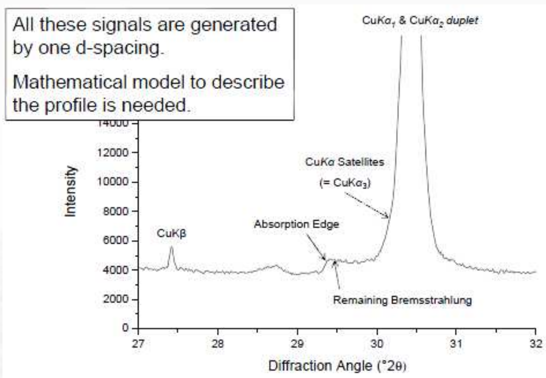
Peak Shape Modelling

Bish & Post Chap 8

Young Chap 7

Jenkins & Snyder page 302

Peak shape modelling



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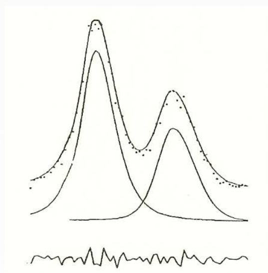


The Rietveld Method, RA Young

- Analytical profile fitting
- Direct convolution approach

Analytical profile fitting

- Fit a numerical function (profile shape function; PSF) to a measured diffraction pattern.
- PSF → 2θ, I, FWHM
- An optimization algorithm is employed to adjust parameters of PSF until the difference between the measured and calculated lines are minimized.

Direct convolution approach (Fundamental Parameters Approach)

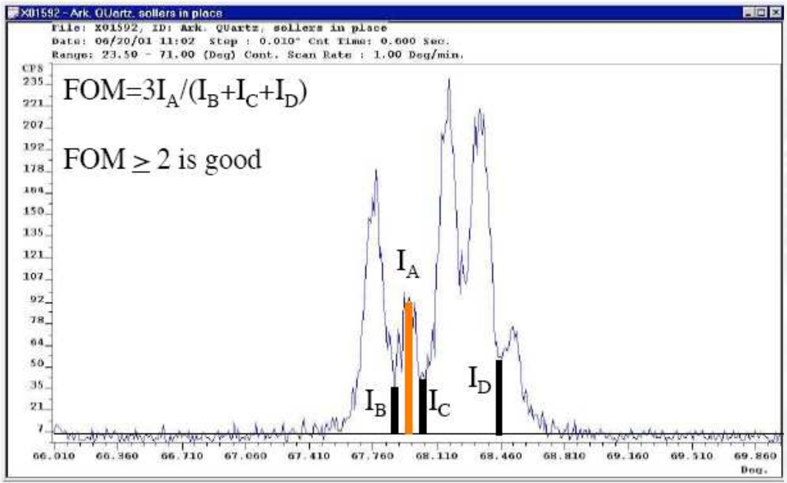
- Profiles are generated by convolution where various functions are convoluted to form the observed profile shape.
- Calculate peak profile from device configuration.

Precision vs. Accuracy

- Precision - reproducibility
- Accuracy – approach to the "true" value
- Improperly calibrated instruments, inadequate correction for systematic errors → highly precise but inaccurate measurement

Resolution test:

Five fingers of quartz: FOM= 2.29



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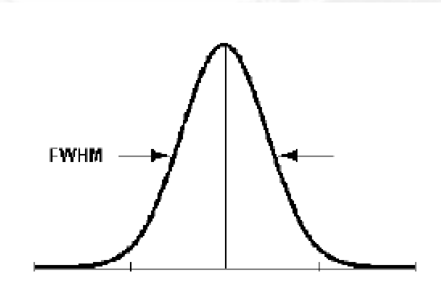
Full Width Half Maximum

- All peak shape functions incorporate dependence of half width of Bragg peaks or FWHM.
- FWHM shows angular dependence expressed by the **Caglioti** function.

