# POWDER DIFFRACTION

Possibilities – Problems

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- Indexing
- Stress/strain
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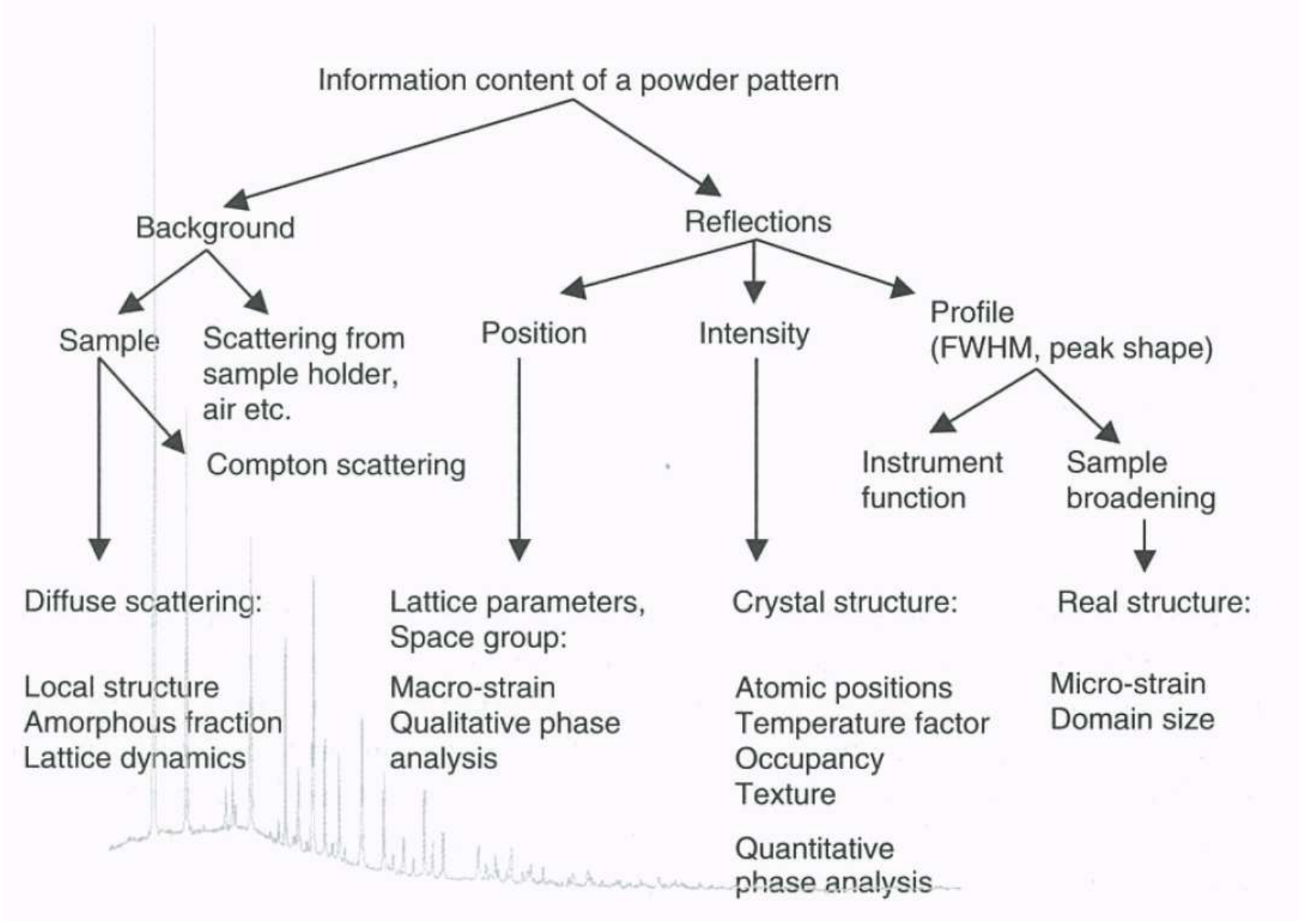
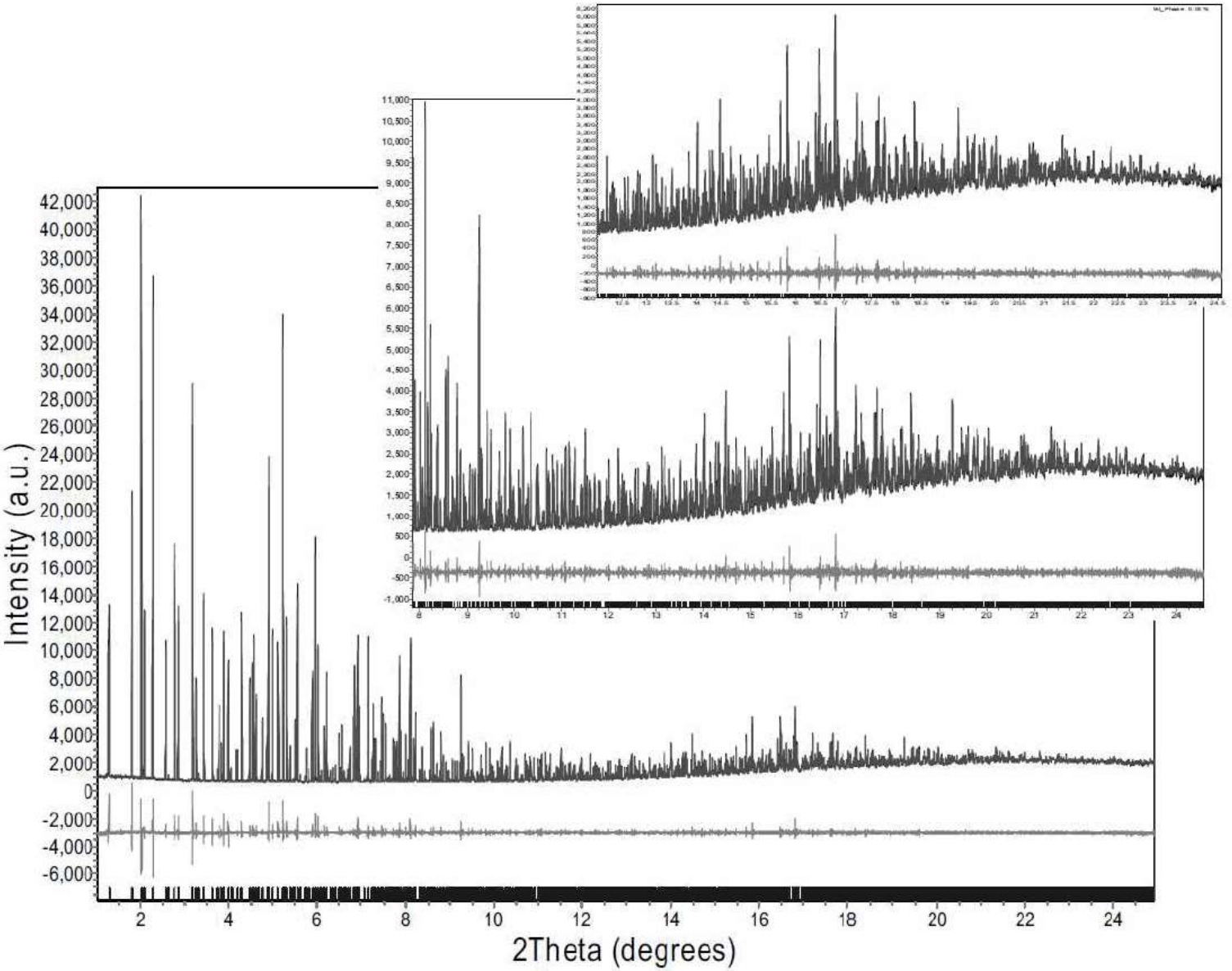
- Axial divergence

