac{\text{RIR}_{\beta,c}}{\text{RIR}_{\alpha,c}} \right), \quad \sum_{j=1}^n X_j = 1.$$

$$X_{\alpha} = \frac{I_{(hkl)\alpha}}{\text{RIR}_{\alpha} I_{(hkl)\alpha}^{\text{rel}}} \left[\frac{1}{\sum_{j=1}^{\text{No. of phases}} (I_{(hkl)j} / \text{RIR}_j I_{(hkl)j}^{\text{rel}})} \right].$$

I_j^{rel} - relative intensity of line j scaled to 100% line

Whole pattern profile matching

- Most useful where overlapping peaks are a problem. Phase to be analysed may not have at least one clearly resolved peak.
- Profile fitting
 - ✓ Groups of overlapping peaks are separated into individual peaks and integrated intensities extracted. Knowledge of peak profiles, positions required but not crystal structure or composition.
- Structure refinement
 - ✓ Either using conventional methods developed for single crystal structure analysis (extraction of integrated intensities, refinement of derived structure factors against a model) or by Rietveld methods
 - ✓ Both structure refinement methods require knowledge of crystal structure

The quantity minimized

$$R = \sum_j w_j |I_{j(0)} - I_{j(c)}|^2$$

$$I_{j(c)} = S_\alpha \sum_{(hkl)} K_{(hkl)\alpha} G(\Delta\theta_{j,(hkl)\alpha}) P_{(hkl)} + I_{b(c)}$$

Profile shape
function

Preferred orientation
function

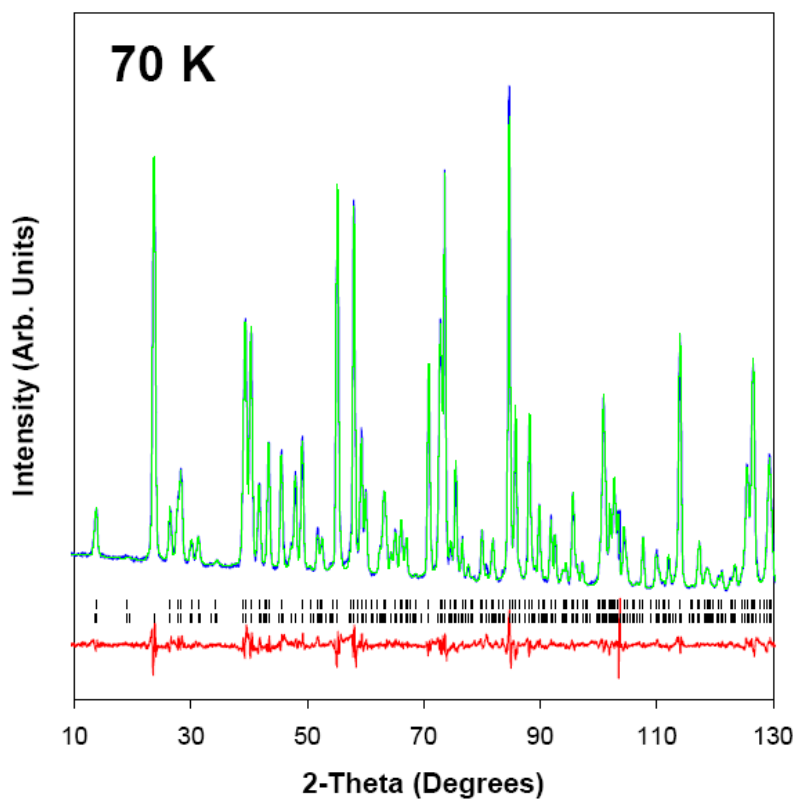
background

$$S_\alpha = \frac{I_{(hkl)\alpha}}{K_{(hkl)\alpha}}$$

Rietveld scale factor

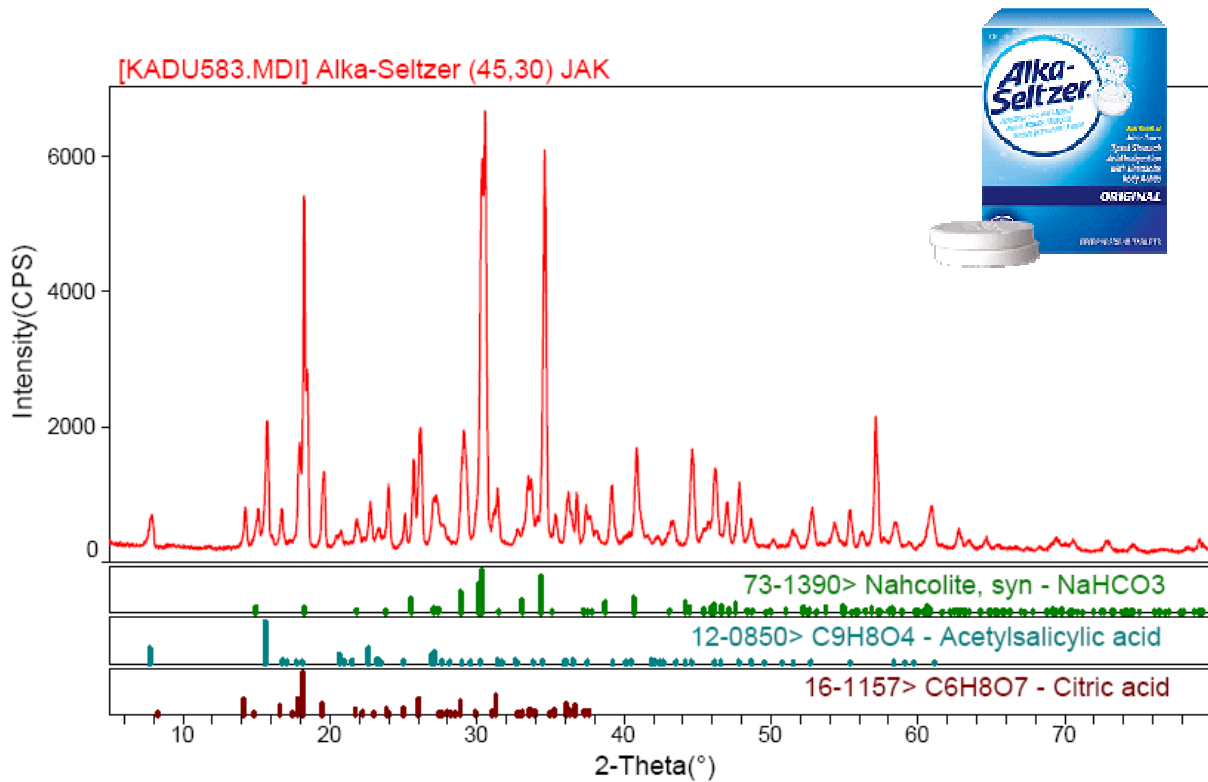
➤ Rietveld scale factor contains the weight fraction of each phase