$$H^2 = U \tan^2\theta + V \tan\theta + W$$

- ✓ *H* = half width
- ✓ U, V, W = refinable parameters



- Convolution – product of two functions is integrated over all spaces.
- Deconvolution

$$(f*g)(t) = f(t)*g(t) = \int_0^t f(t-\tau)g(\tau)\,d\tau = \int_0^t f(\tau)g(t-\tau)\,d\tau$$

- Intrinsic profile (specimen profile) (S)
- Spectral distribution (radiation source contribution) (W)
- Instrumental contribution (G)

- Observed profile; h(x)
- h(x) = (W * G) * S + background

Intrinsic profile (specimen profile) (S)

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- Darwin width
  - ✓ Inherent width of a diffraction peak
  - ✓ Result of uncertainty principle ($\Delta p \Delta x = h$)
    - Location of a photon in a crystal is restricted to a small volume. (← absorption coefficient) → Δp must be finite. → $\Delta\lambda$ ($\Delta p = h/\Delta\lambda$; de Broglie relation) must be finite. → produces a finite width to a diffraction peak.

- Two sample effects which broaden the profile shape functions
  - ✓ Size $\beta_{size} = l/(t\cos\theta)$
  - ✓ Microstrain $\beta_{strain} = 4e\tan\theta$

Spectral Distribution (radiation source contribution) (W)

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- The inherent spectral profile of the K-alpha1 line from a Cu target has a breadth of 0.518 x 10^{-3} Å (approximately Lorenzian and asymmetric).
- The inherent width & asymmetry is usually overwhelmed by the fact that various components of radiation ($K_{\alpha 1}$, $K_{\alpha 2}$, $K_{\alpha 3,4}$, ---) in a polychromatic beam will each spread out as 2theta increases.
- This spectral dispersion is so great that it can dominate the diffraction profiles at high angle, making them quite broad & relatively symmetric.
- Monochromatization can limit the breadth of W to the Darwin width of the monochromator crystal and its mosaicity.

$$H^2 = U \tan^2\theta + V \tan\theta + W$$

Instrumental contribution (G), Observed profile h(x)

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- 5 principal non-spectral contribution to the instrumental profile (G)

X-ray source image

Flat specimen → asymmetry

Axial divergence of incident beam → asymmetry

Specimen transparency → asymmetry

Receiving slit

- Intrinsic profile (S)
- Spectral distribution (radiation source contribution) (W)
- Instrumental contribution (G)

- h(x) = (W * G) * S + background (*; convolution)
- (W * G) ; fixed for a particular instrument/target system → instrumental profile g(x)
- h(x) = g(x) * S + background

LaB_6 (SRM 660c)

- Very asymmetric profile in sealed tube parafocusing system
- Symmetric Gaussian profile in neutron & synchrotron X-ray

Analytical profile shape functions (PSFs)

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Table 1.2 Some symmetric analytical profile functions that have been used[a]

Function	*Name*
(a) $\frac{C_0^{1/2}}{H_K\pi^{1/2}}\exp(-C_0(2\theta_i-2\theta_K)^2/H_K^2)$	Gaussian ('G')
(b) $\frac{C_1^{1/2}}{\pi H_K}1\bigg/\left[1+C_1\frac{(2\theta_i-2\theta_K)^2}{H_K^2}\right]$	Lorentzian ('L')
(c) $\frac{2C_2^{1/2}}{\pi H_K}1\bigg/\left[1+C_2\frac{(2\theta_i-2\theta_K)^2}{H_K^2}\right]^2$	Mod 1 Lorentzian
(d) $\frac{C_3^{1/2}}{2H_K}1\bigg/\left[1+C_3\frac{(2\theta_i-2\theta_K)^2}{H_K^2}\right]^{3/2}$	Mod 2 Lorentzian
(e) $\eta L+(1-\eta)G$ The mixing parameter, η, can be refined as a linear function of 2θ wherein the refinable variables are NA and NB: $\eta = NA + NB*(2\theta)$	pseudo-Voigt ('pV')
(f) $\frac{C_4}{H_K}\left[1+4*(2^{1/m}-1)\frac{(2\theta_i-2\theta_K)^2}{H_K^2}\right]^{-m}$ m can be refined as a function of 2θ, $m = NA + NB/2\theta + NC/(2\theta)^2$, where the refinable variables are NA, NB, and NC.	Pearson VII
(g) Modified Thompson–Cox–Hastings pseudo-Voigt, 'TCHZ' $\mathrm{TCHZ} = \eta L + (1-\eta)G$ where $\eta = 1.36603q - 0.47719q^2 + 0.1116q^3$ $q = \Gamma_L/\Gamma$ $\Gamma = (\Gamma_G^5 + A\Gamma_G^4\Gamma_L + B\Gamma_G^3\Gamma_L^2 + C\Gamma_G^2\Gamma_L^3 + D\Gamma_G\Gamma_L^4 + \Gamma_L^5)^{0.2} = H_K$ $A = 2.69269$ $B = 2.42843$ $C = 4.47163$ $D = 0.07842$ $\Gamma_G = (U\tan^2\theta + V\tan\theta + W + Z/\cos^2\theta)^{1/2}$ $\Gamma_L = X\tan\theta + Y/\cos\theta$	(Mod-TCH pV)

