



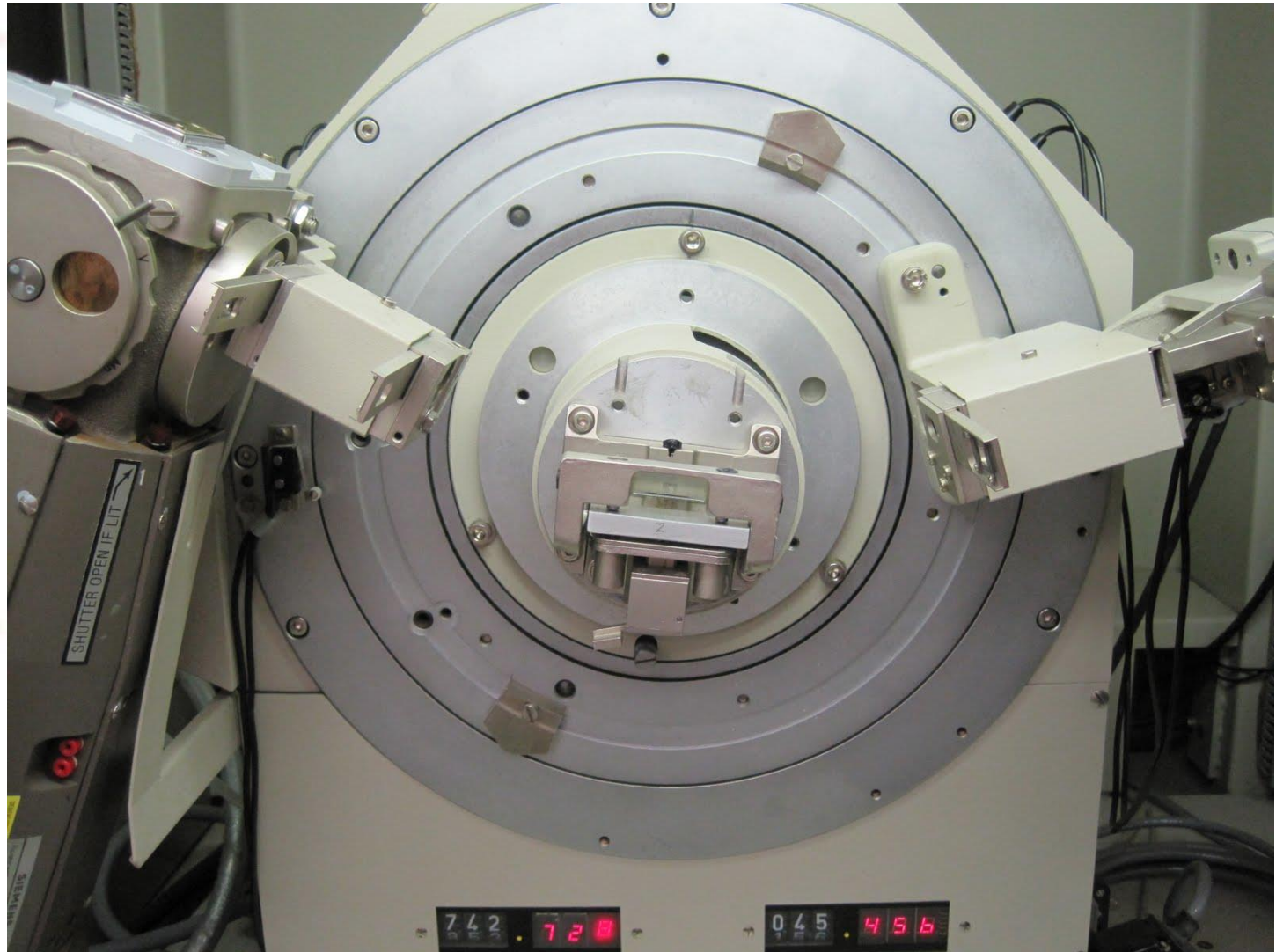
chem 5390

Advanced X-ray Analysis

LECTURE 10

Dr. Teresa D. Golden
University of North Texas
Department of Chemistry

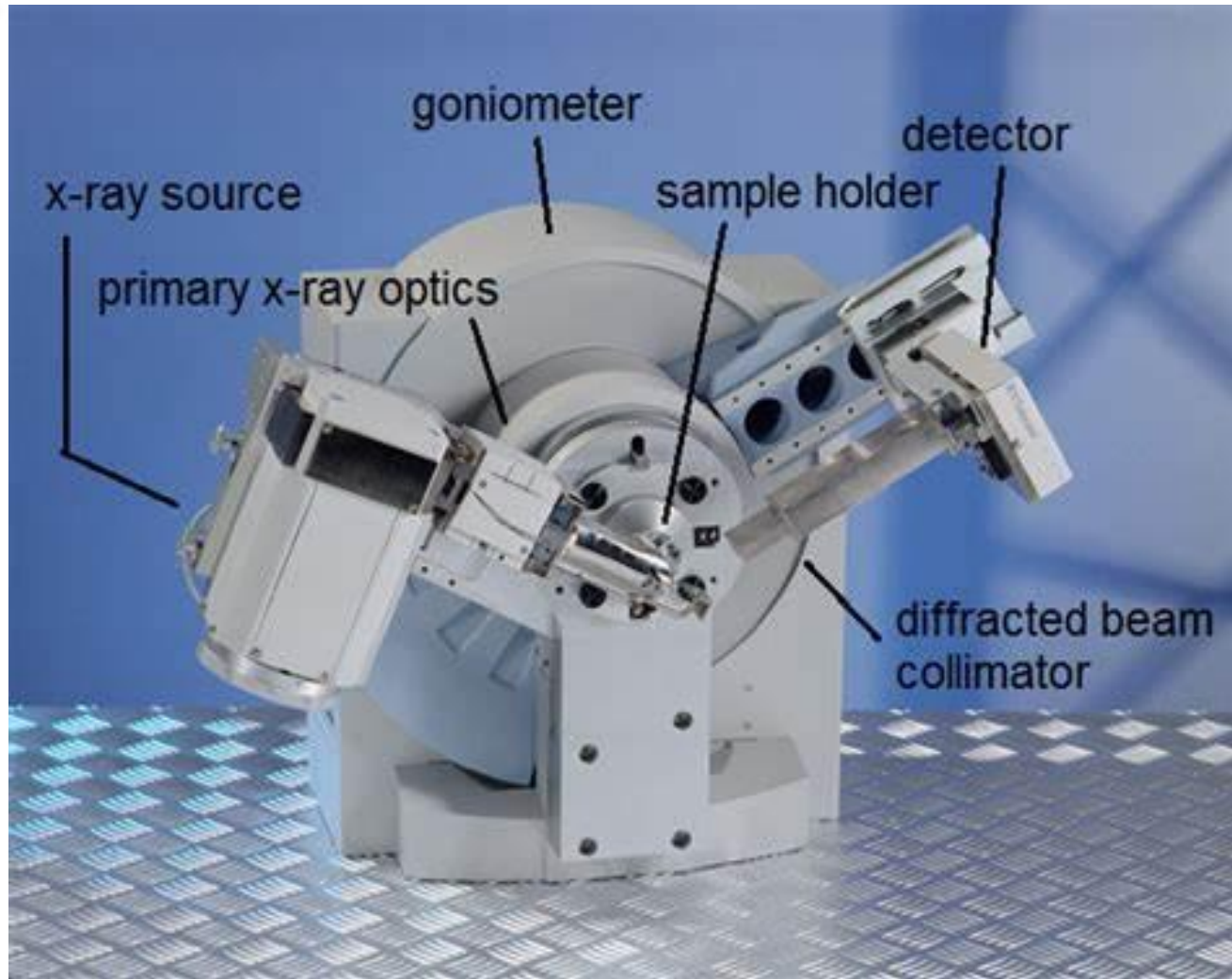
Instrumentation



chem 5390

Advanced X-ray Analysis

Instrumentation



Instrumentation

Optics

Includes a variety of slits, filters, mirrors, monochromators

Purpose: to reduce stray radiation, produce x-ray spectra which display diffraction from a single wavelength. (each unique d-spacing will diffract different wavelengths at different angles).

Instrumentation

Optics

For Cu radiation, the basic emission contains the α_1 , α_2 doublet and the β_1 , β_3 transition. Usually the β radiation can be reduced to a few % of the α radiation by using filters, monochromator, or energy resolving detector.

Most diffraction work uses the Cu $K\alpha_1$, $K\alpha_2$ doublet, which can be inconvenient at some angles.

Instrumentation

Optics

The angular dispersion of a diffractometer, $d\theta/d\lambda$, can be obtained by differentiating Bragg's law:

$$d\theta/d\lambda = 1/2d\cos\theta$$

$$d\theta/d\lambda = \tan\theta/2d\sin\theta$$

$$d\theta/d\lambda = \tan\theta/\lambda$$

Instrumentation

Optics

The angular dispersion increases as the 2θ value increases.

At low 2θ values, the α doublet is not resolved.

At high 2θ values, the α doublet is completely separated.

At mid range angular values ($30-60^\circ$), there is partial resolution, leading to distortion of the line profiles.

Instrumentation

Optics

Absolute value of the angular dispersion ranges from 100 eV at low 2θ to 2 eV at high 2θ .

The energy difference between $K\alpha_1$ and $K\alpha_2$ for Cu is ~ 20 eV.

Instrumentation

Optics

Besides the wanted x-ray wavelengths, a diffraction pattern is also made up of scatter and fluorescence.

