Precise lattice parameter

Structure Analysis

Materials Science & Engineering

Seoul National University

CHAN PARK

variance, weight, mean, weighted mean

- standard deviation (σ) ; a measure of how spread out numbers are
- variance (σ^2) ; the average of the squared differences from the mean (square of expected error)

$$\sigma^2 = \frac{1}{n-1}\sum_{i=1}^{n}(x_i - \overline{x})^2$$

- weight (ω_i) $w_i = \frac{1}{\sigma_i^2}.$

$$\sigma^2 = \frac{n}{n-1}\frac{\sum_{i=1}^{n} w_i (x_i - \overline{x})^2}{\sum_{i=1}^{n} w_i}$$

- weighted mean $\bar{x} = \frac{\sum_{i=1}^{n} w_i x_i}{\sum_{i=1}^{n} w_i},$

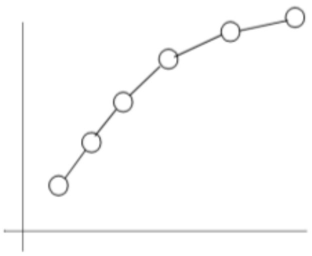
- Minimizing the sum of the squares of the deviations from the mean → **<u>"least square minimization"</u>**

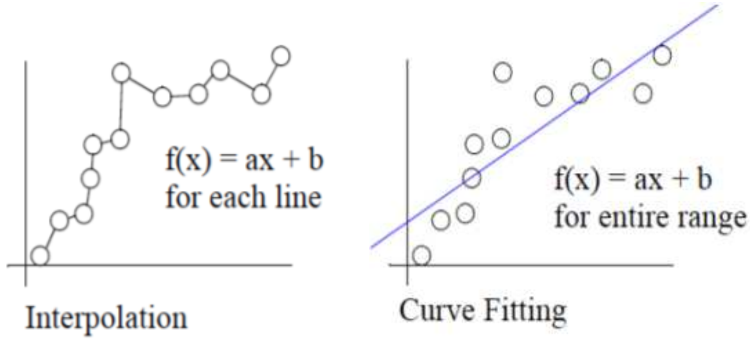
Crystal Structure Analysis, ed. Clegg Chap 12

Curve fitting

- Interpolation
  - ✓ connect the data-dots
  - ✓ If data is reliable, we can plot it and connect the dots

- Depicting the trend in the data variation by assigning a single function to represent the data across its entire range





The goal is to identify the coefficients 'a' and 'b' such that f(x) 'fits' the data well

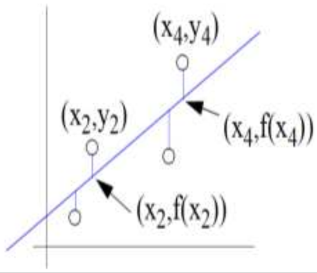
Linear curve fitting, linear regression

A straight line function $f(x) = ax + b$

How can we pick the coefficients that best fits the line to the data?

First question: What makes a particular straight line a 'good' fit?

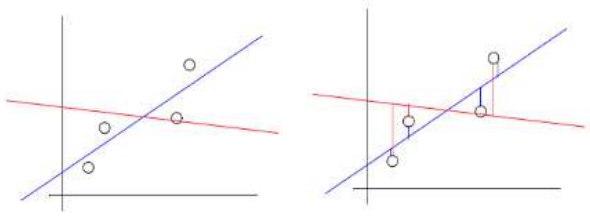
- Square the distance
- Denote data values as (x, y) and points on the fitted line as (x, f(x))
- Sum the error at the four data points



The 'best' line has minimum error between line and data points.

least square minimization

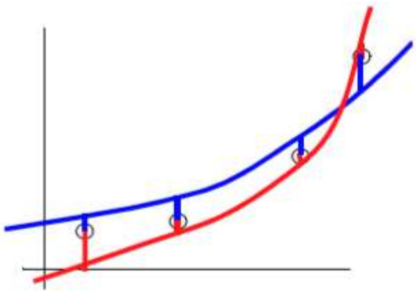
the square of the error is minimized

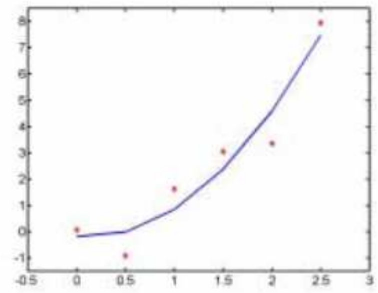


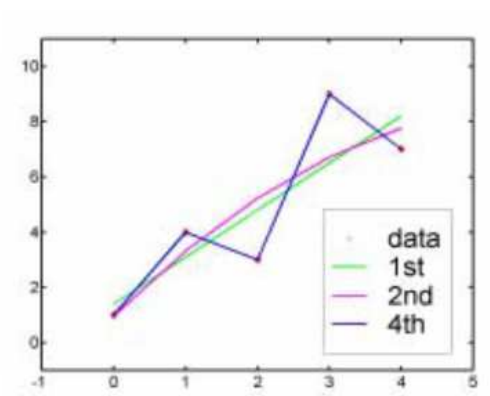
Non-linear curve fitting

- Just as was the case for linear regression;
- How can we pick the coefficients that best fit the curve to the data?
- The curve that gives minimum error between data → fit is 'best'

- Quantify the error for these two second order curves…
  - ✓ Add up the length of all the red and blue vertical lines
  - ✓ pick curve with minimum total error







From presentatin of Ashish Garg of IIT Kanpur

Linear least square

4 measurements (observations)
2 unknown parameters

4 (x,y) data sets

(1,6), (2,5), (3,7), (4,10)

$\boxed{\beta_1 + \beta_2 x = y}$ Fundamental Equation form

$$\beta_1 + 1\beta_2 = 6$$
$$\beta_1 + 2\beta_2 = 5$$
$$\beta_1 + 3\beta_2 = 7$$
$$\beta_1 + 4\beta_2 = 10$$

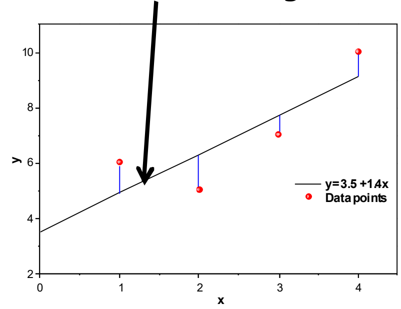
<u>More equations than the # of unknowns</u>

→There are no values of β_1 and β_2 that satisfy the equations exactly

→ can get the β_1 and β_2 that satisfy the equations as much as possible (best straight line thru the points)

→ best fit ≡ values of β_1 and β_2 that minimizes $\sum \varepsilon_i^2$ when residual (error) $\varepsilon_i = y - \beta_1 - \beta_2 x$

Line of linear regression



$\pm\Delta 2\theta$

Linear least square

$$S(\beta_1,\beta_2)=[6-(\beta_1+1\beta_2)]^2+[5-(\beta_1+2\beta_2)]^2+[7-(\beta_1+3\beta_2)]^2+[10-(\beta_1+4\beta_2)]^2$$

