Diffractometers Generally Used In a Modern Powder X-ray Diffraction Laboratory - Chapter 6 Diffractometer Measurements

1. $\theta$–2$\theta$ Diffractometers

2. $\theta$–$\theta$ Diffractometers

With and without Sample Rotation Capability

The diffractometers on the left are when used in $\theta$–2$\theta$ configuration are called Bragg Brentano Diffractometer
Typical Diffractometer Scan on a Bragg Brentano Diffractometer

Figure 6-5 Diffraction pattern of NaCl powder. Copper Kα radiation, monochromator, variable divergence slit diffractometer. About one-half of the entire range of 2θ is shown here. The vertical axis shows the square root of the number of counts.
Sample Preparation Methods

Figure 6-6  Steps in one method of diffractometer sample preparation: place holder face down on a slightly rough surface (frosted end of a glass microscope slide, matte cardboard, etc.) pour powder into sample holder from behind, press until powder is self-supporting in the holder, lift holder from surface and flip so that face B (the front of the sample holder) is exposed.
Figure 6-7  High resolution diffractometers for single crystal samples, (a) schematic of a double axis diffractometer used for recording rocking curves and (b) diagram of a Bede Scientific triple axis diffractometer for recording rocking curves and for high resolution reciprocal space mapping.
Focusing, Para focusing, Parallel Beam Optics for Diffraction Systems

Focusing Optics for Diffraction Systems

Figure 6-8  Focusing-geometry.
Diffractometer Circle or Rowland Circle

1. Focusing Circle and Diffractometer Circle Differences:

2. Focusing Circle is connects the Center of the X-ray target-Sample-receiving slit. It need not be actually a circle.

3. @ 0° – It is straight line

4. @ high angles ellipse

Figure 6-9 Focusing geometry for flat specimens in (a) forward reflection and (b) back reflection.
Soller Slits

1. Keeps beam nearly parallel …they are placed in front of the X-ray tube.

Figure 6-10  Soller slit (schematic). For simplicity, only three metal plates are shown; actual Soller slits contain about a dozen.
Bragg Brentano Diffractometer

Figure 6-1 X-ray diffractometer (schematic).
Diffractometer Geometry

1. Focusing Circle, Soller slits, Sample positions and receiving slits.
Detection Systems Operations

1. If a Cu Kα radiation is used then there is specific voltage is generated and all signals are roughly of the same voltage.

2. These signals come in pulses as Pulse - signal for the detectors

3. Note if there is some other type radiation then the voltage of the pulse is different

Figure 6-12  Randomly spaced voltage pulses produced by a detector.
Figure 6-13  The effect of counting rate on counting losses for three kinds of detectors (schematic).
Figure 6-14 Calibration curve of a multi-chamber Geiger counter. Cu Kα radiation. Nickel foils, each 0.01 mm thick, used as absorbers.
X-Ray Diffraction

MSE 416 and Graduate Students

Chapter No. 6

Diffractometer Measurements

Prof. Dhanesh Chandra

Metallurgical and Materials Engineering

University of Nevada, Reno

Phone: 775-784-4960

E-mail: dchandra@unr.edu
Types of Detectors

1. Proportional Detector → Used in Old systems and now in New XRD systems
2. Geiger Counter → Used in Surveying X-radiation
3. Scintillation Detector → Used in Modern XRD systems*
4. Solid State Detector-Si → Used in Modern XRD systems*
5. Position Sensitive Detectors
   • Used in Modern High Temperature Diffraction systems
   • Replace Films in Camera’s
   • To detect Texture in Materials
   • Laue Cameras
   • Single Crystal Systems
Efficiency of Detectors

Windows: Mica or Be or Polymer Seal

Overall Efficiency, \( E = (E_{\text{absorption}} \times E_{\text{Detector}}) \)

\[
E = E_{\text{abs}} \cdot E_{\text{Det}} = (1 - f_{\text{abs,}W})(f_{\text{abs,d}})[1 - f_{\text{losses}}]
\]

\( E_{\text{abs}} = (1 - f_{\text{abs,}W})(f_{\text{abs,d}}) \)

\( E_{\text{Det}} = [1 - f_{\text{losses}}] \)

Here,

\( E_{\text{Det}} = 100\% \) for most detectors in XRD

\( \therefore E \) is determined by \( E_{\text{abs}} \), which is calculated from dimensions and absorption coefficient of the Windows

\( E_{\text{abs}} \) varies as the wavelength

Due to dependence on wavelength
Detector Efficiencies as a function of Wavelength of X-rays