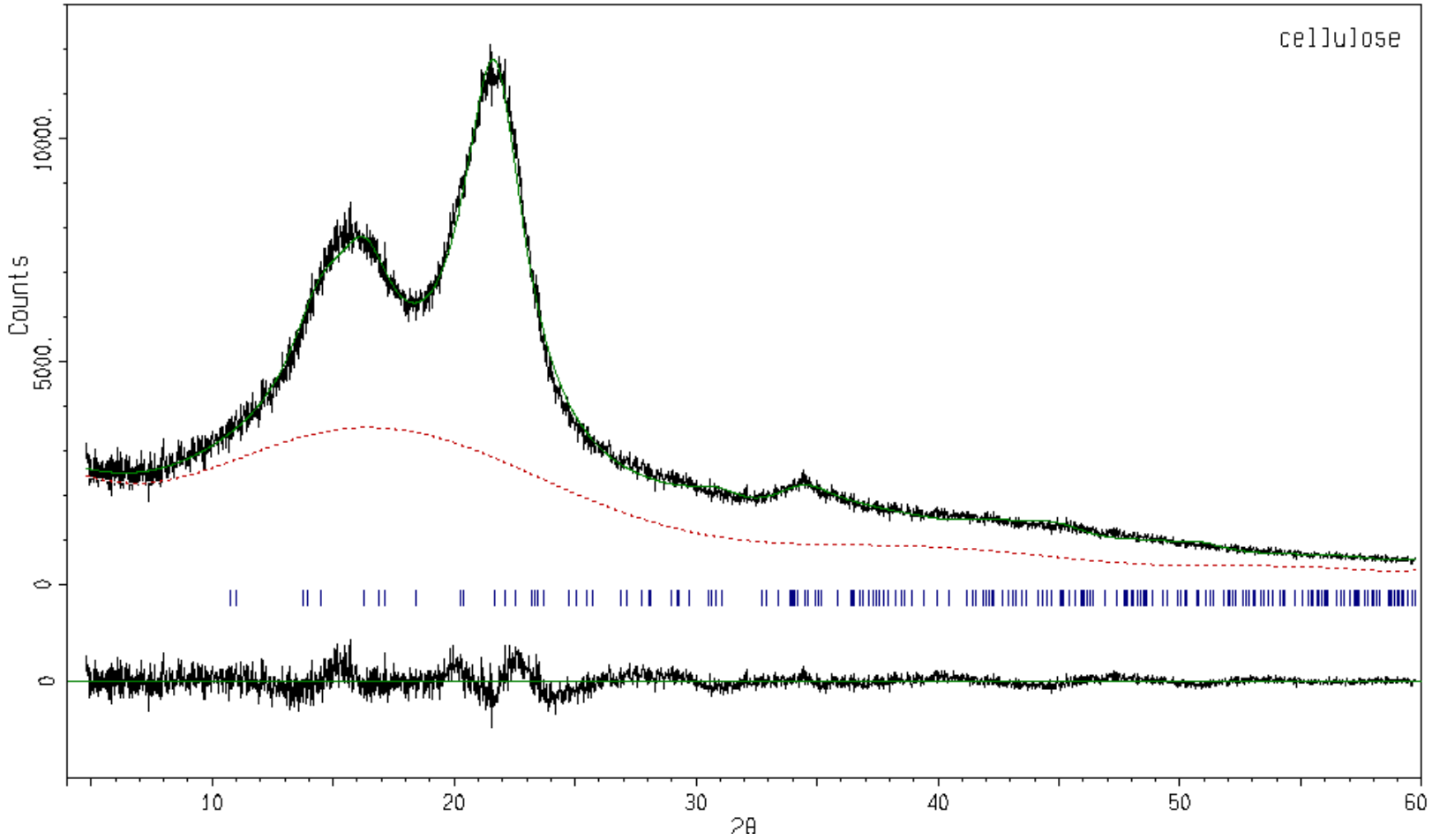
# POSSIBILITIES



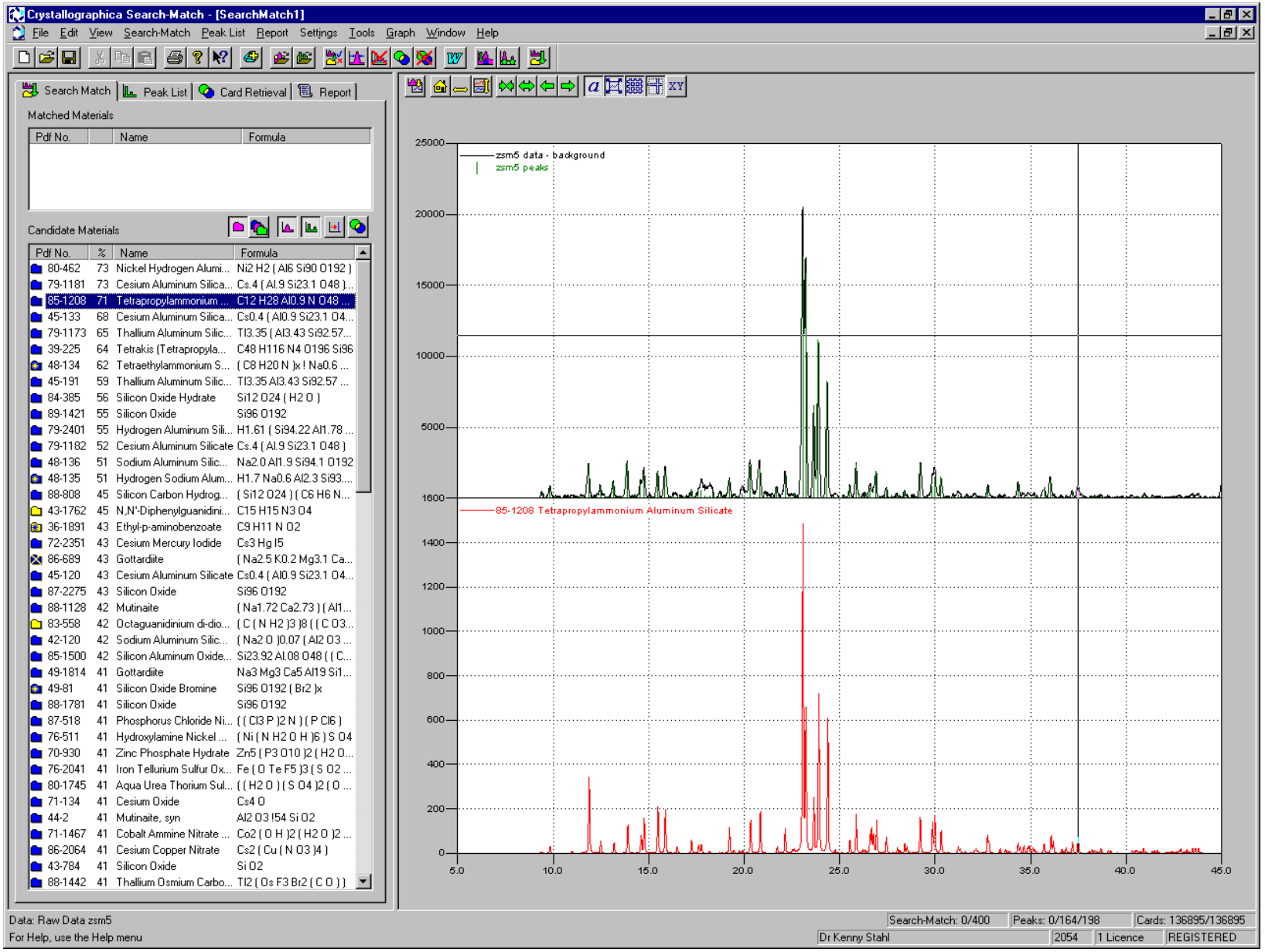
# POWDER DIFFRACTION



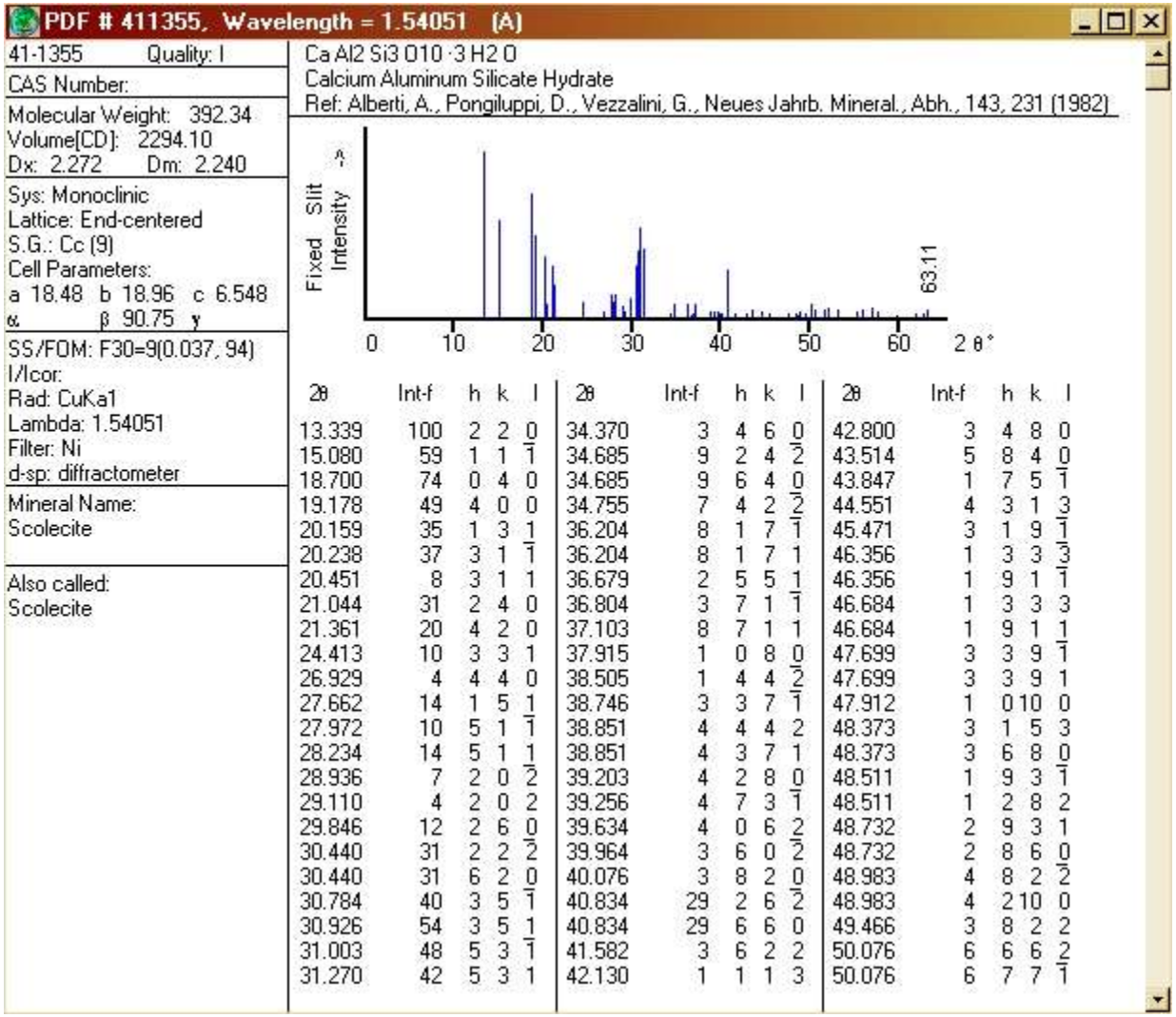
# POWDER DIFFRACTION



# PHASE IDENTIFICATION

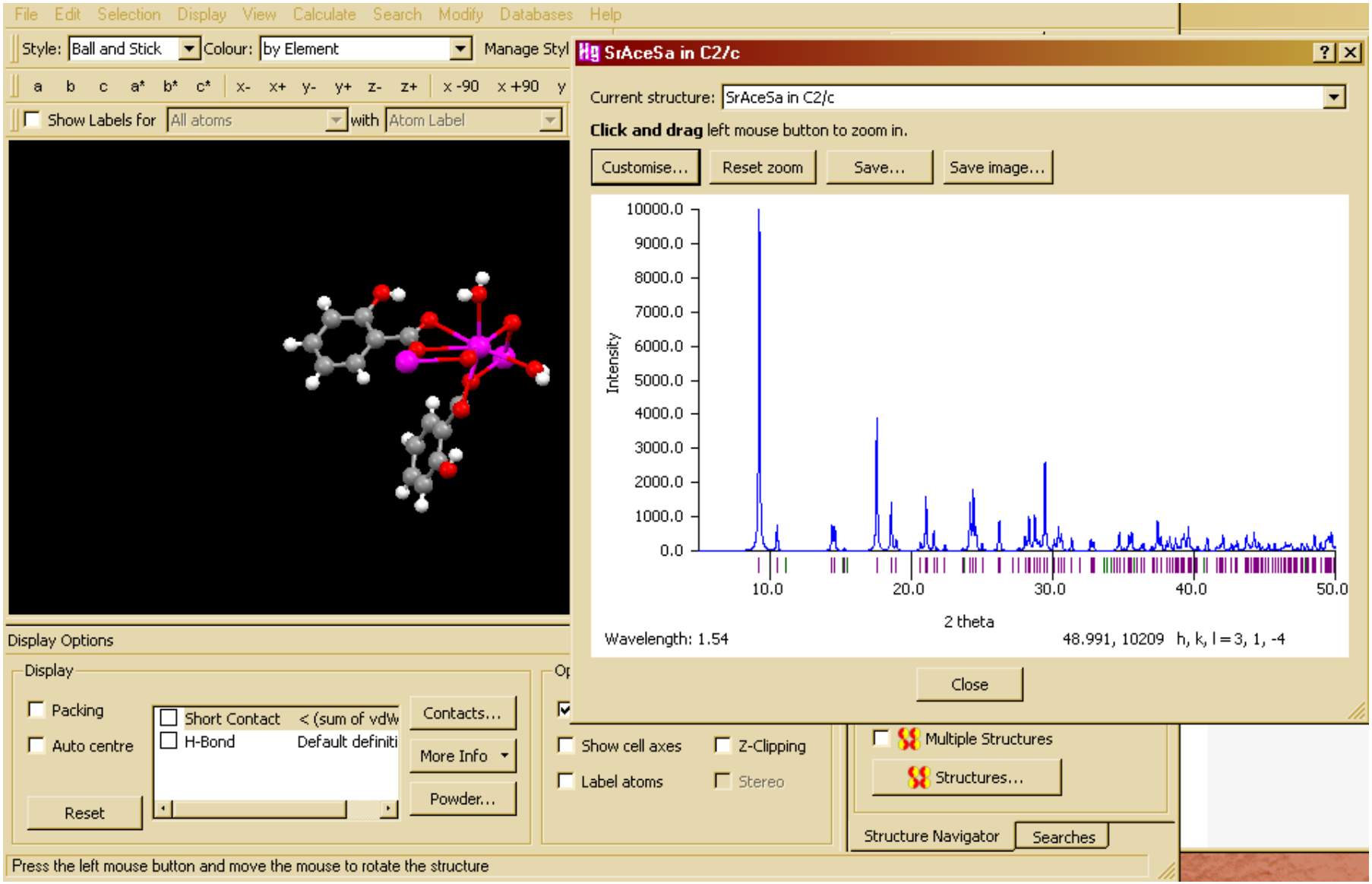


# PHASE IDENTIFICATION




The PDF4 database contains about 250000 entries

# PATTERN CALCULATION



# INDEXING

Cubic:

$(1 / d_{hkl})^2 = (h^2 + k^2 + l^2) / a^2$

$2\, d_{hkl} \sin\theta_{hkl} = \lambda$

$\sin^2 \theta_{hkl} = (h^2 + k^2 + l^2)\, \lambda^2 /(4a^2)$

| $2\theta$ | $\sin^2 \theta$ | $(h^2 + k^2 + l^2)$ | h k l |
|---|---|---|---|