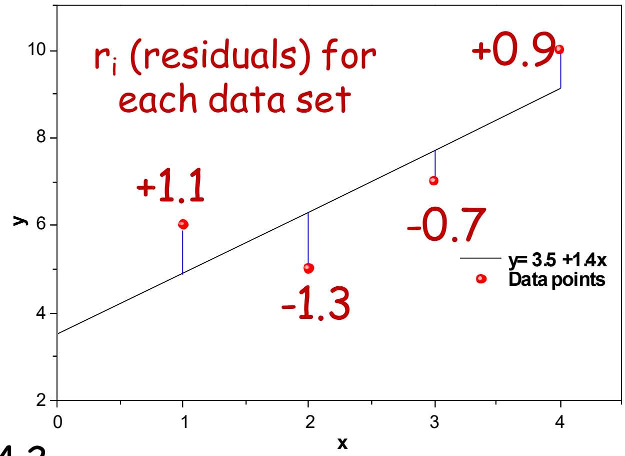
For errors to be minimum

$$\frac{\partial S}{\partial \beta_1} = 2\beta_1 + 5\beta_2 - 14 = 0$$

$$\frac{\partial S}{\partial \beta_2} = 10\beta_1 + 30\beta_2 - 77 = 0$$

$\beta_1 = 3.5$, $\beta_2 = 1.4$

→ y = 1.4 x + 3.5



S (3.5 , 1.4)
= $1.1^2 + (-1.3)^2 + (-0.7)^2 + (0.9)^2 = 4.2$

Least square fitting

- a way of finding the best curve to fit a given set of observations
- it gives the best values of the constants in the equation selected

Cullity chap 13

Linear least square analysis

- ✓ q is a function of 3 variables x, y and z
- ✓ measurement of q at various values of x, y and z
- ✓ 3 unknown parameters a, b and c

➢With only 3 measurements at various x, y and z, 3 equations can be uniquely solved for a, b and c

➢When number of measurements > 3,
→ (1) can use only 3 measurements (equations) to solve for a, b, and c
→ (2) can get more accurate values of a, b and c by taking advantage of the redundancy of the data; the best line that fits the experimental points

$$q_j = ax_j + by_j + cz_j \quad (j > 3)$$

For every measurement q_j, the error E_j is given by $E_j = ax_j + by_j + cz_j - q_j$

The sum of the squares of errors for all q_j must be minimum w.r.t. unknowns $\sum_j E_j^2 = \sum_j \left(ax_j + by_j + cz_j - q_j\right)^2$

Linear least square analysis

$\sum_j E_j^2 = \sum_j \left(ax_j + by_j + cz_j - q_j\right)^2$ must be minimum w.r.t. unknowns

At minimum, $\dfrac{\partial \sum_j E_j^2}{\partial a} = \dfrac{\partial \sum_j E_j^2}{\partial b} = \dfrac{\partial \sum_j E_j^2}{\partial c} = 0$

$$\frac{\partial \sum_j E_j^2}{\partial a} = 2\sum_j x_j \left(ax_j + by_j + cz_j - q_j\right) = 0$$

$$\boxed{\begin{aligned} a\sum_j x_j^2 + b\sum_j x_j y_j + c\sum_j x_j z_j - \sum_j q_j x_j &= 0 \\ a\sum_j x_j y_j + b\sum_j y_j^2 + c\sum_j y_j z_j - \sum_j q_j y_j &= 0 \\ a\sum_j x_j z_j + b\sum_j y_j z_j + c\sum_j z_j^2 - \sum_j q_j z_j &= 0 \end{aligned}}$$

3 equations can be solved for 3 unknowns

Linear least square analysis

n measurements
2 unknown parameters

$y_i = mx_i + c$

$y_1 = mx_1 + c$
$y_2 = mx_2 + c$

$y_n = mx_n + c$

observation equation

$$\underset{\mathbf{A}}{\begin{pmatrix} x_1 & 1 \\ x_2 & 1 \\ .. & . \\ x_n & 1 \end{pmatrix}} \underset{\mathbf{x}}{\begin{pmatrix} m \\ c \end{pmatrix}} = \underset{\mathbf{b}}{\begin{pmatrix} y_1 \\ y_2 \\ .. \\ y_n \end{pmatrix}}$$

$$\mathbf{Ax = b}$$
$$\downarrow$$
$$\mathbf{(A^TA)x = A^Tb}$$

# of equations = # unknowns

Least square solution is that which minimizes the sum of squares of residuals of the observation equations

w_i ; inversely proportional to the (expected error)^2 of each observation equation

W weight matrix

$$\mathbf{WAx = Wb}$$
$$\downarrow$$
$$\mathbf{(A^TWA)x = (A^TW)b}$$

n linear equations & m unknown parameters

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + \ldots + a_{1m}x_m &= y_1 \\ a_{21}x_1 + a_{22}x_2 + \ldots + a_{2m}x_m &= y_2 \\ \ldots \\ a_{n1}x_1 + a_{n2}x_2 + \ldots + a_{nm}x_m &= y_n \end{aligned}$$

$$\mathbf{Ax = y}$$

$$\mathbf{A} = \begin{pmatrix} a_{11} & a_{12} & \ldots & a_{1m} \\ a_{21} & a_{22} & \ldots & a_{2m} \\ \ldots & \ldots & \ldots & \ldots \\ a_{n1} & a_{n2} & \ldots & a_{nm} \end{pmatrix}; \quad \mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \\ \ldots \\ x_m \end{pmatrix}; \quad \mathbf{y} = \begin{pmatrix} y_1 \\ y_2 \\ \ldots \\ y_n \end{pmatrix}$$

When n > m, vector x can be found, which will be the best solution for all n existing equations using the least square technique.

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + \ldots + a_{1m}x_m - y_1 &= \varepsilon_1 \\ a_{21}x_1 + a_{22}x_2 + \ldots + a_{2m}x_m - y_2 &= \varepsilon_2 \\ \ldots \\ a_{n1}x_1 + a_{n2}x_2 + \ldots + a_{nm}x_m - y_n &= \varepsilon_n \end{aligned}$$

Find the minimum of

$$\Phi(x_1, x_2, \ldots x_m) = \sum_{i=1}^{n} \varepsilon_i^2$$

Pecharsky page 475

Linear least square analysis

$$a_{11}x_1 + a_{12}x_2 + \ldots + a_{1m}x_m - y_1 = \varepsilon_1$$
$$a_{21}x_1 + a_{22}x_2 + \ldots + a_{2m}x_m - y_2 = \varepsilon_2$$
$$\ldots$$
$$a_{n1}x_1 + a_{n2}x_2 + \ldots + a_{nm}x_m - y_n = \varepsilon_n$$