Source

Diffraction of required λ

Diffraction of other λ 's

Coherent scatter from sample

Incoherent scatter from sample

Scatter from sample support

Fluorescence from sample

Result

Wanted peaks

Unwanted peaks

General background

General background

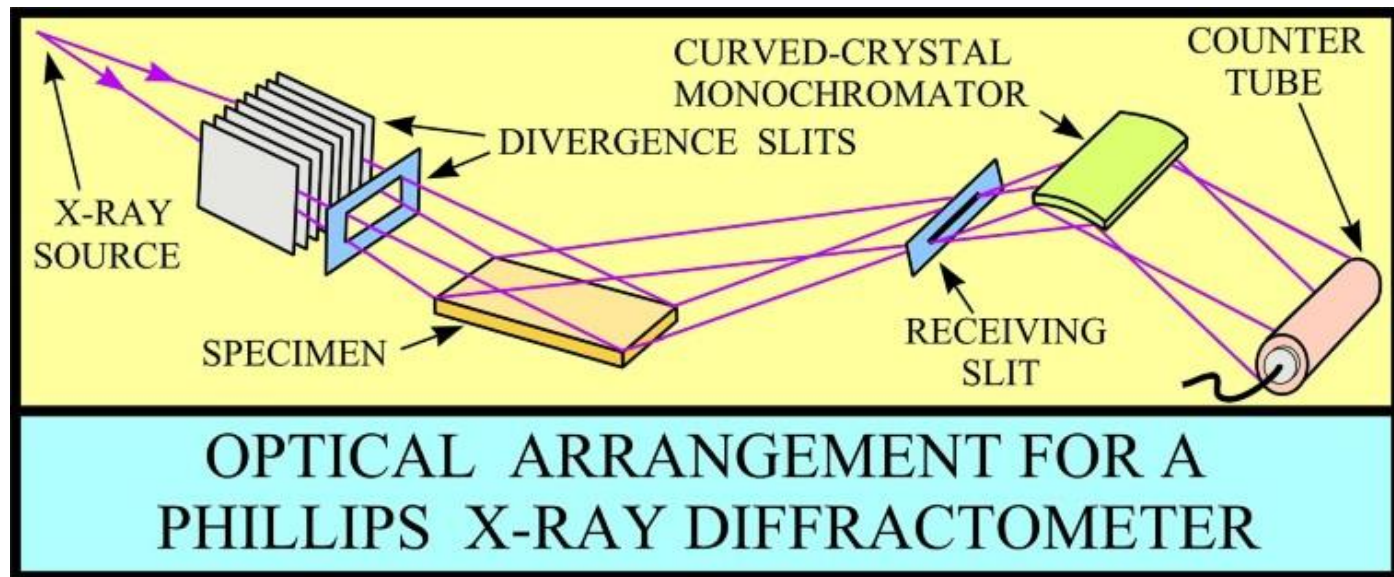
Extra low-angle
background

General background

Instrumentation

Optics

The fluorescence background is relatively constant, since it is not diffracted and angle independent, a fixed divergent slit can decrease this problem.



Instrumentation

Optics

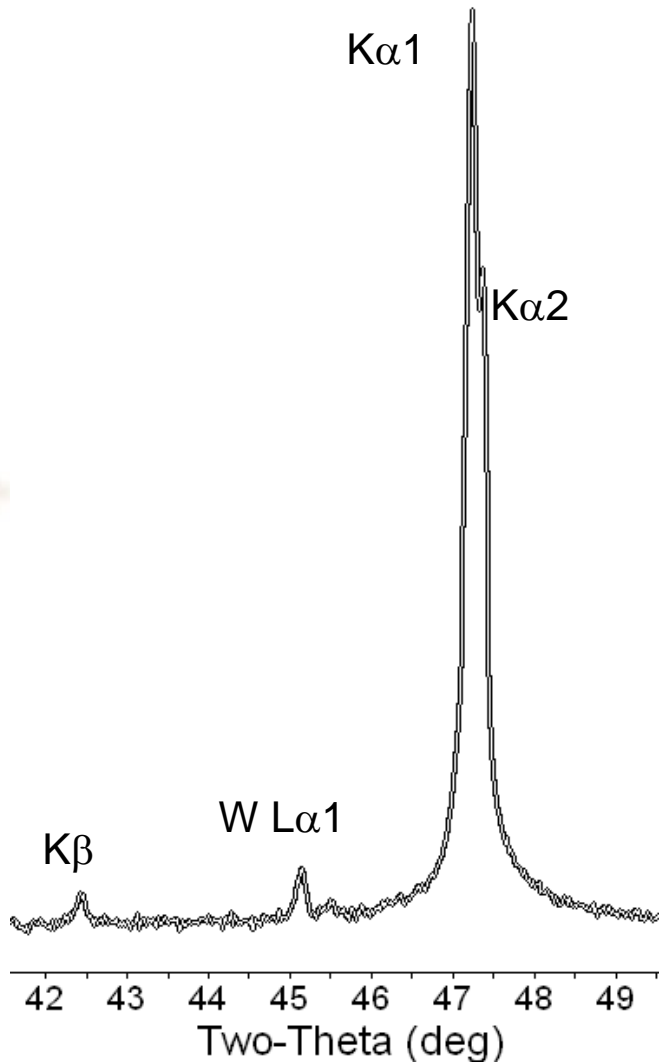
Additional lines in the diffraction pattern occur because of an impure source. These can include Fe $K\alpha$, W $L\alpha$, and W $L\beta$.

Potential interfering Lines for Quartz

| d-Value | (hkl) | 2θ | | | |
|---------|---------|--------------|-------------|-------------|------------|
| | | Cu $K\alpha$ | Cu $K\beta$ | W $L\alpha$ | W $L\beta$ |
| 4.257 | (100) | 20.850 | 18.823 | 19.967 | 17.231 |
| 3.342 | (101) | 26.652 | 20.044 | 25.515 | 22.116 |
| 2.457 | (110) | 36.542 | 32.917 | 34.959 | 30.245 |
| 2.282 | (102) | 39.456 | 35.522 | 37.737 | 32.627 |
| 2.237 | (111) | 40.284 | 36.261 | 38.526 | 33.302 |

Instrumentation

Spectral Contamination in Diffraction Patterns

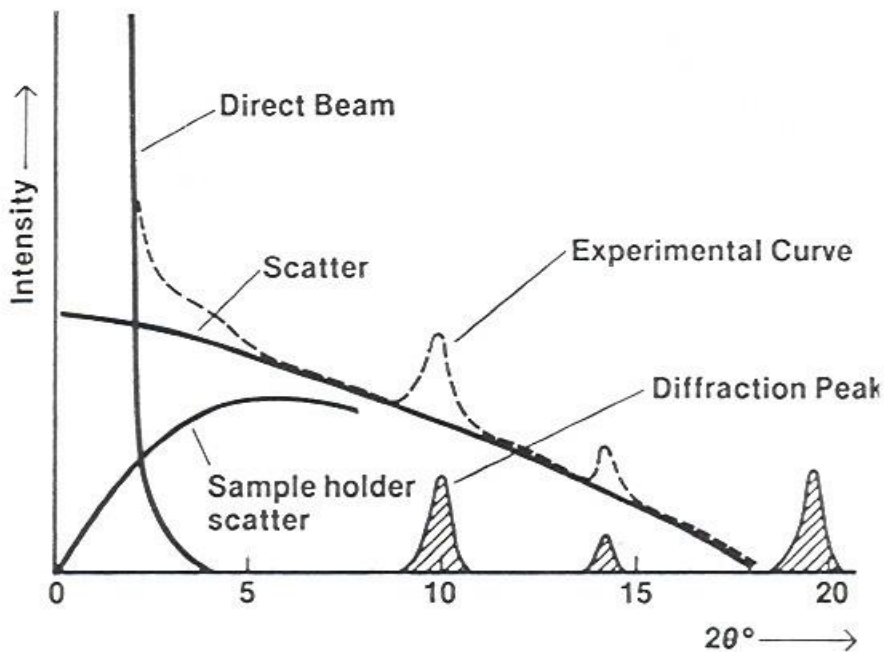


Additional lines in the diffraction pattern occur because of an impure source. These can include $Fe K\alpha$, $W\alpha$, and $W LB$.

Instrumentation

Optics

The low-angle region (0 to 20°) is especially difficult to clean up. The sample holder interferes at these angles.



Instrumentation

Optics

1. β - Filter

A bandpass device used mainly to improve the ratio of Cu $K\alpha$ to Cu $K\beta$.

If a polychromatic beam of radiation is passed through a filter, then preferential transmission of certain λ 's will occur.

So need to find materials that has an absorption edge between the $K\alpha$ doublet and the $K\beta$ doublet, to increase the α/β transmission ratio.

Instrumentation

1. β - Filter

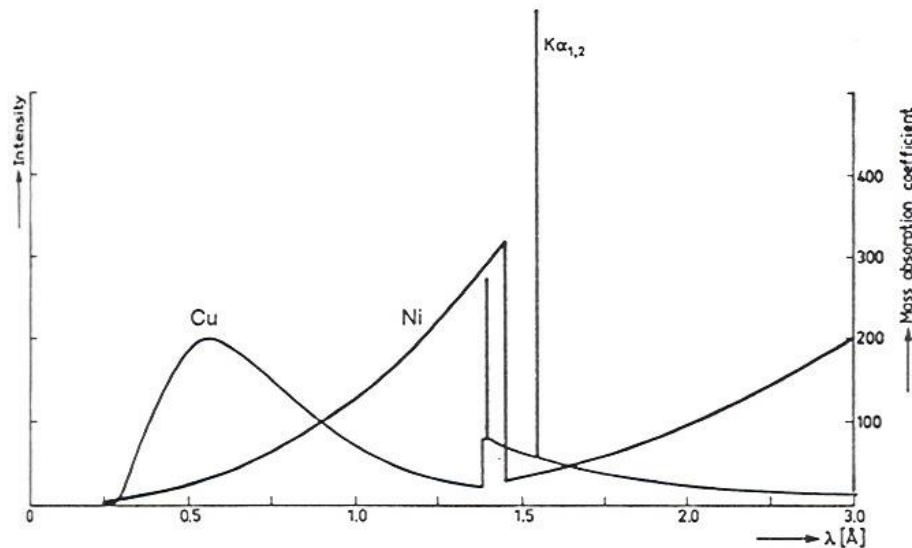
$K\beta$ and $K\alpha_2$ will cause extra peaks in XRD pattern, and shape changes, but can be eliminated by adding filters.