Figure 6-15  Calculated values of absorption efficiency $E_{abs}$ (in percent) of various kinds of detectors, photographic x-ray film (black dots). After Parrish [6.5] and pp. 538-555 of Vol. C of [G.1].
Energy Resolution of Detectors

Consider a Incident wavelength ($\lambda$) of Cu $K\alpha$ → produces “V” volts

Then the voltage Pulse of Mo-$K\alpha$ quantum develops a pulse of:

$$\frac{\text{Mo } K_{\text{edge}}}{\text{Cu } K_{\text{edge}}} = \frac{20}{9} \text{ keV} = 2.2 \text{ Volts}$$

$$R = \frac{W}{V}$$

Smaller the $R$ ……better the resolution
**Ionization Chambers (IC)**

Ionization Chambers (IC) are devices used to detect and measure ionizing radiation. The process involves the following steps:

1. **Valence electrons stripped from gas atoms**: When x-rays or other ionizing radiation pass through the IC, they remove valence electrons from the noble gas atoms (e.g., Kr, Xe). This leaves a positively charged core in the atom.

2. **RC Circuit**: The ionized gas is connected to a resistor-capacitor (RC) circuit. The RC circuit is designed to amplify the charge signal produced by the ionization process.

3. **Charged Positive Cores of atoms**: The positively charged cores of the atoms are accelerated towards one of the electrodes, creating a current that is detected by the RC circuit.

These chambers are often used in various applications, including medical imaging, radiotherapy, and environmental monitoring.
Proportional Counters – Practical Detectors used older M/cs

- Gas Amplification Factor
- Linear region is used for Proportional counters
- Bottom part is called the Counter Tube
- Higher voltage leads to Geiger Muller Counters

Figure 6-18 Effect of voltage on the gas amplification factor. Friedman [6.7].
To set the detector voltage

1. Wavelength of incoming radiation is important as the “Size of the voltage” pulses depend on the wavelength of the incoming x-ray as shown below.

2. Then you need increase the dial voltage until a plateau is obtained, and stop beyond the Threshold voltage.

1. If Cu has a Pulse of = 1 V

2. Then Mo will have a Pulse = 20/9=2.2 Volts
1. As the electrons flow through the anode wire in case of the Proportional detector there is a current flow and the recorded at the rate meter.

2. As the rate of impingement of x-rays increases the signal increases.

3. All the detectors work on these principles.

4. However, the sources of pulses or ionization process is different.

For Ex: Gas proportional counters we ionize the a “Gas atom”

In scintillation counter we produce light from NaI crystal by impingement of x-rays.
1. Voltages around 1500 V the proportional counter will act as a Geiger Muller Counter.

2. Not only are atoms ionized but there is ultraviolet radiation produced. These UV rays travel at 10 cm/ nanosec. And knock off electrons from cathode casing of the detector. And the current production is not limited to a spot on the wire but it is through out the wire.

3. Gas Amplification is raised to $10^8$ to $10^9$ which is much larger than the Proportional counter.

4. Used in Survey meter. It has a slow count rate.

**Figure 6-20** Differences in the extent of ionization between proportional and Geiger counters. Each plus (or minus) symbol represents a large number of positive ions (or electrons).
1. X-rays strike NaI (activated small amount of Tl+) crystal - the electrons jump into the conduction band of NaI and then transfer energy to Tl\(^+\) ion; where the Tl\(^+\) electron is excited and when it returns it goes back to its ground level produces light.

2. Every time an x-ray strikes the crystal, light is emitted due to recombination. This light strikes the photocathode (Cs-Sb) and produces photoelectrons.

3. These strike, what are called “Dynodes,” of Cs-Sb and produce millions of electrons and directed towards other dynodes which are maintained at higher potential.

4. Gain is about 4 to 5 and usually 10 dynodes are used. Multiplication factor = \(5^{10} = 10^7\). Final pulse is of order of Volts … large as Geiger Counter.

5. But the process requires microseconds- rates as high as \(10^5\) c/s can be achieved….good
Detector Resolution

Energy Resolution \( R = \frac{W}{V} \)

Smaller \( R \) is better

1. Scintillation  FWHM = 3070 eV
2. Scintillation  FWHM = 1000 eV
3. Si(Li)  FWHM = 150 eV

Incident Beam

\[ Mn - K_\alpha \approx 5.9 \text{ keV} \]
\[ \lambda = 2.10 \text{ Å} \]

Figure 6-22 Pulse-height distribution curves for three kinds of detector. Incident radiation is Mn \( K_\alpha (\lambda = 2.10 \text{ Å}, h\nu = 5.90 \text{ keV}) \) from a radiative \( ^{55}\text{Fe} \) source. Data from Frankel and Adams [6.8] and [p. 540, Vol. C of G.1].