The best solution is found by calculating the minimum condition of $\Phi(x_1, x_2, \ldots x_m) = \sum_{i=1}^{n} \varepsilon_i^2$

$$\frac{\partial \Phi(x_1, x_2, \ldots, x_m)}{\partial x_1} = 0$$
$$\frac{\partial \Phi(x_1, x_2, \ldots, x_m)}{\partial x_2} = 0$$
$$\ldots$$
$$\frac{\partial \Phi(x_1, x_2, \ldots, x_m)}{\partial x_m} = 0$$

$$x_1 \sum_{i=1}^{n} a_{i1}^2 + x_2 \sum_{i=1}^{n} a_{i1}a_{i2} + \ldots + x_m \sum_{i=1}^{n} a_{i1}a_{im} = \sum_{i=1}^{n} a_{i1}y_i$$
$$x_1 \sum_{i=1}^{n} a_{i2}a_{i1} + x_2 \sum_{i=1}^{n} a_{i2}^2 + \ldots + x_m \sum_{i=1}^{n} a_{i2}a_{im} = \sum_{i=1}^{n} a_{i2}y_i$$
$$\ldots$$
$$x_1 \sum_{i=1}^{n} a_{im}a_{i1} + x_2 \sum_{i=1}^{n} a_{m}a_{i2} + \ldots + x_m \sum_{i=1}^{n} a_{im}^2 = \sum_{i=1}^{n} a_{im}y_i$$

ex) m=2, $\frac{\partial S}{\partial x_1} = a_{11}^2 x_1 + a_{11}a_{12}x_2 - a_{11}y_1 = 0$

Linear least square analysis

$$x_1 \sum_{i=1}^{n} a_{i1}^2 + x_2 \sum_{i=1}^{n} a_{i1}a_{i2} + \ldots + x_m \sum_{i=1}^{n} a_{i1}a_{im} = \sum_{i=1}^{n} a_{i1}y_i$$
$$x_1 \sum_{i=1}^{n} a_{i2}a_{i1} + x_2 \sum_{i=1}^{n} a_{i2}^2 + \ldots + x_m \sum_{i=1}^{n} a_{i2}a_{im} = \sum_{i=1}^{n} a_{i2}y_i$$
$$\ldots$$
$$x_1 \sum_{i=1}^{n} a_{im}a_{i1} + x_2 \sum_{i=1}^{n} a_{m}a_{i2} + \ldots + x_m \sum_{i=1}^{n} a_{im}^2 = \sum_{i=1}^{n} a_{im}y_i$$

$$\underbrace{\begin{pmatrix} a_{11} & a_{21} & \ldots & a_{n1} \\ a_{12} & a_{22} & \ldots & a_{n2} \\ \ldots & \ldots & \ldots & \ldots \\ a_{1m} & a_{2m} & \ldots & a_{nm} \end{pmatrix}}_{A^T} \underbrace{\begin{pmatrix} a_{11} & a_{12} & \ldots & a_{1m} \\ a_{21} & a_{22} & \ldots & a_{2m} \\ \ldots & \ldots & \ldots & \ldots \\ a_{n1} & a_{n2} & \ldots & a_{nm} \end{pmatrix}}_{A} \mathbf{x} = (A^T y)$$

$$(A^T A)\mathbf{x} = A^T y$$

$$\therefore \mathbf{x} = (A^T A)^{-1}(A^T y)$$

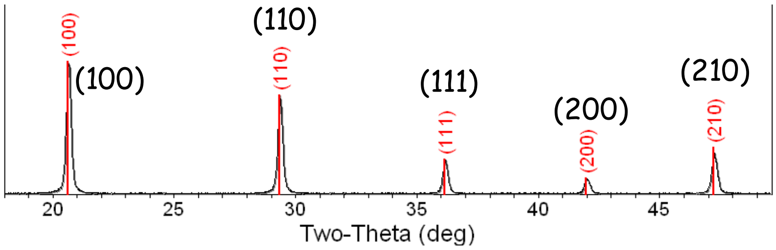
d-value vs. lattice constants

Bragg´s law $\lambda = 2\, d\, sin\, \theta$

- λ, θ known → d can be calculated

$$1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2$$

d-value of a tetragonal elementary cell



- Best values of a & c can be obtained by least square minimization

(100) $1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2$

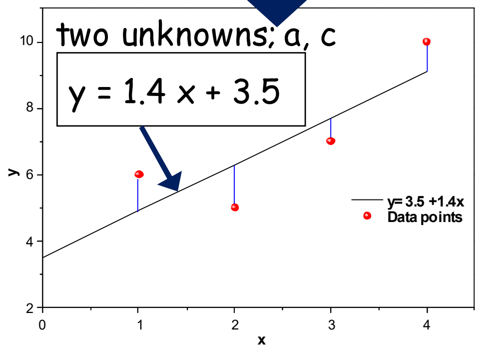
(110) $1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2$

(111) $1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2$

(200) $1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2$

(210) $1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2$

two unknowns; a, c



Evaluation of F_N

- 50 possible lines
- 42 have observable intensity
- $2\theta_{calc}$; calculated 2θ values based on the known lattice parameters
- $\Delta 2\theta = 2\theta_{calc} - 2\theta_{obs}$

$$F_N = \frac{1}{|\Delta 2\theta|} \frac{N}{N_{poss}}$$

SS figure of merit

$2\theta_{calc}$ $2\theta_{obs}$ $\Delta 2\theta$

Use of the Smith–Snyder FOM for the Evaluation of the Metric Aspects of a Powder Pattern[a]

No.	$2\theta_{calc}$	I^{rel}	d (Å)	$2\theta_{obs}$	$\Delta 2\theta$
1	6.710	21	13.162	6.790	0.080
2	8.820	48	10.018	8.780	−0.040
3	11.710	12	7.551	11.760	0.050
4	14.320	37	6.180	14.360	0.040
5	17.210	100	5.148	17.200	−0.010
6	18.950	25	4.679	18.970	0.020
7	20.230	95	4.386	20.210	−0.020
8	20.730	45	4.281	20.760	0.030
9	21.819	11	4.070	21.809	−0.010
10	26.263	5	3.391	26.283	0.020
11	31.721	12	2.818	31.727	0.006
12	32.618	—	2.743	—	—
13	34.618	78	2.589	34.602	−0.016
14	38.210	31	2.353	38.221	0.011
15	46.262	3	1.961	46.260	−0.002
16	47.183	—	1.925	—	—
17	47.523	39	1.912	47.517	−0.006
18	48.325	68	1.882	48.318	−0.007
19	49.199	21	1.850	49.200	0.001
20	50.999	4	1.789	51.003	0.004
21	52.503	27	1.741	52.509	0.006
22	56.215	—	1.635	—	—
23	56.973	26	1.615	56.991	0.018
24	58.201	11	1.584	58.200	−0.001
25	59.000	3	1.564	59.012	0.012
26	59.421	2	1.554	59.460	0.039

N; # experimental lines (peaks) considered

N_{poss}; # possible, space group-allowed diffraction lines

Jenkins & Snyder, page 314, 315

Evaluation of F_N

(Cont'd.)

