chem 5390

Advanced X-ray Analysis

LECTURE 12

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Acquisition of Diffraction Data

A. Steps in Data Acquisition

Typical steps for acquisition, treatment, and storage of diffraction data includes:

1. **Sample preparation (covered earlier)**
2. **Selection of instrument variables, i.e. source, kV, mA, slits (covered earlier)**
3. **Data collection, i.e. range, step size, count time**
4. **Pattern reduction, i.e. smoothing, Kα2 strip, peak locate, peak correction, storage, report**
5. **Interpretation**

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection, i.e. range, step size, count time.

a. Choice of d-spacing range and Two Theta

A large enough number of d-spacings must be measured to ensure complete identification of a material. Patterns can contain up to 50 lines, but higher symmetry gives less lines.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection, i.e. range, step size, count time.

a. Choice of d-spacing range and Two Theta

Also the largest d-spacings are generally the most useful in pattern identification and indexing. It is important not to miss low angle lines.

Important to take a survey scan first to determine 2θ range and lines of interest.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

b. Choice of Wavelength

Copper Kalpha the most popular.

$K\alpha 1 = 1.54060$ Å

$K\alpha 2 = 1.54439$ Å

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

b. Choice of Wavelength

Table 10.3. Maximum and Minimum *d*-Values Measurable with Various Wavelengths

Radiation	Wavelength	Maximum *d*	Minimum *d*
Cr $K\alpha$	2.291	65.6	1.16
Co $K\alpha$	1.790	51.3	0.91
Cu $K\alpha$	1.542	44.2	0.78
Mo $K\alpha$	0.709	20.3	0.36

Acquisition of Diffraction Data

A. Steps in Data Acquisition

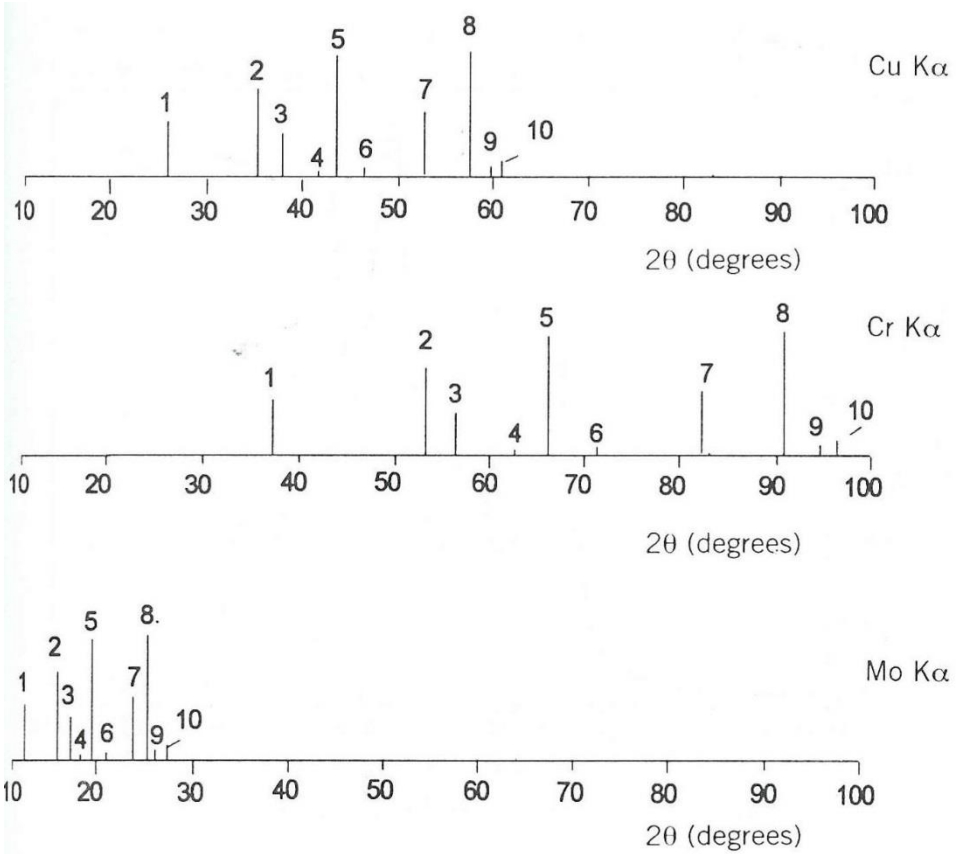

Figure 10.3. Pattern for corundum measured with chromium, copper, and molybdenum radiation.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

b. Choice of Wavelength

An error in d-spacing calculation is proportional to an error in measurement of wavelength.

