

# Quantitative phase analysis

Jenkins & Snyder Chap 13

Cullity Chap 12

Bish & Post Chap 5

Klug & Alexander Chap 7

Krawitz Chap 8

## QPA - reference

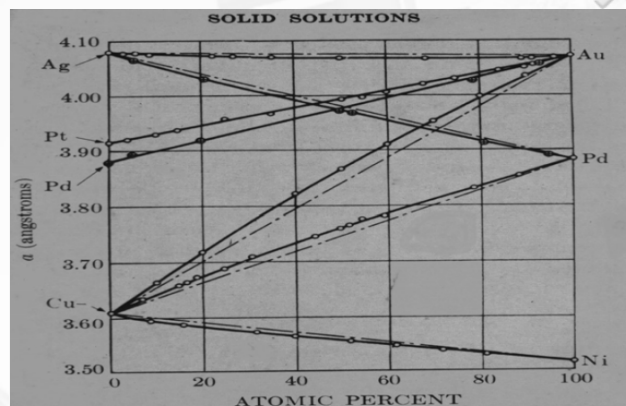
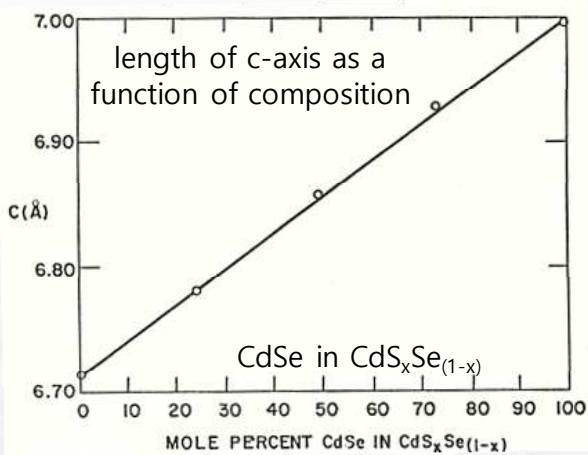
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  - ✓ Hill, R.J. (1992): "Rietveld Refinement Round Robin. I. Analysis of Standard X-ray and Neutron Data for PbSO<sub>4</sub>". J. Appl. Cryst., 25, 589-610
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- QPA Round Robin (<http://www.iucr.org/iucr-top/comm/cpd/>)
  - ✓ 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
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- 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"

CHAN PARK, MSE, SNU Spring-2022 Crystal Structure Analyses

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**

- 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%

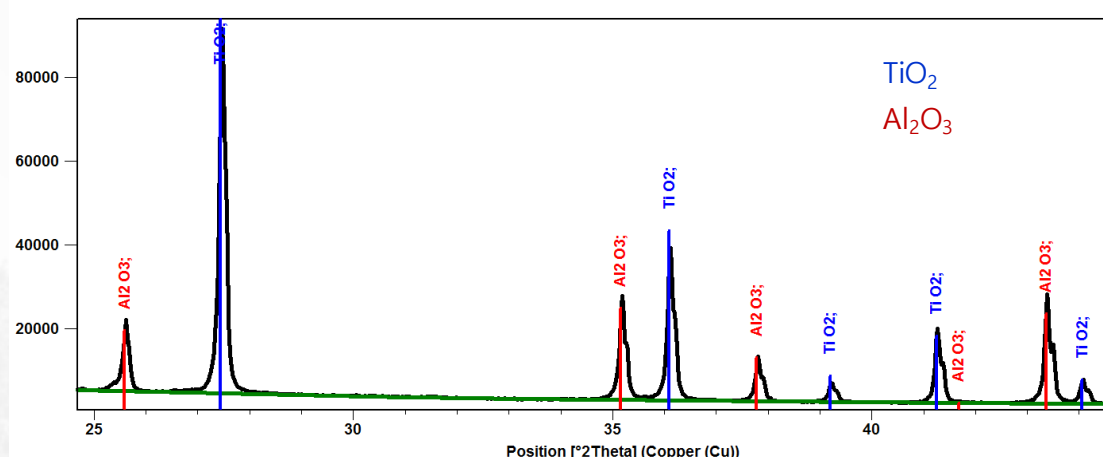
RIR ; reference intensity ratio

## Factors affecting line intensities of XRPD peaks

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

- 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

## Intensity vs. phase quantity



- A mixture of equal amounts of  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$
- The  $\text{TiO}_2$  pattern is more intense because  $\text{TiO}_2$  diffracts X-rays more efficiently.
- With proper calibration, the amount of each phase present in the sample can be calculated.