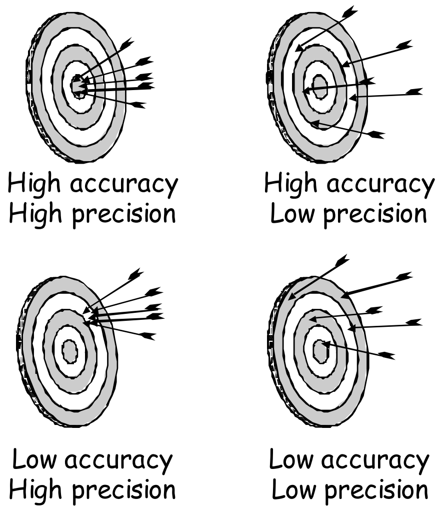
No.	$2\theta_{calc}$	I^{rel}	d (Å)	$2\theta_{obs}$	$\Delta 2\theta$
40	80.253	5	1.195	80.238	−0.015
41	81.772	9	1.177	81.776	0.004
42	82.025	1	1.174	—	—
43	84.002	1	1.151	—	—
44	84.923	1	1.141	84.916	−0.007
45	85.773	3	1.132	85.770	−0.003
46	8.246	6	1.106	88.249	0.003
47	89.114	2	1.098	89.110	−0.004
48	90.002	1	1.089	—	—
49	90.734	4	1.082	90.720	−0.014
50	91.720	1	1.073	91.726	0.006
Avg $\Delta 2\theta$ [a]	0.0066	0.0066	0.0083	0.0104	0.0084
N_{poss}	50	50	40	30	20
N_{obs}	50	42	35	27	18
FOM	151.6	127.4	104.9	86.2	107.3

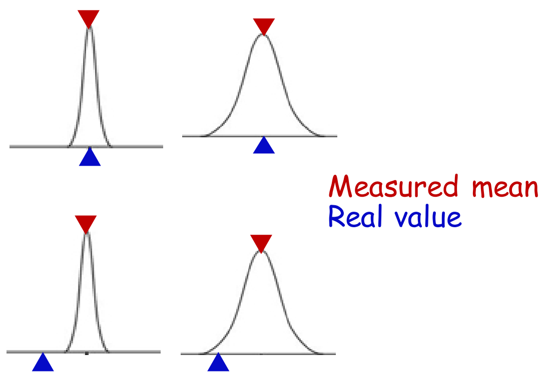
[a] Wavelength = 1.54056.

$$F_N = \frac{1}{|\Delta 2\theta|} \frac{N}{N_{poss}}$$

Jenkins & Snyder, page 314

Accurate vs. Precise





Precision - reproducibility

Accuracy – approach to the "true" value

- **Precision** ; the degree to which further measurements show the same or similar results
- **Accuracy** ; the degree of conformity of a measured quantity to its true value.

celebrating200years.noaa.gov/magazine/tct/accuracy_vs_precision_220.jpg

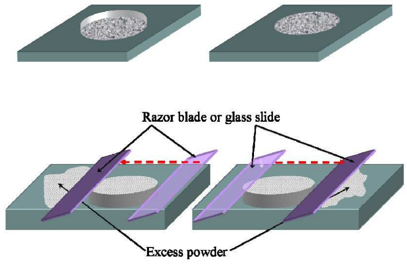
Arnt Kern of BRUKER

- How to prepare powder?
  - ✓ Grind in mortar & pestle (wet or dry)
  - ✓ Crush (percussion mill)
  - ✓ Cryo-grind
  - ✓ Micronising mill
  - ✓ Treatments/separations
- Mounting specimen
  - ✓ Front, side, back-loaded powders
  - ✓ Films & disks
  - ✓ Diluents & dispersants
  - ✓ Adhesives
  - ✓ Reactive samples (windows)
  - ✓ Capillaries
  - ✓ Odd shapes
  - ✓ Zero-background holders (ZBH)

Panalytyical

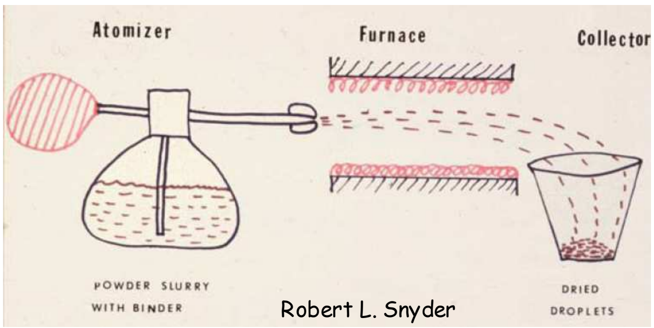
BRUKER

BRUKER

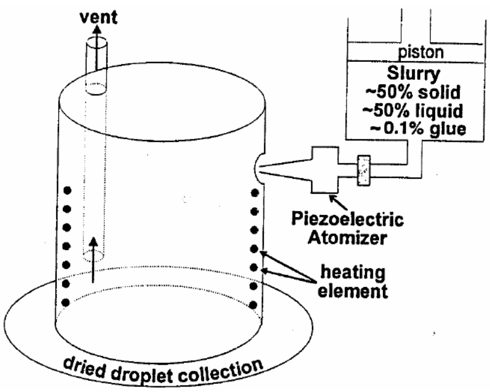


www2.arnes.si/~sgszmera1/html/xrd/preparation2.html

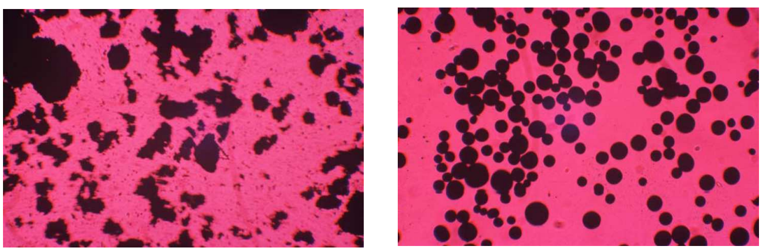
Spray drying – can eliminate preferred orientation



Robert L. Snyder



Jenkins & Snyder, page 252



Hematite before & after spray drying

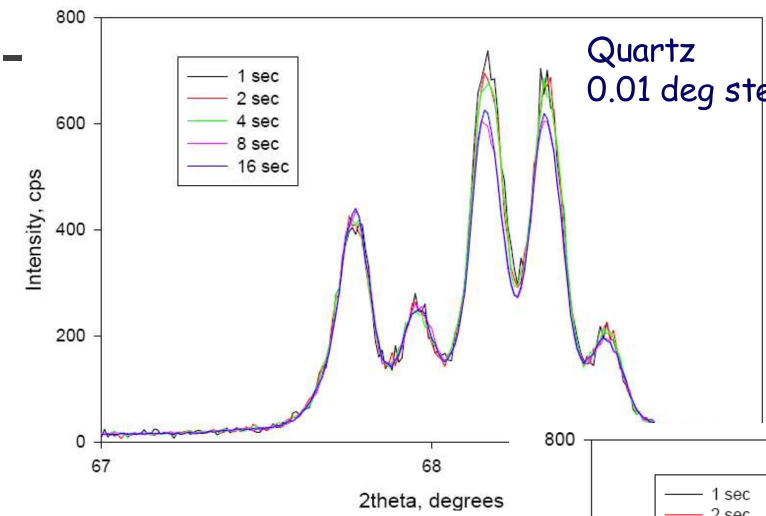
Jenkins & Snyder, page 253

- Specimen preparation
  - Specimen should represent the bulk
  - 1um < Particle size < 15um
  - Method should not distort the lattice
  - Avoid solid state reactions