- Gaussian
- Lorentzian
- Modified Lorentzian
- Intermediate Lorentzian
- Pseudo-Voigt
- Pearson VII
- Split Pearson VII

Analytical profile fitting > Gaussian, Lorentzian, Pseudo Voigt profile

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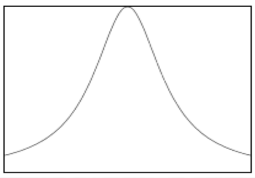
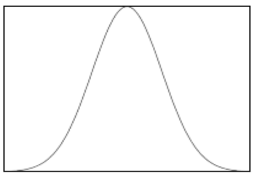
- Most instruments are more Gaussian at low angles and more Lorentzian at high angles (wavelength dispersion).

Pseudo Voigt profile; nL + (1-n)G

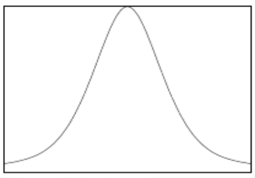
Lorentzian profile　　Gaussian profile



Lorentzian (n = 1.0)



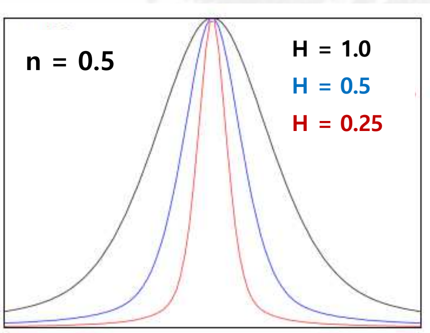
Gaussian (n = 0)



Pseudo Voigt (n = 0.5)

Same FWHM (H) in

$H^2 = U\tan^2\theta + V\tan\theta + W$



Analytical profile shape functions

(a) $\frac{C_0^{1/2}}{H_K\pi^{1/2}} \exp(-C_0(2\theta_i - 2\theta_K)^2/H_K^2)$ Gaussian ('G')

(b) $\frac{C_1^{1/2}}{\pi H_K} 1\Big/\left[1 + C_1\frac{(2\theta_i - 2\theta_K)^2}{H_K^2}\right]$ Lorentzian ('L')

(c) $\frac{2C_2^{1/2}}{\pi H_K} 1\Big/\left[1 + C_2\frac{(2\theta_i - 2\theta_K)^2}{H_K^2}\right]^2$ Mod 1 Lorentzian

(d) $\frac{C_3^{1/2}}{2H_K} 1\Big/\left[1 + C_3\frac{(2\theta_i - 2\theta_K)^2}{H_K^2}\right]^{3/2}$ Mod 2 Lorentzian

(e) $\eta L + (1-\eta)G$ pseudo-Voigt ('pV')

The mixing parameter, η, can be refined as a linear function of 2θ wherein the refinable variables are NA and NB:

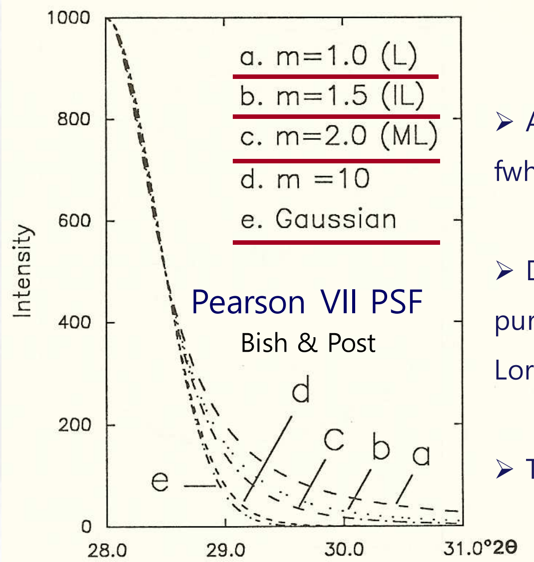
$\eta = NA + NB*(2\theta)$

(f) $\frac{C_4}{H_K}\left[1 + 4*(2^{1/m}-1)\frac{(2\theta_i - 2\theta_K)^2}{H_K^2}\right]^{-m}$ Pearson VII

m can be refined as a function of 2θ,

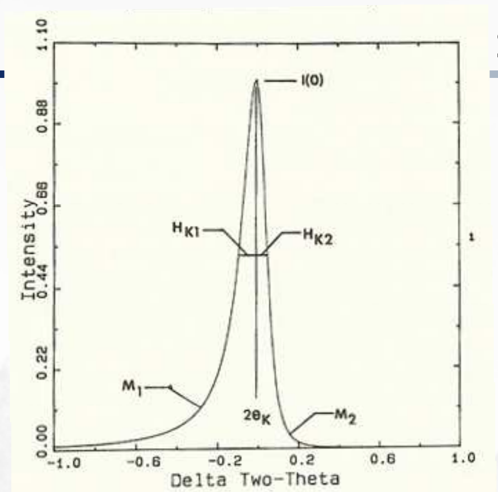
$m = NA + NB/2\theta + NC/(2\theta)^2$,

where the refinable variables are NA, NB, and NC.

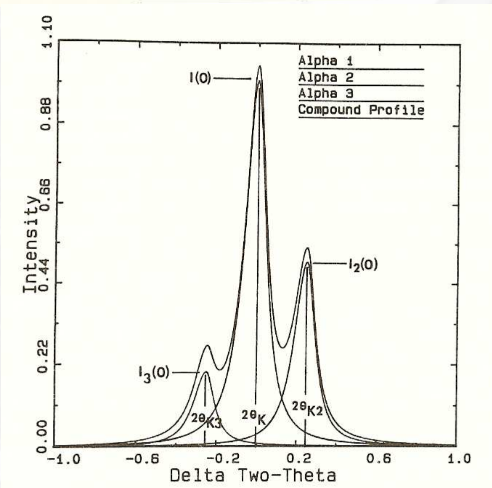


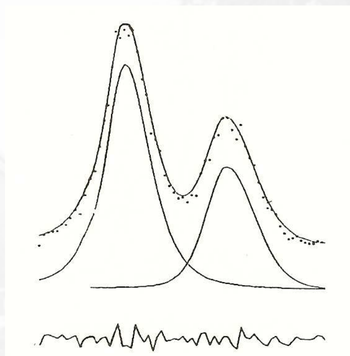
- A series of Pearson VII profiles generated with the same fwhm but with different values of exponent m
- Depending on the value of m, the function replicates the pure Lorenzian (L), Intermediate Lorenzian (IL) and Modified Lorenzian (ML) profiles.
- The shape is essentially Gaussian when m > ~ 10.

Split Pearson VII



- The two half profiles share a common Bragg angle $2\theta_k$ and peak intensity I(0).
- Their different fwhm's H_K, and exponents m, allow the profile to model an asymmetric line.