50:50 mixture of Si and Al<sub>2</sub>O<sub>3</sub>

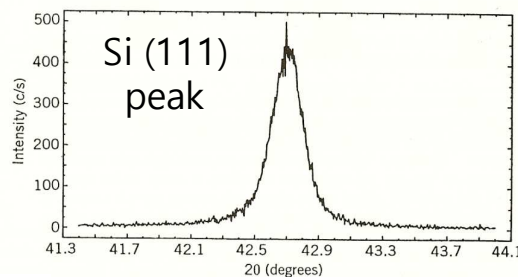
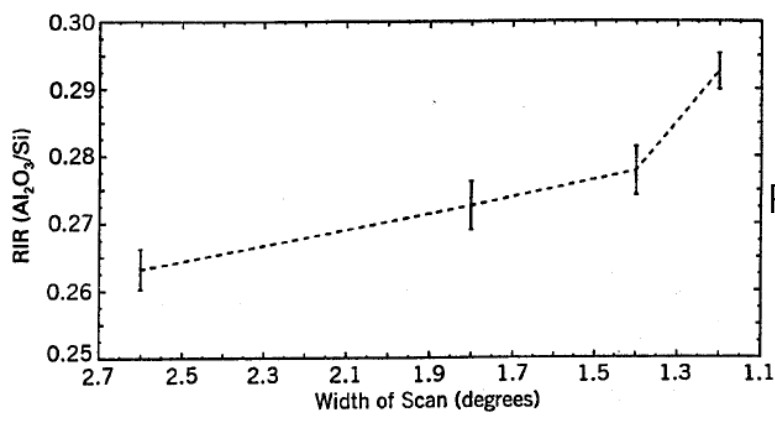


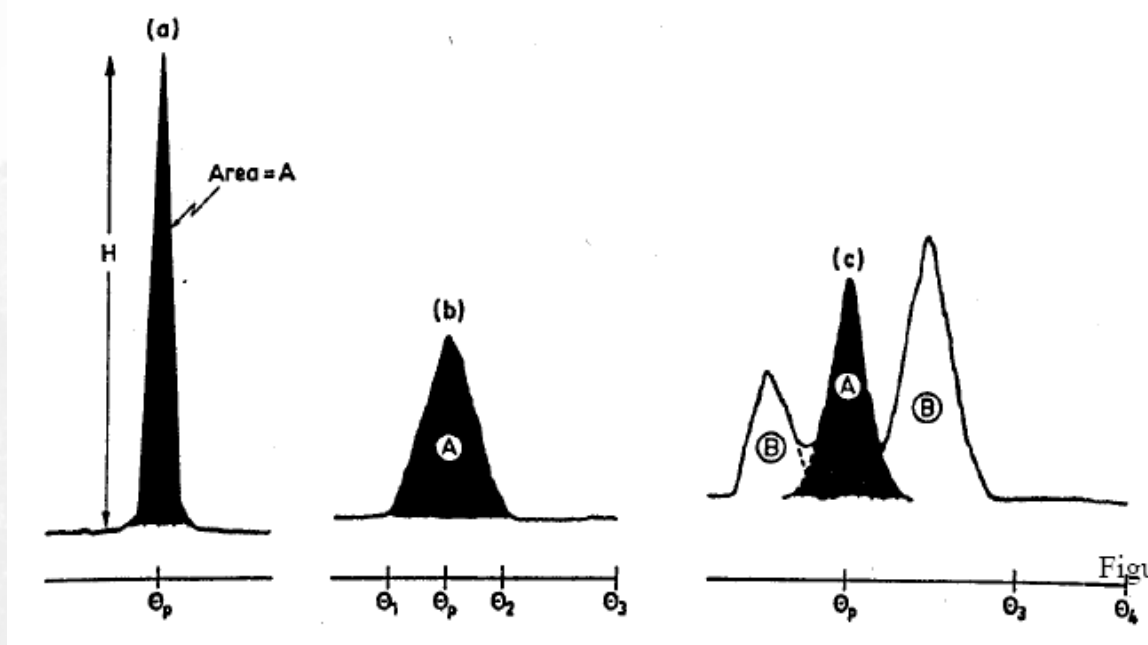
Figure 13.3. Trace of the Si (111) peak using Cr radiation.