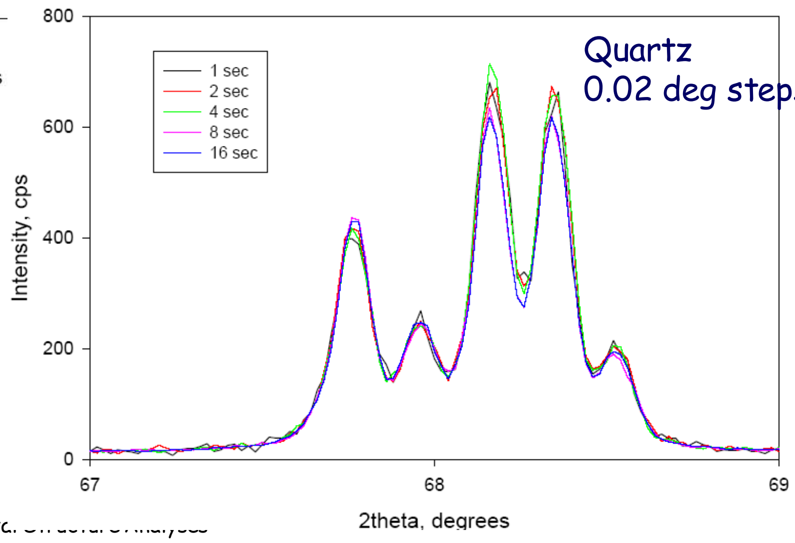
- Diffractometer specimen requirements
  - Flat specimen surface
  - Smooth specimen surface
  - Area greater than that irradiated by beam
  - Specimen support gives zero diffraction or zero contribution

- Common problems in specimen preparation
  - Preferred orientation
  - Crystallite statistics
  - Crystallite & particle size
  - Particle morphology
  - Specimen configurations
  - Crystallite perfection
  - Absorption effects

5 fingers of quartz



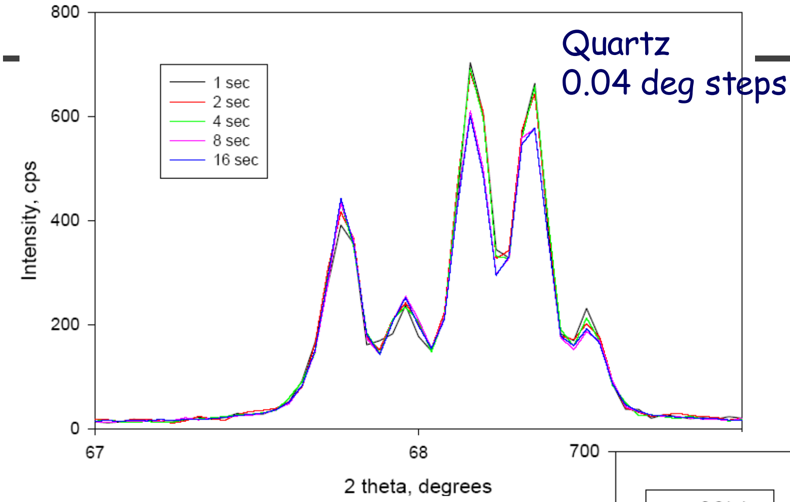
Quartz
0.01 deg steps

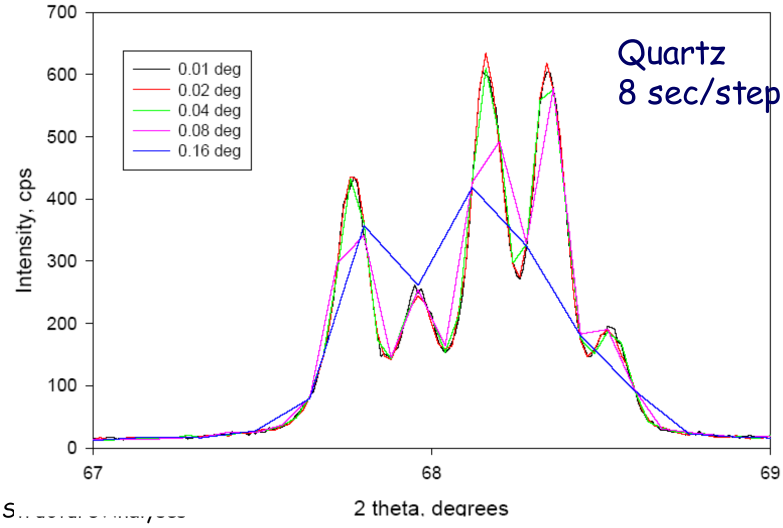


Quartz
0.02 deg steps

Jenkins & Snyder, page 268

5 fingers of quartz





$\Delta 2\theta$ & Δd

- Typical error windows
  - ✓ Debye Scherrer camera $\pm\Delta 2\theta$ = 0.1°
  - ✓ diffractometer $\pm\Delta 2\theta$ = 0.05°
  - ✓ diffractometer (internal standard corrected) $\pm\Delta 2\theta$ = 0.01°
  - ✓ diffractometer (internal standard corrected & peaks profile fitted) $\pm\Delta 2\theta$ = 0.005°
- $\Delta 2\theta$ – d relationship is non-linear
  - ✓ Low angle (low 2θ, large d-value) lines have large error

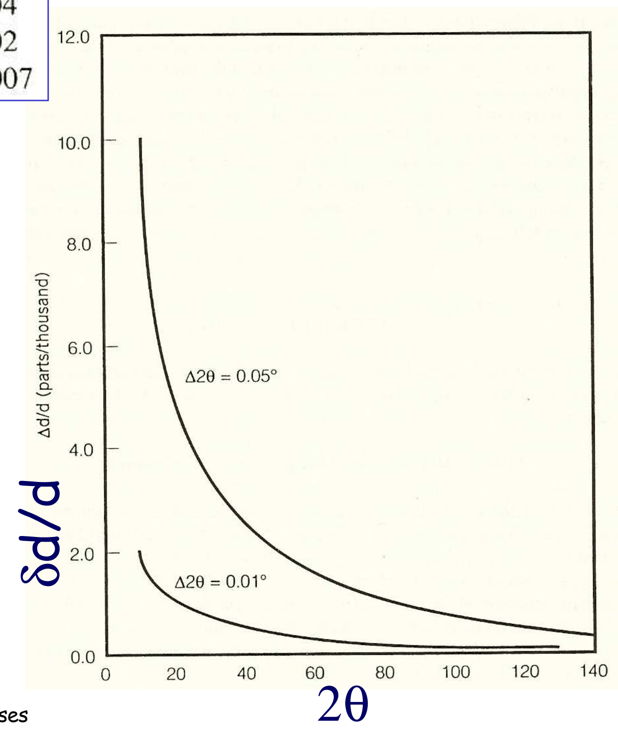
Table 12.2. Errors in *d*-Values Resulting from Fixed 2θ Errors

d (Å)	2θ (degrees)	$\pm\Delta 2\theta$ (degrees)	$\pm\Delta d$ (Å)	$\pm\Delta 2\theta$ (degrees)	$\pm\Delta d$ (Å)
5	17.73	0.1	0.04	0.05	0.014
4	22.20	0.1	0.02	0.05	0.008
3	29.76	0.1	0.01	0.05	0.005
2	45.30	0.1	0.004	0.05	0.002
1.5	61.80	0.1	0.002	0.05	0.0011
1.0	100.76	0.1	0.0007	0.05	0.0004