To obtain an 1/1000 accuracy must either weight average Kα1 and Kα2 or strip Kα2 or measure separately.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

b. Choice of Wavelength

For lattice parameter measurements utilize internal standards to calibrate out errors.

If the diffraction pattern is very complex, can collect the data using Kβ instead to simplify the pattern.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

b. Choice of Wavelength

Example: superlattices

Intensity for β is a factor of 5 lower compared to α.

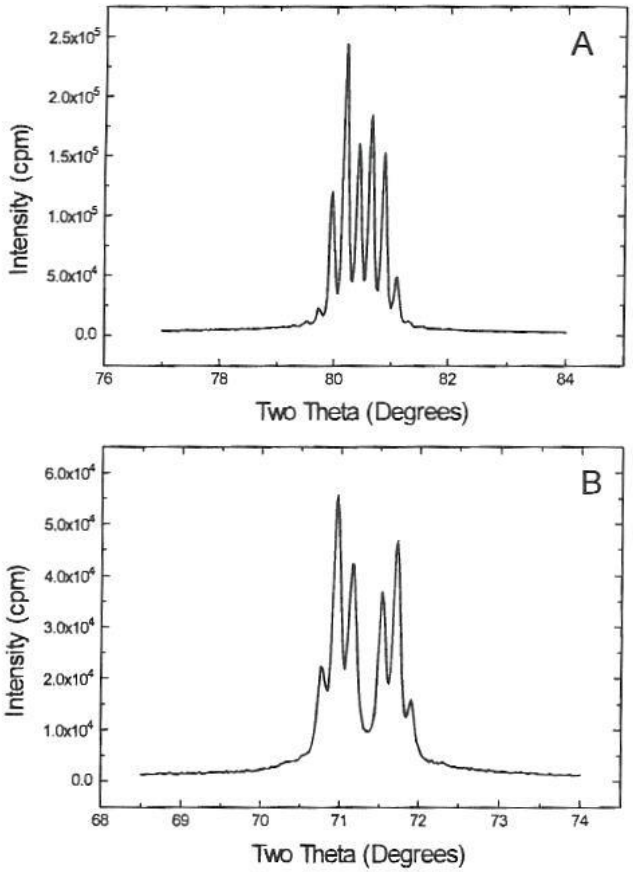

Figure 14. (A) X-ray diffraction pattern of a [210]-textured superlattice in the Pb–Tl–O system using Cu Kα radiation as the X-ray source. The modulation wavelength was calculated as $\Lambda_F = 50$ nm by Faraday's law. (B) Same as (A), except using Cu Kβ radiation for the X-ray source.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

c. Choice of Scan Rate

During a scan – pulses are counted at each angle for a set time. These pulses are integrated for a time related to the RC time constant of the ratemeter. Time constant must be matched with the scanning speed. Too small an RC leads to noisy recording, too large an RC leads to severe distortion of the line profiles.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

c. Choice of Scan Rate

Since the ratemeter is integrating the x-ray photons at the detector, the integration time must be sufficient to allow a correct measure at a given angle.

General rule to establish RC:

Rc $\leq$ 30 x receiving slit width (degrees)/scan speed (degrees/min)

Ex. slit width – 0.2^{o} scan speed – 2 ^{o}/min Rc $\leq$ 3.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

c. Choice of Scan Rate

Must translate this for a pulse stepping motor and step scanning.