| 25.96 | 0.05043 | | |
| 30.01 | 0.06704 | | |
| 43.06 | 0.13468 | | |
| 50.97 | 0.18517 | | |
| 53.41 | 0.20196 | | |
| 62.54 | 0.26941 | | |
| 68.88 | 0.31984 | | |
| 70.97 | 0.33693 | | |
| 78.92 | 0.40391 | | |

$$\sin^2 \theta_{hkl} = h^2 X_1 + k^2 X_2 + l^2 X_3 + hk X_4 + hl X_5 + kl X_6$$

# PARTICLE SIZE - STRESS / STRAIN (DEFECTS)

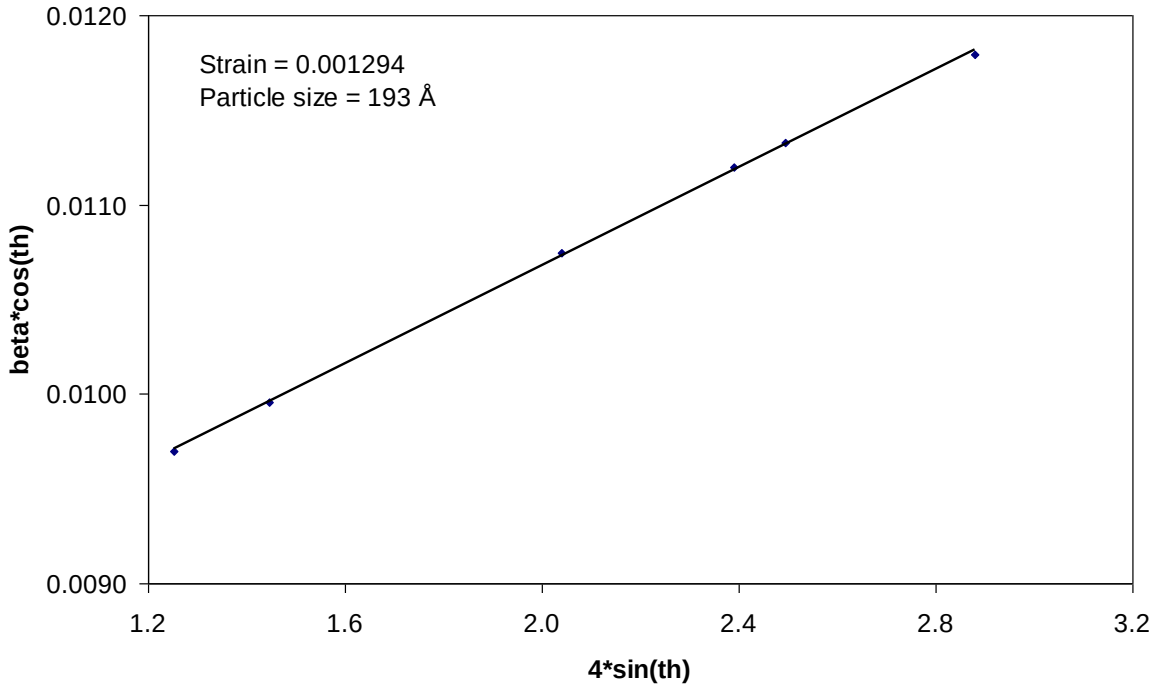
**Size ($\tau$) (Sherrer) :** $\beta = k \lambda / \tau \cos(\theta)$

$\beta^2 = FWHM_{obs}^2 - FWHM_{ref}^2$ (rad)

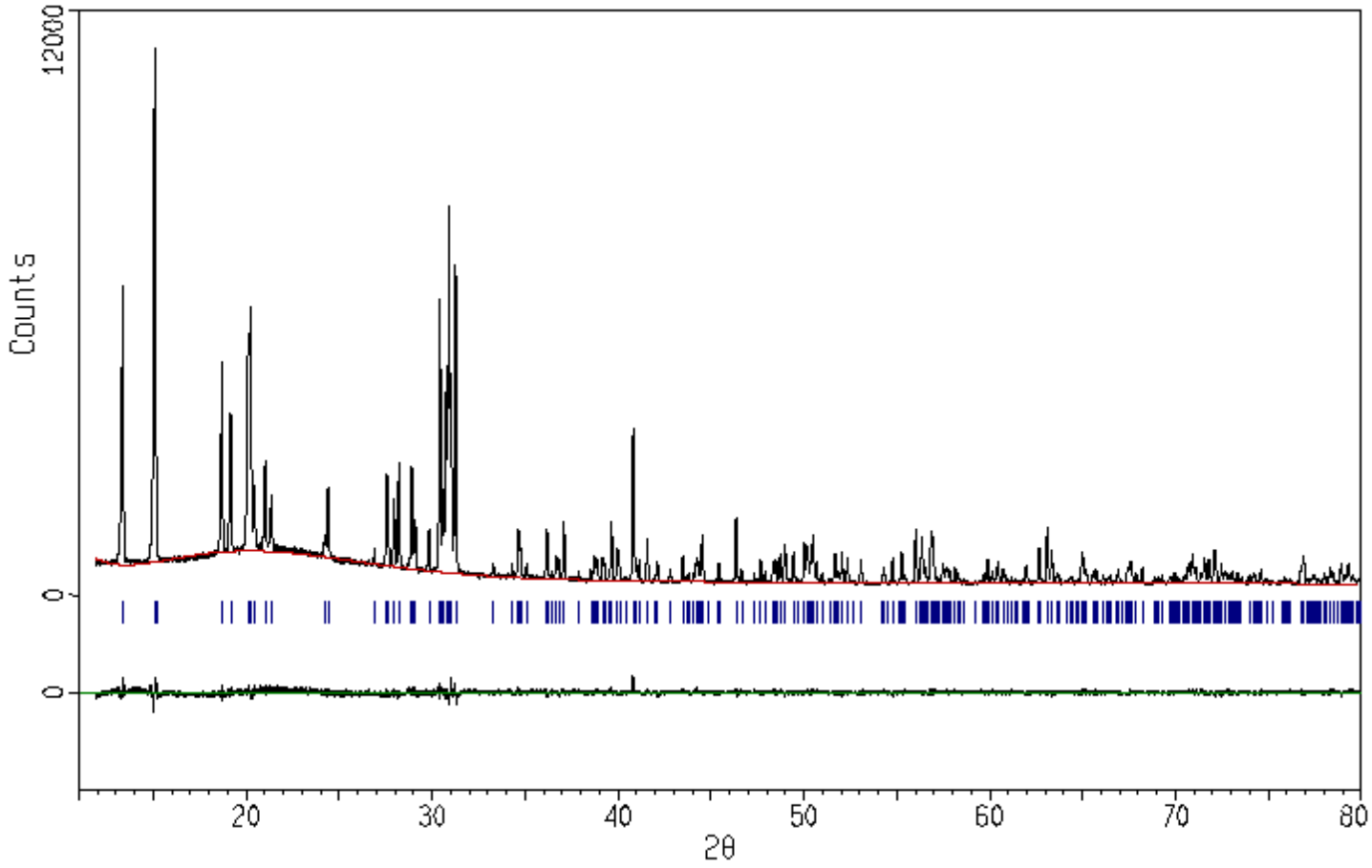
**Stress/strain ($\varepsilon$):** $\beta = 4 \varepsilon \tan(\theta)$