1. If Cu has a Pulse of = 1 V
2. Then Mo will have a Pulse = 20/9=2.2 Volts
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Metallurgical and Materials Engineering
University of Nevada, Reno
Phone: 775-784-4960
E-mail: dchandra@unr.edu

2nd. Lecture on Diffractometer

Modern Diffractometer
1. Li ions are deposited on the n side and Boron on the other “p” side.

2. A Reverse Bias voltage is applied such that Li ions drift towards the positive side and the charge cancels out because of combination

3. Leaving behind an intrinsic area in the Center of the crystal

**Av. Ionization Energy of Si ~3.8 eV**

If Mn Kα Radiation is used: Emission= 5900 eV

So absorption of an Quanta should produce ion pairs~5900/3.8=1550

In comparison with Ar gas Ionization using MnKα Ex:

No. of ion pairs = 5900 eV/26 eV = 230 (It takes 20 eV to ionize argon gas atom).

Figure 6-23  Si(Li) detector and FET preamplifier, very schematic. Both are in a cooled evacuated space, and x-rays enter through a beryllium window. The detector is operated at about 1000 volts. ⊖ = electron, ⊕ = hole.
Resolution of Detectors

Geiger counter:

No of ion pairs or electron – hole pairs are dependent on the Energy of the Incoming X-ray Quanta.

\[ R = \frac{W}{V} = \frac{k^3}{\sqrt{n}} \]

\[ R \] where, \( k = \) constant and \( n = \) No. of ion pairs.

Proportional Counter

\[ R = k_5 \cdot \sqrt{n} \]

Si Detector

\[ R = \frac{W}{V} = \frac{[(100eV)^2 + 2.62E]}{E} \]

\[ E \]

\[ R \] where, \( k = \) constant and \( n = \) No. of ion pairs. E units are in eV. and the 100 eV is the noise level
**Pulse Height Analyses**

1. **Pulse Height Discriminator:**
   Each pulse is of a particular Voltage (i.e. different wavelengths). The PHD rejects the Pulse A and passes the Pulse B and C through the circuit.

   The short wavelength components may not be weakened by this PHD.

   ![Diagram](Image)

   *Figure 6-24* Pulse-height discrimination and analysis. The statistical spread in pulse size, measured by the width W of Fig. 6-16, is suggested above by the variable heights of each pulse.

2. **Single Channel PULSE Height Analyzer**

3. **Multichannel Pulse Height Analyzer**

   1. **Pulse Height Analyzer:**
      Each pulse is of a particular Voltage (i.e. different wavelengths). The PHA rejects the Pulse A and C and passes the Pulse B through the circuit.

      The short wavelength components may not be weakened by this PHD.

      This help reduce the background.
Escape Peaks Observed in a Detector

For Mo Kα - $V_{a} = k \cdot E_{1} = k \cdot 17.4$ Absorption of other Quanta will involve reduction in energy.

Escape Peak Pulse will be $V_{\text{esp.}} = k \cdot (E_{1} - E_{2})$

$= k \cdot (17.4 - 12.6) = 4.8k$

Intensity of the Pulse is a different matter depends on if it is Kα or Lα.

Lα escape peaks are weak.

Figure 6.25 Pulse-height distribution curves showing escape peaks (ep) in proportional counters for (a) Mo Kα radiation incident on a krypton counter and (b) Cu Kα radiation incident on a xenon counter, Parrish [6.5].
Multi Channel Pulse Height Analyzer usually has ~1024 channels and energy scale is linear with the increase from channel to channel is linear. These are used in Energy Dispersive analyzers.
Energy Dispersive Diffractometry

1. Both Emission and Diffraction Peaks are observed in this case.
2. One uses All wavelengths for this purpose

$$E = h \nu = \frac{h.c}{\lambda} = \frac{h.c}{2d \sin \theta}$$

$$E(\text{keV}) = \frac{6.2}{d \cdot \sin \theta}$$

$d$ is in Angstroms

Finally there are position sensitive Detectors also available

![Energy Dispersive Diffractometry Diagram](image)

Figure 6-26 Energy-dispersive diffractometry. (a) Experimental arrangement. The x-ray tube is seen end on. Diffracted beam collimator not shown. (b) Diffraction pattern of polycrystalline platinum at $2\theta = 21.4^\circ$ obtained with a Si(Li) detector and an iron-target x-ray tube operated at 45 kV and 8 mA. SWC = short wave cutoff = short-wavelength limit of incident beam. Giessen and Gordon [6.14].
Integrated Intensity an XRD Bragg Peak

1. New machines have manual windows that can be adjusted to cover the peak, and it will give you the c/s for the peak. (Old M/c’s had mechanical angle traversing devices).