Correct procedure to select parameters:

1. Take note of average count rate of the background.

Ex. 25 c/s.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

c. Choice of Scan Rate

2. Calculate statistical error needed to reveal small peaks.

Ex. 10% error

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

c. Choice of Scan Rate

3. Calculate ratemeter setting.

Ex. $\sigma(RM) = 100/(r \times 2RC)^{1/2}$

$\sigma(RM) = 10 = 100/(25 \times 2 \times RC)^{1/2}$

$RC = 2$

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

c. Choice of Scan Rate

4. Allowing for receiving slit used, calculate maximum scan speed.

Ex. 0.2 slit

Rc $\leq$ 30 x receiving slit width (degrees)/scan speed (degrees/min)

scan speed = (30 x 0.2)/2 = 3^{o}/min

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

c. Choice of Scan Rate

Rc $\leq$ 30 x receiving slit width (degrees)/scan speed (degrees/min)

scan speed = (30 x 0.2)/2 = 3º/min

In the lab: a 0.05 step size and 1 sec scan rate will translate into:
20 steps per degree = 20 sec in 3 degrees = 1 minute

If unsure – scan a prominent peak
at high and low scan speeds

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

d. Choice of Step Width

For step scans: the goniometer is moved in fixed angular increments, the timer/scaler counts for a fixed time increment when the goniometer is stationary.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

d. Choice of Step Width

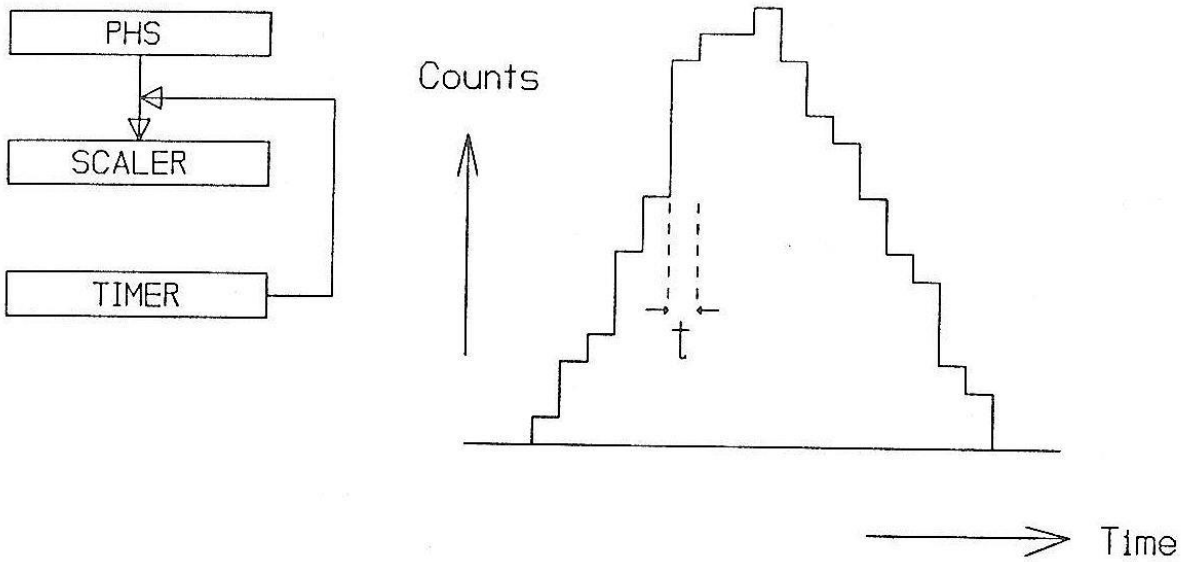

Figure 10.8. Step scanning with the timer/scale (PHS = pulse height selector).

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

d. Choice of Step Width

Timer/scaler, goniometer, and the registering device are three separate processes.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

3. Data collection

d. Choice of Step Width

If the step size is too large, a high degree of smoothing will decrease peak intensity and resolution.

If the step size is too small, then too little smoothing will give peak shifts.

