chem 5390

Advanced X-ray Analysis

LECTURE 9

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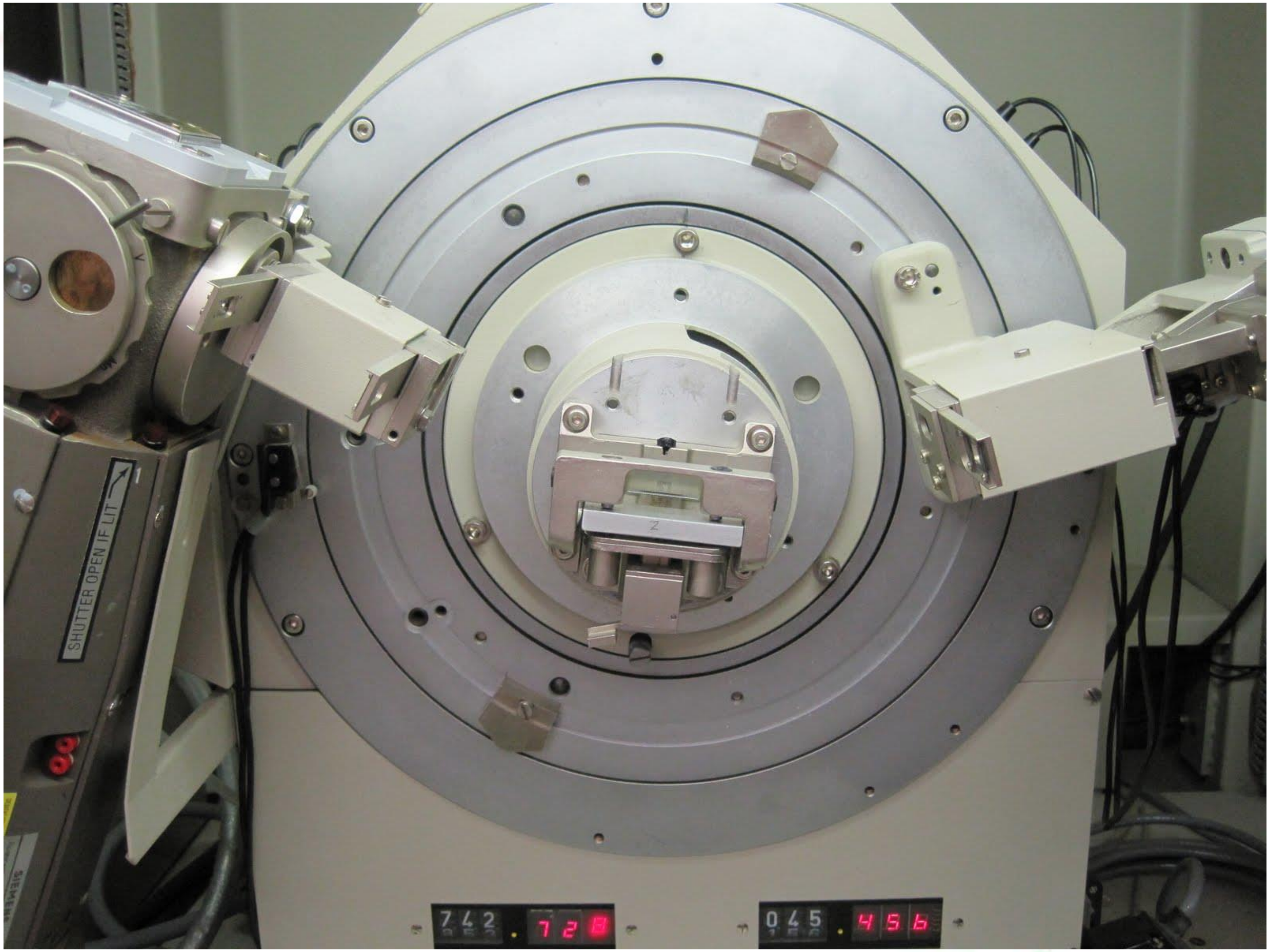
Instrumentation



Instrumentation

D. Optics

Includes a variety of slits, filters, monochromaters

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

D. 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, monochromater, 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

D. 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

D. 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 (30-60º), there is partial resolution, leading to distortion of the line profiles.