Rietveld refinement



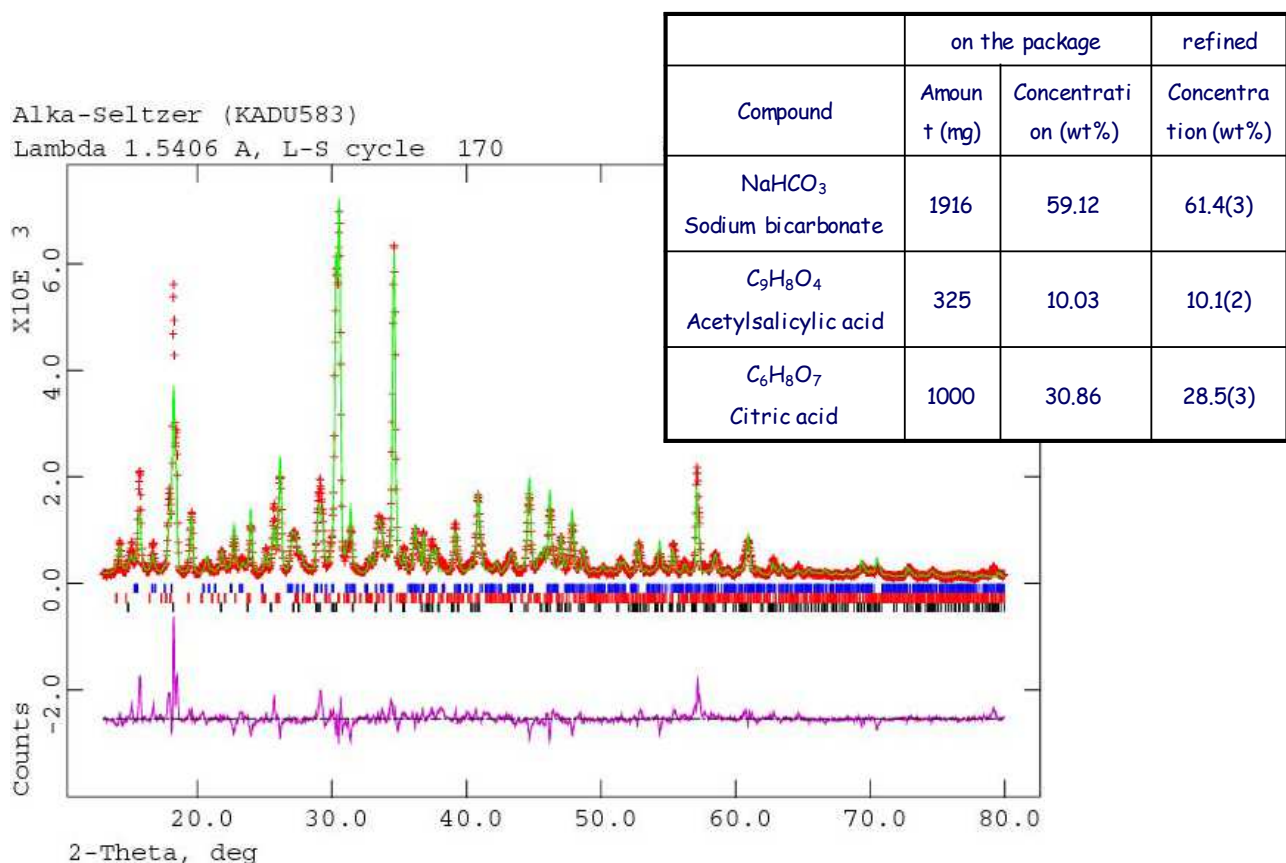
Blue = Observed
Green = Calculated
Red = Difference
Black = Expected
peak positions

Example > Alka-Seltzer 1 > phase ID



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Example > Alka-Seltzer 2 > Quant using Rietveld refinement



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