RIR (Al<sub>2</sub>O<sub>3</sub>/Si)

RIR; Ratio of the **background-corrected integrated intensities** of Si(111) peak to the 100% line of Al<sub>2</sub>O<sub>3</sub>

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



Figure

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

- $I(hkl)$  = 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
- $\lambda$  = 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
- $\theta$  = Bragg angle                       $e^{-2M}$  = temperature factor
- $\mu$  = **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  $\alpha$  &  $\beta$

$$I_\alpha(hkl) = I_\alpha = \frac{K_1 c_\alpha}{\mu_m}$$

$c_\alpha$  = volume fraction of alpha phase in the mixture  
 $\mu_m$  = linear attenuation coefficient of the mixture

- $c_\alpha$  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  $\alpha$
  - ✓ 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.

- $i, j, k, \dots$  lines in diffraction pattern
- $I, J, K, \dots$  components of a mixture
- $S$  subscript referring to component used as reference standard
- $\rho_J$  density of components  $J$
- $f_J$  volume fraction of component  $J$  in a mixture
- $x_J$  weight fraction of component  $J$  in a mixture
- $\mu_J$  linear absorption coefficient of component  $J$  for X-ray wavelength  $\lambda$
- $\mu_J^* = \mu_J/\rho_J$  mass absorption coefficient of component  $J$  for X-ray wavelength  $\lambda$
- $\mu$  linear absorption coefficient of sample with  $N$  components
- $\mu^*$  mass absorption coefficient of sample with  $N$  components  $\mu^* = \sum x_J \mu_J^*$
- $I_{ij}$  intensity of  $i^{\text{th}}$  line of component  $J$  in mixture
- $(I_{ij})_0$  intensity of  $i^{\text{th}}$  line of pure component  $J$
- $I/I_{\text{cor}}$  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  $S$

## 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 a 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  $\mu^*$  of sample
- ✓ Determining calibration constant  $K_{ij}$

$f_J$  volume fraction of component  $J$  in a mixture  
 $x_J$  weight fraction of component  $J$  in a mixture  
 $\mu_J$  linear absorption coefficient of  
 $\mu_J^* = \mu_J/\rho_J$  mass absorption coefficient of  $J$   
 $\mu$  linear absorption coefficient of sample with  $N$  components  
 $\mu^*$  mass absorption coefficient of sample with  $N$  components  
 $\mu^* = \sum x_J \mu_J^*$



- 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), and 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)

## External standard method

Mixture of phase  $\alpha$  &  $\beta$ 

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

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

 $c_\alpha$  = volume fraction of  $\alpha$  in the mixture $w$  = weight fraction,  $\rho$  = densityin a unit volume of mixture,weight of the mixture =  $\rho_m$       weight of the  $\alpha$  phase =  $w_\alpha \rho_m$ volume of phase  $\alpha$  =  $c_\alpha = (w_\alpha \rho_m) / \rho_\alpha \rightarrow w_\alpha = (\rho_\alpha c_\alpha) / \rho_m$  $\mu_m$  = linear attenuation coefficient of the mixture

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

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

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

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

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

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

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

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

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

For a pure phase  $\alpha$ ,  $I_{\alpha p} = \frac{K_1}{\mu_\alpha}$ ; (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  $w_\alpha$  from  $(\mu/\rho)_\alpha$ ,  $(\mu/\rho)_m$ , and  $\frac{I_\alpha}{I_{\alpha p}}$