Narrow peaks require smaller step sizes.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

4. Pattern reduction

   Reduction includes:

   -converting raw data to tables

   i.e. d-spacings and intensities (absolute intensities values are converted to relative intensities where the strongest line is set to 100%).

d-I list is referred to as the “reduced” pattern

Acquisition of Diffraction Data

A. Steps in Data Acquisition

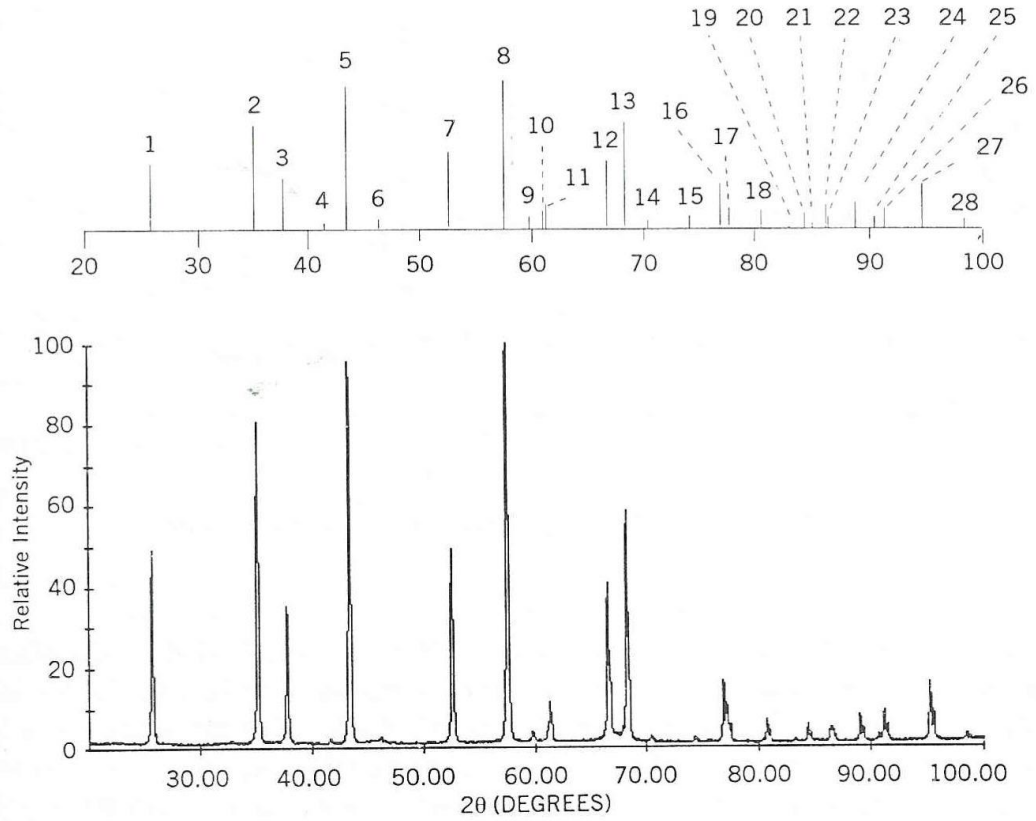

Figure 10.1. The experimental (bottom) and reduced (top) diffraction patterns of Al_2O_3.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

4. Pattern reduction

   Steps in Data Treatment

   1. Data collection
   2. Smoothing
   3. Background subtraction
   4. alpha2 stripping
   5. Peak location
   6. Two theta calibration
   7. Calibration and reporting of d