**Williamson-Hall:** $\beta = k \lambda / \tau \cos(\theta) + 4 \varepsilon \tan(\theta)$

$\beta \cos(\theta) = k \lambda / \tau + 4 \varepsilon \sin(\theta)$



# RIETVELD REFINEMENT




Scolecite

# RIETVELD REFINEMENT

Least-squares: $D = \Sigma_j w_j (Y_{oi} - Y_{ci})^2$

$$Y_{ci} = B_i + S \Sigma_{hkl} A(2\theta) P_{hkl} Lp(2\theta) \Phi(2\theta - 2\theta_{Bragg}) |F_{hkl}|^2$$

$Y_{ci}$ = Calculated intensity

$B_i$ = Background intensity

$S$ = Scale factor

$A(2\theta)$ = Absorption correction

$P_{hkl}$ = Preferred orientation correction

$Lp(2\theta)$ = Lorentz and polarization correction

$\Phi(2\theta - 2\theta_{Bragg})$ = Profile function

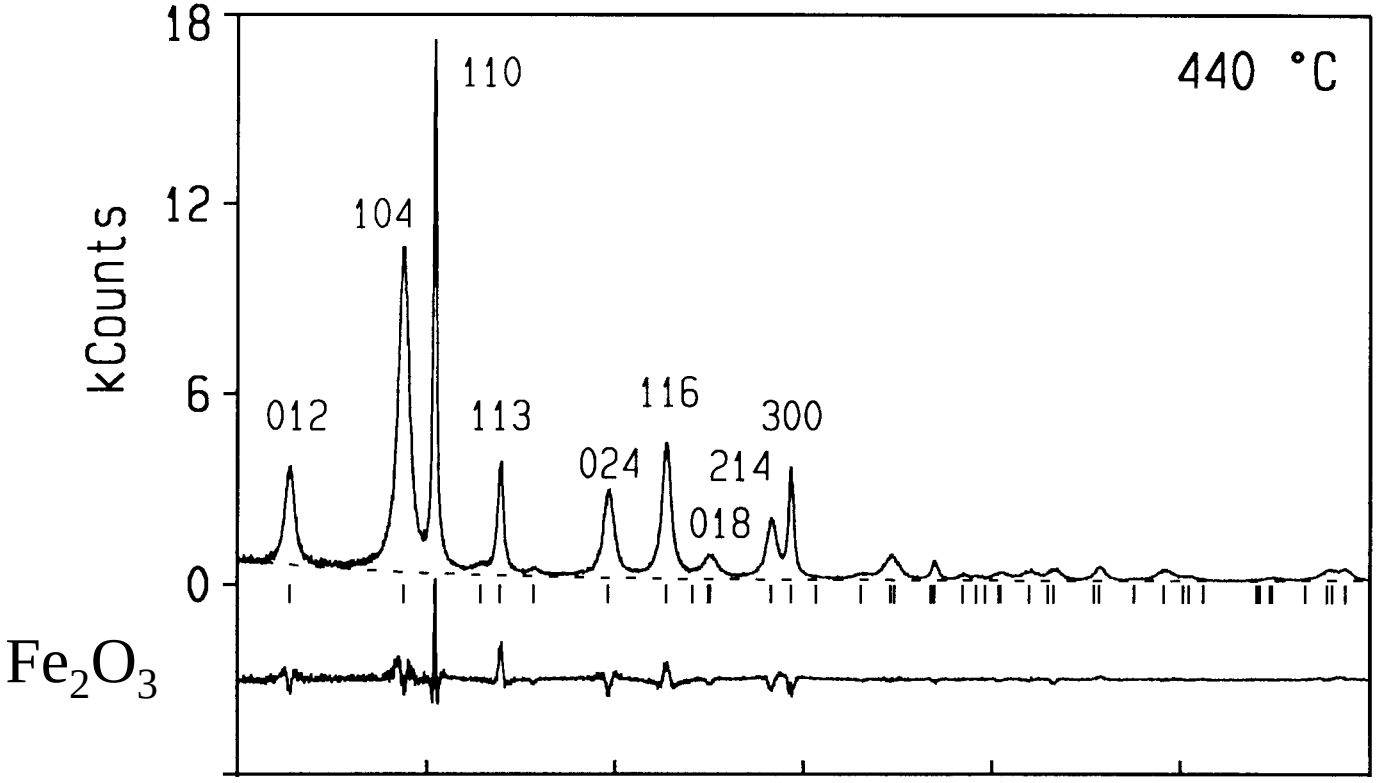
$|F_{hkl}|^2$ = Diffracted (single-crystal) intensity

# RIETVELD REFINEMENT

Scolecite, Huber data

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Si(1) | - O(1) | 1.632(7) | | | | | |
| | - O(2) | 1.593(6) | | Al(1) | - O(1) | 1.694(8) | |
| | - O(9) | 1.597(6) | | | - O(3) | 1.691(7) | |
| | - O(10) | 1.609(7) | | | - O(5) | 1.786(8) | |
| Si(2) | - O(3) | 1.676(8) | | | - O(7) | 1.748(8) | |
| | - O(6) | 1.642(7) | | Al(2) | - O(2) | 1.775(8) | |
| | - O(7) | 1.610(7) | | | - O(4) | 1.768(8) | |
| | - O(9) | 1.636(8) | | | - O(6) | 1.739(7) | |
| Si(3) | - O(4) | 1.586(8) | | | - O(8) | 1.730(8) | 1.75 Å |
| | - O(5) | 1.621(8) | | | | | |
| | - O(8) | 1.622(7) | | | | | |
| | - O(10) | 1.641(8) | 1.62 Å | | | | |

# ANISOTROPIC SIZE EFFECTS



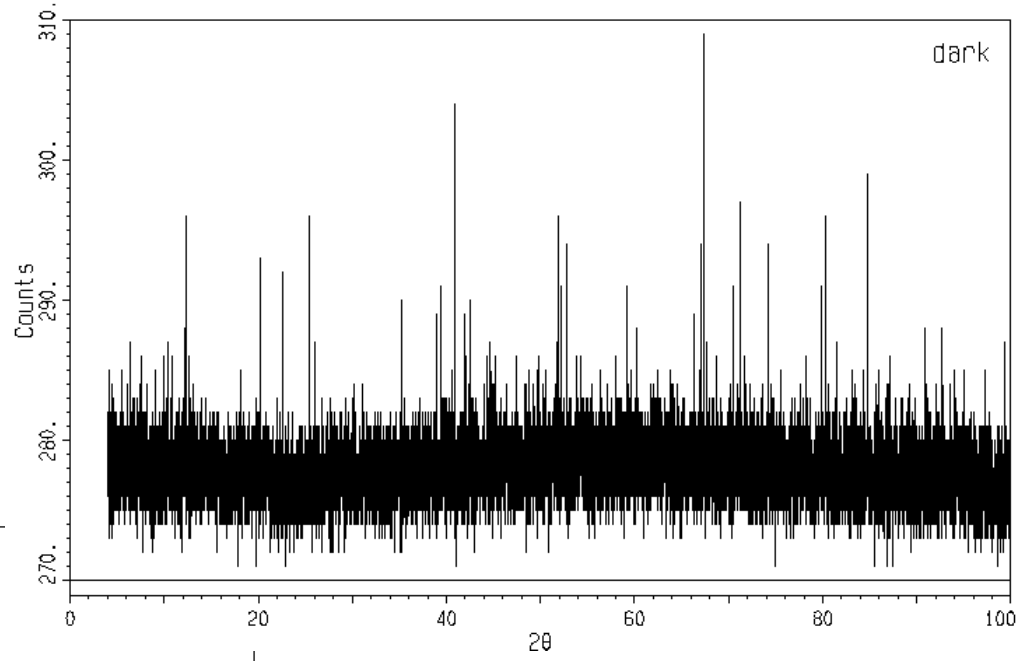

a = 5.0364(8), c = 13.750(2) Å  D(a) = 399(3) Å, D(c) = 87(2) Å

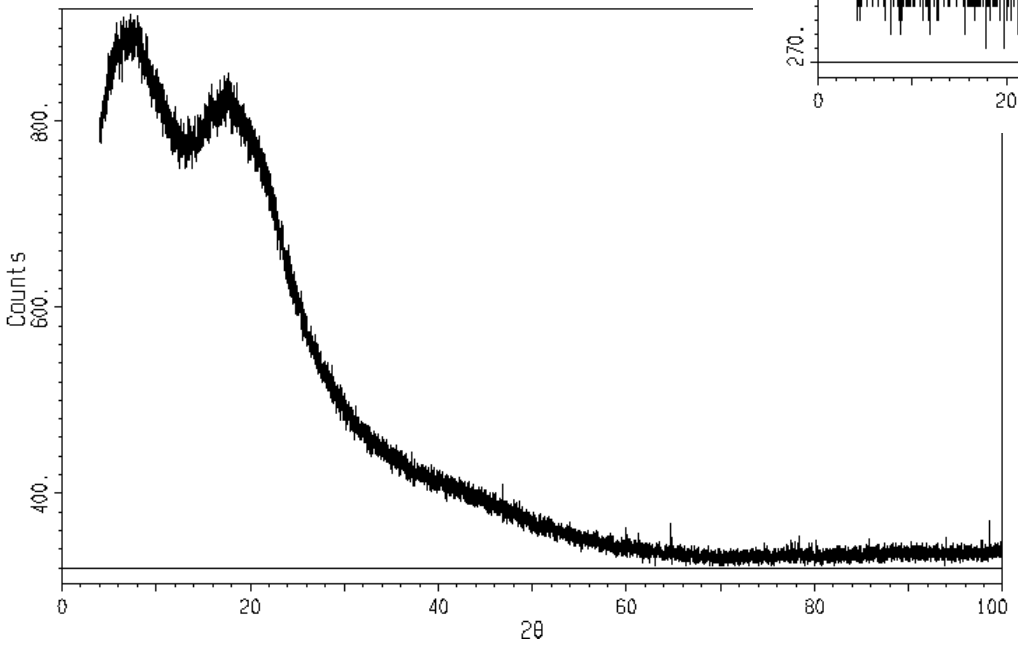
# PROBLEMS - ERRORS

| | |
|---|---|
| Background | General |
| | Fluorescence/incoherent scattering |
| | Counting statistics |
| Preferred orientation | Poor sample |
| | Texture |
| Systematic errors | Absorption – intensities |
| | Absorption – peak positions |
| | Axial divergence |