Instrumentation

D. 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

D. Optics

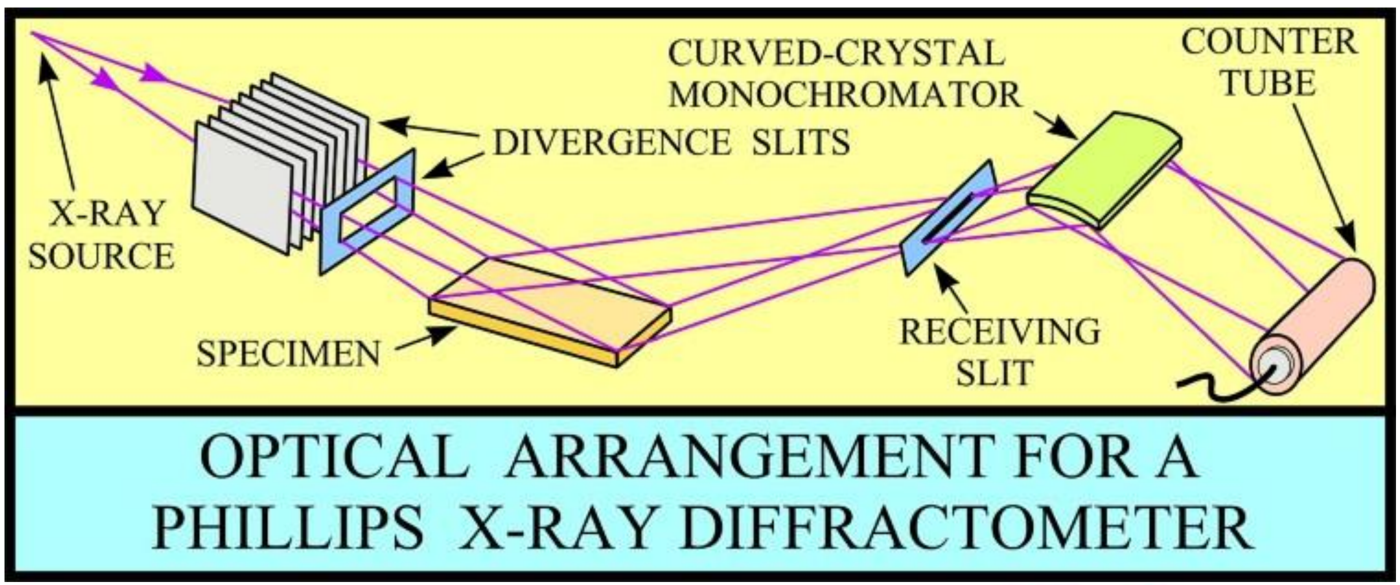
Besides the wanted x-ray wavelengths, a diffraction pattern is also made up of scatter and fluorescence.

Source	Result
Diffraction of required λ	Wanted peaks
Diffraction of other λ's	Unwanted peaks
Coherent scatter from sample	General background
Incoherent scatter from sample	General background
Scatter from sample support	Extra low-angle background
Fluorescence from sample	General background

Instrumentation

D. Optics

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



Instrumentation

D. Optics

Additional lines in the diffraction pattern occur because of an impure source. These can include Fe Kα, W Lα, and W LB.