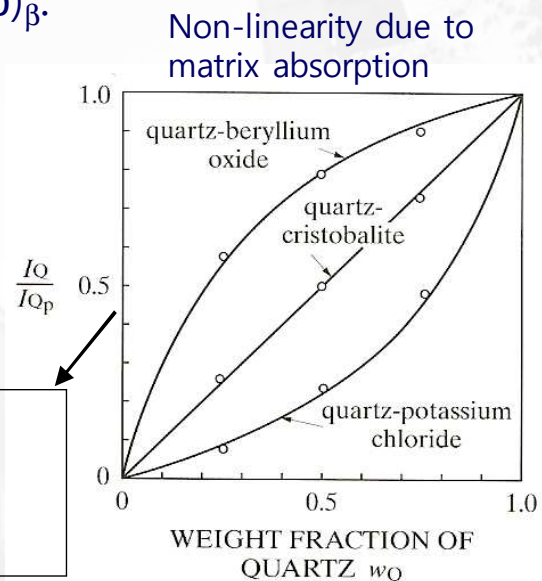
$$\frac{I_\alpha}{I_{\alpha p}} = \frac{w_\alpha(\mu/\rho)_\alpha}{w_\alpha [(\mu/\rho)_\alpha - (\mu/\rho)_\beta] + (\mu/\rho)_\beta}$$

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

When  $\mu/\rho$  of  $\alpha$  &  $\beta$  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.

- 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

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

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

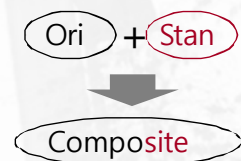
$I = \frac{K_2 R}{2\mu}$   $K_2$  constant, independent of the kind & amount of the diffracting substance  
 $R$  depends on  $\theta$ ,  $hkl$ , and the kind of substance.

<p>2 phase mixture <math>\alpha, \gamma</math></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 <math>c_\gamma/c_\alpha</math></p> <p>can get <math>c_\gamma</math> and <math>c_\alpha</math> from <math>c_\gamma + c_\alpha = 1</math></p>	<p>3 phase mixture <math>\alpha, \gamma, c</math></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 <math>c_\gamma/c_\alpha</math> and <math>c_\gamma/c_c</math></p> <p>can get <math>c</math>'s from <math>c_\gamma + c_\alpha + c_c = 1</math></p>
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- 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.

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  $\alpha$  &  $\beta$

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

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

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

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

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

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

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

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

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

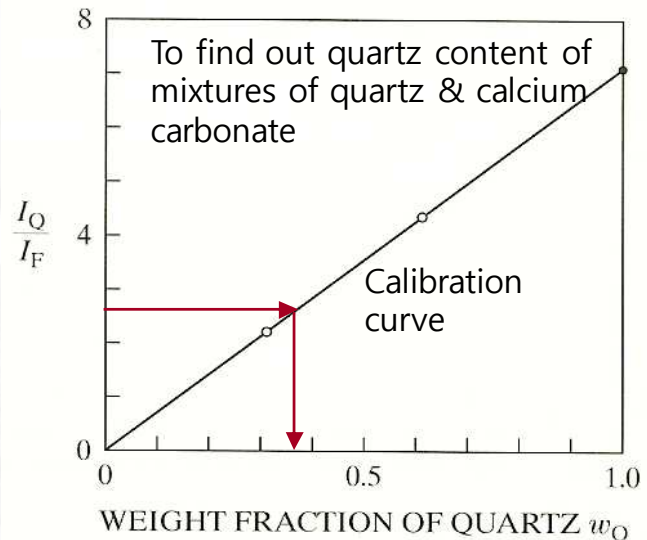
$w_S$  is kept constant in all composite samples.

- 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.