2. These are used in Quantitative X-ray diffraction analyses.

3. Ex: If you have mixture of Al + Si mixed in some unknown proportions. The integrated intensities of the standards (Pure Si and Al) and unknown (Al+Si) powders are compared.
RC Circuits Used in X-ray Counting systems

1. Typical circuit consists of R, and C.

- Charge the Capacitor (Connect a-c)
- Short Circuit (connect b-c)
- When RC reaches 63% or 0.63V of the charge..this is called **Time Constant** for the circuit.
- To reach 99% + it takes 4.6 RC
- Product RC has the dimension of time (but actual the R is in Megaohms and C is in Microfarads).
- The discharge also occurs slowly, and discharge is 0.37 V

![Diagram of RC circuit](image)
1. **Rate constants (RC)** are generally set to 1 sec.

The rate constants are set such that the charge – discharge process is complete very rapidly during the window of time taken for the peak to transverse through the receiving slit.

2. If the rate constants are too large then the time taken is more to collect the data and there are shifts in the peaks.

3. Generally it is better to have a relatively short Time constant
• Monochromators are generally used in Modern Diffractometers

• These replace the Filters to eliminate $K\beta$ Peaks in Bragg-Brentano diffractometers, using mosaic Graphite crystals that are large grains with slight tilt in orientation of the grain (or may think of it as a preferred orientation peak situation.)

• In Case of Guinier Systems, a Ge single crystal is used that actually eliminates the $K\alpha_2$, as well as $K\beta$, giving pure $K\alpha_1$ radiation. These use what are called Johansson type focusing crystals.
Flat Crystal Monochromators:
Used in Spectrometry and INEL Position sensitive detectors

Curved Crystal (Johansson Monochromators)
Curved crystals of: Ge or NaCl, LiF, SiO2

\[ SC = 2R \cdot \cos \left( \frac{\pi}{2} - \alpha \right) \]

\[ SC = R \cdot \frac{\lambda}{d} \]

\[ R = 30 \text{ cms.} \]

For Diffraction of Cu - K\(\alpha\) from 10.1 plane of quartz.
Polarization Factor for Guinier Cameras

Usual Polarization Factor: \( \left( \frac{1 + \cos^2 2\theta}{2} \right) \)

and LP Factor for ordinary diffraction system:

\[
LPFactor = \left( \frac{1 + \cos^2 2\theta}{(\sin^2 \theta \cdot \cos \theta)} \right)
\]

For Polarization using Johansson Monochromator:

\[
\left[ \frac{1 + \cos^2 2\alpha \cdot \cos^2 2\theta}{(1 + \cos^2 2\theta)} \right]
\]

where: \( 2\alpha \) – monochromator diffraction angle

So, Lorenz Polarization Factor, LP Factor

\[
= \left[ \frac{1 + \cos^2 2\alpha \cdot \cos^2 2\theta}{(\sin^2 \theta \cdot \cos \theta)} \right]
\]
There are 4 different ways to evaluate Peak positions:

1. **Peak maximum**
2. **Mid Point of FWHM**
3. **Av. Of Inflection Points**
4. **2theta median**

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**Figure 6-35** Different methods of defining peak position. a) peak maximum $2\theta_{\text{max}}$, b) mid-point of half-maximum intensities $2\theta_{\text{mid}}$, c) average of the points of inflection $2\theta_{\text{infl}}$, d) peak median $2\theta_{\text{median}}$ and (not shown graphically) peak centroid $<2\theta>$. Equations for a) - c) are shown below the plots; note that $K\alpha_2$ and background stripping is assumed in all calculations except $2\theta_{\text{max}}$ where it is indicated explicitly.
1. Equation of a Parabola: with axis parallel to the y-axis and vertex at h,k.

2. \((x-h^2) = p (y-k)\)

3. \( @ x=2\theta, y=I \)

A Simpler Method is by Koistinen and Marburger:

in which

\[
h = x_1 + \frac{c}{2} \left( \frac{3a + b}{a + b} \right)
\]

where, \( a = y_2 - y_1 \)

\( b = y_2 - y_3 \)

\( y \)-coordinate may be Intensity

\( I = c / s \)

counts, \( n \) for a fixed time

This ends Chapter 6