Rietveld Method for Quantitative Phase Analysis

Innovation with Integrity

History of Rietveld Analysis

Milestones

1966 7th Congress of the IUCr in Moscow

1969 publication in J.Appl.Crystallogr.
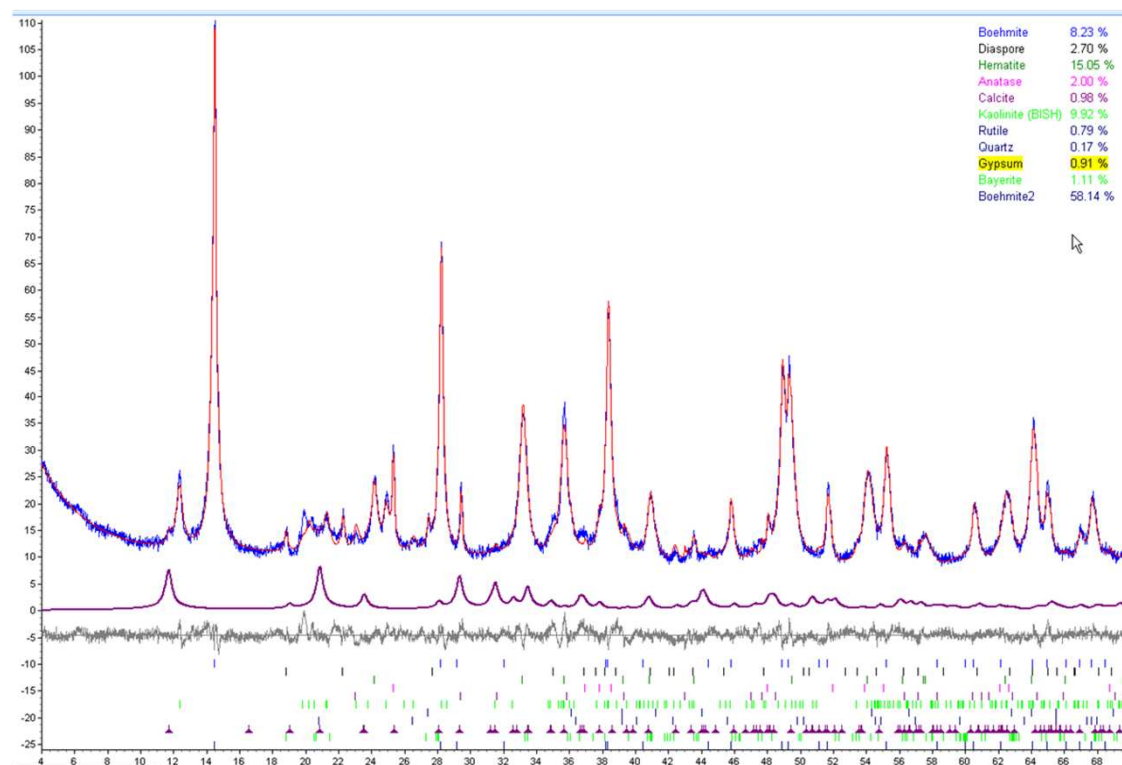
1977 acceptance for X-ray diffraction

1983 Quantitative Phase Analysis

Dr. Hugo M. Rietveld

pictures by courtesy of Hugo Rietveld (http://home.wxs.nl/~rietv025/)

Rietveld Method

- Full profile fitting
- Using crystallographic constraints
    - Lattice parameters and space group to constrain peak positions
    - Crystal structure to constrain peak intensities

Profile Fitting

- An accurate description of the line profile shapes in a powder pattern is critical to the success of any profile fitting application!

- Today's profile fitting techniques:
  - Analytical profile fitting
  - Direct convolution approach

Profile Fitting Methods
# Analytical Profile Fitting

- Characterized by peak shape functions (PSFs) with an explicit and relatively simple mathematical form which can be differentiated analytically with respect to each of the refined parameters

- Most common are the Gaussian, Lorentzian, sums of Gaussians or Lorentzians, Voigt, pseudo-Voigt and PearsonVII functions

- Convenient to use

- No physical meaning

- Large number of parameters required to fit profiles well over the whole 2θ range pattern frequently leading to:

  - Correlation problems

  - Loss of uniqueness

  - Instability of the refinement procedure

Profile Fitting Methods
Direct Convolution Approach

- PSFs are generated by convoluting functions together to form the observed profile shape $Y(2\theta) = F_1(2\theta) \times F_2(2\theta) \times \ldots \times F_i(2\theta) \times \ldots \times F_n(2\theta)$
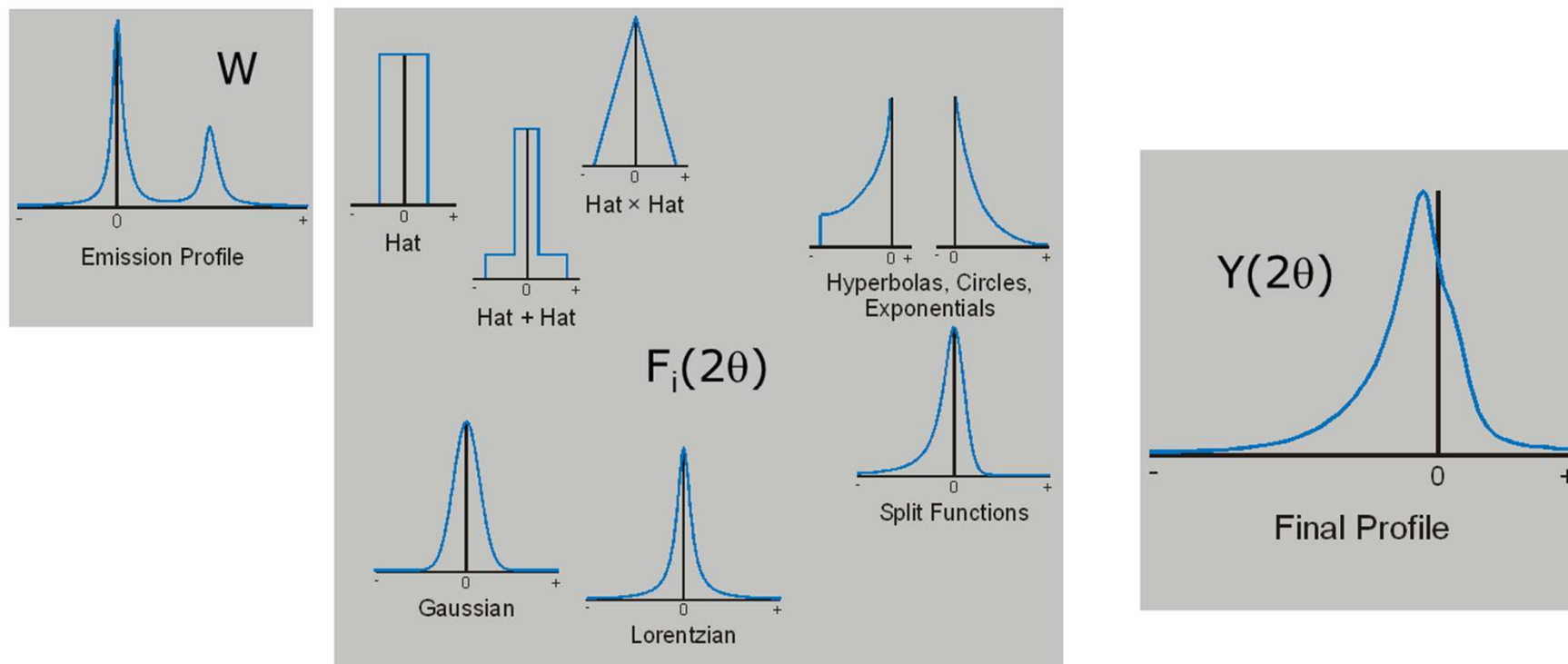
$$W \times F_1(2\theta) \times F_2(2\theta) \times \ldots \times F_i(2\theta) \times \ldots \times F_n(2\theta) = Y(2\theta)$$
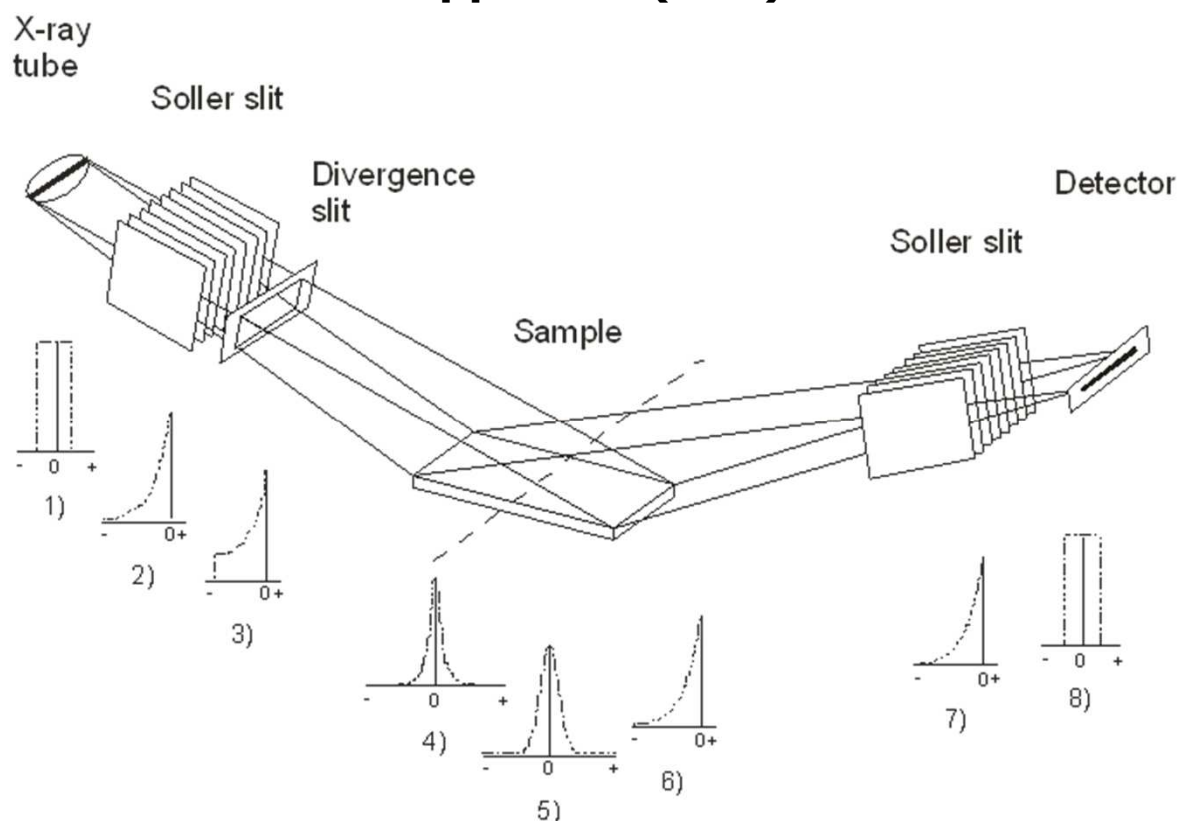
Profile Fitting Methods
Direct Convolution - FPA

- In powder diffractometry the functions $F_i(2\theta)$ can be interpreted as the aberration functions of the diffractometer:

Fundamental Parameters Approach (FPA)

Profile Fitting Methods
Direct Convolution - FPA

Benefits:

- The ideal approach for all profile fit applications -

  not only if micro-structure information is of interest

- The Bragg Brentano geometry is the most convenient

- Micro-structure information can be derived

- Allows to deal with higher degrees of peak overlap

  (with significant impact on e.g. quantitative Rietveld analysis)

- Uses a minimal number of profile parameters

  (specimen contributions such as size/strain/...) – stabile refinement

- Refined profile parameters have a physical meaning

  (size/strain/...)