Instrumentation

Optics

1. β - Filter

For copper radiation, nickel is used since the nickel absorption edge (1.488 \AA) lies between the Cu $K\alpha$ (1.542 \AA) and Cu $K\beta$ (1.392 \AA) radiation.

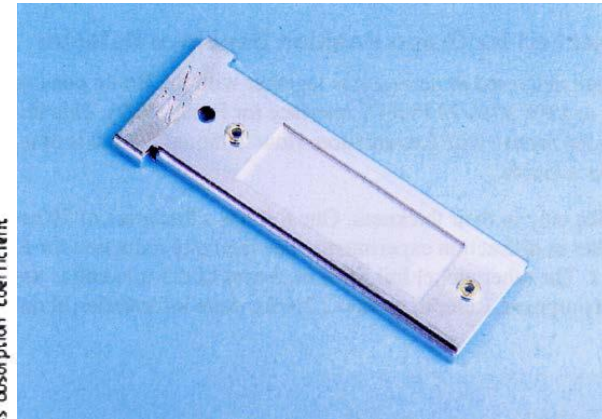
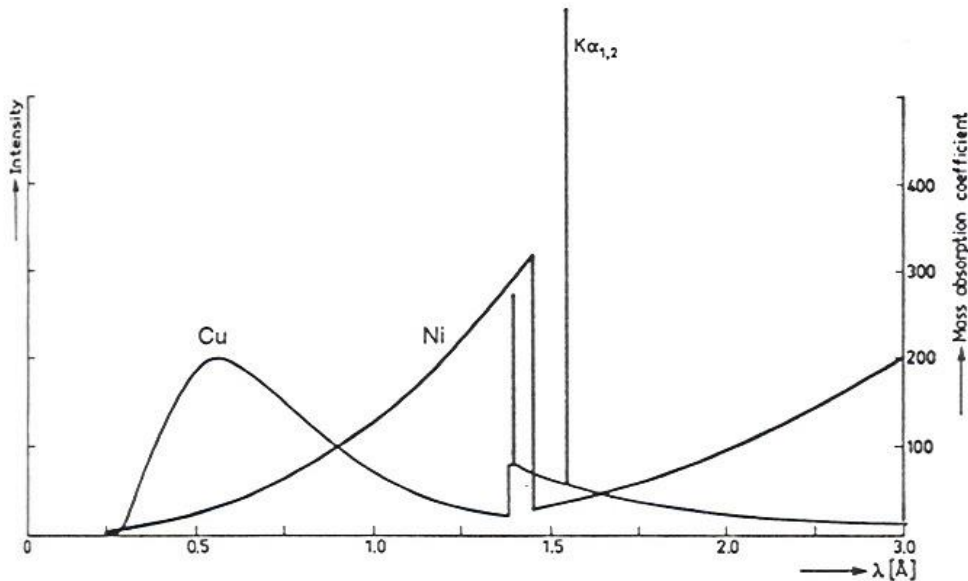


Instrumentation

Optics

1. β - Filter

The Cu $K\beta$ is strongly absorbed (mass attenuation coefficient = 286 cm^2/g) and the Cu $K\alpha$ is weakly absorbed (mass att. coef. = 49.2 cm^2/g).



Instrumentation

Optics

1. β – Filter

Also some of the less intense continuous radiation λ 's is absorbed, this helps decrease noise, since it cuts down on scatter.

| Target | $K\alpha$ (Å) | β -Filter | Thickness (μm) | Density (g/cc) | $K\alpha$ (%) | $K\beta$ (%) |
|--------|------------------|-----------------|--------------------------------|-------------------|------------------|-----------------|
| Cr | 2.291 | V | 11 | 6.0 | 58 | 3 |
| Fe | 1.937 | Mn | 11 | 7.43 | 59 | 3 |
| Co | 1.791 | Fe | 12 | 7.87 | 57 | 3 |
| Cu | 1.542 | Ni | 15 | 8.9 | 52 | 2 |
| Mo | 0.710 | Zr | 81 | 6.5 | 44 | 1 |

Instrumentation

Optics

1. β – Filter

Notice that the filter is about one atomic # less than the x-ray radiation source.

| Target | $K\alpha$ (Å) | β -Filter | Thickness (μm) | Density (g/cc) | $K\alpha$ (%) | $K\beta$ (%) |
|--------|------------------|-----------------|--------------------------------|-------------------|------------------|-----------------|
| Cr | 2.291 | V | 11 | 6.0 | 58 | 3 |
| Fe | 1.937 | Mn | 11 | 7.43 | 59 | 3 |
| Co | 1.791 | Fe | 12 | 7.87 | 57 | 3 |
| Cu | 1.542 | Ni | 15 | 8.9 | 52 | 2 |
| Mo | 0.710 | Zr | 81 | 6.5 | 44 | 1 |

Instrumentation

Optics

1. β – Filter

The transmission efficiency of a filter of given thickness can be calculated by:

$$I = \exp[2 - (0.434 \mu \rho x)]$$

Where I = the % transmission

ρ = density

μ = mass att. coef.

x - thickness of filter

Instrumentation

Optics

1. β – Filter

For Cu radiation using a Ni filter of 15 μm , with a density of 8.92 g/cm^3 :

$$I_{\text{K}\alpha} = \exp[2 - (0.434 \times 49.2 \text{ cm}^2/\text{g} \times 8.92 \text{ g}/\text{cm}^3 \times 0.0015 \text{ cm})]$$

$$I_{\text{K}\alpha} = 52\%$$

$$I_{\text{K}\beta} = \exp[2 - (0.434 \times 286 \text{ cm}^2/\text{g} \times 8.92 \text{ g}/\text{cm}^3 \times 0.0015 \text{ cm})] = 2\%$$

Usually a filter thickness that gives a ratio of $\text{K}\alpha/\text{K}\beta = 50:1$ or $25:1$ is employed.

Instrumentation

Optics

1. β – Filter

Balanced - Filter Technique

Alternate between two filters whose absorption edge lies just above and just below the λ of $K\alpha$ radiation, while taking the intensity measurements.

Take the difference of the plots, resulting plot is due to almost monochromatic λ .

Instrumentation

Optics

1. β – Filter

Example: for Cu $K\alpha$ (1.542 Å), use Ni (1.488 Å) for low wavelength side and Co (1.608 Å) for high λ side. The thickness of the two materials must be carefully adjusted, i.e Ni 0.0100 mm and Co 0.0108 mm.

This technique not used much anymore for regular diffraction scans, but still finds use in photographic (film) work.

Instrumentation

Optics

1. β – Filter

Of course can use a PHA (pulse height selector - electronics) alone or in conjunction with a β -filter to help eliminate β -radiation.

Or can use a monochromater.

Instrumentation

Optics

Various Slits

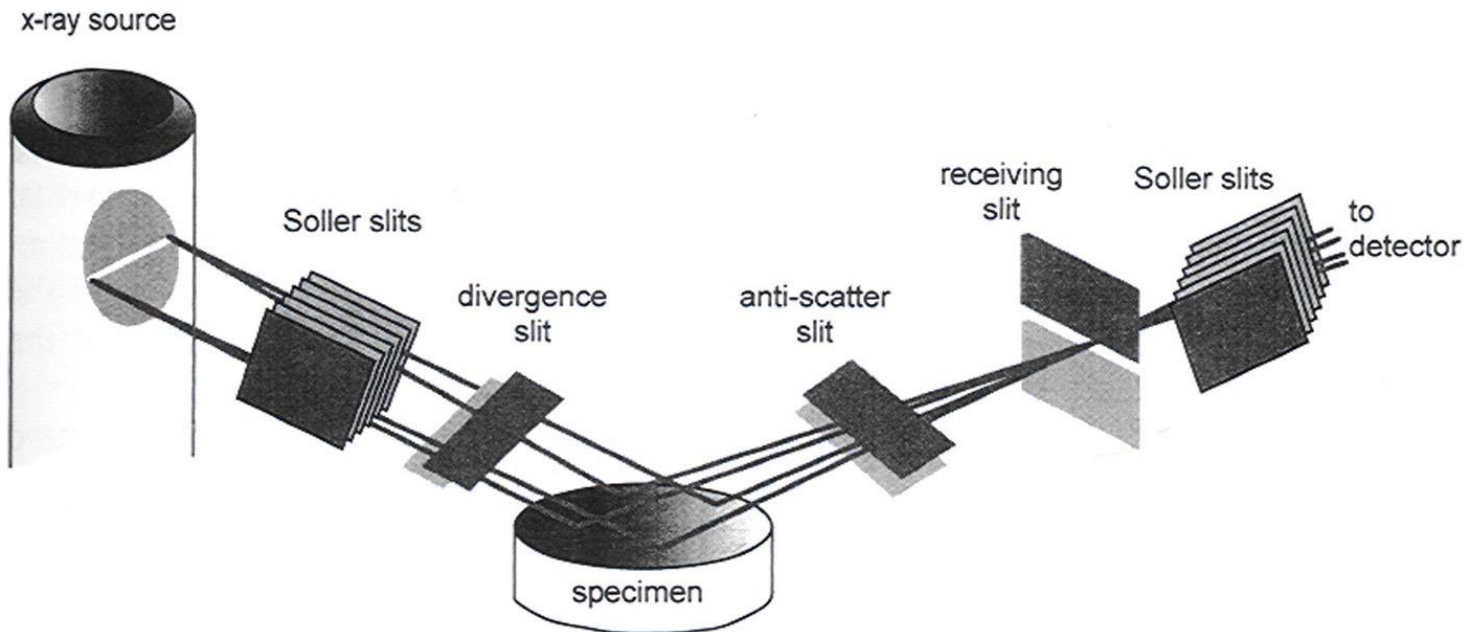
The x-ray radiation passes through a series of slits on both the source side and the detector side.

These slit width can be varied depending on the sample and x-ray scan parameters.

Instrumentation

Optics

Various Slits



Instrumentation

Optics

Various Slits

2. Soller slits – are a series of closely spaced metal plates which are parallel to each other. These plates collimate (make parallel) the incident beam.