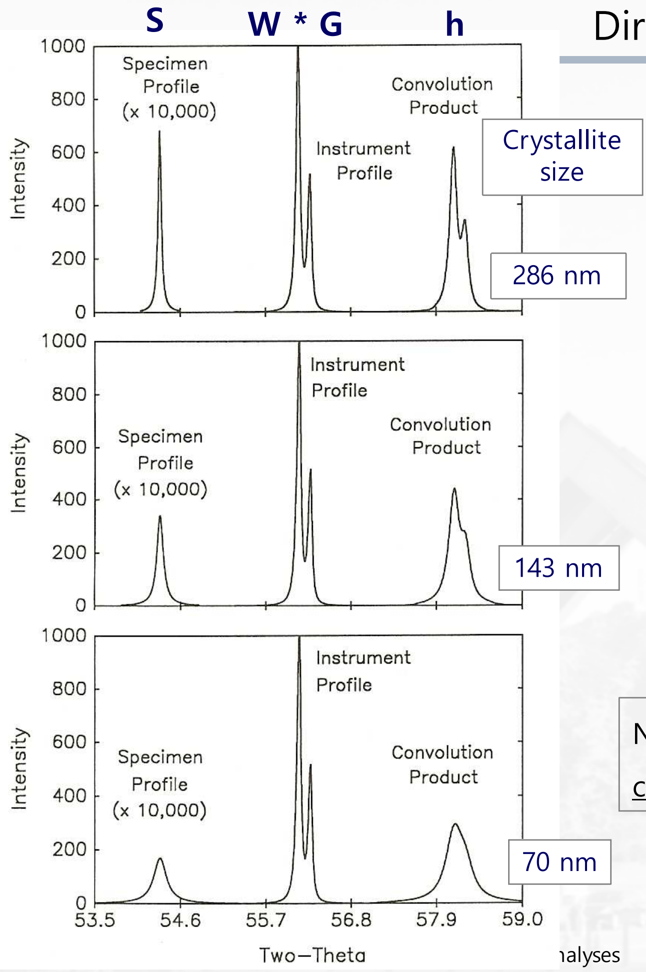




Page 120~122, figure 7.3, 7.4, 7.5, 7.6

Unconstrained profile fitting

Direct convolution approach



$$h = (W * G) * S$$

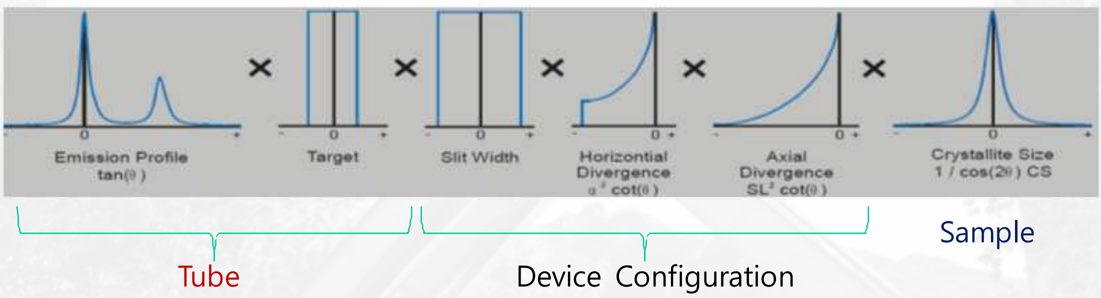
- Line shape ← convolution of (W*G) and (S) contributions
  - S; Intrinsic profile (specimen profile)
  - W; Spectral distribution (radiation source contribution)
  - G; Instrumental contribution
  - W*G; instrument

Integrated intensity of the peak remains the same while the peak broadens and the peak intensity decreases.

Need to know precisely the nature of <u>contributions from both instrument & specimen.</u>

Direct convolution approach > Fundamental Parameters Approach (FPA)

- Calculate the peak profile from the device configuration.
- Take into account the contributions of:
  - ✓ Source emission profile (X-ray wavelength distribution from Tube).
  - ✓ Every optical element in the beam path (position, size, etc.).
  - ✓ Sample contributions (peak broadening due to crystallite size & strain).