- …

Profile Fitting Methods
FPA vs. Analytical Profile Fitting
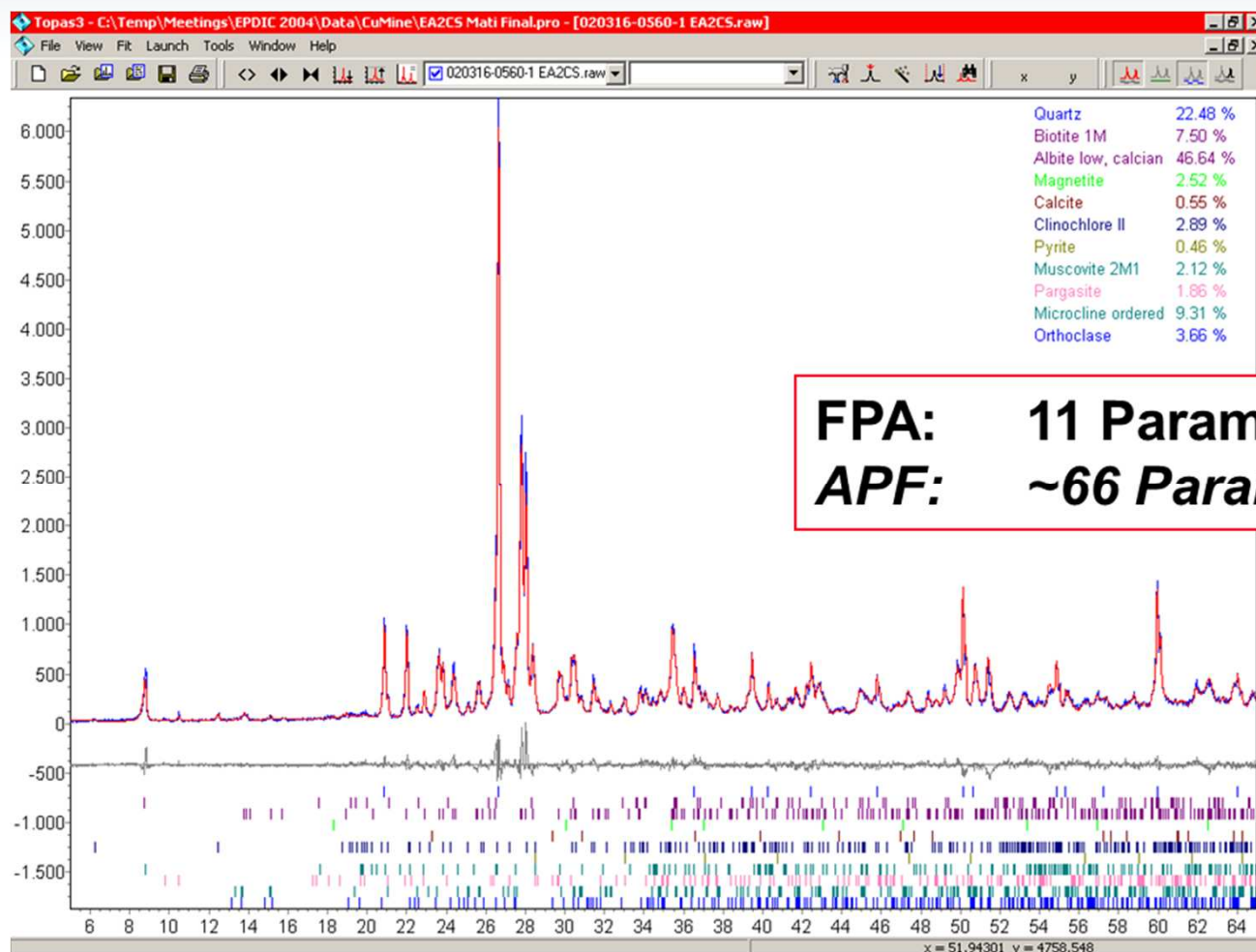
Fitting

- Single peak fitting

- Full pattern fitting

    - Le Bail / Pawley methods

    - Rietveld method
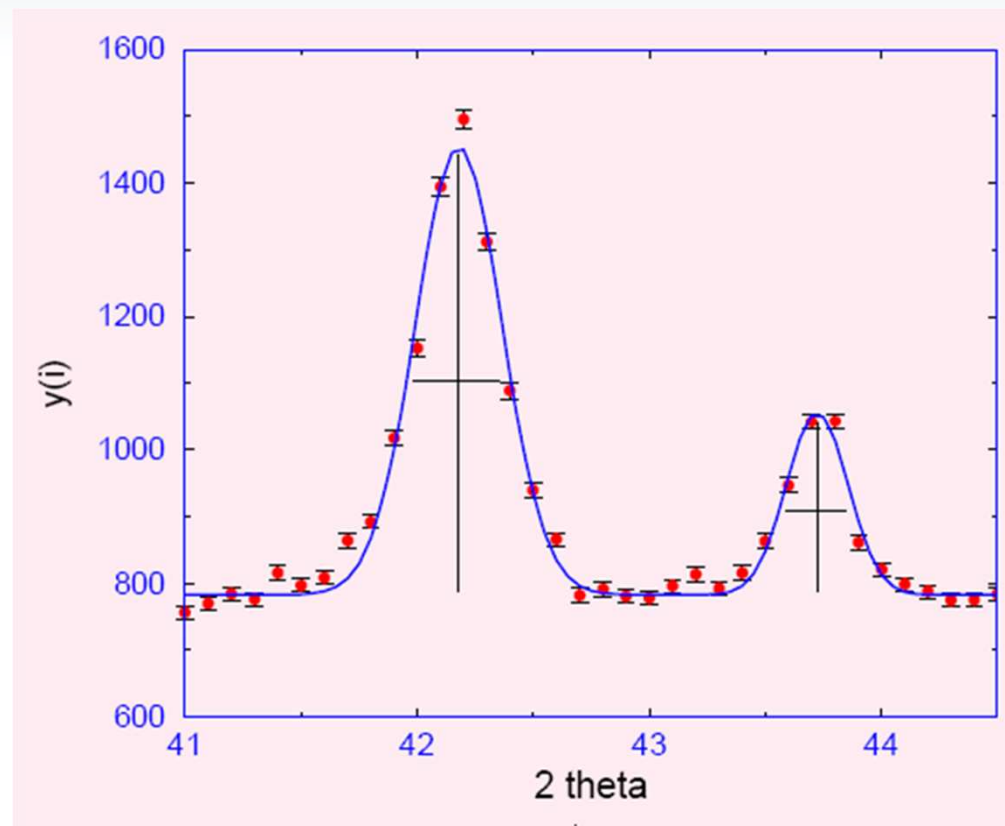
Single Peak Fit

- Results:

    - Positions
    - Intensity (amplitude, integral)
    - Width, shape

- Calculate:

$$\sum (y_i^o - y_i^c)^2 \rightarrow \text{Min.}$$

y_i^o observed step intensity
y_c^o calculated step intensity

- Needs profile function

Single Peak Fit - Parameters

- Profile functions P_i
- Gaussian $G(2\theta_i, I_i, w_i)$
- Lorentzian $L(2\theta_i, I_i, w_i)$
- Pseudo-Voigt $xG_i + (1-x)L_i$
- Asymmety function (one or two parameters)
  split-functions: two independent functions
  P_i^l for $2\theta < 2\theta_i$
  P_i^r for $2\theta > 2\theta_i$