The slits are typically 30 mm long and 0.05 mm thick, the distance between the plates is about 0.5 mm.

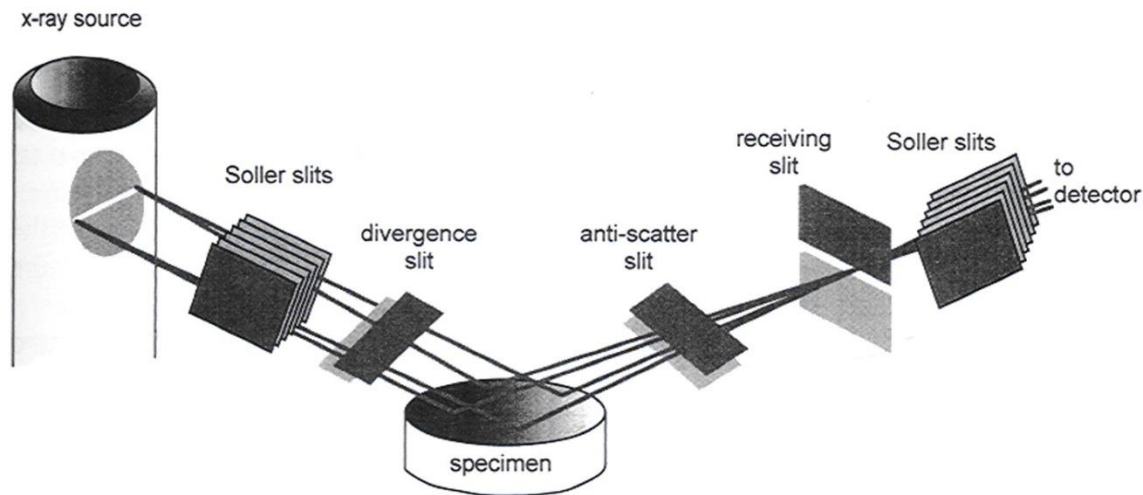
These plates are made up of a high atomic number element such as Mo or Ta.

Instrumentation

Optics

Various Slits

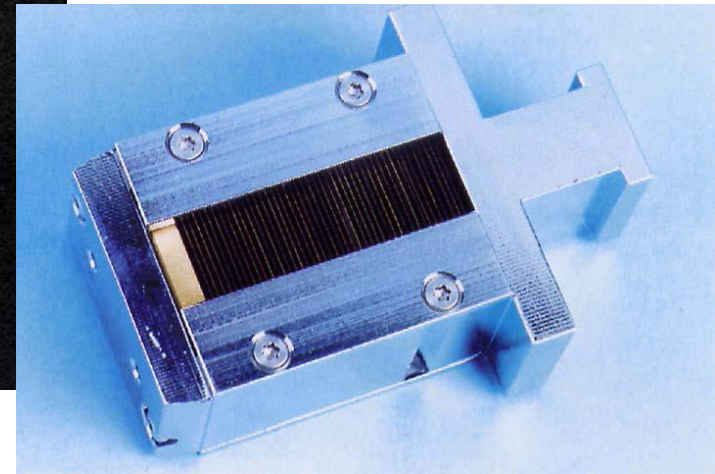
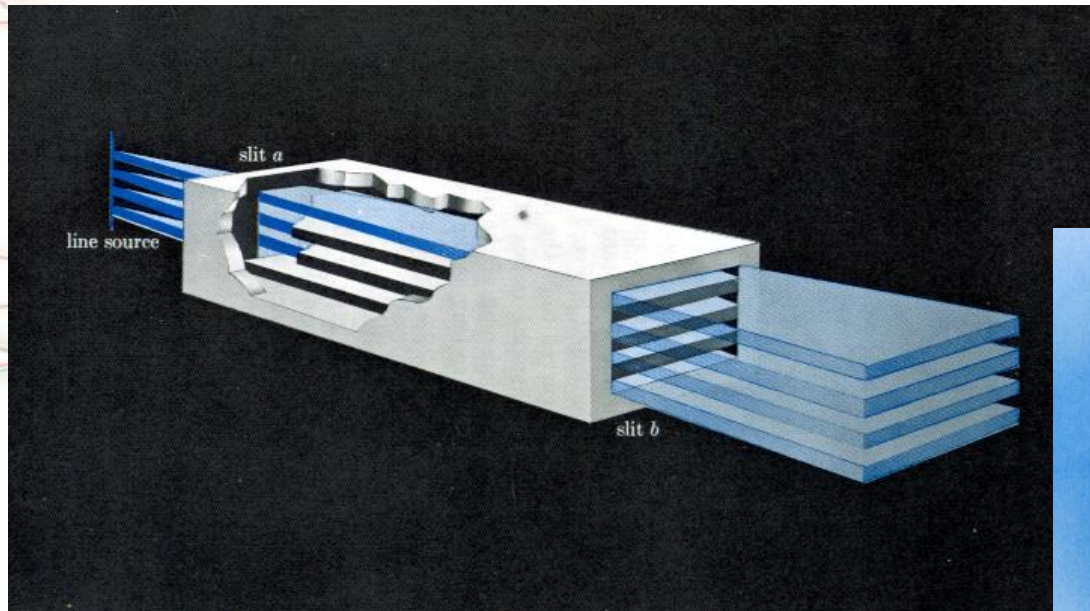
Soller slits – sometimes a second set is present before the monochromator.



Instrumentation

Optics

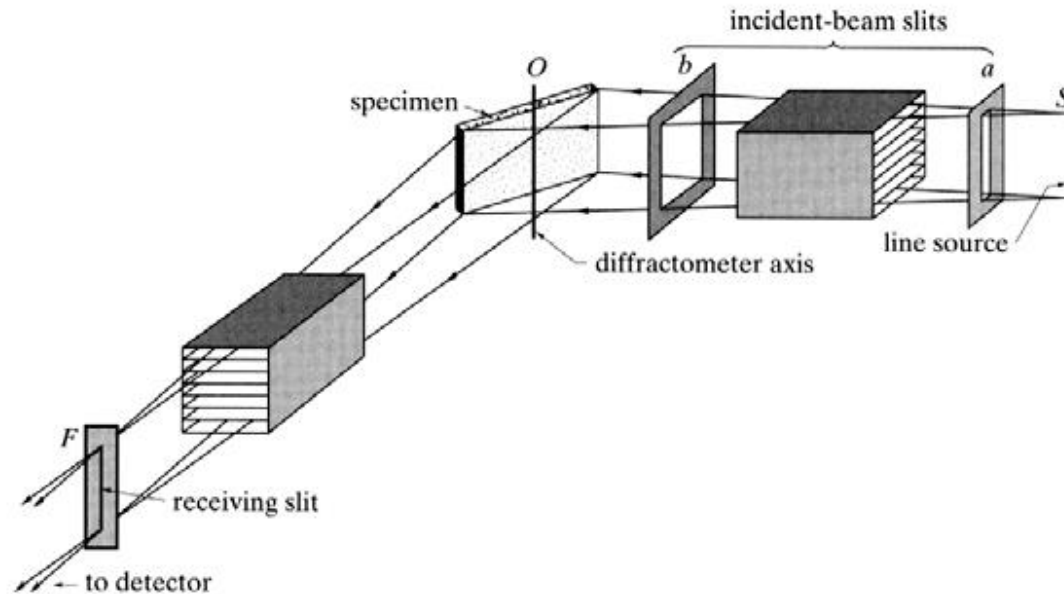
Soller slits - take a line source of radiation and slice it into smaller, parallel beams. This reduces axial divergence of the beam.



Instrumentation

Optics

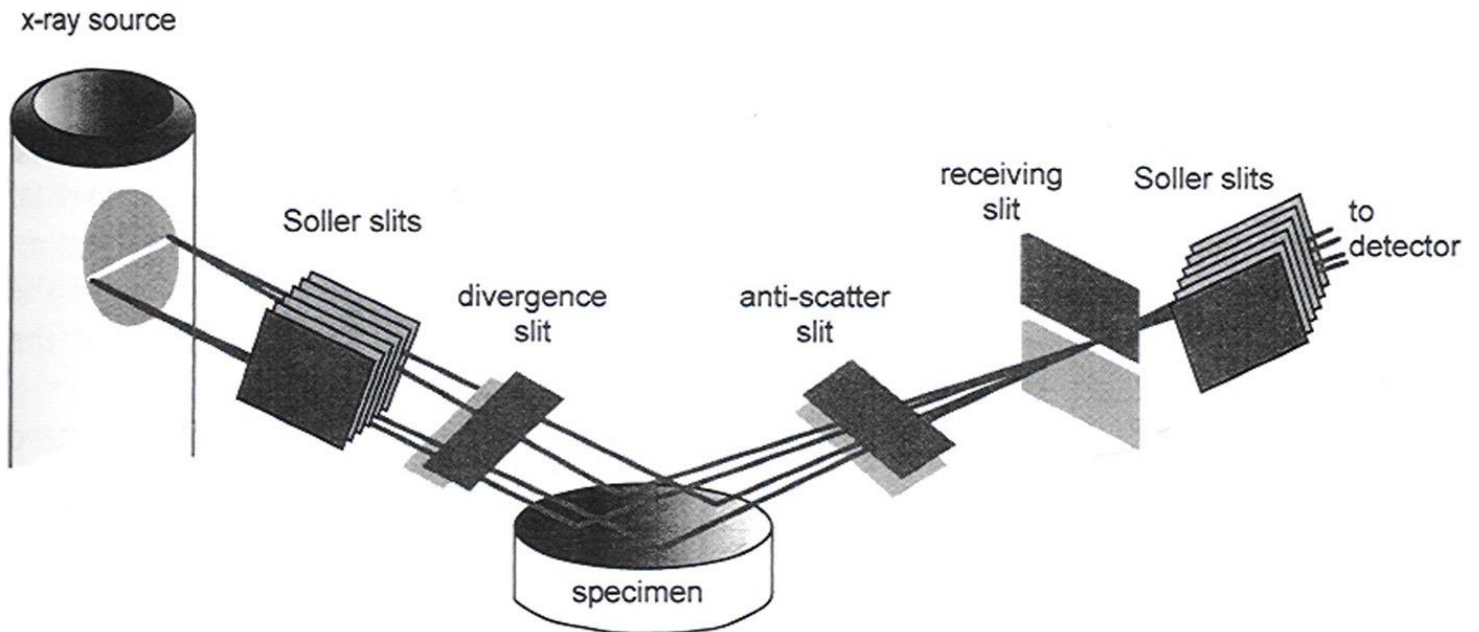
Soller slits - The sizes of the slits determine the intensity of the peaks measured in the diffraction pattern and also their shapes. Narrow slits reduce the intensity but they also produce sharper peaks.