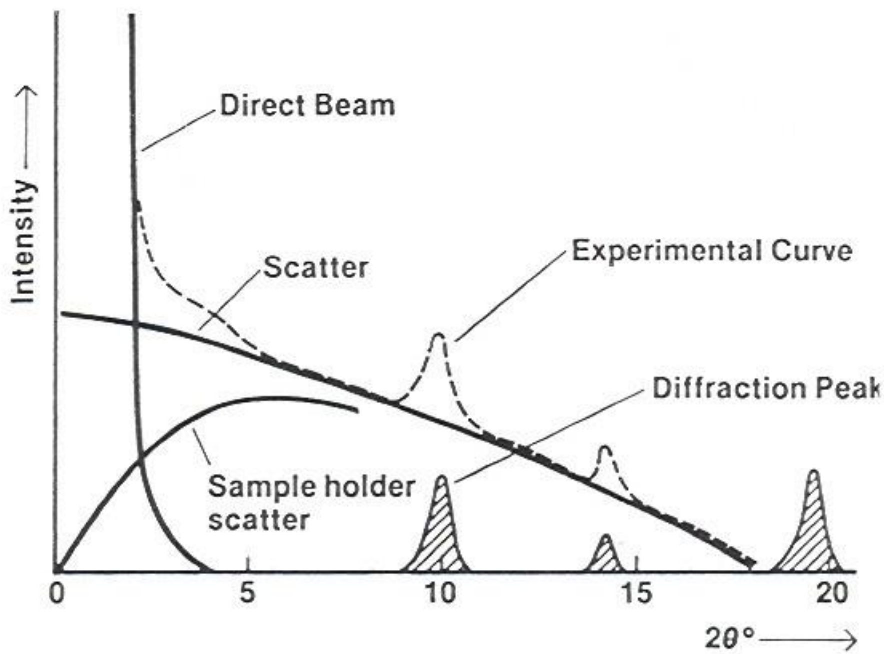
Potential interfering Lines for Quartz

		2θ			
d-Value	(*hkl*)	Cu *Kα*	Cu *Kβ*	W *Lα*	W *Lβ*
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

D. Optics

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



Instrumentation

D. Optics

1. β - Filter

A bandpass device used mainly to improve the ratio of Cu Kα to Cu Kβ.

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

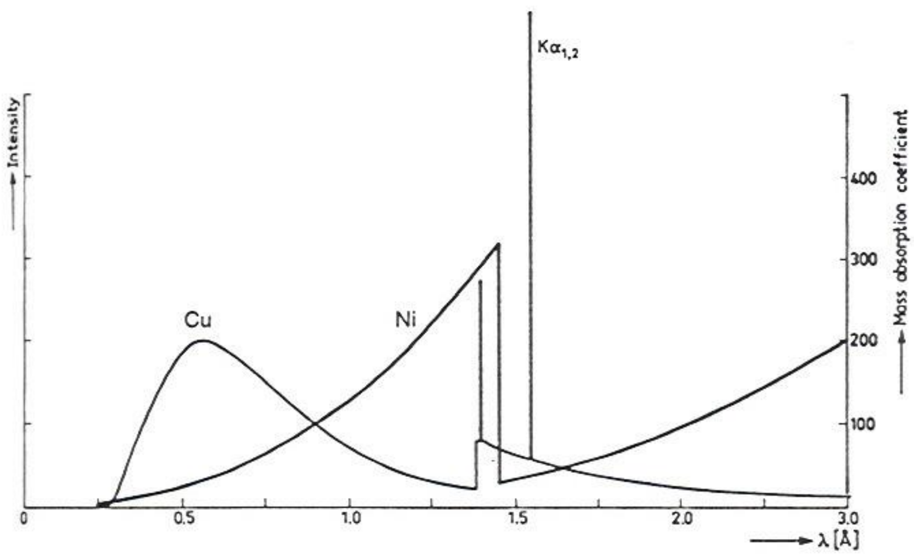
So need to find materials that has an absorption edge between the Kα doublet and the Kβ doublet, to increase the α/β transmission ratio.

Instrumentation

D. Optics

1. β - Filter

For copper radiation, nickel is used since the nickel absorption edge (1.488 Å) lies between the Cu Kα (1.542 Å) and Cu Kβ (1.392 Å) radiation.