Jenkins & Snyder

Δ2θ & Δd

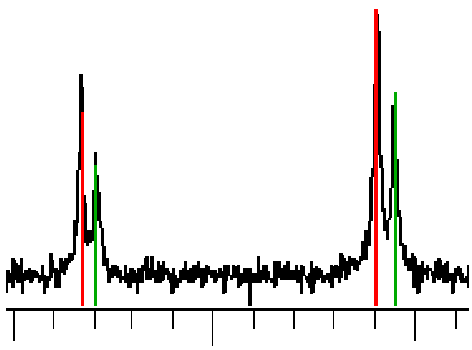
d (Å)	2θ (degrees)	$\pm\Delta 2\theta$ (degrees)	$\pm\Delta d$ (Å)
5	17.73	0.1	0.04
4	22.20	0.1	0.02
3	29.76	0.1	0.01
2	45.30	0.1	0.004
1.5	61.80	0.1	0.002
1.0	100.76	0.1	0.0007

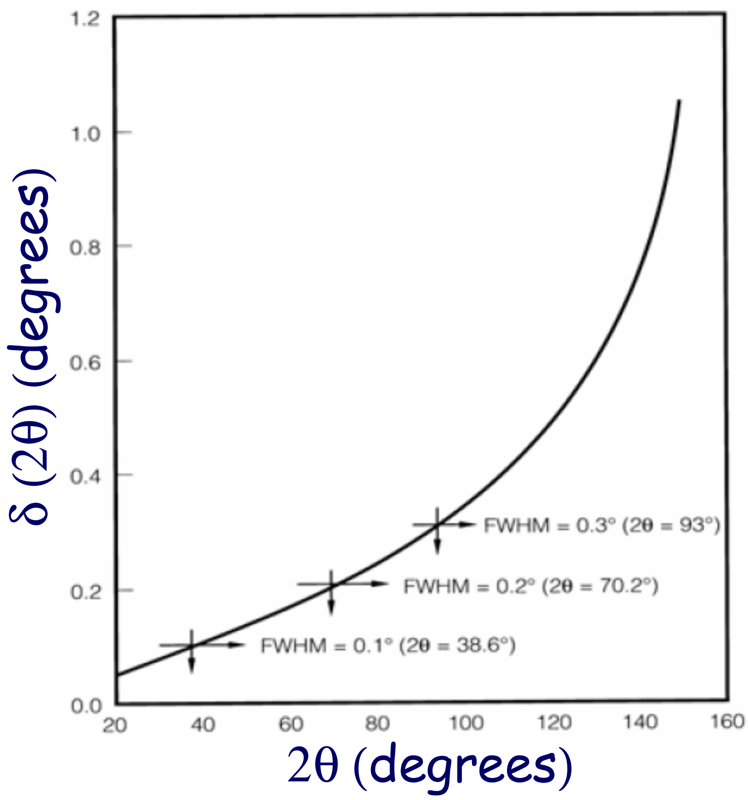


$$\Delta d/d = -\Delta\theta \cot\theta$$

Jenkins & Snyder, page 307

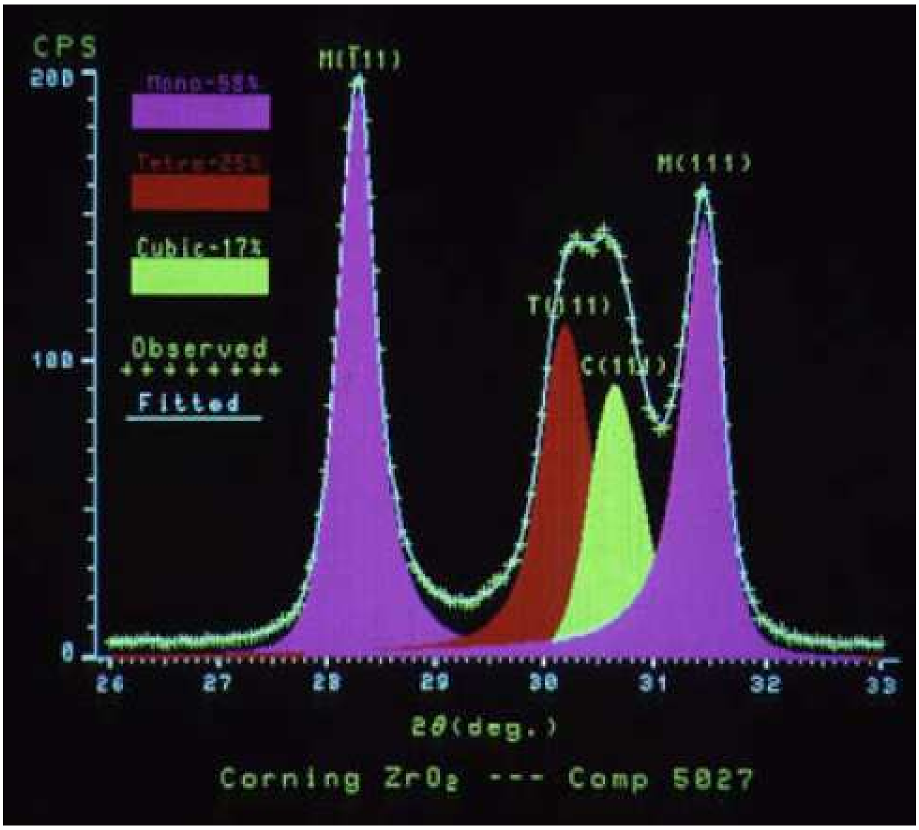
Spectral dispersion; peak breadth increases with 2θ





Jenkins & Snyder, page 306

Line (peak) profile analysis



Smith & Snyder FOM

$$F_N = \frac{1}{|\Delta 2\theta|} \frac{N}{N_{\text{poss}}}$$

De Wolff FOM

$$M_{20} = \frac{\mathbf{d}^{*2}_{20}}{2|\Delta \mathbf{d}^{*2}|} \frac{1}{N_{\text{poss}}}$$

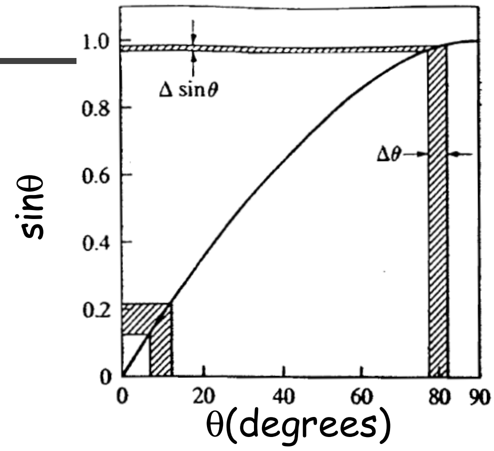
Jenkins & Snyder, page 316

Intensity FOM

$$R_I = \sum \frac{I_{\text{obs}} - I_{\text{calc}}}{I_{\text{obs}}}$$

Precise lattice parameter

- Composition of a solid solution
- Thermal expansion coefficients
- Solubility limit
- -----