# BACKGROUND

Read-out-noise

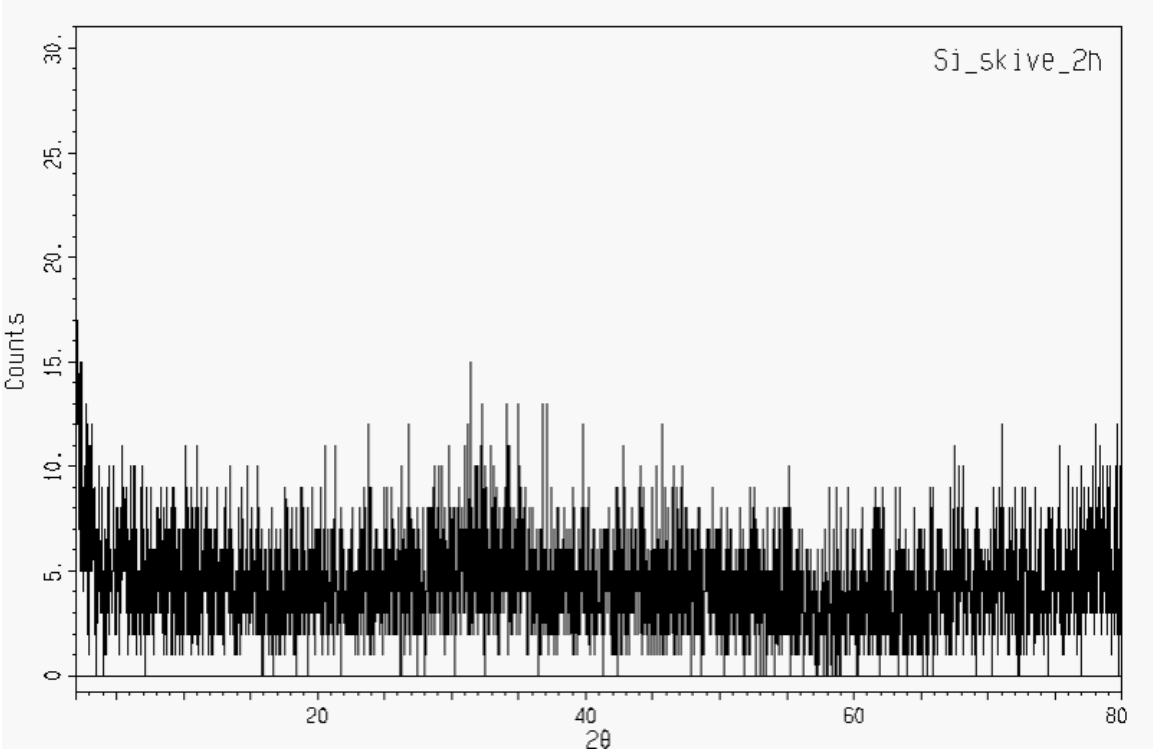



Sample holder (transmission mode)

# BACKGROUND

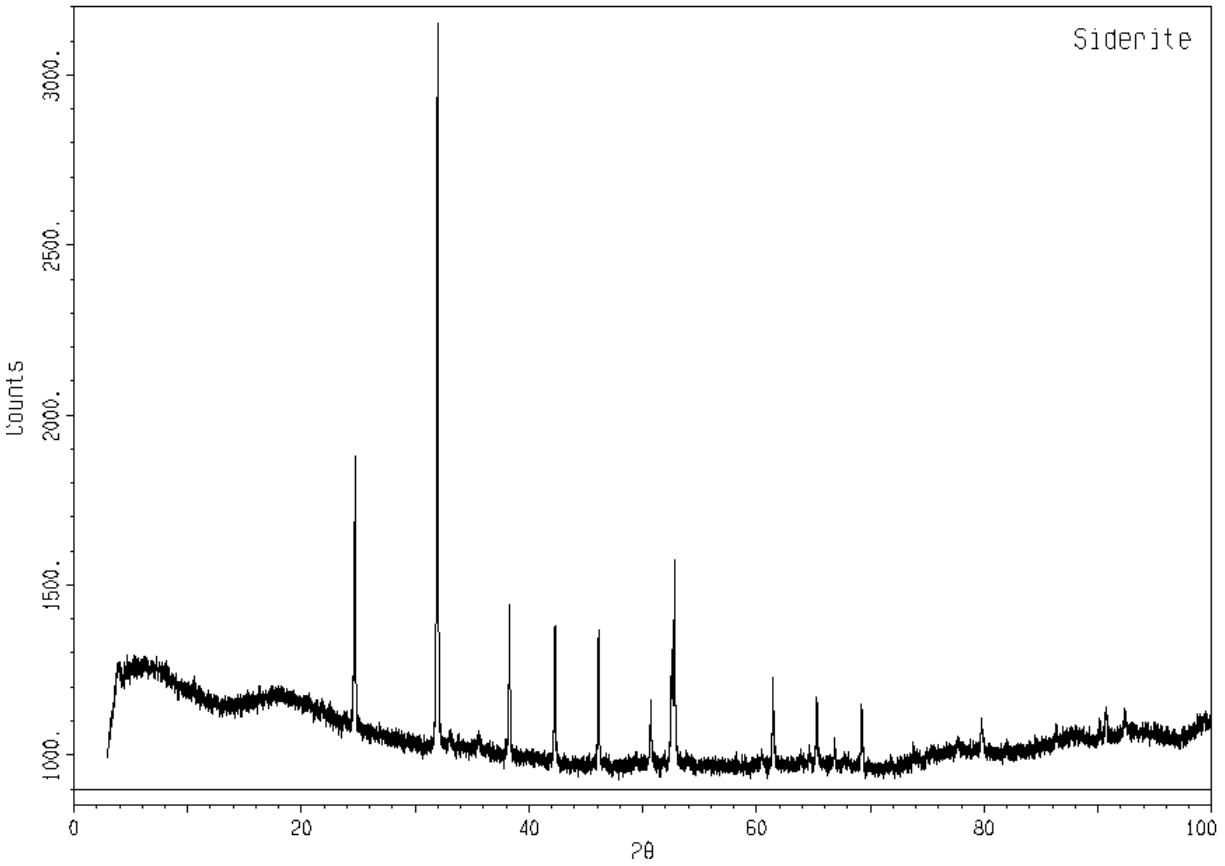
Reflection mode




Si single crystal (711 reflection tilted 5°)