FPA needs:

- Very detailed and complete description of the instrument configuration.
- Very well aligned instrument.

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Factors that affect the integrated peak **intensity** and **not the peak shape**

- Background fitting (this should not affect the apparent Bragg intensities if it is done correctly)
- Extinction
- Preferred Orientation (Texture)
- Absorption & Surface Roughness
- Other Geometric Factors

- Need to know precisely the nature of contributions from both instrument and specimen.
- PSF representing instrument can be obtained by measuring a set of lines from a specimen.
  - ✓ Free of crystallite size broadening and lattice defects
  - ✓ Sufficiently small mean particle size and narrow size distribution without having particles so small as to introduce line broadening
  - ✓ Line profile standard, LaB_6 NIST SRM

Standard Reference Materials (SRMs)

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- Powder Line Position + Line Shape Std for Powder Dif
  - ✓ **Silicon (SRM 640f)**; \$745/7.5g
- Line position - Fluorophlogopite mica (SRM 675); \$809/7.5g
- Line profile - **LaB_6 (SRM 660c)**; \$907/6g

No broadening from size & strain

- Intensity
  - ✓ ZnO, TiO_2 (rutile), Cr_2O_3, CeO_2 (SRM 674b); out of stock
- Quantitative phase analysis
  - ✓ Al_2O_3 (SRM 676a); out of stock, Silicon Nitride (SRM 656); \$580/ 20g
- Instrument Response Std
  - ✓ Alumina plate (SRM 1976c); \$721/1 disc

Prices; 2021-06-17
www.nist.gov/srm/index.cfm

Gold
\$58.66 / gram
(2021-06-17)
goldprice.org

Line (peak) profile analysis

The danger of profile fitting

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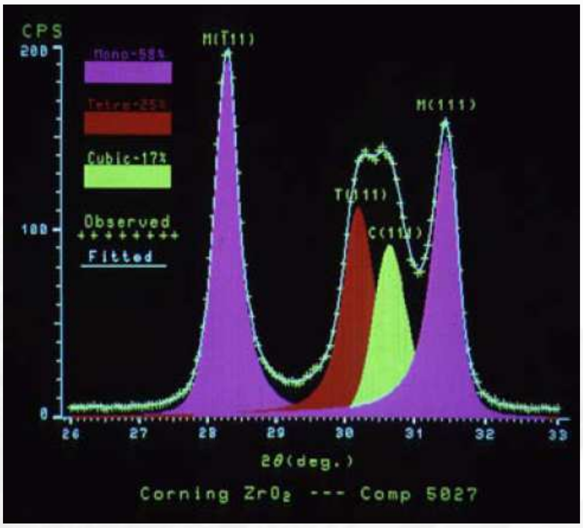
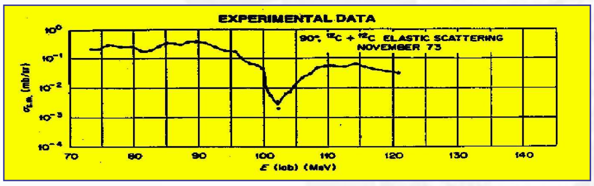
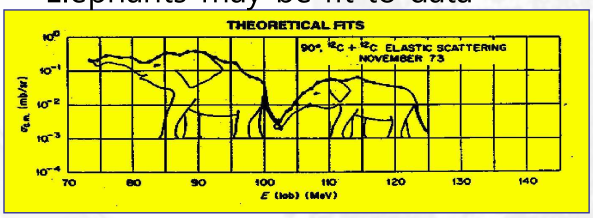
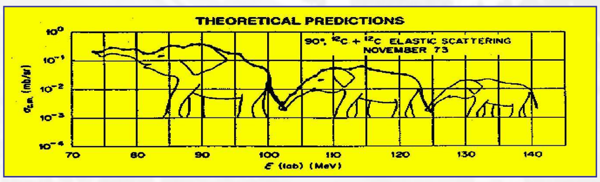




Elephants may be fit to data





Extrapolation ?????

Robert L. Snyder