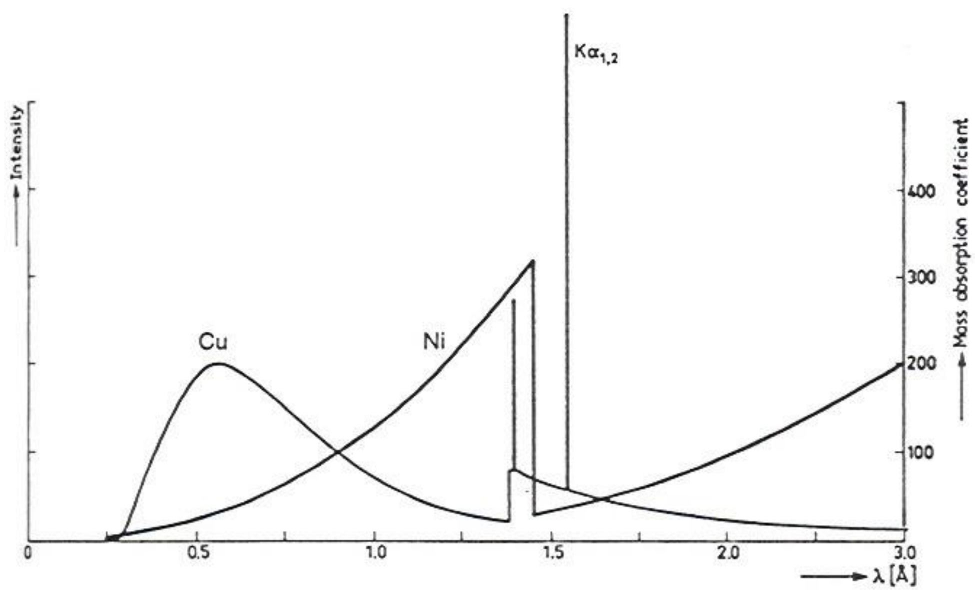


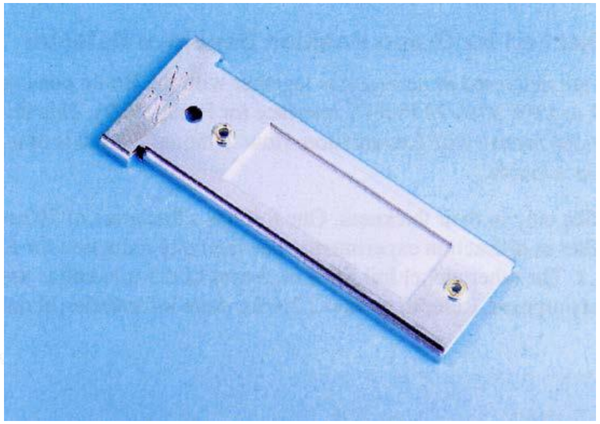
Instrumentation

D. Optics

1. β - Filter

The Cu Kβ is strongly absorbed (mass attenuation coefficient = 286 cm^2/g) and the Cu Kα is weakly absorbed (mass att. coef. = 49.2 cm^2/g).





Instrumentation

D. 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

D. 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
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Mo	0.710	Zr	81	6.5	44	1

Instrumentation

D. 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

D. Optics

1. β – Filter

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

$$I_{K\alpha} = \exp[2 - (0.434 \times 49.2\ cm^2/g \times 8.92\ g/cm^3 \times 0.0015\ cm)]$$
$$I_{K\alpha} = 52\%$$

