Diffractometer

Geometry
Optics
Detectors
Diffractometers

Debye Scherrer Camera

Diffractometers

- Ewald sphere and powder diffraction

\[ |OC| = \frac{1}{\lambda} \sin \theta = \frac{1}{2} |d_{hkl}^*| = \frac{1}{2d_{hkl}} \Rightarrow \lambda = 2d_{hkl} \sin \theta \]

\[ |OB| = d_{hkl}^* \]
Diffractometers

- Ewald sphere and powder diffraction

Diffractometers

- Ewald sphere and powder diffraction

\[ d = \frac{\sin \theta}{\lambda} \]

Diffractometers

- Powder Diffractometer

La(Ni$_{4.85}$Sn$_{0.15}$), Cu Kα

Intensity, Y (10^3 counts)

Bragg angle, 2θ (deg.)

113, Kα$_1$
032, Kα$_4$
131, Kα$_1$
113, Kα$_2$
032, Kα$_2$
131, Kα$_2$

Diffractometers

- PANalytical X’Pert Materials Research Diffractometer
X-ray Powder Diffractometer

Powder diffractometers working in the Bragg-Brentano (θ-2θ) geometry utilize a parafocusing geometry to increase intensity and angular resolution.
Diffractometers

Goniometer for Powder Diffraction – $\theta$-$\theta$ scan
Diffractometers

Goniometer for Powder Diffraction – $\theta$-2$\theta$ scan
X-ray Powder Diffractometer

Parafocusing geometry of the Bragg-Brentano diffractometer. $S$ is the sample, $R$ is the radius of the goniometer circle, $r$ is the radius of a focusing circle and $\theta$ is the Bragg angle. The x-ray beam is emitted from point $A$ and is focused at the detection point $D$. 
X-ray Powder Diffractometer

Powder Diffraction of Cu, Ni, Fe and Si.
X-ray Powder Diffractometer

Sample length
Sample irradiated area

\[
\frac{l_1}{\sin \frac{\varphi}{2}} = \frac{R}{\sin(\theta + \frac{\varphi}{2})}
\]

\[
\frac{l_2}{\sin \frac{\varphi}{2}} = \frac{R}{\sin(\theta - \frac{\varphi}{2})}
\]

\[L = l_1 + l_2\]
X-ray Powder Diffractometer

Sample length

Sample irradiated area

\[ \varphi = 2^\circ \]

\[ \varphi = 1/2^\circ \]

\[ \varphi = 1/4^\circ \]

R = 320 mm

Irradiated length, \( l + \frac{l}{2} \) (mm)

Bragg angle, \( 2\theta \) (deg)
Beta-filters

A beta-filters are used to keep as much as possible of the characteristic $K\alpha$ radiation from the tube whilst suppressing $K\beta$ and white radiation.

$$I_t = I_0 \exp(-\mu x)$$

<table>
<thead>
<tr>
<th>Tube anode material</th>
<th>Beta-filter material</th>
<th>Thickness [µm]</th>
<th>$K\beta$ intensity reduction [%]</th>
<th>$K\alpha$ intensity reduction [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>Zr</td>
<td>75</td>
<td>97</td>
<td>54</td>
</tr>
<tr>
<td>Cu</td>
<td>Ni</td>
<td>20</td>
<td>99</td>
<td>58</td>
</tr>
<tr>
<td>Co</td>
<td>Fe</td>
<td>16</td>
<td>99</td>
<td>51</td>
</tr>
<tr>
<td>Cr</td>
<td>V</td>
<td>13</td>
<td>98</td>
<td>45</td>
</tr>
</tbody>
</table>
Collimators

Simplest collimation is achieved by placing a slit between x-ray source and the sample.

\[ \alpha \approx \frac{D+S}{L} \]

if \( L \gg D \)
Divergence slits are fitted in the incident beam path to control the equatorial divergence of the incident beam, and thus, the amount (length) of the sample that is irradiated by the incident x-ray beam.