Instrumentation

Optics

Various Slits



Instrumentation

Optics

Various Slits

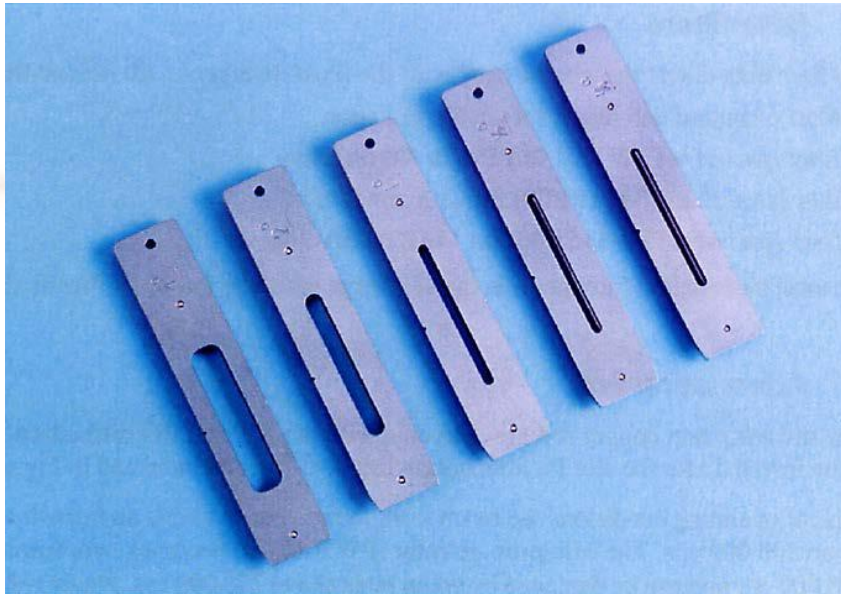
3. Divergence slit – defines the width of the incident beam.

Divergence slit - limits the vertical divergence of the x-ray beam, to irradiate as much as sample as possible while avoiding the sample support.

Instrumentation

Optics

Divergence slit – slits are fitted in the incident beam path to control the amount (length) of the sample that is irradiated by the incident x-ray beam. Can be fixed or variable.

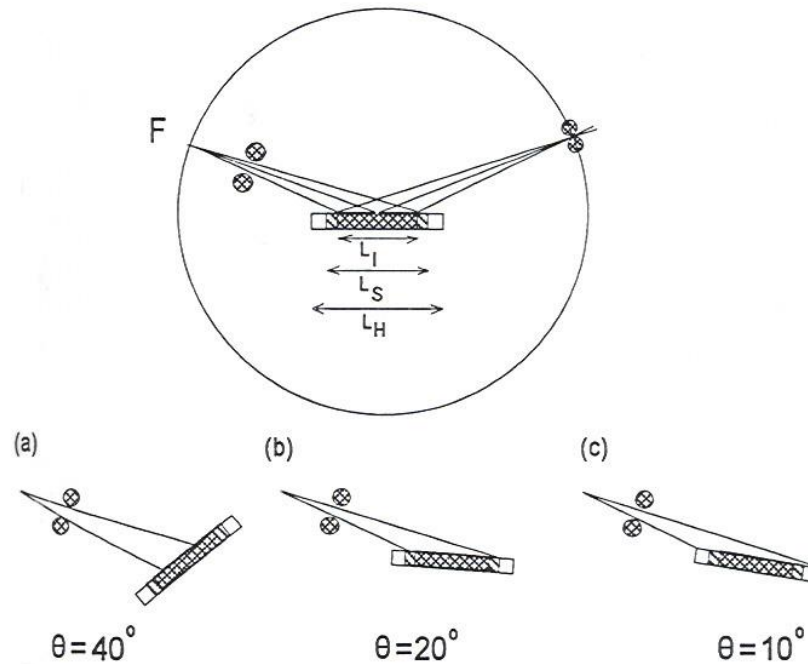


Instrumentation

Optics

Divergence slit

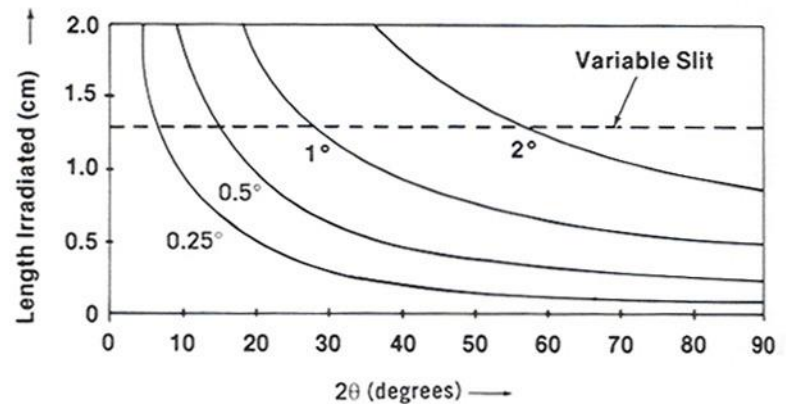
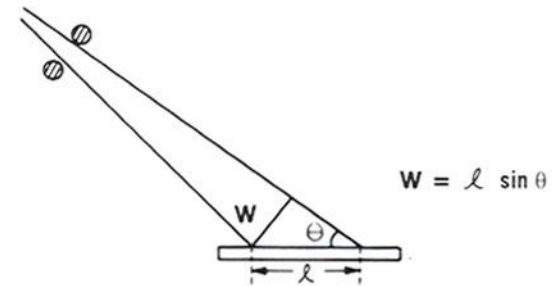
If the divergence slit is fixed, the irradiation area of the sample will change with angle.



Instrumentation

Optics

Divergence slit



At 40° , only the sample is irradiated

At 20° , sample and some support is irradiated, increasing background.

At 10° , larger part of sample holder is irradiated, increase background.

Instrumentation

D. Optics

Divergence slit

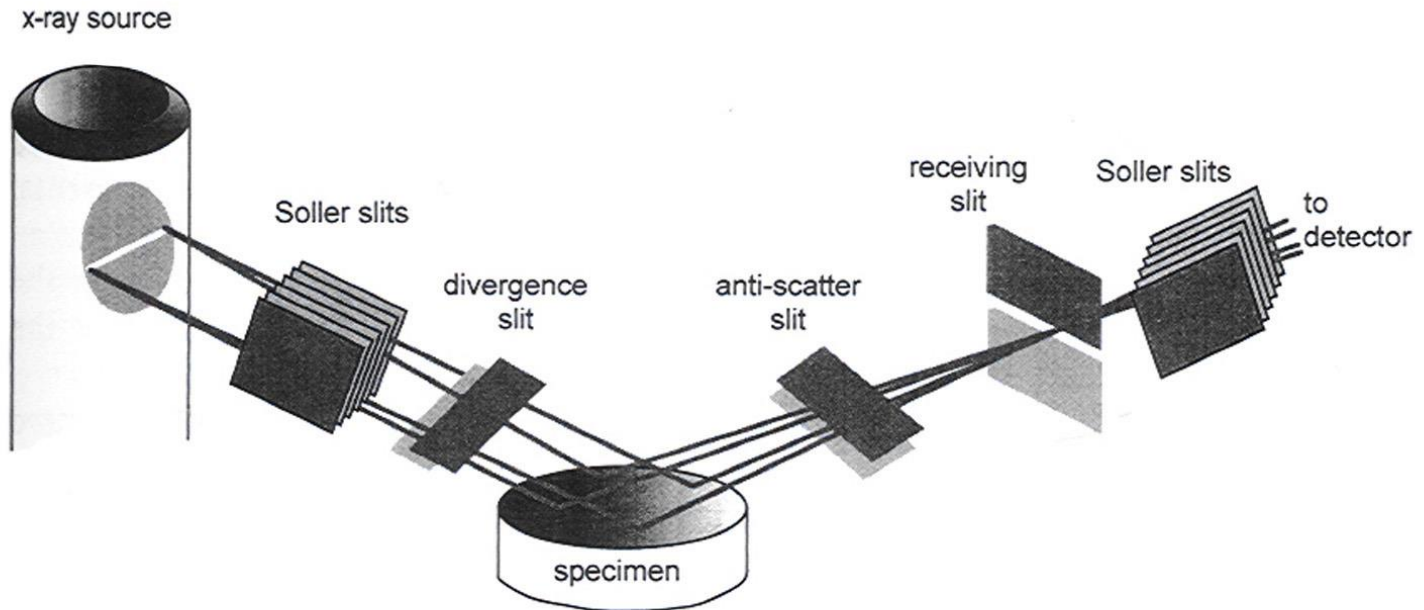
Too wide a divergence slit, or too small a sample holder, can lead to a small scatter peak (ghost) at $4\text{-}5^\circ 2\theta$, which can be confused with a clay peak.

So the choice of divergence slit is critical, especially at low angles.