- About 6 parameters per peak

Single Peak Fit

range: single reflections, reflection groups

independent parameters: peak area, position and shape

prior knowledge: none

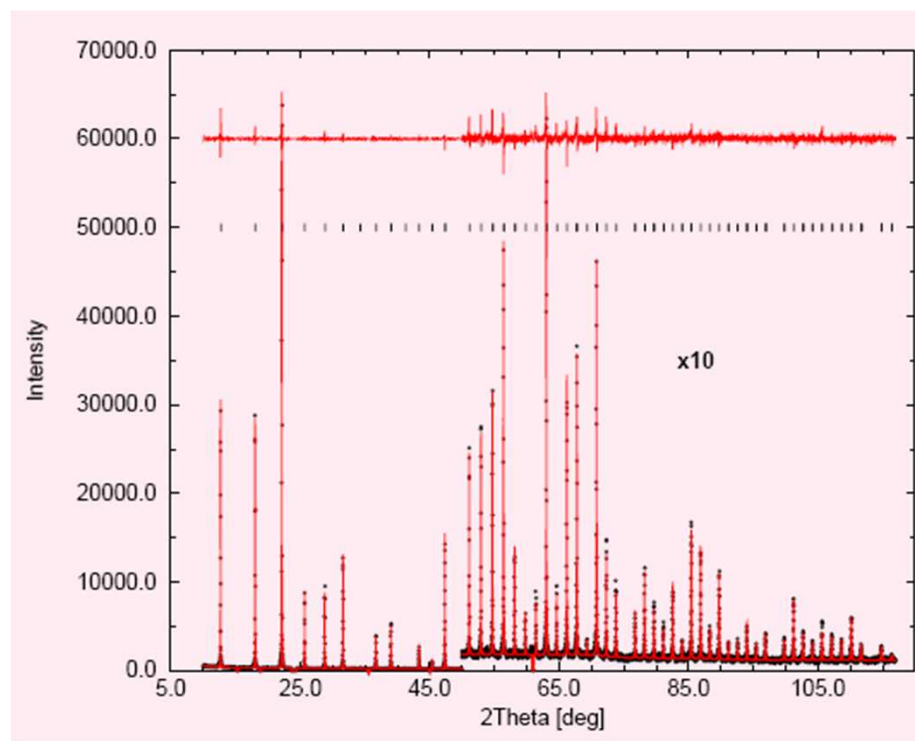applications: indexing, cell parameters, $|F|$-determination, line shape analysis

Huge number of parameters for many peaks

Full Pattern Fitting

- WPPF

- Whole Powder Pattern Fit

  - Pawley
  - LeBail
  - Pattern matching

- Use lattice parameters and spacegroup info to constrain peak positions

- calculate

$$\sum (y_i^o - y_i^c)^2 \rightarrow \text{Min.}$$

Peak Shape Functions

models for the peak shape:

- fundamental parameters approach
- analytical functions (Gauss, Lorentz, pseudo-Voigt, Pearson VII, TCH, split-type, …)

$$G(\Delta 2\theta_{ik})^G = \frac{4\ln 2}{\sqrt{\pi}H_k}\exp\left[-4\ln 2\frac{(2\theta_i - 2\theta_k)^2}{H_k^2}\right]$$

$$G(\Delta 2\theta_{ik})^L = \frac{2}{\pi H_k}\Bigg/\left[1 + \frac{4(2\theta_i - 2\theta_k)^2}{H_k^2}\right]$$

$$G(\Delta 2\theta_{ik})^{PV} = \eta G(\Delta 2\theta_{ik})^L + (1-\eta)G(\Delta 2\theta_{ik})^G$$

- asymmetry correction
- peak half width $H_k = \left[u\tan^2(\theta) + v\tan(\theta) + w\right]^{1/2}$

WPPF

range: total diffraction pattern,

independent parameters: peak area

dependent parameters:

$$2\theta(\mathsf{hkl}) = f(a, b, c, \alpha, \beta, \gamma),$$
$$\lambda = 2d\sin(\theta), \; d = 1/|\vec{H}|,$$
$$\vec{H} = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$$

profile parameters $= f(2\theta)$

prior knowledge: approximate unit cell

applications: $|F|$, cell parameters

structure solution

WPPF vs. Rietveld

Aim: find best aggreement between measured y_i^o and calculated y_i^c diffraction pattern

$$\sum (y_i^o - y_i^c)^2 \rightarrow \text{Min.}$$

non-linear optimization problem

Method: simultaneous refinement of models for

- diffraction optics, instrumental parameters
  (resolution function, instrument offsets, ...)
- Background
- phase specific parameters
  (cell parameters, crystal structure (x,y,z,B,n))
- sample specific parameters
  (crystallite size, stress, preferred orientation)

Rietveld

Step Intensity

intensity y_i^c at the ith step consists of:

$$y_i^c = y_{bi}^c + S \sum_{k=1}^{n} m_k \, L_k \, |F_k|^2 \, G(\Delta 2\theta_{ik}) \, P_k$$

$\underbrace{\qquad\qquad}_{n \text{ overlapping reflections}}$

y_{bi}^c	...background
S	...scale factor
n	...number of overlapping reflections (hkl)
m_k	...multiplicity of reflection k
L_k	...Lorentz-, polarisation correction
F_k	...structure factor
$G(\Delta 2\theta_{ik})$	...peak shape function
P_k	...preferred orientation correction

Rietveld Refinement -
Lorentz-polarisation correction

- **Lorentz**

  reciprocal lattice nodes needs different times to pass the Ewald sphere

- **Polarization**

  depends on polarization state of the incident beam and scattering angle of the diffracted beam

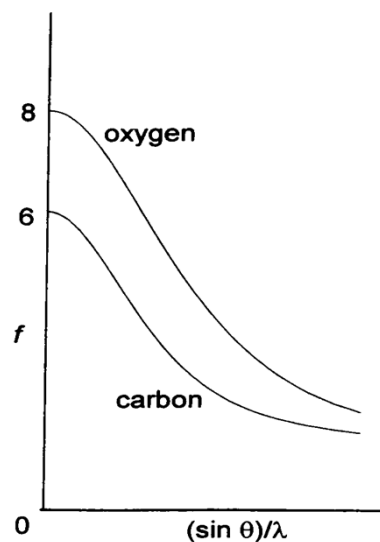$\Rightarrow$ **synchrotron radiation: LP = 90 (totally polarized)**

filters, energy dispersive detector: LP = 0 (not polarized)

monochromator cystals: LP = Bragg angle

Rietveld Refinement -
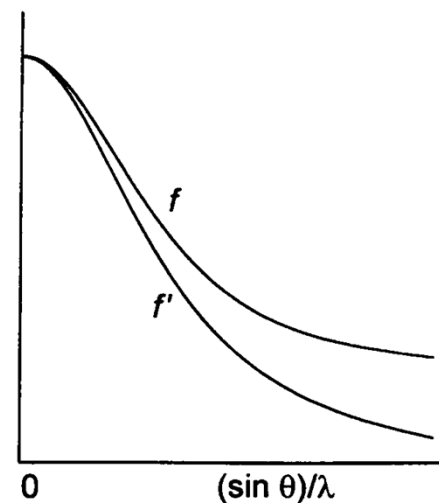# Structure factor

$$F(hkl) = \sum_j^N f_j \, \exp\left[2\pi i \left(hx_j + ky_j + lz_j\right)\right]$$

$$f = 4\pi \int \rho(r)\left(\frac{\sin Kr}{r}\right) dr$$

$$f_j = {}^0 f_j \, \exp\left(\frac{-B \sin^2 \theta}{\lambda^2}\right)$$

Structure Model

- Cell parameters (edge lengths, angles)
  a,b,c, alpha, beta, gamma

- Symmetry group, space group
- Asymmetric unit i.e. atom coordinates, TDPs, occupancy:

TABLE 1.   ATOMIC POSITIONS

	x	y	z	B equiv
T(1)	0.3968(2)	-0.0001(1)	0.1906(1)	0.648
T(2)	0.8970(2)	0.1667(1)	0.1908(1)	0.686
M(1)	0.0	0.0	0.0	0.336
M(2)	-0.0009(2)	0.3334(1)	0.00006(9)	0.555
M(3)	0.0012(2)	0.1666(1)	0.50314(9)	0.430
M(4)	0.5	0.0	0.5	0.949

TABLE 2.   ANISOTROPIC THERMAL PARAMETERS*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
T(1)	54(3)	14(1)	10.5(5)	1(1)	3(1)	0.8(5)
T(2)	58(3)	15(1)	10.9(5)	-1(1)	3(1)	0.5(5)
M(1)	39(3)	11(2)	9.7(8)	-0(2)	3(2)	0.4(9)
M(2)	41(4)	12(1)	9.7(5)	1(2)	2(1)	0.4(6)
M(3)	36(4)	6(1)	8.3(5)	0(1)	2(1)	0.4(6)
M(4)	88(3)	23(1)	13.1(5)	0(1)	4(1)	0.7(5)

NOTE ! Rietveld is structure refinement, not structure determination

Structure Model
Where to get it from?

- Literature, journals (e.g. Acta Cryst., Z. Krist., …)
- CSD (Cambridge Structural Database)
- ICSD (Inorganic Crystal Structure Database)
- PDF-4
- COD
- PDB (Protein Data Bank)
- From structure solution

Close starting model necessary!

Rietveld Refinement

Preferred Orientation

- **March Dollase function**

$$P_k = \left[G^2 \cos^2 \alpha_k + \left(\frac{1}{G} \right) \sin^2 \alpha_k \right]^{-3/2}$$

α_K = angle between (hkl) and preferred orientation vector
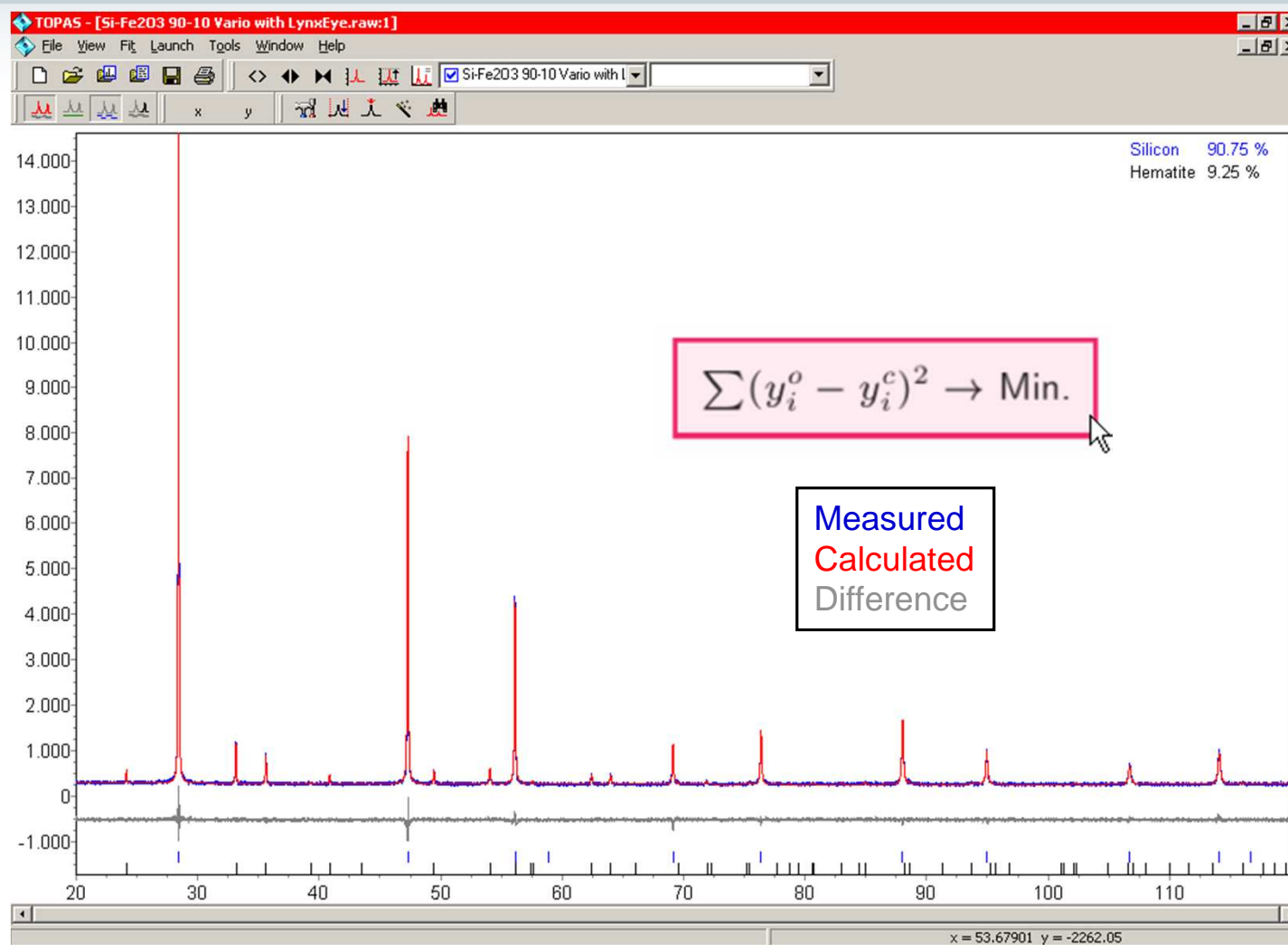
- **Spherical harmonics**

only even orders (Friedel's Law)
start always with lowest order
increase order until no improvement of R_{wp} is obtained
!!! Check plot of phase intensity for negative values !!!