# BACKGROUND

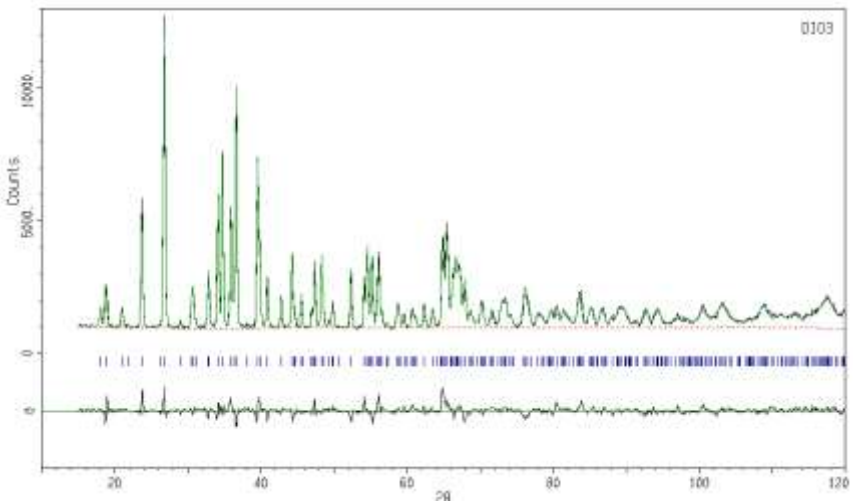
Siderite, $FeCO_3$




Fluorescence scattering

# BACKGROUND

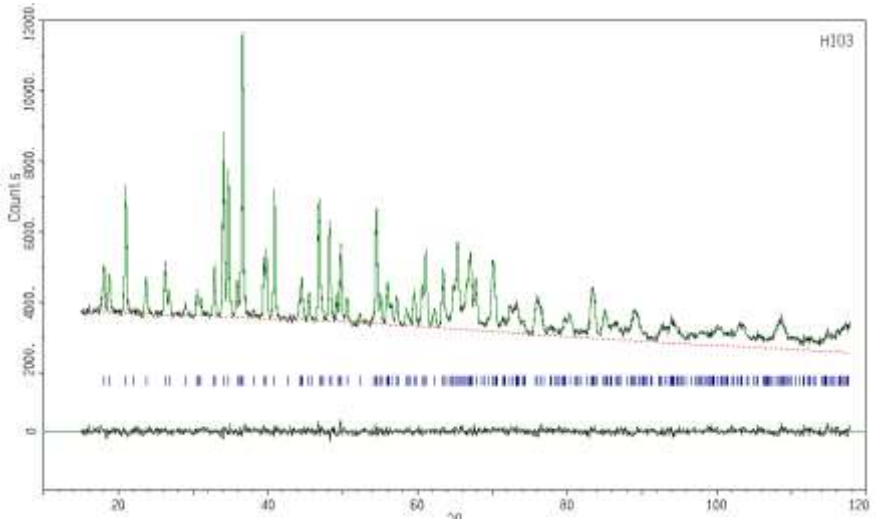
$DIO_3$




b(D) = 6.671 fm

Rp = 4.65 %

$HIO_3$




b(H) = -3.739 fm

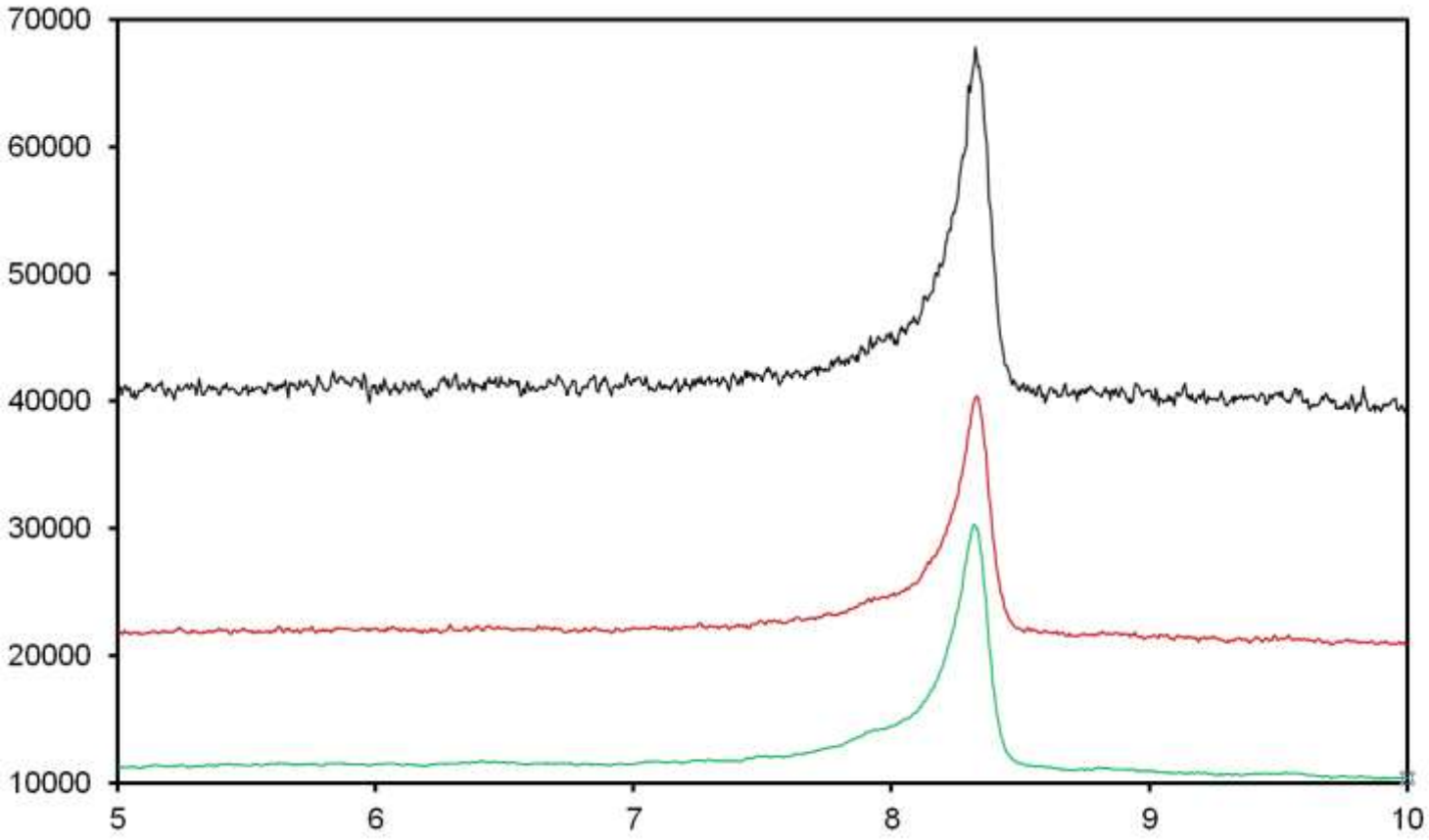
Rp = 1.52 %

Incoherent scattering!