Instrumentation

Optics

4. Antiscatter slits – reduces background radiation.



Instrumentation

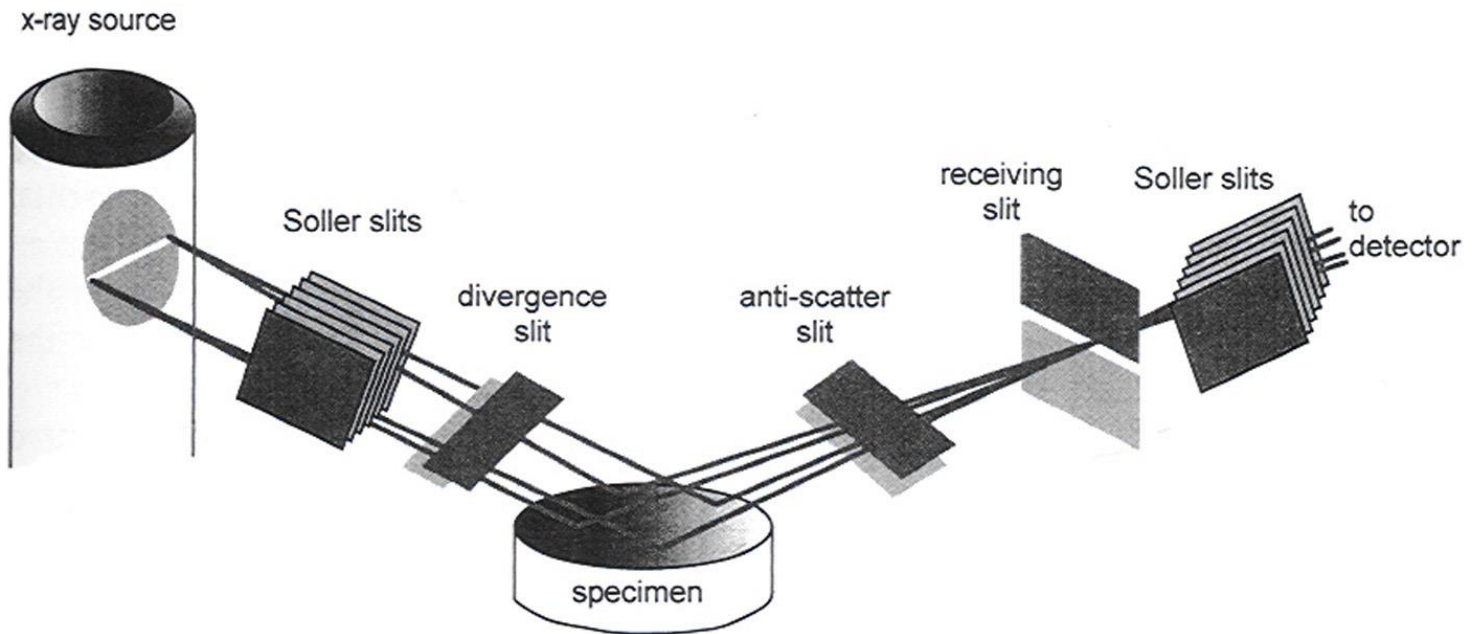
Optics

Antiscatter slits – The anti-scatter slit not only reduces the height divergence but also reduces diffusely scattered x-rays which are due to amorphous or air scattering. This results in a reduction in noise of the output.

Instrumentation

Optics

Various Slits



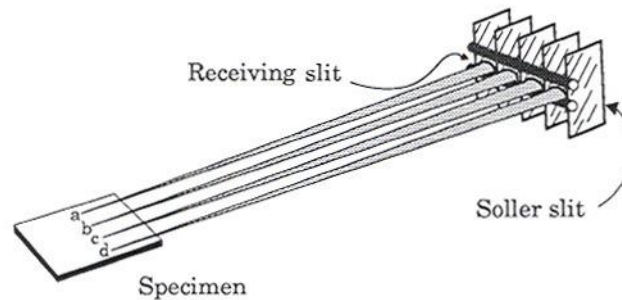
Instrumentation

Optics

Various Slits

5. Receiving slit – defines the width of the diffracted beam.

The receiving slit size can be varied, and has a dramatic effect on the peak shape and intensity.



Instrumentation

Optics

Receiving slits



Instrumentation

Optics

Receiving slit

There is only one optimum size receiving slit.
Want to choose the beam width close in size to the receiving slit for optimum intensity and resolution.

Receiving slit is smaller than the beam width - intensity is reduced with slight improvement of resolution.

Receiving slit is larger than the beam width - slight increase in intensity but very poor resolution.

Instrumentation

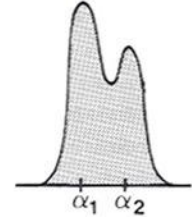
Optics

Receiving slit

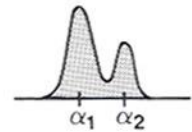
Receiving slit is smaller than the beam width - intensity is reduced with slight improvement of resolution.

Receiving slit is larger than the beam width - slight increase in intensity but very poor resolution.

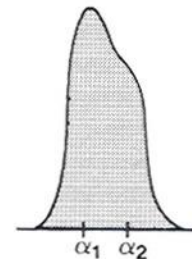
(a) Beam is exactly coincident with receiving slit



(b) Receiving slit smaller than image



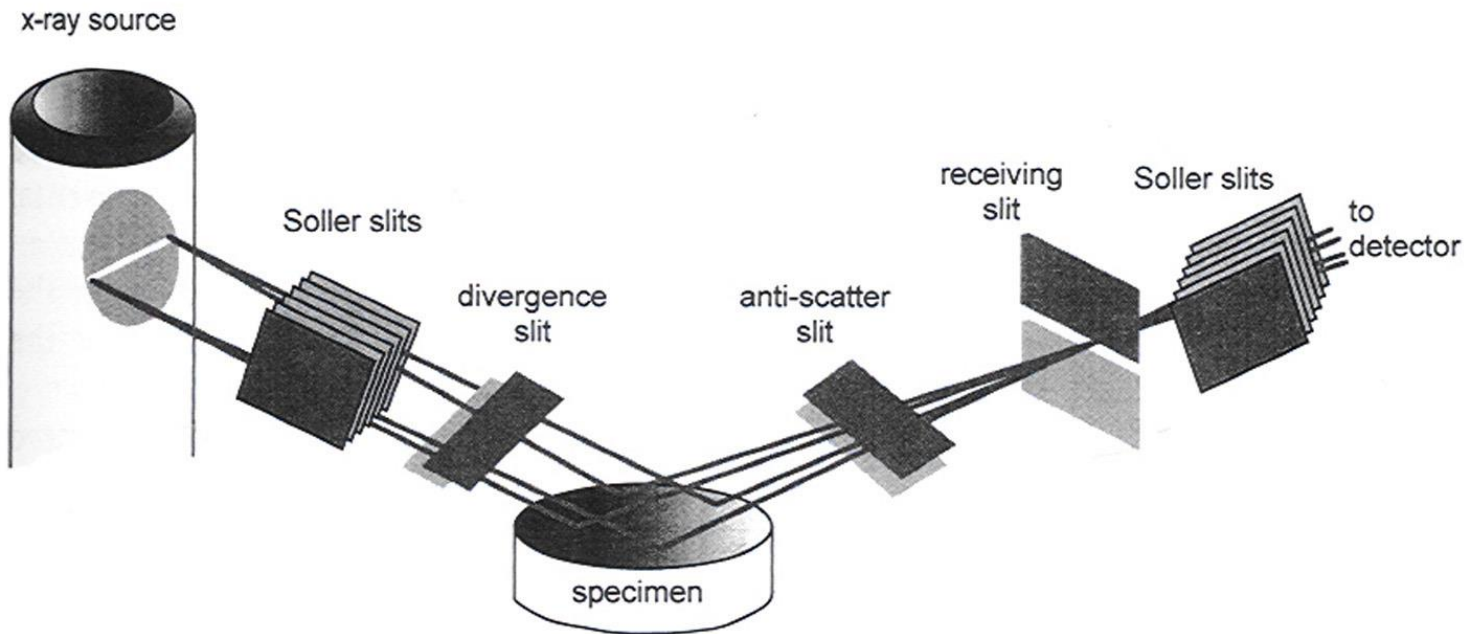
(c) Receiving slit larger than image



Instrumentation

Optics

Various Slits



Instrumentation

Optics

Various Slits

6. Detector slit - a slit situated right before the detector. This slit is part of the monochromator system and can be adjusted to allow the α doublet to pass through the slit, while excluding the β radiation.

Instrumentation

Optics

Monochromators

Remove unwanted radiation.

The crystals used for monochromators need to be mechanically strong, not affected by exposure to x-rays, and stable in air.

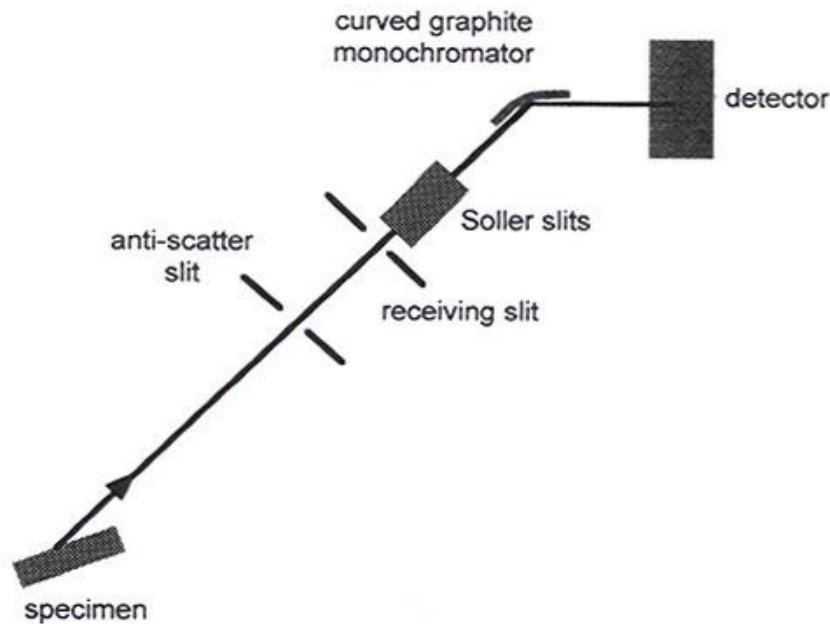
Plane crystal monochromators are used in camera work, while curve (bent) crystal monochromators are used in powder diffractometers.