Rietveld Refinement
Principal and Visual Quality Check

Rietveld Refinement
Numerical Quality Criteria

Criteria of fit	Definition
"R-pattern", R_p	$R_p = \sqrt{\dfrac{\sum \left| Y_{o,m} - Y_{c,m} \right|}{\sum Y_{o,m}}}$ $\qquad$ $R_p' = \sqrt{\dfrac{\sum \left| Y_{o,m} - Y_{c,m} \right|}{\sum \left| Y_{o,m} - Bkg_m \right|}}$
"R-pattern", R_p' (background corrected)	
"R-weighted pattern", R_{wp}	$R_{wp} = \sqrt{\dfrac{\sum w_m \left(Y_{o,m} - Y_{c,m} \right)^2}{\sum w_m Y_{o,m}^{\;2}}}$ $\qquad$ $R_{wp}' = \sqrt{\dfrac{\sum w_m \left(Y_{o,m} - Y_{c,m} \right)^2}{\sum w_m \left(Y_{o,m} - Bkg_m \right)^2}}$
"R-weighted pattern", R_{wp}' (background corrected)	
"R-expected", R_{exp}	$R_{exp} = \sqrt{\dfrac{\sum M - P}{\sum w_m Y_{o,m}^2}}$ $\qquad$ $R_{exp}' = \sqrt{\dfrac{\sum M - P}{\sum w_m \left(Y_{o,m} - Bkg_m \right)^2}}$
"R-expected", R_{exp}' (background corrected)	
"Goodness of fit", GOF	$GOF = chi^2 = \dfrac{R_{wp}}{R_{exp}} = \sqrt{\dfrac{\sum w_m \left(Y_{o,m} - Y_{c,m} \right)^2}{M - P}}$
"R-Bragg", R_B	$R_B = \dfrac{\sum \left| I_{"o",k} - I_{c,k} \right|}{\sum I_{"o",k}}$

Quantitative Phase Analysis

step intensity y_i of k overlapping reflections from a multiphase mixture of p phases

$$Y_i = y_b + \sum_p S_p \sum_k m_{kp} L_{kp} |F_{kp}|^2 G_{ikp} P_{kp}$$

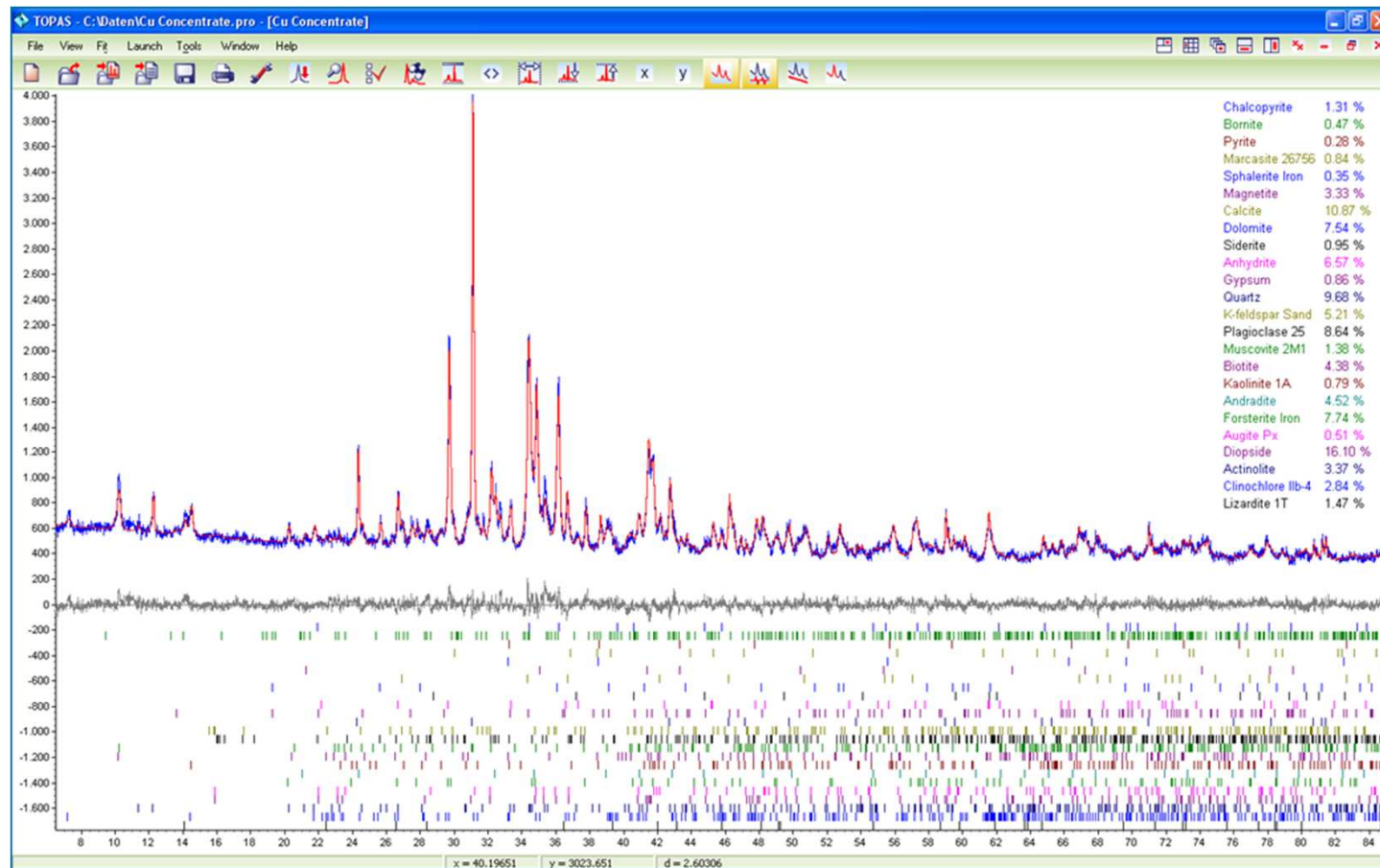the scale factors S_p yield the mass m_p of phase p

$$m_p \propto S_p/(Z_p M_p V_p)$$

M_p ...mass per formula unit
Z_p ...number of formula units per unit cell
V_p ...volume of the unit cell