Acquisition of Diffraction Data

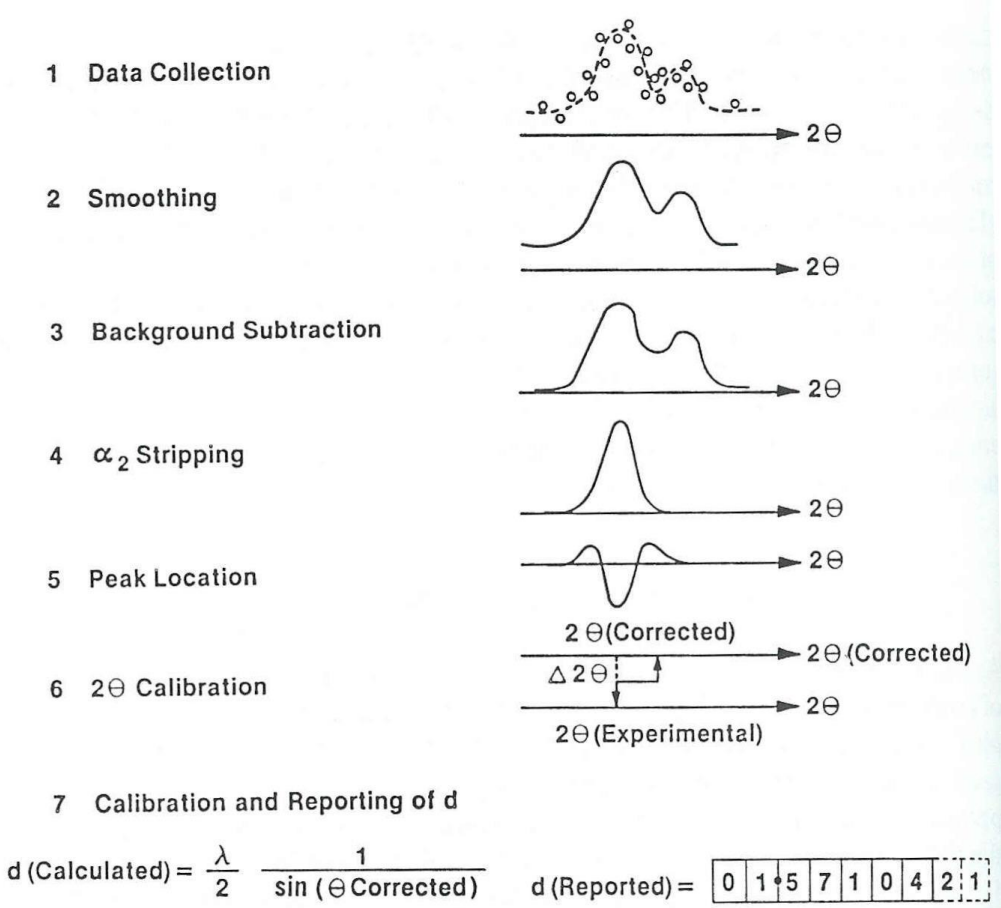

Figure 11.1. Steps in the treatment of diffraction data. From R. Jenkins, Experimental procedures. In *Modern Powder Diffraction* (D. L. Bish and J. E. Post, eds.), p. 59, Fig. 8. Mineralogical Society of America, Washington, DC, 1989. Reprinted by permission.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

4. Pattern reduction

Computer software can be used to treat data or can be done manually. Different software packages give different results.

Acquisition of Diffraction Data

Table 11.2. Experimentally Reduced Data from Two Different Software Programs

Lines Used		User 1		User 2	
Line No.	(*hkl*)	*d* (Å)	I/I^{rel}	*d* (Å)	I/I^{rel}
1	(012)	3.479	75	3.472	43
2	(104)	2.552	90	2.547	71
3	(110)	2.379	40	2.376	34
4	(006)	2.165	1	2.162	1
5	(113)	2.085	100	2.085	96
6	(202)	1.964	2	1.962	2
7	(024)	1.740	45	1.739	52
8	(116)	1.601	80	1.602	100
9	(211)	1.546	4	1.546	5
10	(122)	1.514	6	1.511	8
11	(018)	1.510	8	1.510	11
12	(214)	1.404	30	1.510	43
13	(300)	1.374	50	1.373	73
14	(125)	1.337	2	1.336	3
15	(208)	1.276	4	1.275	6
16	(10, 10)	1.239	16	1.239	26
17	(119)	1.2343	8	1.235	13
18	(220)	1.1898	8	1.189	13
19	(306)	1.1600	1	1.160	2
20	(223)	1.1470	6	1.147	10

Acquisition of Diffraction Data

A. Steps in Data Acquisition

4. Pattern reduction

Steps in Data Treatment

a. Data collection

Pattern is stored along with all parameters.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

4. Pattern reduction

Steps in Data Treatment

b. Smoothing

Counting processes introduces random fluctuations in the raw data. These fluctuations are partially removed by data smoothing, i.e. 3pt or 5 pt smooth.