Instrumentation

Optics

Monochromators

Curved crystal monochromators provide monochromatic radiation with low background, and furnish high intensity (compared to plane) and high resolving power. Materials used as crystals are: mica, gypsum, quartz, graphite, Si, Ge, LiCl.

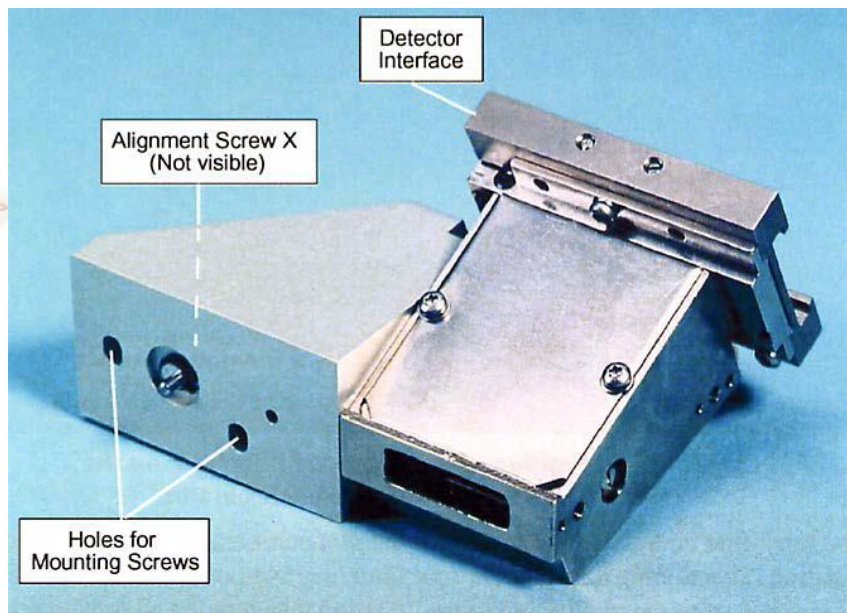


Instrumentation

Optics

Curved crystal monochromators

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) pyrolytic graphite crystal.



Instrumentation

Optics

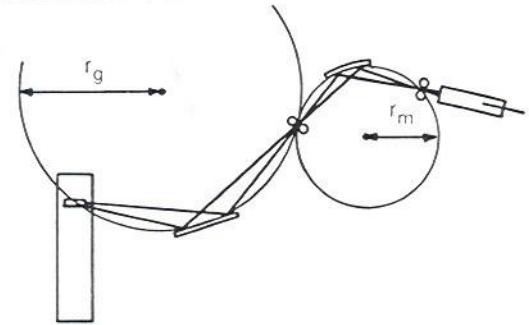
Monochromators

Most common configurations of the monochromator are parallel, antiparallel, and primary beam.

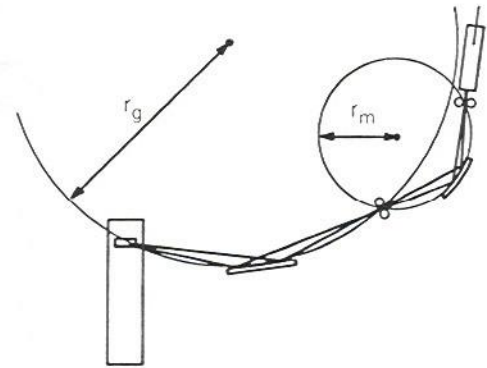
r_g – radius of the goniometer circle.

r_m – radius of the monochromator circle.

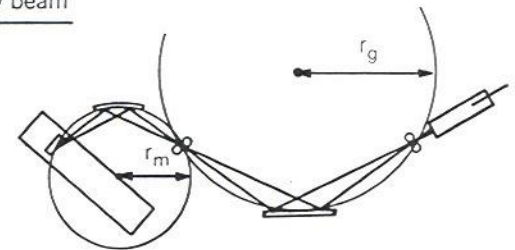
(a) Diffracted-beam, parallel



(b) Diffracted-beam, antiparallel



(c) Primary beam



Instrumentation

Optics

Monochromators

The antiparallel puts the lowest torque on the detector arm.

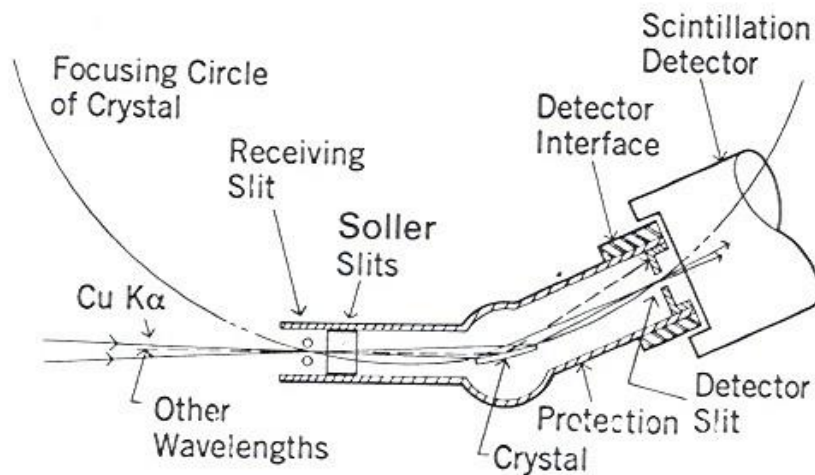
Primary beam monochromator main advantage is the ability to isolate the $K\alpha_1$ from the $K\alpha_2$. Disadvantage much more difficult to align.

Instrumentation

Optics

Monochromators

Diffracted beam monochromator is made up of: a receiving slit, with a single crystal behind that, the detector is set at an angle to collect the λ of interest diffracted by the crystal. The surface of the crystal, receiving slit, and detector slit all lie on the focusing circle of the monochromator.



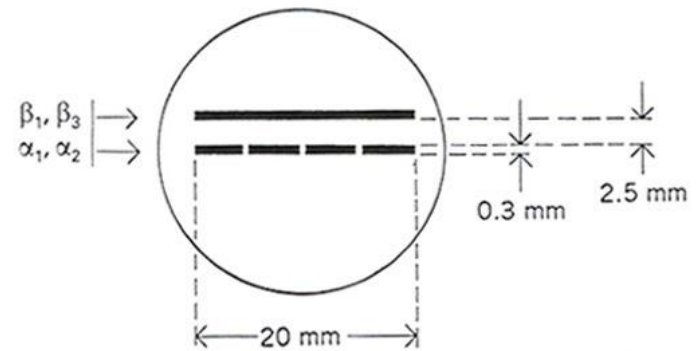
Instrumentation

Optics

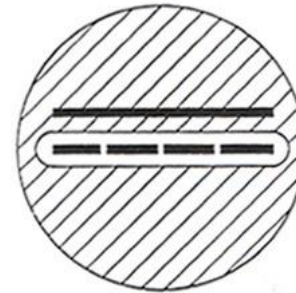
Monochromators

If the monochromator is correctly aligned, the α doublet is exactly at the center of the detector slit, while the β radiation would miss the slit.

Intensity Distribution at Detector Window



Intensity Distribution passed by Detector Slit



Instrumentation

Optics

Monochromators

a. Graphite crystal – suppress the background radiation, i.e. fluorescence from the sample.

The crystal is oriented to diffract only $K\alpha$ radiation.

It is pyrolytic graphite with the hexagonal basal planes aligned parallel.

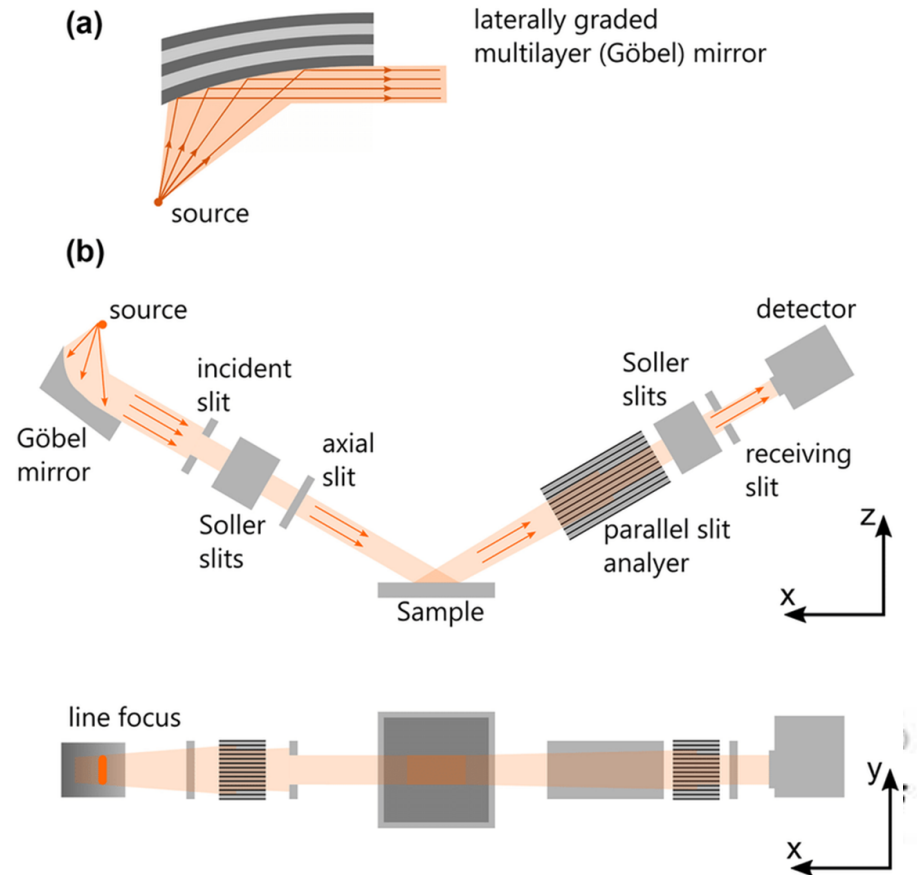
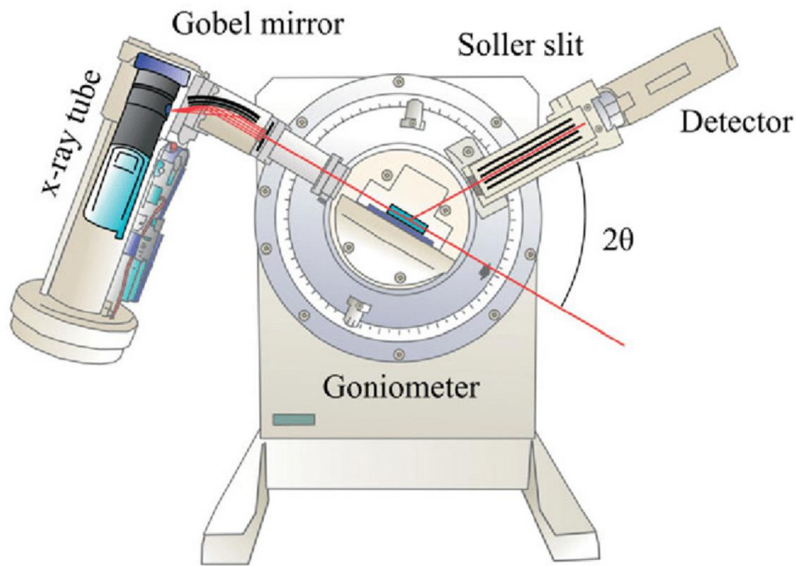
It is 4-6 times more reflective than the LiF crystal and gives a more uniform distributed diffracted beam.