# COUNTING STATISTICS

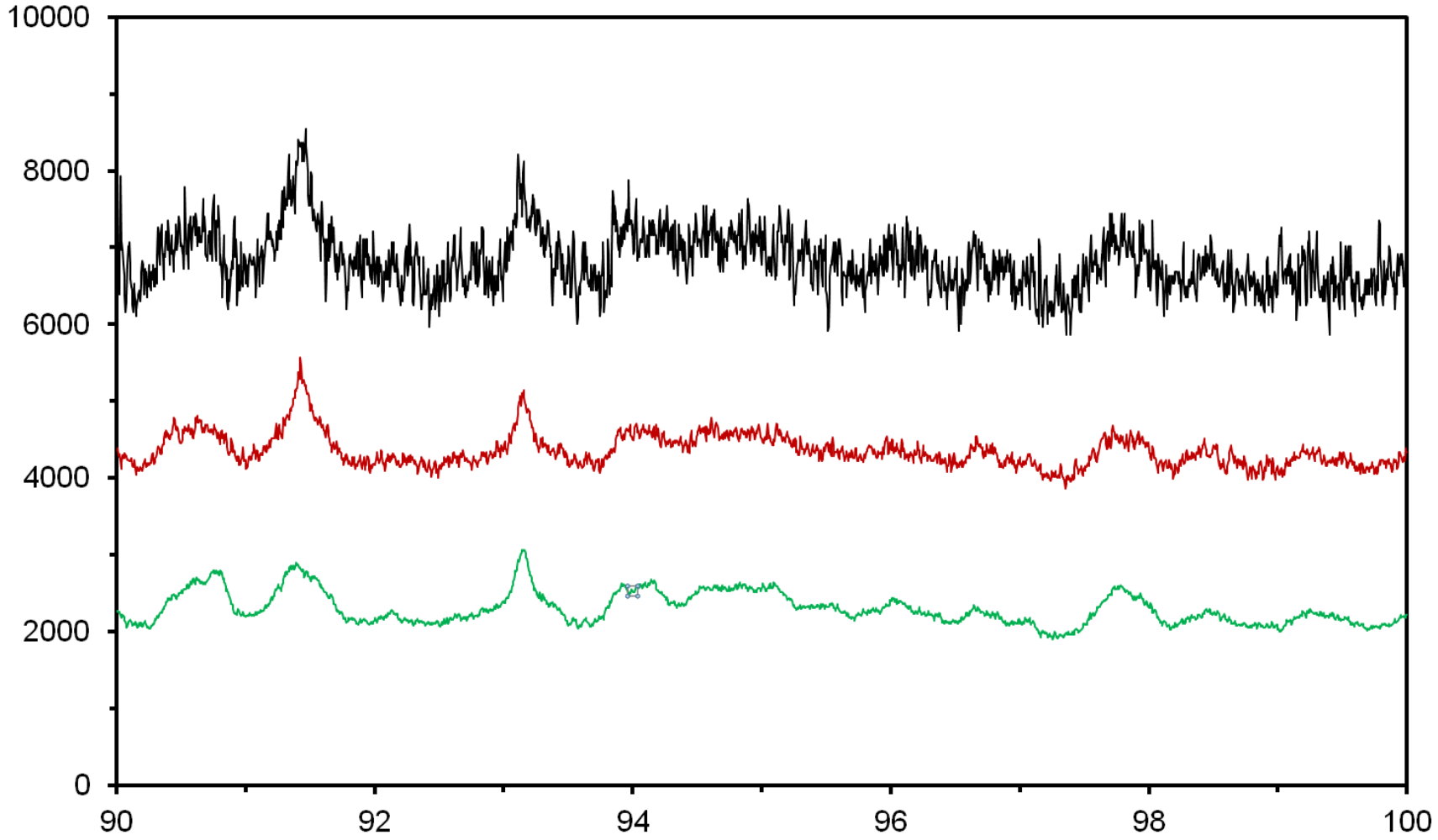
Poisson statistics: $\sigma^2(I) = I$

$\sigma(I) / I = 1 / \mathrm{sqrt}(I)$



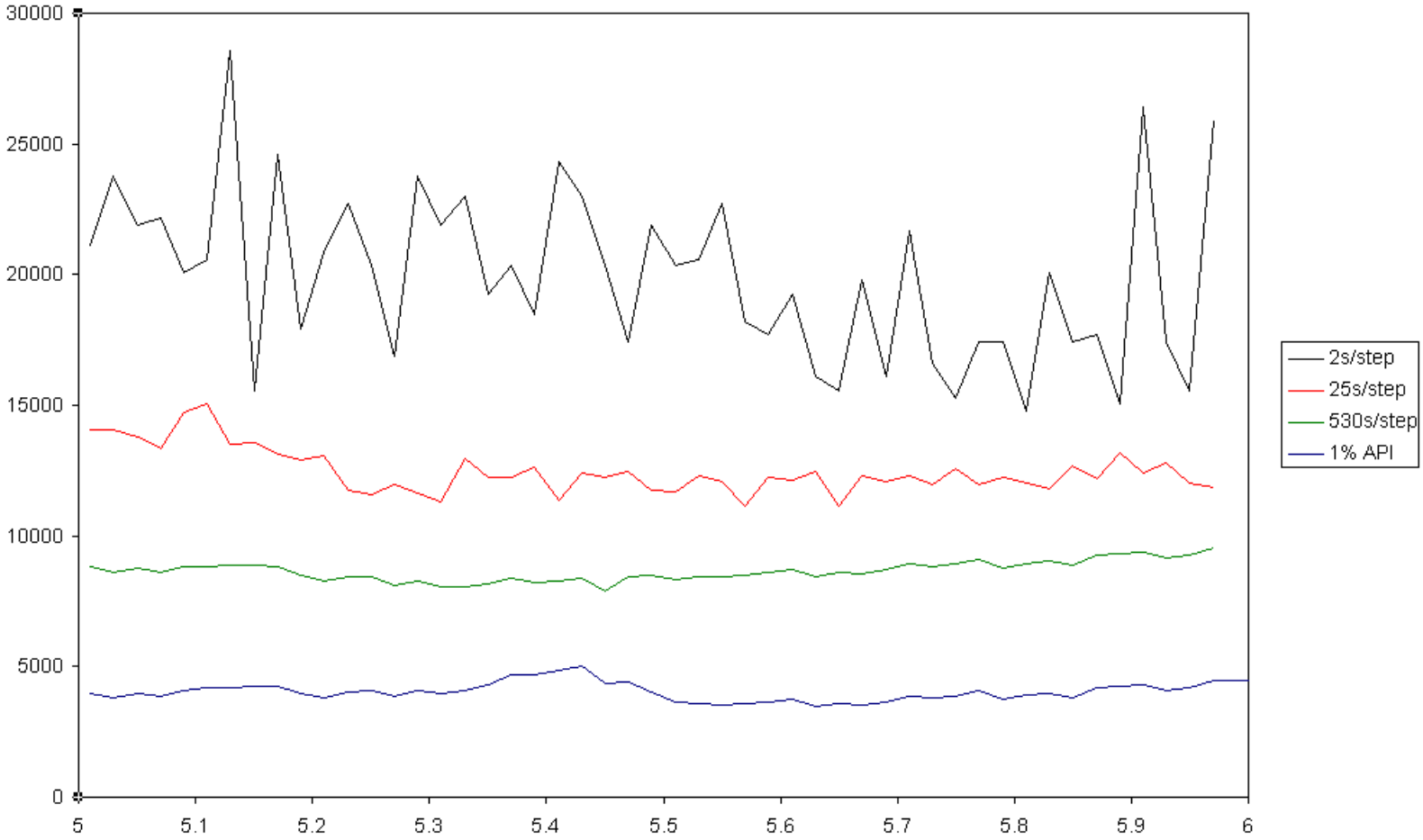

Huber data on sugar. 10 / 60 / 480 min

# COUNTING STATISTICS



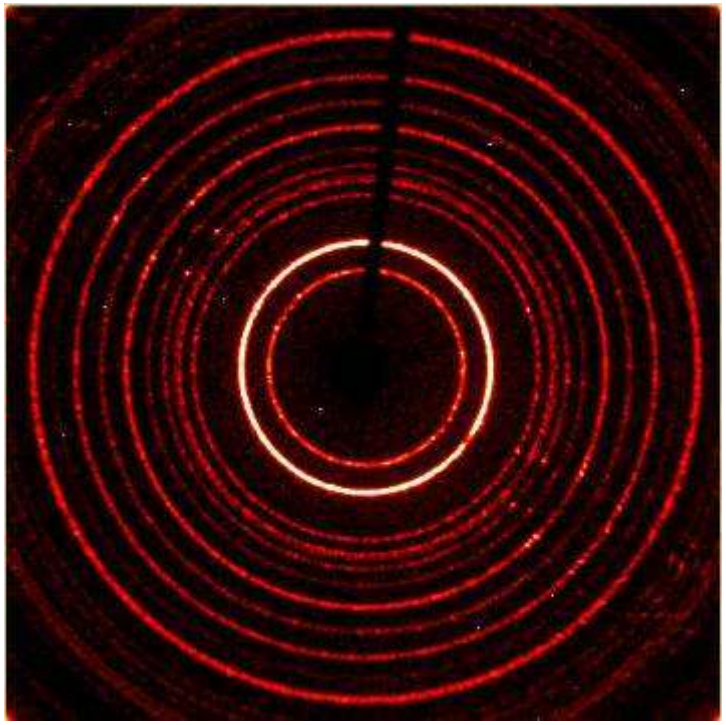

Huber data on sugar. 10 / 60 / 480 min

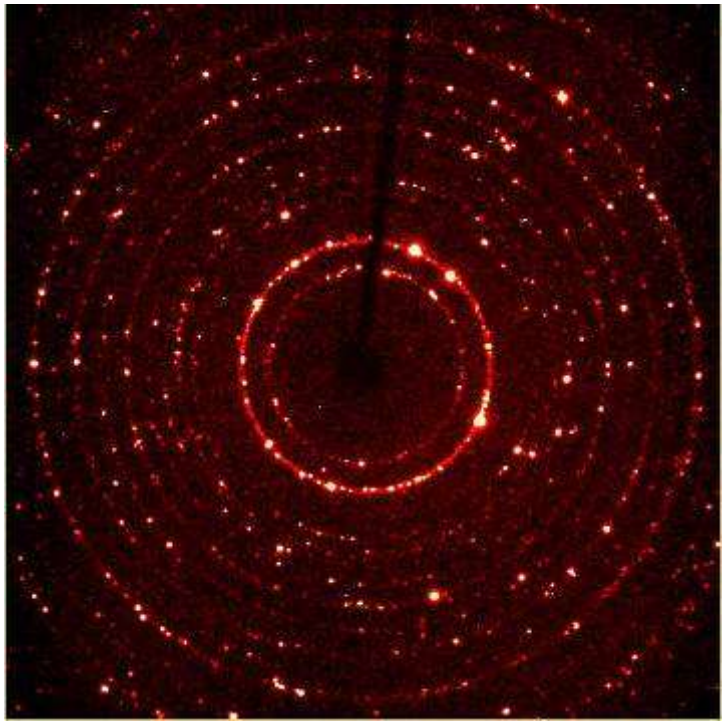
# COUNTING STATISTICS



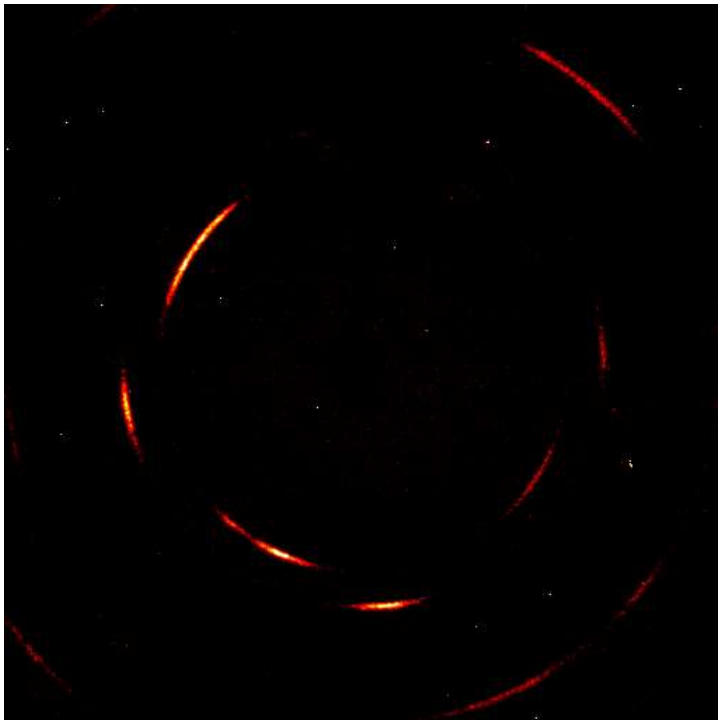

1°= 50 steps, 530 s/step → 7 hours

# POOR SAMPLE

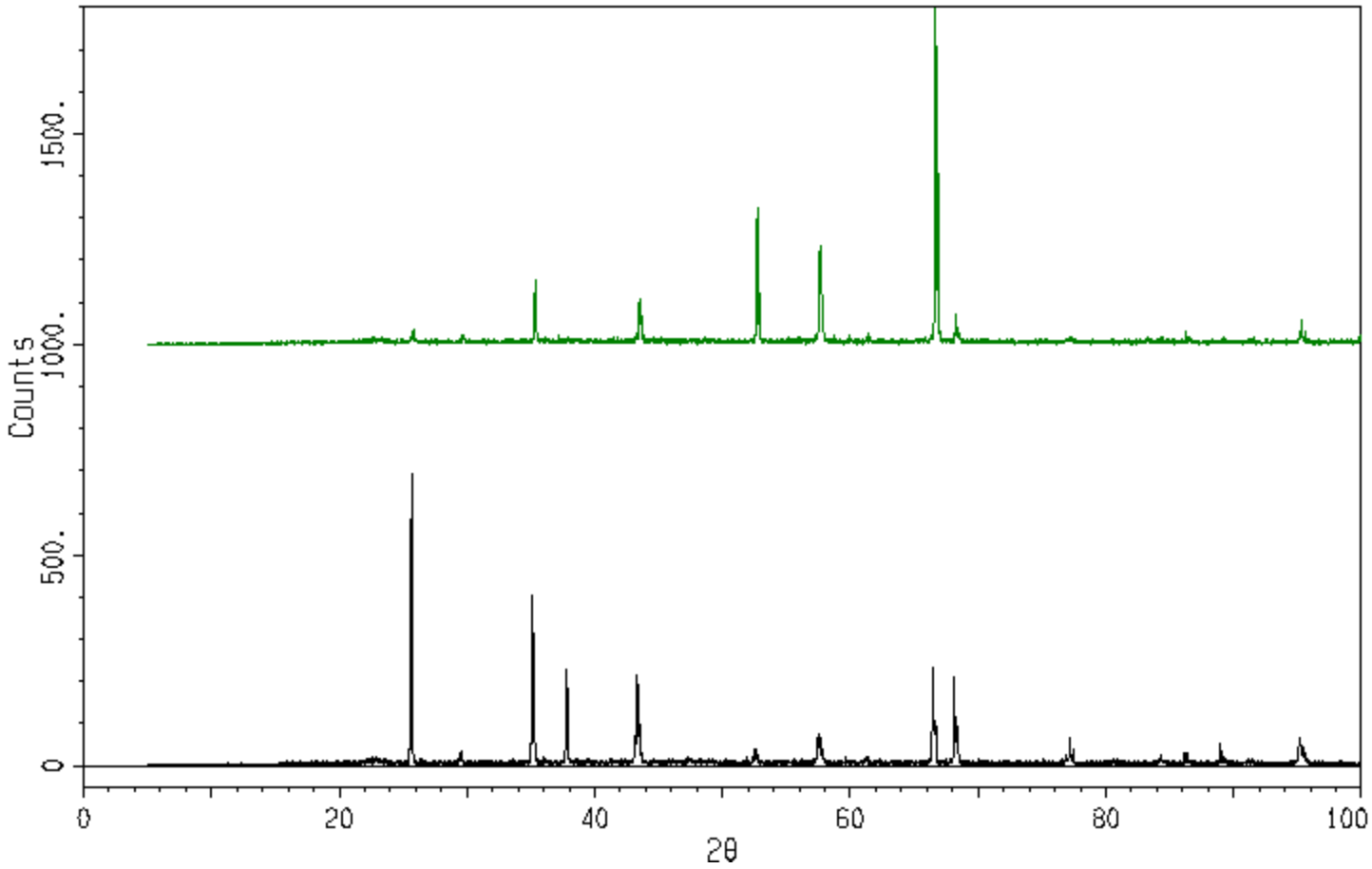




# PREFERRED ORIENTATION (TEXTURE)

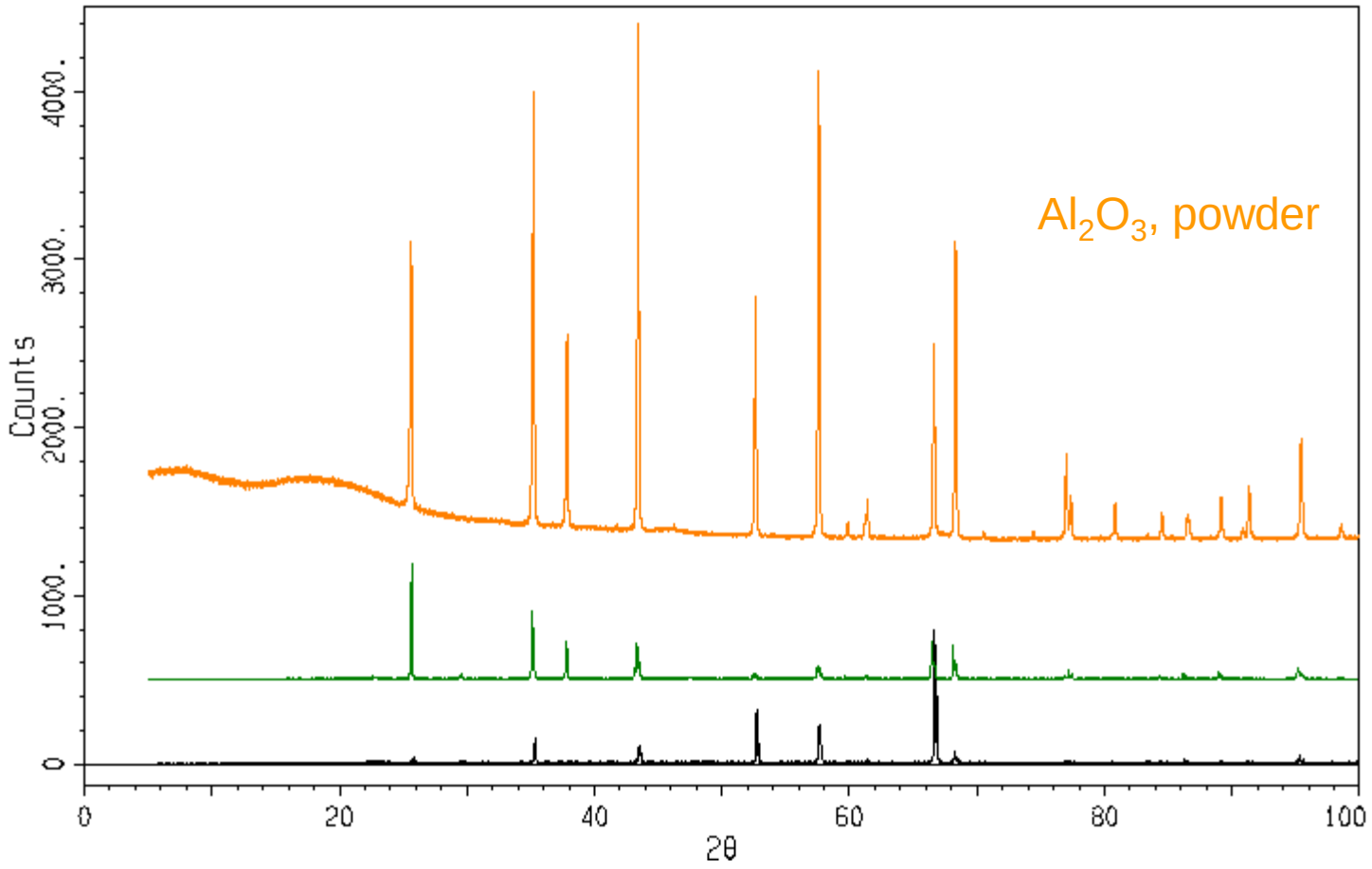