- 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)
- $w_S = 0.2$



- 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
- $x'_j = x_j (1 - x_s)$
- $I_{ij} = (K_{ij} x_j) / \mu_d^*$  ----- (Q1)
- $I_{ij} = K_{ij} x_j (1 - x_s) / \mu_d^*$  (for phase J)
  - ✓  $\mu_d^*$  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](http://www.ccp14.ac.uk/poster-talks/david-hay-quant-notes-axaa99/html/sld001.htm)

# Quantitative analysis – Jenkins & Snyder

Intensity of line hkl of phase  $\alpha$

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

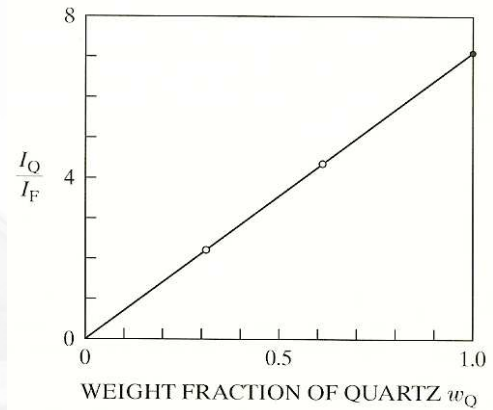
$$I_{(hkl)\alpha} = \frac{K_e K_{(hkl)\alpha} X_\alpha}{\rho_\alpha \left( \frac{\mu}{\rho} \right)_s}$$

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

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

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

- The ratio of a line from phase  $\alpha$  to a line from phase  $\beta$  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)

- $\mu^*$  (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  $\mu^*$  (include phase transitions where chemical composition remains unchanged during the transition)

- 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  $(I_{ij})$ ,  $(I_{ij})_0$ ,  $\mu^*$ , and  $\mu_j^*$ .
- $\log x_j - \log [(I_{ij}) / (I_{ij})_0] = \log [\mu^* / \mu_j^*]$  → should be a straight line, but deviates (due to microabsorption).
  - $x_j = (I_{ij}) / (I_{ij})_0 \cdot (\mu^* / \mu_j^*)^\alpha$
- $\alpha$  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.

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

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

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



$$\frac{I_{i\alpha}}{I_{i\alpha}^\circ} = \left( \frac{\mu}{\rho} \right)_\alpha X_\alpha \left( \frac{\mu}{\rho} \right)_m$$

In case of polymorph,

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

- Cristobalite in quartz and amorphous SiO<sub>2</sub> matrix
- Cubic, tetragonal, & monoclinic forms of ZrO<sub>2</sub> in pure ZrO<sub>2</sub> body
- Anatase in rutile (TiO<sub>2</sub>)



Use of Klug's equation for any two phase mixture

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

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

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

$$X_\alpha + X_\beta = 1$$

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

Klug's equation

Can determine the amount of a single phase in a binary mixture where values of both  $(\mu/\rho)$ 's are known.

Can use  $(\mu/\rho)$  measured or derived from elemental chemical analysis data.

Spiking method (method of standard addition)

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

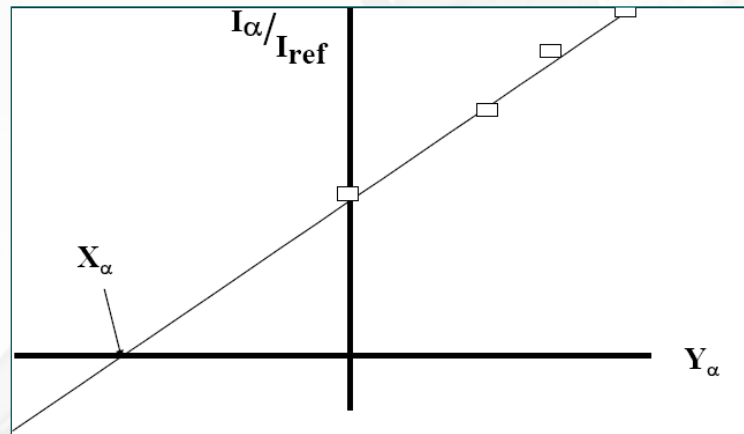
Add  $Y_\alpha$  grams of phase alpha per gram of unknown.

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

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

- $X_\alpha$  initial weight fraction of  $\alpha$
- $X_\beta$  initial weight fraction of  $\beta$
- $Y_\alpha$  # 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.