Take odd # of data points and average and replace middle data point with average. Step one increment and continue process.

Acquisition of Diffraction Data

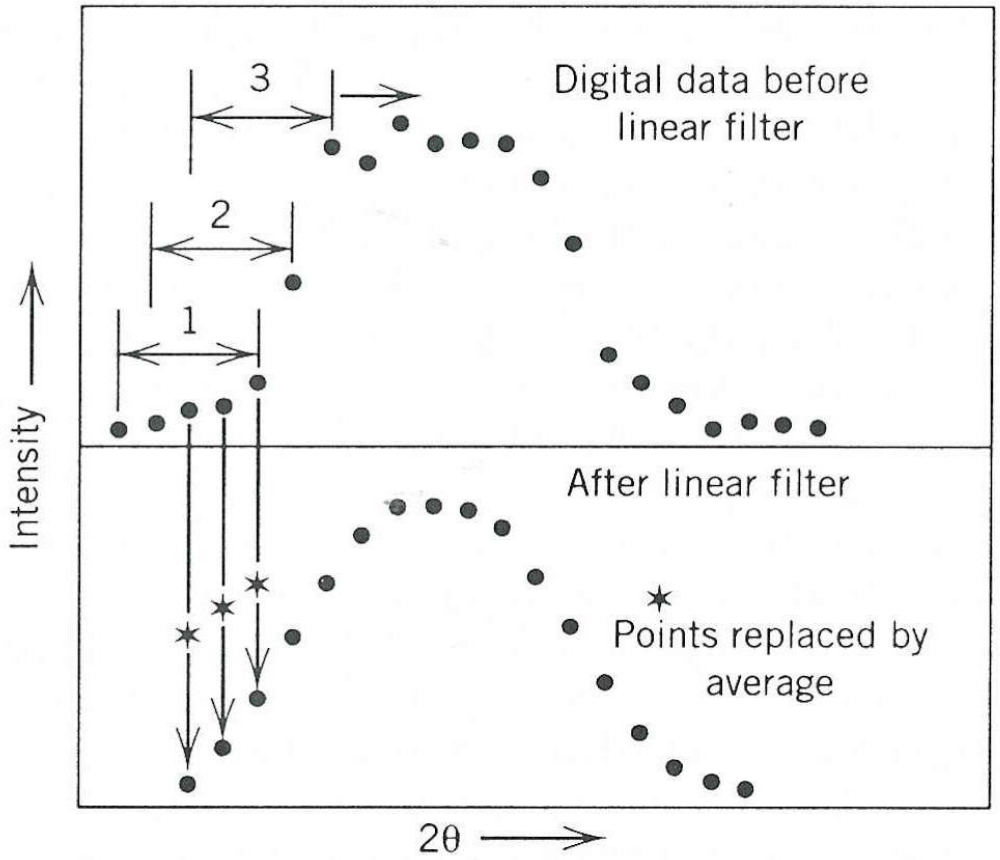

Figure 11.2. Smoothing out statistical noise with a linear digital filter. The five-point-averaged value is indicated with an asterisk.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

4. Pattern reduction

Steps in Data Treatment

b. Smoothing

If the x-ray profile is asymmetric with intensity falling off more rapidly on the high angle side (axial divergence), then a linear digital filter will cause the peak maximum to shift. Better to use a quadratic, cubic, or higher order polynomial type filter. (Savitzky-Golay algorithm quadratic filter).

Acquisition of Diffraction Data

A. Steps in Data Acquisition

4. Pattern reduction

Steps in Data Treatment

c. Background subtraction

Variations in background caused by:

- **scatter from the sample holder (low angles with a too wide divergence slit)**
- **fluorescence from the sample**
- **presence of significant amounts of amorphous material in the sample**
- **scatter from the sample mount substrate (thin samples)**
- **air scatter (greatest effect at low two theta values)**

Acquisition of Diffraction Data

A. Steps in Data Acquisition

4. Pattern reduction

Steps in Data Treatment

c. Background subtraction

To differentiate peaks from the background noise:

- **1st linerarize the pattern to remove typical low-angle maximum of amorphous scattering.**
- **2nd determine threshold of statistically significant data.**

Acquisition of Diffraction Data

A. Steps in Data Acquisition

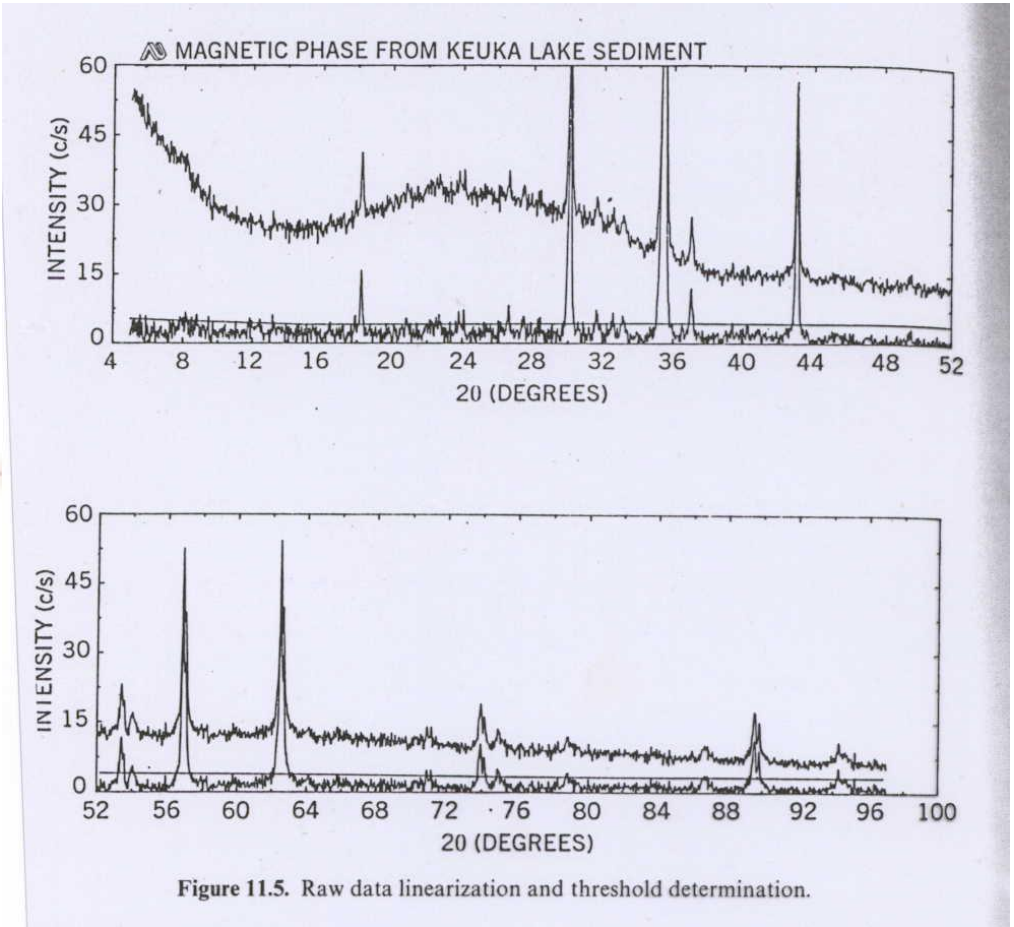

Figure 11.5. Raw data linearization and threshold determination.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

4. **Pattern reduction**

   Steps in Data Treatment

   d. alpha2 stripping (not always beneficial)

   Kalpha2 lines lead to distortion of diffraction profiles, especially in the mid angular region.

   Removal of alpha2

   - Rachinger technique

   - Fourier technique

Acquisition of Diffraction Data

A. Steps in Data Acquisition

4. Pattern reduction

Steps in Data Treatment

e. Peak location

Methods:

-manual

-computer – most programs use the 2nd derivative.

Sample displacement of 10 um lead to a peak shift of 0.001 degrees.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

4. Pattern reduction

Steps in Data Treatment

e. Peak location

Profile Fitting – used to determine shape of diffracted line profile. Peak location methods using profile fitting procedures are popular with many software programs (I.e. Lorentzian function and split Pearson VII function). More precise method for individual lines.