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

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

Instrumentation

D. Optics

1. β – Filter

Balanced - Filter Technique

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

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

Instrumentation

D. Optics

1. β – Filter

Example: for Cu Kα (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

D. 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

D. Optics

2. Various Slits

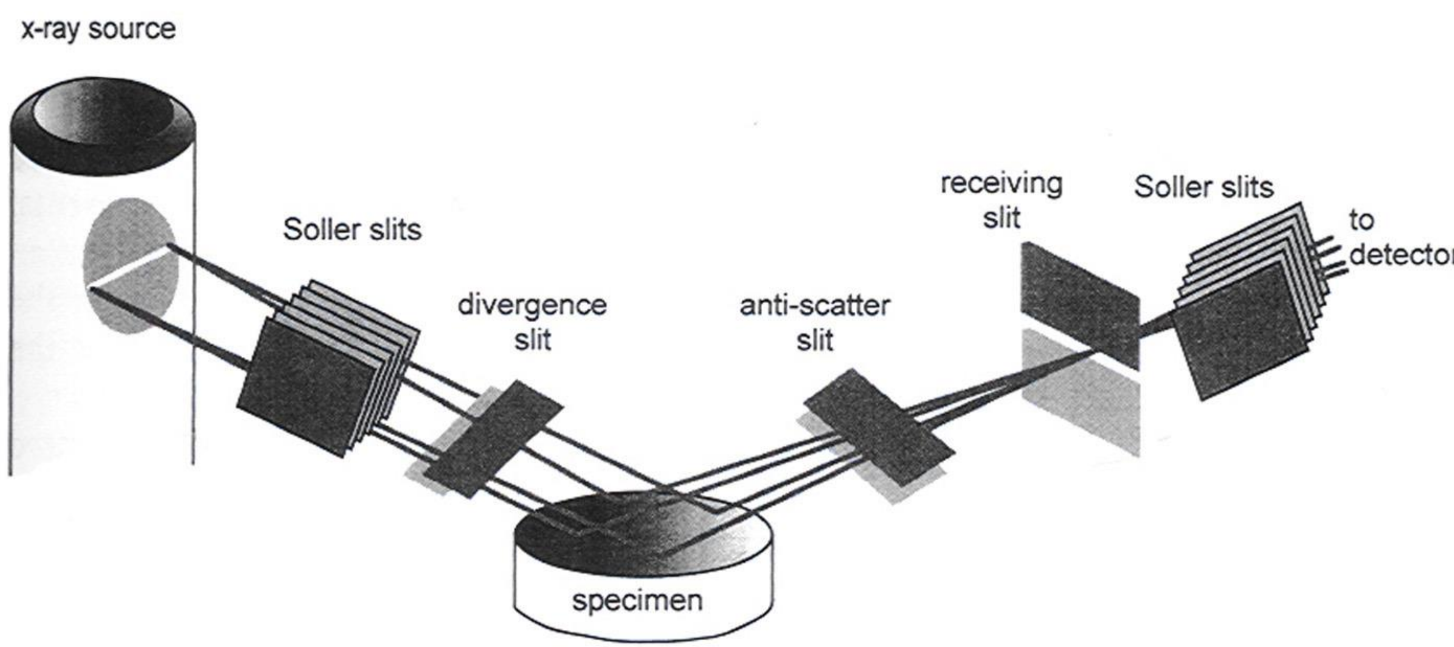
The x-ray radiation passes through a series of slits on both the source side and the detector side.

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

Instrumentation

D. Optics

2. Various Slits



Instrumentation

D. Optics

2. Various Slits

<u>Soller slits</u> – 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.

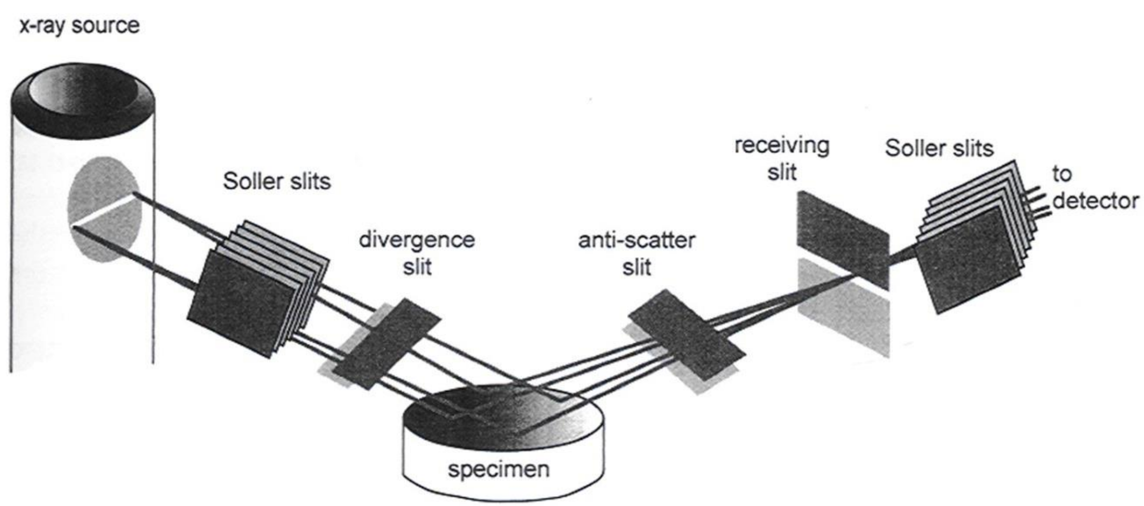
These plates are made up of a high atomic number element such as Mo or Ta.