In cubic,

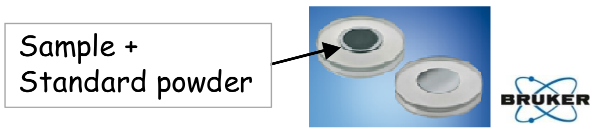
- measure θ for hkl → determine d → calculate a
- Precision in d or a depends on precision in sinθ, not on θ
- Accurate value of sinθ ← measurement of θ near 90°

- Differentiation of Bragg's law w.r.t. θ → Δd/d = -Δθ cotθ = Δa/a
- Δa caused by a given Δθ → zero as θ →90°
- precision when using peaks in 2θ ~ 180°
- precision of 0.001Å possible

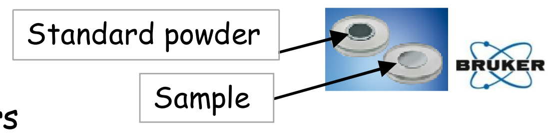
Cullity chap 13

2 theta Calibration

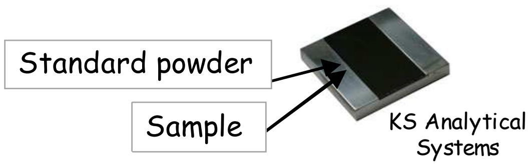
- Internal standard method
  - ✓ Δ2θ = 0.01
  - ✓ Can eliminate <u>both displacement and transparency errors</u>
  - ✓ <u>Both instrument & specimen errors</u> are corrected



- External standard method
  - ✓ Δ2θ = 0.25
  - ✓ Do not correct displacement errors
  - ✓ With ZBK holder, can correct all errors → Δ2θ = 0.01



- Zero background holder method



- Profile fit peak positions

Jenkins & Snyder page 249, 281 & 308

Zero Background Holder

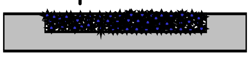
- A single crystal of quartz that is cut and polished in an orientation such that it produces no diffraction peaks.

KS Analytical Systems

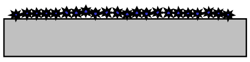
Panalytical

MTI

- Thick specimens
  - ✓ Good intensity…but problems defining depth (position)



- Thin specimens
  - ✓ No penetration depth effect (good position)… but low intensity



From presentation of Dr. Mark Rodriguez @ DXC 2017 "What usually causes trouble?"

2θ calibration techniques

The Effects of Calibration on the Figure of Merit F_N

Method	Arsenic Trioxide ($N = 29$)		Quartz ($N = 30$)	
No correction	9.9	(0.049,59)	16.4	(0.052,35)
External standard	15.4	(0.026,59)	30.0	(0.028,35)
Internal standard	42.0	(0.012,59)	66.1	($\boxed{0.013}$,$\boxed{35}$)

$$F_N = \frac{1}{|\Delta 2\theta|}\frac{N}{N_{poss}}$$

$|\Delta 2\theta|$ N_{poss}

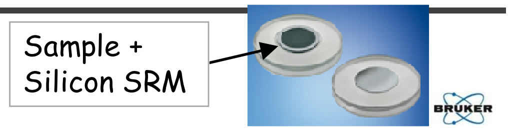
N; # experimental lines (peaks) considered

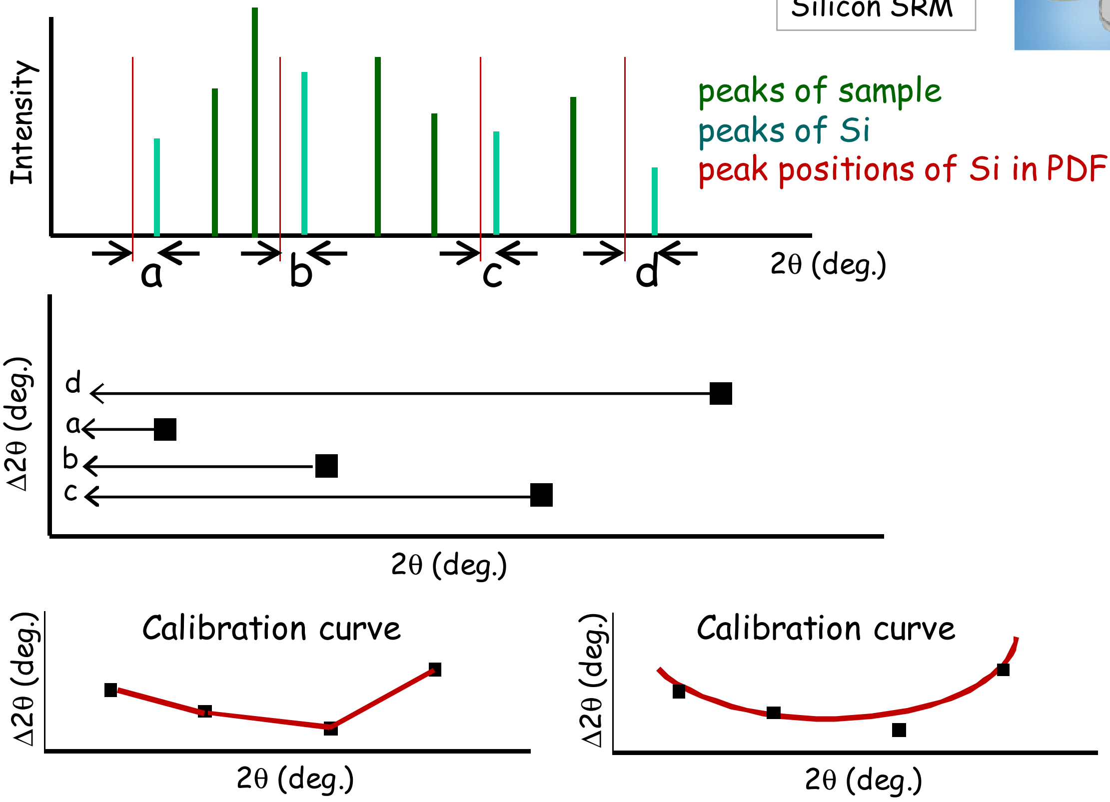
N_{poss}; # possible, space group-allowed diffraction lines