**Divergence Slits**

- Fixed divergence slit
- Programmable divergence slit

![Fixed divergence slit](image1.png)

![Programmable divergence slit](image2.png)
Diffractometers

Fixed Slits

Divergence Slit:
• Match the diffraction geometry and sample size
• At any angle beam does not exceed sample size

Receiving Slit:
• As small as possible to improve the resolution
• Very small slit size reduces diffracted beam intensity

\[ \alpha \approx \frac{L \sin \theta}{R} \text{ (rad)} \]
Diffractometers

Variable Slits

- Vary aperture continuously during the scan
- Length of the sample is kept constant
Soller Slits

- Soller slits used to limit the axial (vertical / out-of-plane) divergence of the incident & diffracted X-ray beams.
- Using soller slits improves peak shape and the resolution in 2θ-type scans, especially at low scattering angles.

\[ \alpha \approx \frac{2d}{l} \]
Beam Attenuators

The beam attenuator is an absorber which is placed in the x-ray beam to reduce its intensity by a specific factor.

Attenuation factors:
- Copper (0.1 mm) ≈ 100
- Combined copper + nickel (0.2 mm / 0.02 mm) ≈ 10,000

\[ I_t = I_0 \exp(-\mu x) \]
Collimators

- Second slit can be added to provide additional collimation
The focusing geometry can be used to provide a monochromatic source of x-rays. Used in Bragg-Brentano geometry and consist of a curved (Johann) pyrolitic graphite crystal.
Crystal Monochromator

Three different sample-monochromator geometries used in powder diffraction:

- Flat diffracted beam monochromator
- Curved diffracted beam monochromator
- Flat primary beam monochromator
Crystal Monochromator

- X-ray beam monochromatization can be achieved by diffraction from single crystals: Si, Ge, LiCl, and graphite.

\[ 2d \sin \theta = \lambda \]

- Sufficient to separate $K\alpha$ and $K\beta$
- Not sufficient to separate $K\alpha_1$ and $K\alpha_2$
An incident beam collimator is a device that combines a divergence slit and a beam width mask in one optical module. It is used in combination with the point focus x-ray tube.

Main applications:
- Texture analysis
- $\psi$-stress analysis
Point Source Geometry

\[ L = \left\{ \frac{R h + p_h (R - f)}{f \sin \omega} \right\} + W \sin \psi \cot \omega \]

where
- \( L \) = the irradiated length on the sample,
- \( R \) = the radius of the goniometer,
- \( h \) = the height of the incident X-ray beam, as set by the divergence slit on the crossed slits assembly,
- \( p_h \) = the height of the point focus of the X-ray tube, usually 1.2 mm,
- \( f \) = the distance from the focus of the X-ray tube to the crossed slits,
- \( \psi \) = the tilt angle, which is the angle between the sample surface normal and the equatorial plane,
- \( \omega \) = the angle between the incident beam and the sample surface.

\[ W = \frac{R w + p_w (R - f)}{f \cos \psi} \]

where
- \( W \) = the irradiated width on the sample,
- \( R \) = the radius of the goniometer,
- \( p_w \) = the width of the point focus of the X-ray tube, usually 0.4 mm,
- \( w \) = the width of the incident X-ray beam, as set by the axial mask on the crossed slits assembly,
- \( f \) = the distance from the focus of the X-ray tube to the crossed slits,
- \( \psi \) = the tilt angle, which is the angle between the sample surface normal and the equatorial plane.
Point Source Geometry

- X-ray Lens

- X-ray Capillary Lens

- Quasi-parallel Beam
Point Source Geometry

- **X-ray Mono-capillary**
  - Used for microdiffraction
  - Beam sizes 1 mm – 10 μm
Multilayer X-ray Mirrors

Tem micrograph of a multilayer mirror Mo/B₄C with a \( d \)-spacing of 1.4 nm and 500 pairs

Materials:
W/Si, W/B₄C, WSi₂/Si, Ni/Mg and Ni/B₄C

Calculated Cu K\( \alpha \) reflectivity vs. incidence angle for W/Si, WSi₂/Si and Ni/B₄C multilayers (100 layer pairs, 4 nm period.)
Multilayer X-ray Mirrors

Parabolic Mirror

Elliptical Mirror
Parallel Beam Geometry

- Incident Beam:
  - X-ray Göbel Mirror

Parabola

θ = 0.5°

θ < 0.04°
Parallel Beam Geometry

- Incident Beam:
  - X-ray Mirror

\[ \alpha \approx \frac{2d}{l} \]
High resolution double-axis diffractometer:
- Open detector mode
High Resolution Geometry

High resolution triple-axis diffractometer:
High Resolution Geometry

Bartels Monochromator

X-ray Focus
Incident Beam:
- X-ray Hybrid Monochromator

θ < 19 arcsec

θ = 0.5°
The x-ray detector is the last item in the x-ray beam path. It is used to count numbers of photons, that is, the intensity of the diffracted beam at a certain $2\theta$ position of the goniometer.