Instrumentation

D. Optics

2. Various Slits

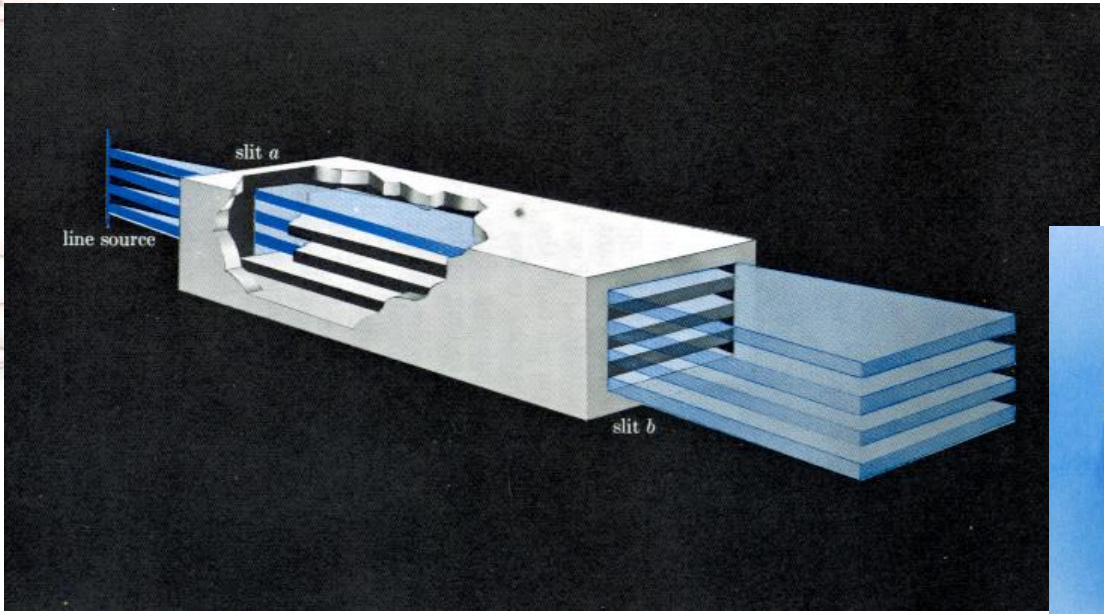
<u>Soller slits</u> – sometimes a second set is present before the monochromator.