Rietveld QPA
State-of-the-Art

- Accurate, standardless quantitative analysis of a Cu concentrate containing 24 phases:
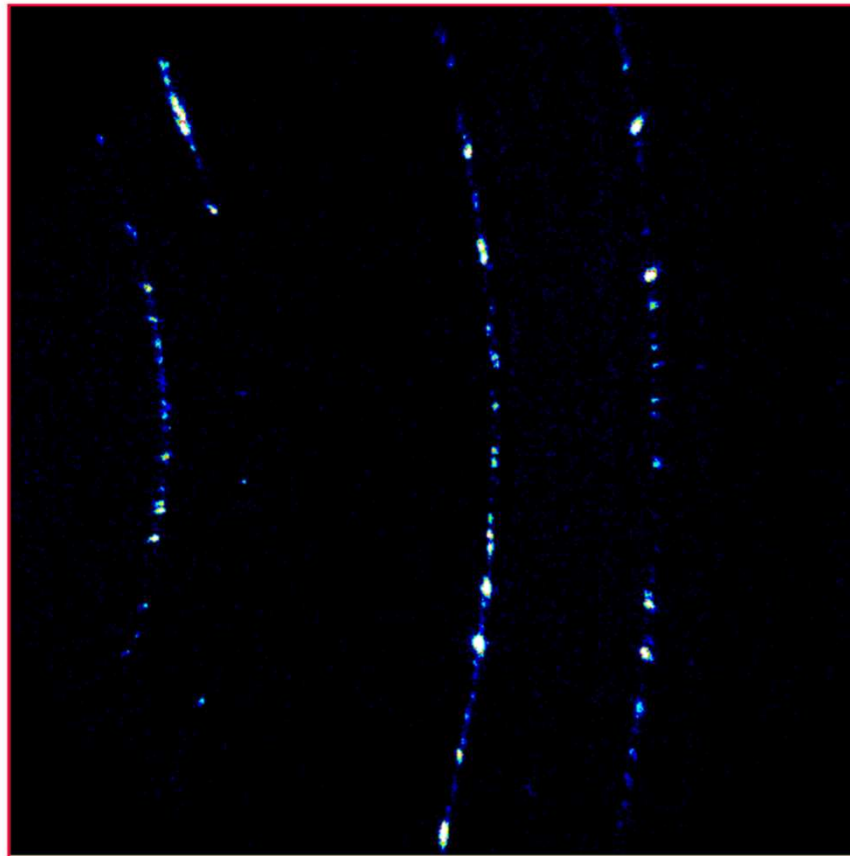
Sample

- The grains in the powder should be randomly oriented!

- Typical sample-related problems:
  - Not enough scattering particles (spotiness)
  - Sample not representative for the bulk
  - Bad sampling / particle heterogeneity / phase separation
  - Preferred orientation
  - Extinction
  - Microabsortion (multiphase samples)
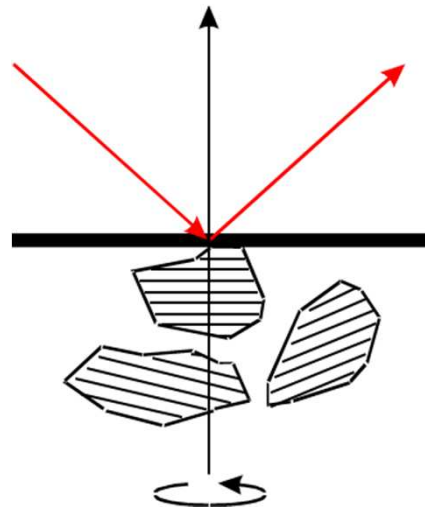
Sample
Not enough scattering particles
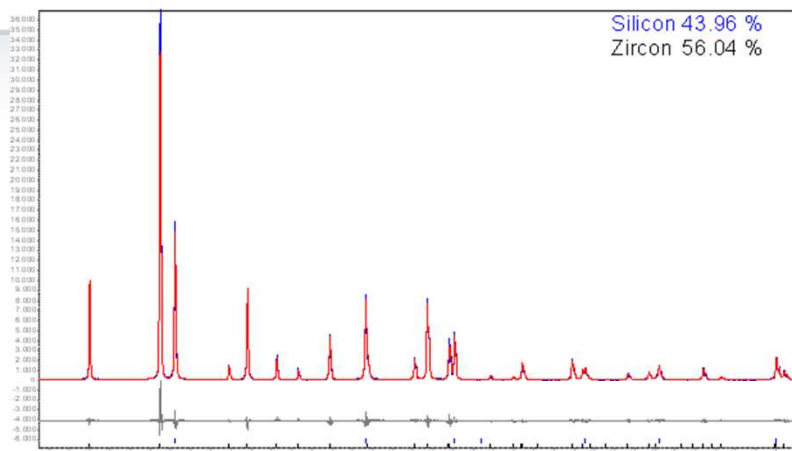
- Spotiness effect

Sample
Preferred Orientation

- Rotation parallel to the scattering vector does not minimize preferred orientation effects!
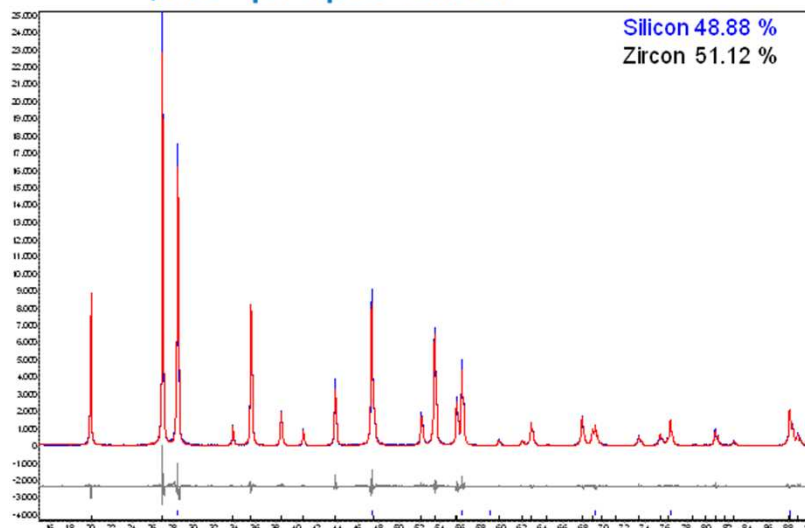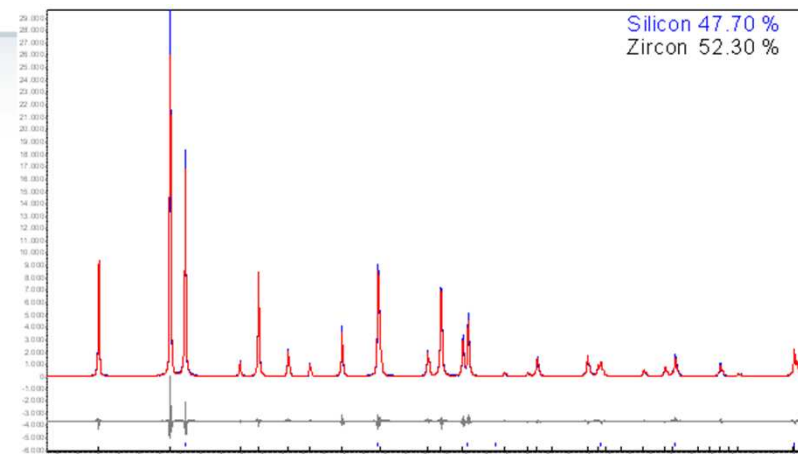
Sample Preparation
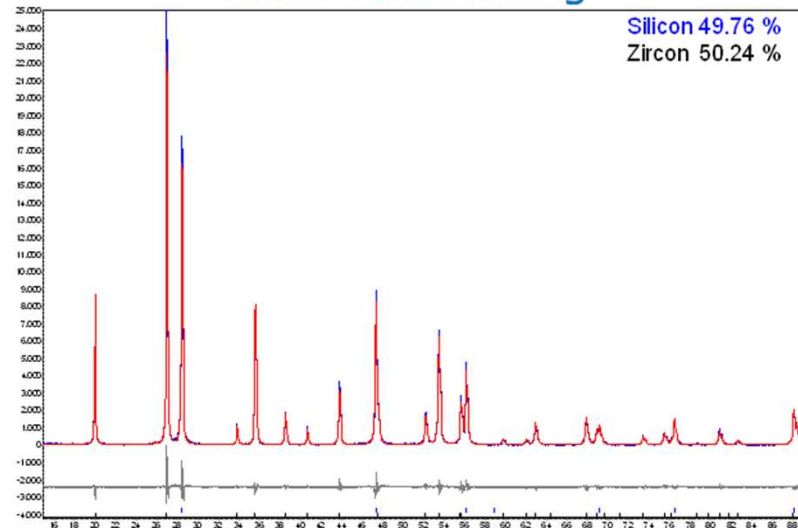# Si/Zr mixture 50/50 – coarse grained