# POOR SAMPLE




Emery paper

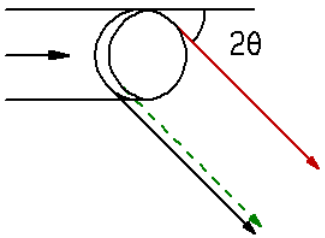
# POOR SAMPLE

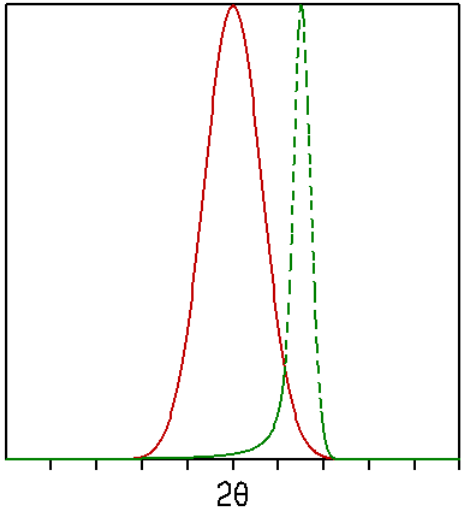



Emery paper

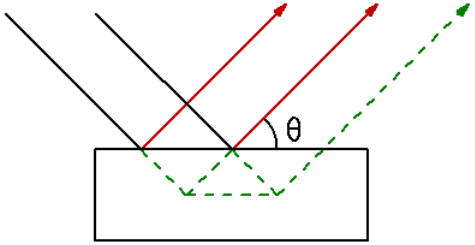
# ABSORPTION EFFECTS

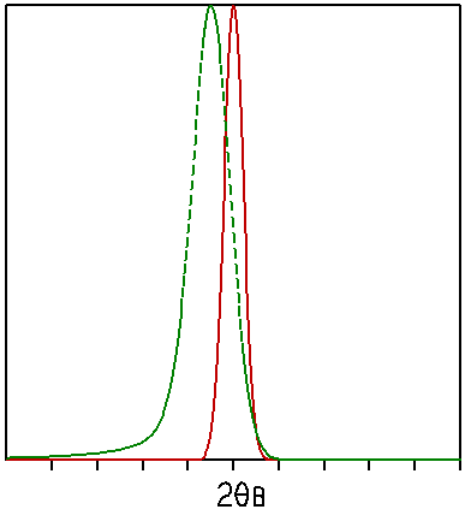
Transmission mode
Capillary sample



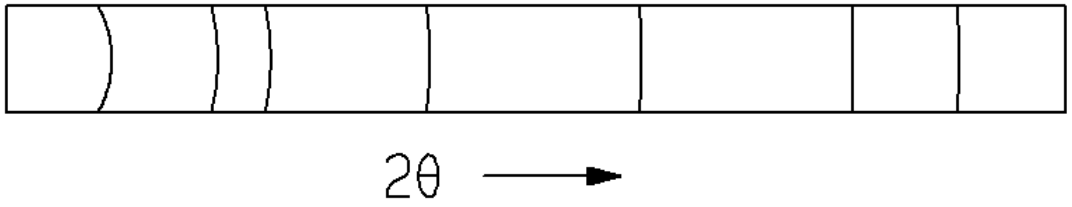



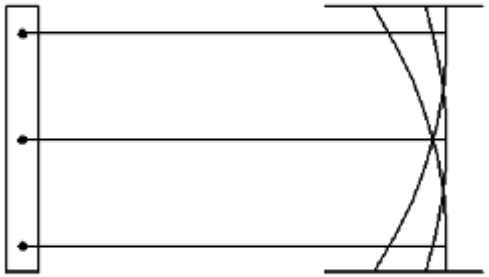

Reflection mode
Flat plate sample

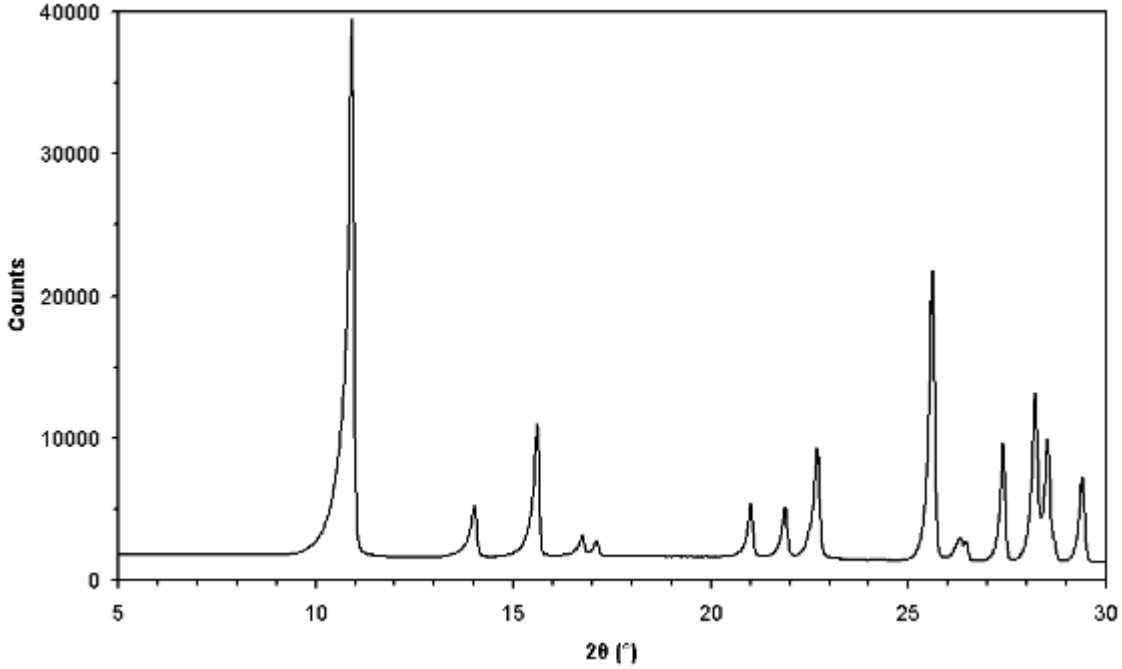


# AXIAL DIVERGENCE





# AXIAL DIVERGENCE

Capillary sample: 1 mm beam height vs. 8 mm beam height