Instrumentation

Optics

Mirrors

If an instrument setup does not use a monochromator, it may use Gobel mirrors instead and have the ability for a parallel beam (PB) setup.

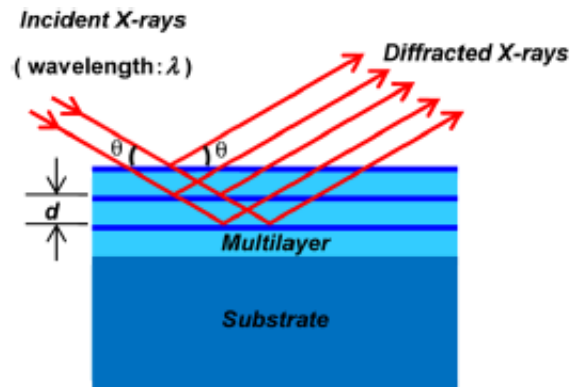


Instrumentation

Optics

Mirrors

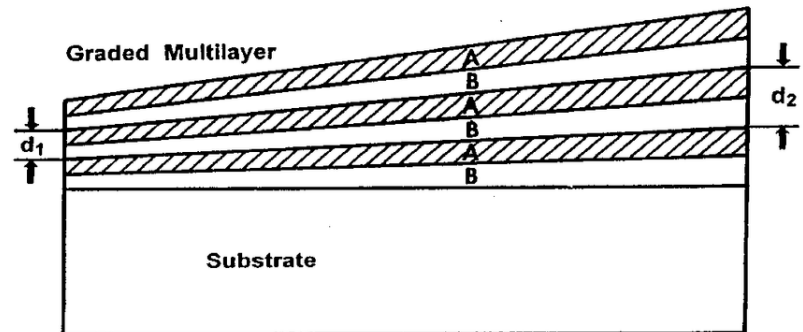
Gobel mirrors are made of a multilayer film, where the periodic thickness of the multilayer continuously changes along a parabolic surface.



$$\text{Bragg equation: } 2d \sin\theta = n\lambda$$

(d : interplanar spacing, θ : incident angle,

n : integer, λ : wavelength)



Instrumentation

Optics

Mirrors

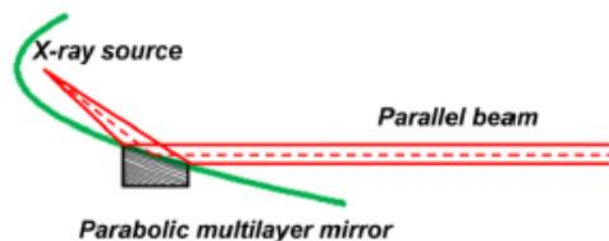


Fig. 2. Parabolic multilayer mirror.

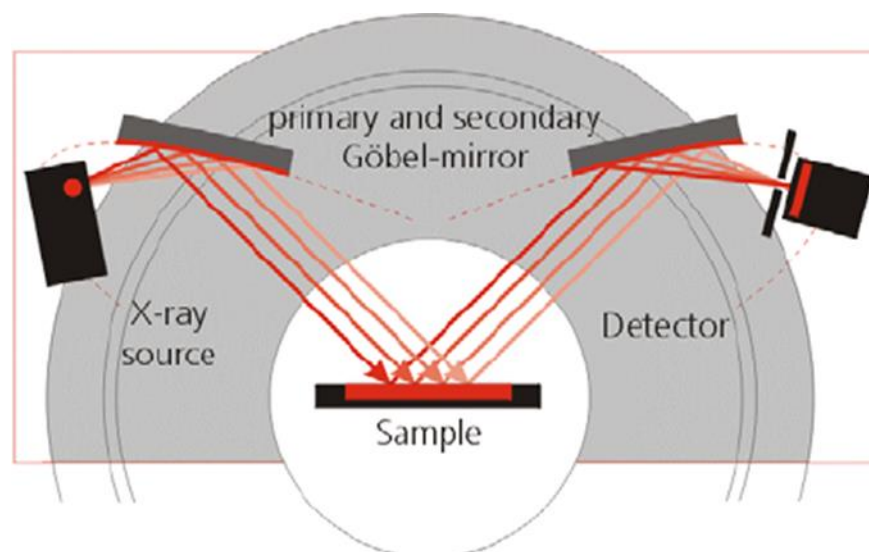


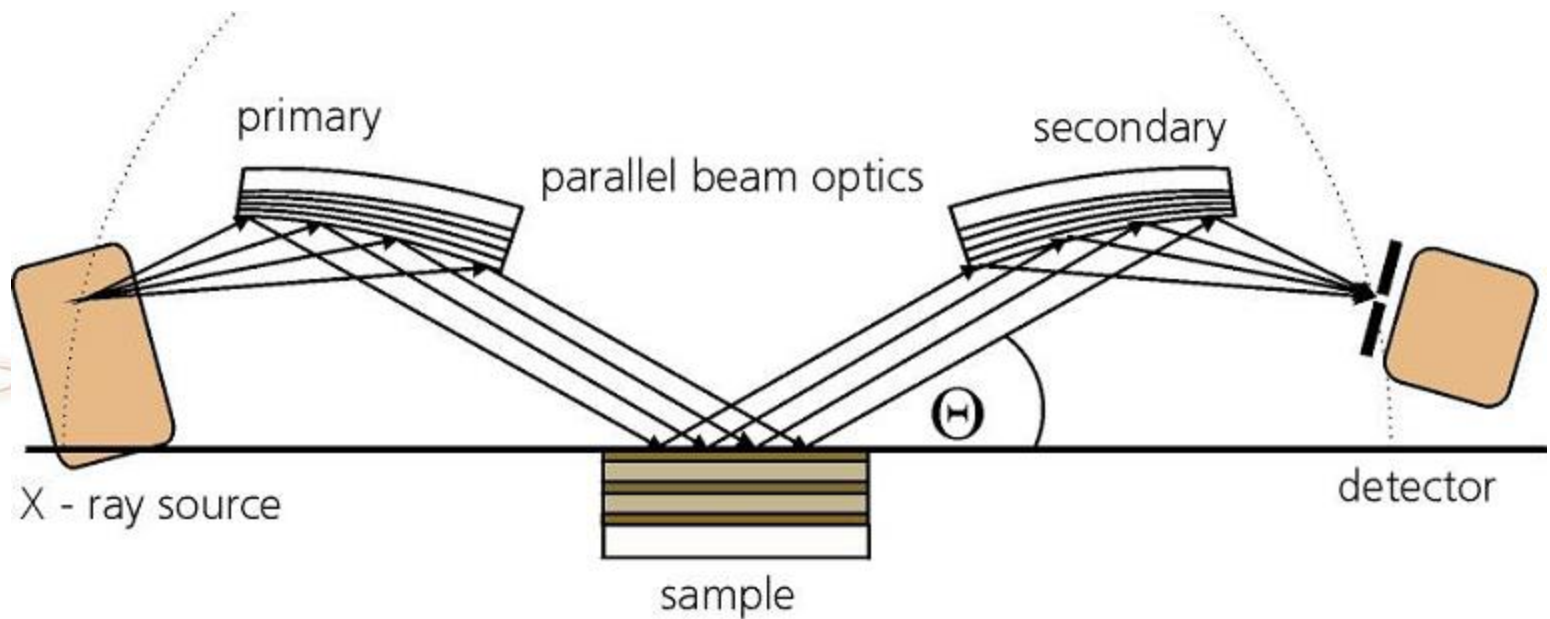
Table 1. Comparison of monochromatization methods.

| Monochromatic method | $K\beta/K\alpha$ intensity ratio | TDI measurement |
|-----------------------|----------------------------------|-----------------|
| $K\beta$ filter | Approx. 1% | Applicable |
| CBO- α | Below 0.2% | Applicable |
| Counter monochromator | Approx. 0.004% | N/A |

Instrumentation

Optics

Mirrors





Reading Assignment:

Read Chapter 3-5, 6, 7, 9, and 13 from:

-Introduction to X-ray powder

Diffraction by Jenkins and Snyder

Read Chapter 3, 4, 6, 13, and 14 from

-Elements of X-ray Diffraction

by Cullity and Stock

Read Chapter 2 from Norton

Homework 5 Due 10/17/24 – Solving a Cubic System