Silicon 43.96 %
Zircon 56.04 %

‚no' preparation

Silicon 47.70 %
Zircon 52.30 %

After 15s milling

Silicon 48.88 %
Zircon 51.12 %

After 30s milling

Silicon 49.76 %
Zircon 50.24 %

After 45s milling

Data Collection Strategy

- For structure refinement, go as far as reasonably possible

- For quantitative refinement, somewhat less strict since generally less parameters are refined

- Use appropriate divergence slits (avoid beam overspill at low angles!)

- No variable slits (for structure refinement)

- 5000 to 10000 counts for main peaks (only as rule of thumb!)

- Step size as to collect 5 to 10 points above FWHM

- Variable counting time strategy (enhance statistics of high angle data)

Refinement Strategy (1)

- Raw data – NO smoothing or $K_{\alpha 2}$-stripping

- Start with Le Bail or Pawley fit $\Rightarrow$ gives the best R_{wP} that can be achieved

- Describe background with as less parameters as possible $\Rightarrow$ correlation

- Do not refine zero-error and sample displacement at the same time, unless lattice parameters are from a certified material

Refinement Strategy (2)

For **qualitative** Rietveld (single phase):

- Heavy atoms first

- As a general rule, use isotropic displacement vectors B_{iso} (in literature sometimes called „thermal parameters")

- Constrain B_{iso} for chemically identical elements

  e.g. B_C and B_O for two independent oxalate ions $C_2O_4^{2-}$

- Use constraints for refinement of occupancy factors

For **quantitative** Rietveld (mixture):

- As a general rule, do not refine positional (x, y, z) and displacement vectors (B)

Possible Problems (1)

- Poor background

  ⇒   increase polynomial coefficients, use peak phase to describe   bumps (e.g. from capillary), use 1/X at low angle

- Poor peak shape description

  ⇒ check instrument set-up

  ⇒ low absorbing material – transparancy

  ⇒ high absorbing material – surface roughness

  ⇒ anisotropic behaviour

- Mismatch calculated vs. observed pattern

  ⇒ unit cell parameters correct?
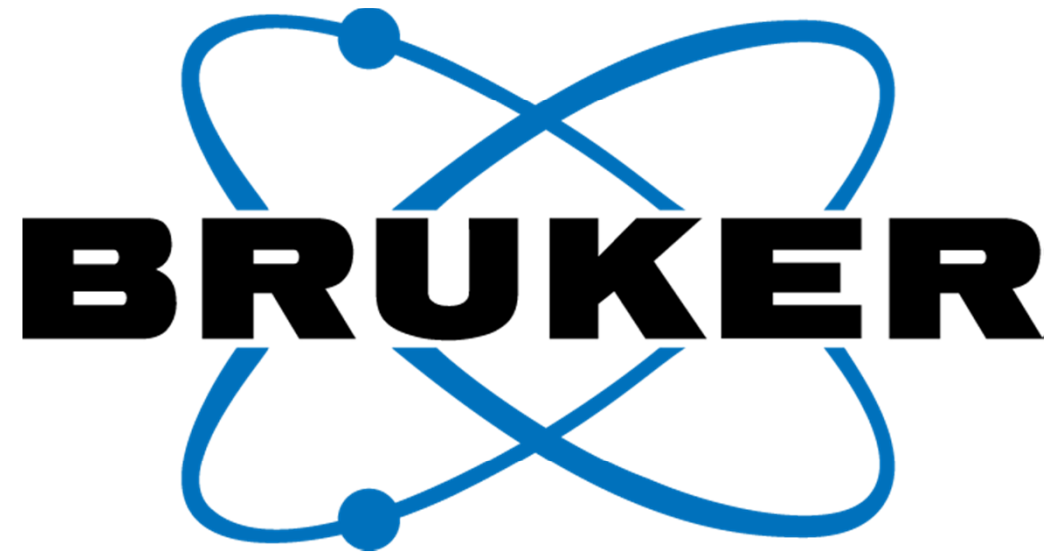
  ⇒ 2θ correction checked?

Possible Problems (2)

- Relative intensities of few reflection too high, none too low

  $\Rightarrow$ poor particle statistics, recollect data after grinding/sieving, sample spinning

- Small unindexed reflections

  $\Rightarrow$ Kβ or W-Lα (if no monochromator)

  $\Rightarrow$ impurity?

  $\Rightarrow$ unit cell parameters correct? Other space group?

- Refinement does not converge

  $\Rightarrow$ check structural model

  $\Rightarrow$ check correlation between parameters

  $\Rightarrow$ use restraints and/or constraints

  $\Rightarrow$ correct space group?

Possible Problems (3)

- Refinement converged, but angle dependent intensity mismatch and/or unreasonable thermal parameters

  $\Rightarrow$ check Lorentz-polarisation correction (monochromator?)

  $\Rightarrow$ absorption correction?

  $\Rightarrow$ surface-roughness correction?

  $\Rightarrow$ preferred orientation?

  $\Rightarrow$ check atoms

More can be found in:

„Rietveld refinement guidelines" Mc. Cusker et al. *Journal of Applied Crystallography* 32 (1999) 36-50

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