- single photon detectors
  - scintillation detectors
  - (gas-filled) proportional counters
  - semiconductor detectors
- linear (position-sensitive) detectors
  - gas-filled (wire) detectors
  - charge-coupled devices (CCD’s)
- area detectors
  - 2-D wire detectors
  - CCD area detectors
- X-ray film (should be obsolete)
**Desired Properties of X-ray Detectors**

- **Quantum counting efficiency** – number of photons detected by the detector to the number of photons entering the detector.

\[ E = E_{abs} E_{det} = \left(1 - f_{abs,w}\right) f_{abs,d} \left[1 - f_{losses}\right] \]
Desired Properties of X-ray Detectors

**Linearity** – the ability of the detector to provide an output that is in direct proportion to the intensity of the x-ray beam (number of x-ray photons entering the detector).
Energy resolution – the ability of the detector to distinguish between energies.

- resolution → input photon of energy $E$ produces an output pulse of height $V \pm \delta V$

\[
R = \frac{W}{V}
\]
Smaller $R$ better resolution
Desired Properties of X-ray Detectors

- **Energy proportionality** – the ability of the detector to produce a pulse with a height proportional to the energy of the x-ray photon detected.

- **Sensitivity** – the ability of the detector to detect low intensity levels.

<table>
<thead>
<tr>
<th>Detector</th>
<th>PW3011/20</th>
<th>PW1964/96</th>
<th>PW3015/20</th>
<th>Braun PSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Sealed Proportional Detector</td>
<td>Scintillation Detector</td>
<td>X’Celerator RTMS Detector</td>
<td>Position Sensitive Detector</td>
</tr>
<tr>
<td>Window size</td>
<td>20 x 24 mm²</td>
<td>30 mm diameter</td>
<td>9 x 15 mm²</td>
<td>50 x 10 mm²</td>
</tr>
<tr>
<td>Efficiency Cu Kα</td>
<td>84%</td>
<td>93%</td>
<td>&gt; 94%</td>
<td>50%</td>
</tr>
<tr>
<td>Efficiency Mo Kα</td>
<td>36%</td>
<td>99%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>99% Linearity range</td>
<td>0 - 1000 kcps</td>
<td>0 - 500 kcps</td>
<td>0 - 900 kcps - Overall 0 - 7000 cps - Local</td>
<td>0 - 2000 cps - Overall 0 - 2000 cps - Local</td>
</tr>
<tr>
<td>Energy resolution around Cu Kα</td>
<td>19%</td>
<td>45%</td>
<td>25%</td>
<td>20%</td>
</tr>
<tr>
<td>Maximum count rate</td>
<td>1000 kcps</td>
<td>1000 kcps</td>
<td>5000 kcps - Overall 250 kcps - Local</td>
<td>50 kcps - Overall 50 kcps - Local</td>
</tr>
<tr>
<td>Maximum background</td>
<td>2 cps</td>
<td>8 cps</td>
<td>&lt; 0.1 cps</td>
<td>1 cps</td>
</tr>
<tr>
<td>Active length</td>
<td>-</td>
<td>-</td>
<td>9 mm</td>
<td>50 mm</td>
</tr>
<tr>
<td>Smallest Step Size</td>
<td>-</td>
<td>-</td>
<td>0.0021° 2θ at 240 mm goniometer radius 0.0016° 2θ at 320 mm goniometer radius</td>
<td>-</td>
</tr>
<tr>
<td>Positional resolution</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>80 μm (0.019° 2θ at 240 mm goniometer radius)</td>
</tr>
</tbody>
</table>
A proportional counter consists of the following main components:
- a gas-filled cylindrical envelope (usually Ar, Kr, or Xe)
- a central anode wire
- a grounded coaxial cylinder (the cathode)
- an X-ray transparent window
When an X-ray photon ionizes a gas molecule, the ejected photoelectrons are accelerated to the anode:

- **Low voltages** – photoelectrons don’t have enough energy to ionize other molecules.
- **Intermediate voltages** – gas amplification occurs (photoelectrons ionize gas molecules on the way to the anode).
- **High voltages** – discharge occurs throughout the gas volume.