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

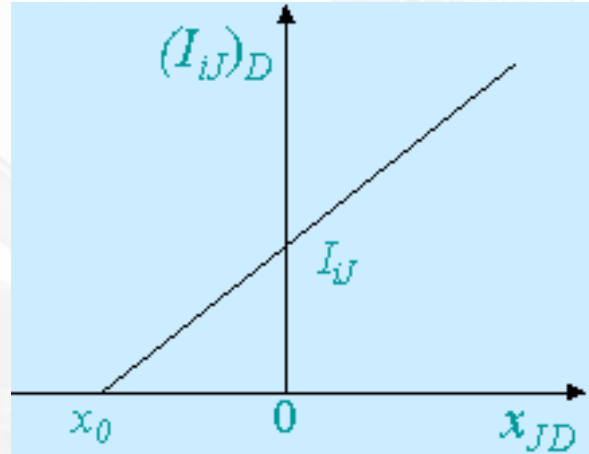


- $X_{\alpha}$  initial weight fraction of alpha
- $X_{\beta}$  initial weight fraction of beta
- $Y_{\alpha}$  # grams of alpha added per gram of original sample

## 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  $\mu^*$  significantly,  $\mu^* \approx \mu_D^*$
- $(I_{ij})_D = K_{ij} [x_J (1 - x_{JD}) + x_{JD}] / \mu^*$
- $(I_{ij})_D = (K_{ij} / \mu^*) x_j + (K_{ij} / \mu^*) (1 - x_j) x_{JD} = I_{ij} + (K_{ij} / \mu^*) (1 - x_j) x_{JD}$

- $I_{ij} = (K_{ij} x_j) / \mu^*$  ---- (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](http://www.ccp14.ac.uk/poster-talks/david-hay-quant-notes-axaa99/html/sld001.htm)

## 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  $\alpha$  &  $\beta$ ,  $RIR_{\alpha,\beta} = I_{i\alpha} / I_{h\beta}$

- 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.

[www.ccp14.ac.uk/poster-talks/david-hay-quant-notes-axaa99/html/sld001.htm](http://www.ccp14.ac.uk/poster-talks/david-hay-quant-notes-axaa99/html/sld001.htm)

- 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.  $X_{\alpha}$  ➔ straight line (slope = k)  
 k; measure of inherent diffracted intensities of the two phases