Rietveld technique used for whole-pattern fitting.

Acquisition of Diffraction Data

A. Steps in Data Acquisition

4. Pattern reduction

Steps in Data Treatment

f. Two theta calibration

g. Calibration and reporting of d

(Includes calibration methods using standards).

Acquisition of Diffraction Data

B. Use of Calibration Standards

Various types of standards are used in x-ray diffraction - these are certified as Standard Reference Materials (SRMs) by NIST. These standards fall into 5 categories:

Type	Use	Material
1. External 2θ Standards		Silicon α-Quartz Gold
2. Internal d-spacing Standards	Primary Primary Secondary	Si (SRM 640b) Fluorophlogopite (SRM 675) W, Ag, quartz, diamond
3. Internal Intensity Standards	Quantitative Intensity Respirable Quartz	Al_2O_3 (SRM 676) α- and β-silicon nitride (SRM 656) Oxide of Al, Ce, Cr, Ti, and Zn (SRM 674a) α-SiO_2 (SRM 1878a) Cristobalite (SRM 1879a)
4. External Sensitivity Standards		Al_2O_3 (SRM 1976)
5. Line profile Standards	Broadening Calibration	Lanthanum hexaboride (SRM 660)

[1]Gaithersburg, MD 20899.

Acquisition of Diffraction Data

B. Use of Calibration Standards

Various types of standards are used in x-ray diffraction - these are certified as Standard Reference Materials (SRMs) by NIST. These standards fall into 5 categories:

Table 10.6. Effectiveness of Standards for the Correction of 2θ Errors

Use of Standard	Type 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

Acquisition of Diffraction Data

B. Use of Calibration Standards

1. **External 2θ Standards**

   Typically silicon, α-quartz, and gold

   Used to check for correct alignment of diffractometer.

   Peaks from the experimental and standard pattern are measured and $\Delta 2\theta$ ($2\theta_{obs}$-$2\theta_{calc}$) is plotted vs 2θ.

   External standard will not correct for sample displacement errors.

Acquisition of Diffraction Data

B. Use of Calibration Standards

2. Internal 2θ and d-spacing Standards

The ideal internal standard properties; good angular coverage, simple pattern, stable, inert, and available in small particle sizes.

Used to correct for instrument alignment, sample transparency and sample displacement.

Typically Si (SRM 640b), Fluorophlogopite (SRM 675), W, Ag, quartz, diamond.

Si (SRM 640b) is good for scans from 24^0 2θ and up.

Fluorophlogopite is good for low angle scans. It is a type of mica that strongly orients in [00l] direction.

Acquisition of Diffraction Data

B. Use of Calibration Standards

3. Internal Intensity Standards

Quantitative standards of high phase purity that exhibit minimal preferred orientation.

These standards include Al_2O_3 (SRM 676), α and β - silicon nitride (SRM 656), Oxides of Al, Ce, Cr, Ti, and Zn (SRM 674a), α - SiO_2 (SRM 1878a), and Cristobolite (SRM 1879a).

The oxides standard (SRM 674a) is unique in that it has a linear range of attenuation coefficients from 126 to 2203 cm^{-1} for CuKα radiation.

Acquisition of Diffraction Data

B. Use of Calibration Standards

4. External Sensitivity Standards

This standard is used to quantify variations in angular sensitivity between different diffractometers.

Usually use Al_2O_3 (SRM 1976). This is a sintered plate of α - alumina.

Acquisition of Diffraction Data

B. Use of Calibration Standards

5. Line Profile Standards

Used for broadening calibration

Typically Lanthanum Hexaboride (SRM 660)

Defines the instrumental broadening of the diffractometer, since this standard is relatively free from strain and particle size effects which lead to broadening. Obtain the FWHM values by use of a split Pearson VII profile shape function.

Can also be used for Rietveld refinement.

Reading Assignment:

Read Chapters 10 and 11 from:

-Introduction to X-ray powder Diffractometry by Jenkins and Synder