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**Gas-filled Proportional Counter**

![Graph showing amplification factor vs voltage](image)

- **Geiger counter**
- **Proportional counter**
- **Avalanche region**
- **Corona discharge**
- **Glow discharge**

- **Ionization chamber**
Aspects of Proportional Counters

- **Proportional counter**
  - Each X-ray photon causes multiple ionizations (29 eV for argon → >300 ion/electron pairs with CuKα)
  - In the gas amplification regime (gain of $10^3$ to $10^5$), a pulse of a few millivolts is produced
  - Pulse amplitude proportional to photon energy
  - Much better energy resolution (15% to 20%) than scintillation detectors

- **Geiger-Müller counter**
  - no longer proportional – entire chamber “light up” with UV
  - large pulse amplitude (~volts) so no amplification needed; good for survey meters
  - slow to relax, so maximum count rate is limited
The Scintillation Detector

The detector has two basic elements:
- a crystal that fluoresces visible light (scintillates) when struck by X-ray photons
- a photomultiplier tube (PMT) that converts the light to electrical pulses

NaI(Tl) scintillator (very sensitive to moisture) – emits around 4200Å

CsSb photocathode – ejects electrons

gain ~5× per dynode (total gain with ten dynodes is $5^{10} \approx 10^7$)
Aspects of Scintillation Detectors

- Relatively inexpensive (~$1500) and rugged
- All necessary electronics are “off the shelf”
- Scintillator crystal can develop “dead spots” over time
- NaI is very hygroscopic and needs careful encapsulation
- Sealed from ambient light with thin Be window
- Energy resolution is poor (~50%)
- Typical noise of < 1 count/sec; advanced detectors can be linear in excess of $10^6$ counts/sec
Aspects of Semiconductor Detectors
Semiconductor Detectors

- Semiconductor detectors are solid-state proportional counters – each photon produces electron-hole (e/h) pairs.
- The detection of e/h pairs would not be possible if the semiconductor has free carriers (n-type or p-type) so it must be intrinsic – this can be done by “lithium drifting”.

Diagram:
- Lightly p-doped Si has Li plated.
- Heat to have the Li diffuse.
- Apply a reverse bias to cause Li$^+$ ions to “drift”.
- A wide central intrinsic region is formed.
Aspects of Semiconductor Detectors

- Originally: Si(Li) and Ge(Li) – “silly” and “jelly”
- Now intrinsic Si and intrinsic Ge are available (Ge better due to higher absorption and better energy resolution)
- Energy resolution about 2%
- Small signal requires a charge-sensitive preamp integrated with the detector
- due to thermal e/h generation and noise in the preamp, cooling to 77K is needed
- New detectors use Si p-i-n photodiodes and large bandgap materials (CdTe and CdZnTe) for room-temperature operation
Detectors

Counts (Arbitrary Units)

Energy (keV)

Scint.
Prop.
Si(Li)

$W_{1/2} = 3070 \text{ eV} = 52\%$
$W_{1/2} = 1000 \text{ eV} = 17\%$
$W_{1/2} = 160 \text{ eV} = 2.7\%$

$K_{\alpha 1} \alpha_2$
$K\beta$
PIXcel Detector

- Resolution better than 0.04° 2Theta
- Efficiency: > 94 % for Cu radiation
- Maximum count rate: > 25,000,000 cps
- Detector noise: < 0.1 cps
- Scan range: from 1° to more than 160° in 2Theta
- Large active length: ~2.5° 2Theta
- Can be used for “static” measurements

Schematic of pixel detector

- 256 x 256 = 65536 pixels
- 55 micron x 55 micron
- 97% count rate linearity up to 100,000 cps per pixel: > 25,000,000 cps per “strip”
- Static measurements possible with all detectors
- 2D possible
PIXcel Detector

Bragg-Brentano geometry  2:30:00 h:m:s
PIXcel detector  0:28:28 h:m:s
Two Dimensional Detector