$\beta$  = corundum  
 1:1 mixture  
 hkl's = 100% intensity lines

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

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

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

$I_j^{\text{rel}}$  – relative intensity of line j scaled to 100% line

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

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

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

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

$I_j^{\text{rel}}$  – 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

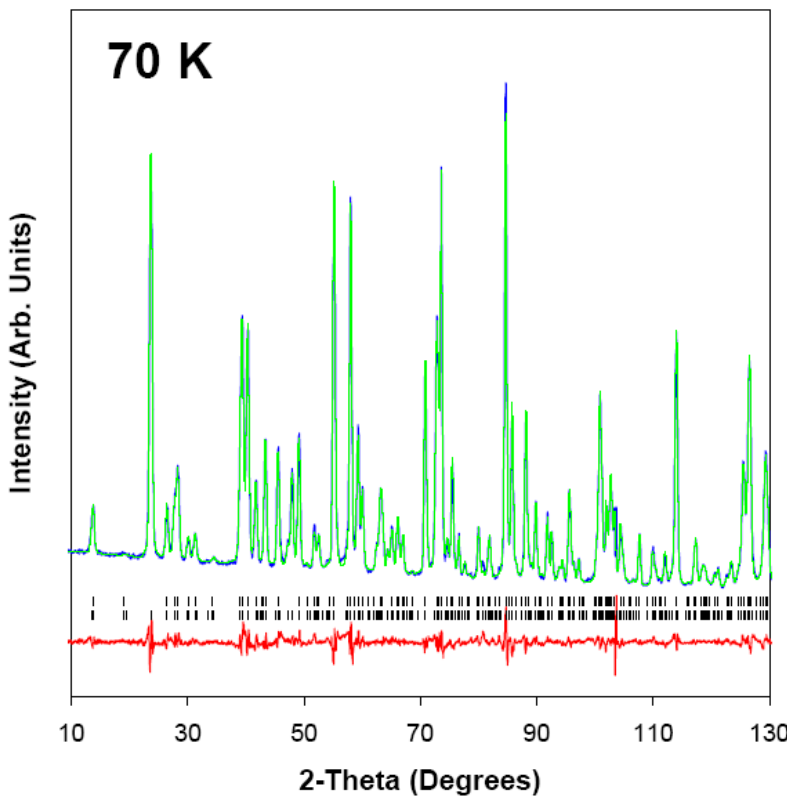
background

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

Rietveld scale factor

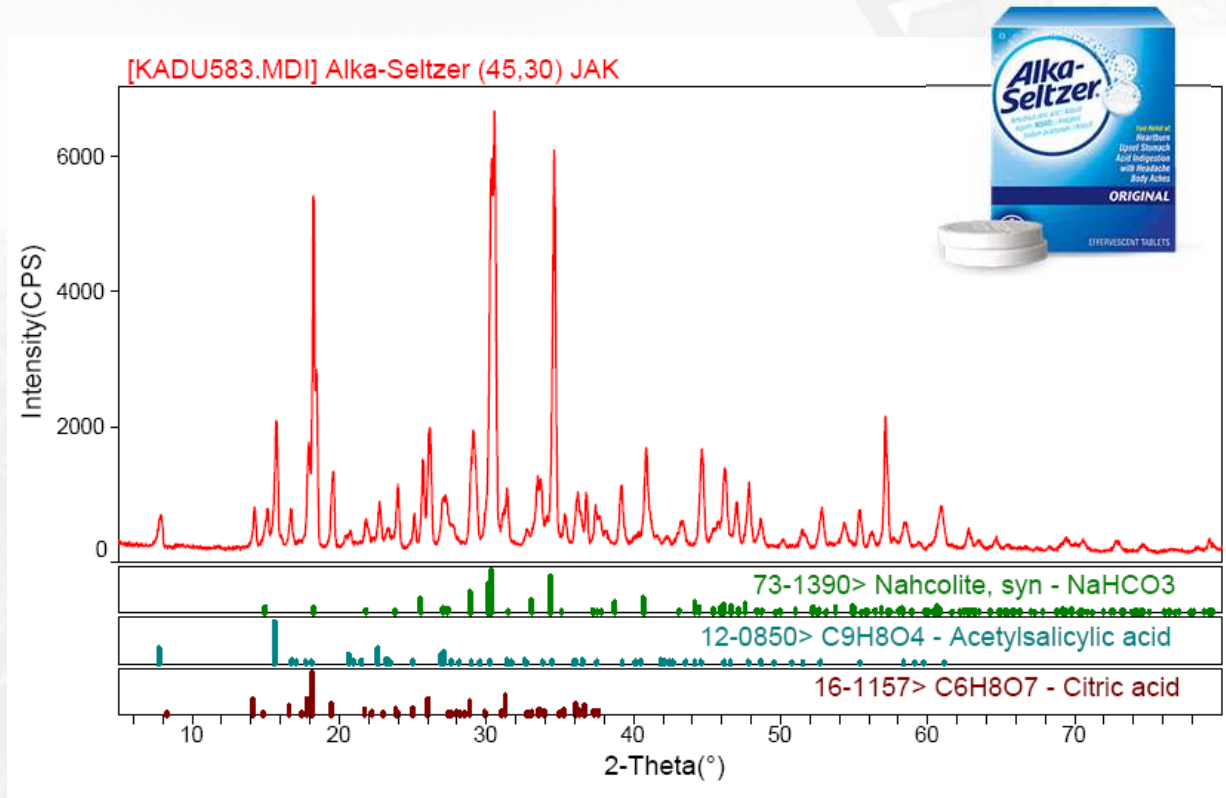
➤ Rietveld scale factor contains the weight fraction of each phase.

Rietveld refinement



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

# Example > Alka-Seltzer 1 > phase ID



# Example > Alka-Seltzer 2 > Quant using Rietveld refinement