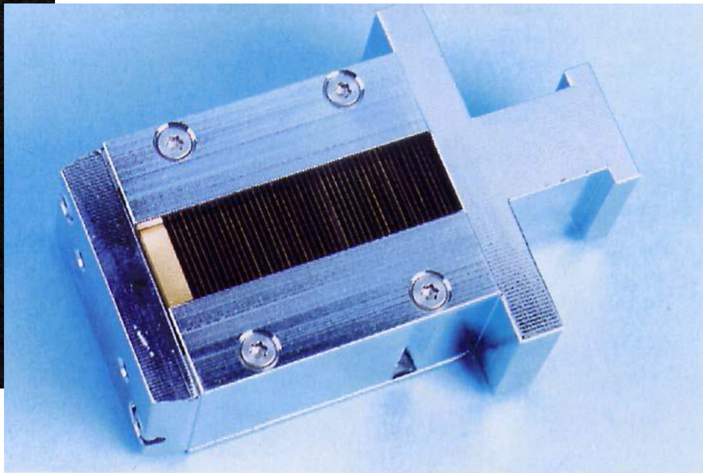


Instrumentation

D. Optics

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

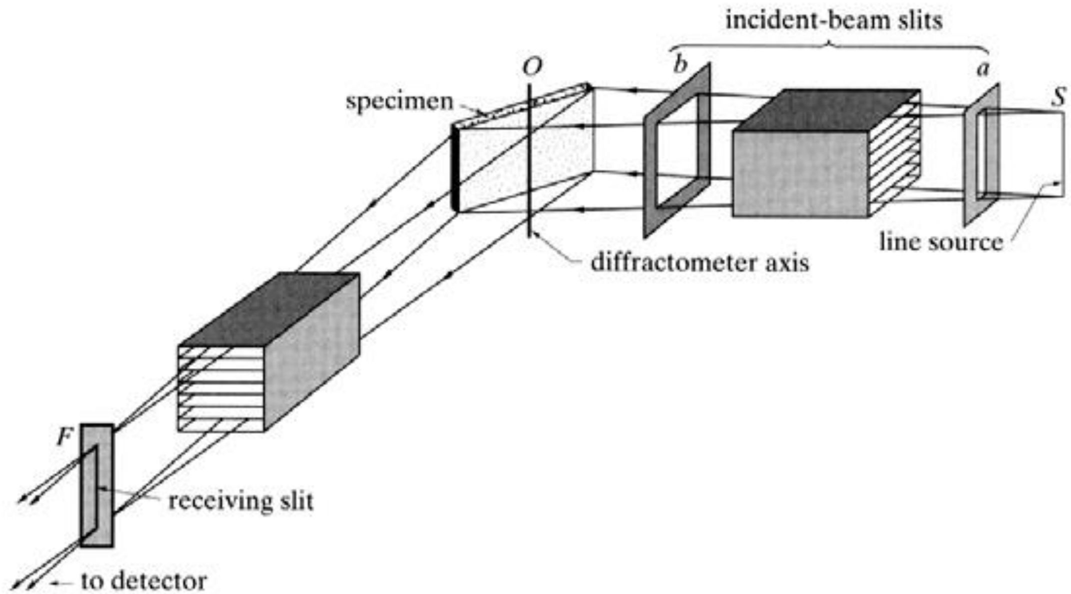




Instrumentation

D. 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

D. Optics

2. Various Slits

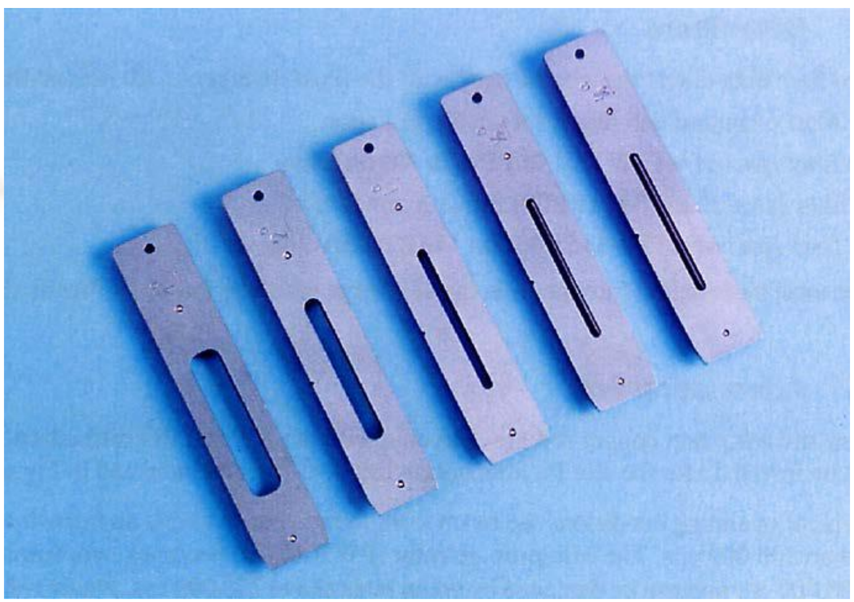
Divergence slit – defines the width of the incident beam.