 Jenkins & Snyder, page 309

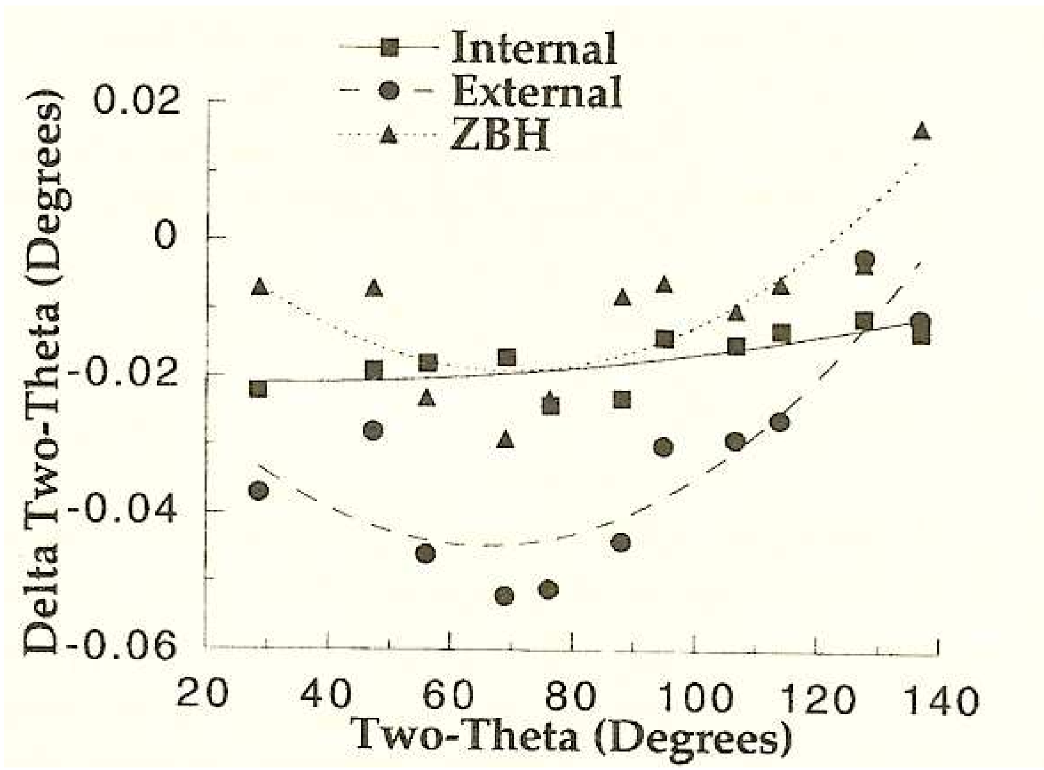
Internal Standard Calibration

- Mix sample powder and silicon SRM





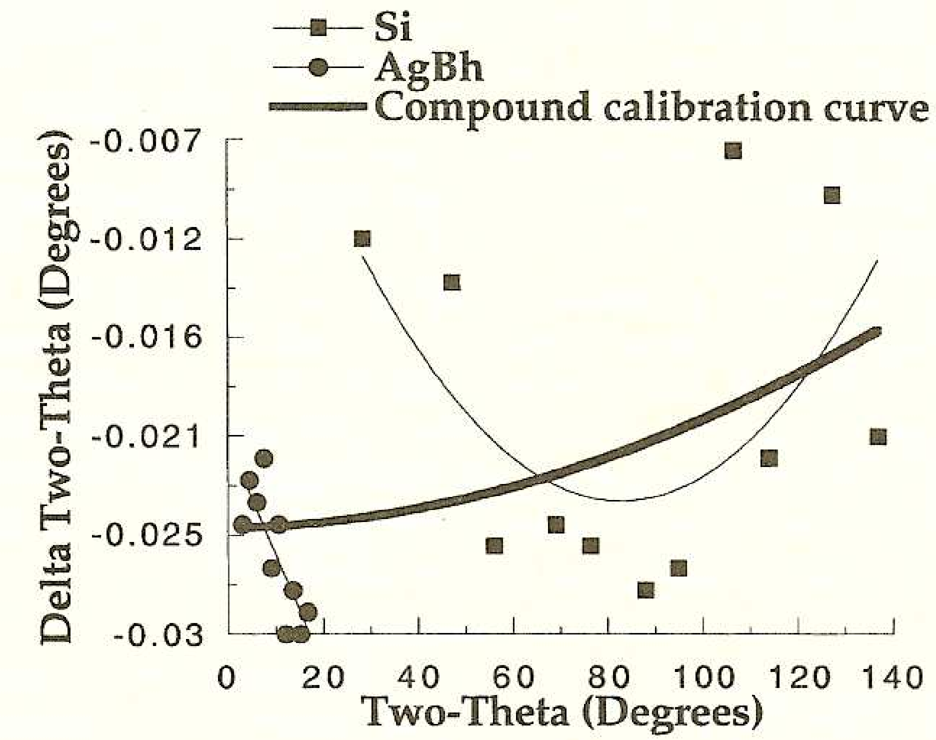
Calibration curve



Jenkins & Snyder, page 252

Misture, etal. Powder Diffraction 9, 172-9 (1994)

Calibration curve



Errors removed by calibration

Effectiveness of Standards for the Correction of 2θ Errors

	Type of Standard				
Use of Standard	None	External (2θ)	Internal (2θ)	ZBH (2θ)	External (Intensity)
Instrument misalignment	No	Yes	Yes	Yes	(Yes)
Inherent aberrations	No	Yes	Yes	Yes	No
Specimen transparency	No	No	Yes	Yes	No
Specimen displacement	No	No	Yes	Yes	No
Instrument sensitivity	No	No	No	No	Yes

Jenkins & Snyder, page 282

Average $\Delta 2\theta$ from different calibration techniques

- None on a random instrument = 0.1°
- None on a well-aligned instrument = 0.05°
- External standard method = 0.025°
- Internal standard method = 0.01°
- Zero background holder method = 0.01°
- Profile fit peak positions = 0.005°

Calibration – quartz crystal

TABLE II. ZBH (mounted quartz crystal) calibrated data.

		2nd-derivative peak location		Profile-fitted peak location
Material	Parameter	Uncalibrated	Calibrated	
Ag	F_N	$F(9)=84$	$F(9)=245$	$F(9)=168$
		(0.0119,9)	(0.0041,9)	(0.0060,9)
	a(Å)	4.0858(14)	4.08616(5)	4.08639(7)
Al_2O_3 (Linde C)	F_N	$F(9)=235$	$F(9)=137$	$F(7)=69$
		(0.0029,13)	(0.0050,13)	(0.0079,13)
	a(Å)	4.7582(2)	4.7598(3)	4.7592(8)
	c(Å)	12.9849(7)	12.9895(11)	12.9951(75)
LaB_6	F_N	$F(13)=172$	$F(13)=190$	$F(13)=274$
		(0.0058,13)	0.0053,13)	(0.0036,13)
	a(Å)	4.1552(1)	4.1562(1)	4.15635(8)
Urea	F_N	$F(11)=57$	$F(11)=56$	$F(11)=53$
		(0.0107,18)	(0.0108,18)	(0.0115,18)
	a(Å)	5.6478(7)	5.6499(7)	5.6493(6)
	c(Å)	4.6972(23)	4.6989(24)	4.6982(22)

Smith & Snyder figure of merit

$$F_N = \frac{1}{|\Delta 2\theta|} \frac{N}{N_{poss}}$$

Jenkins & Snyder page 251