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

D. Optics

<u>Divergence slit</u> – 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.

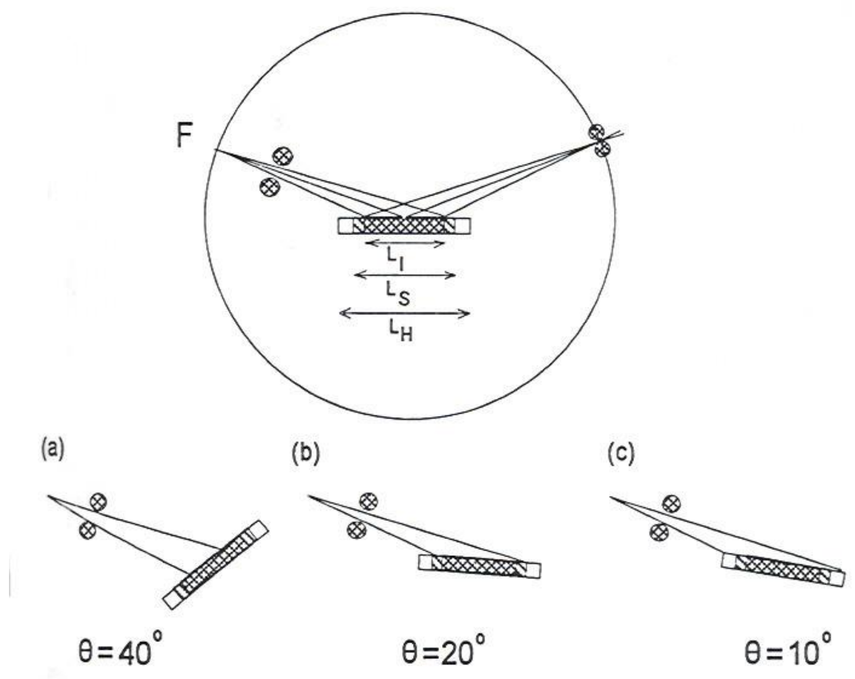


Instrumentation

D. Optics

Divergence slit

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

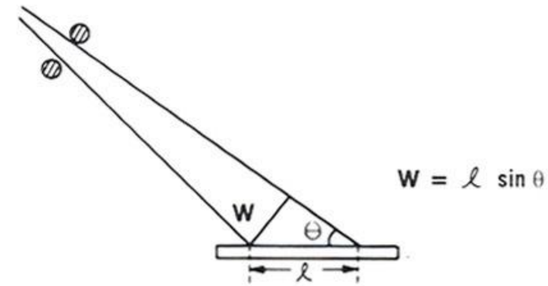


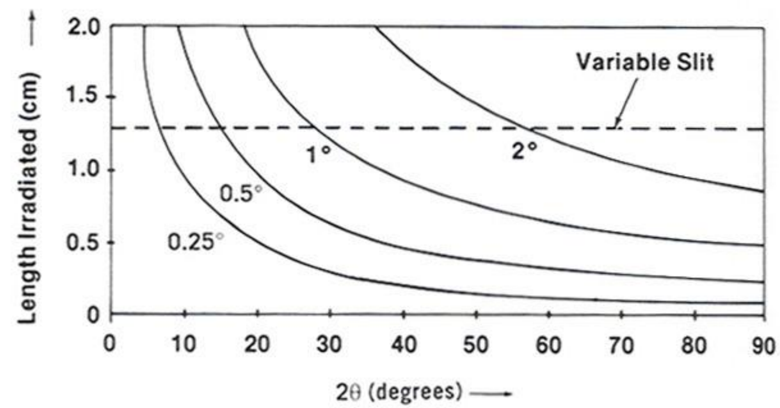
Instrumentation

D. Optics

2. Various Slits

Divergence slit





At 40^o, only the sample is irradiated

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

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

Instrumentation

D. Optics

2. Various Slits

<u>Divergence slit</u>

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

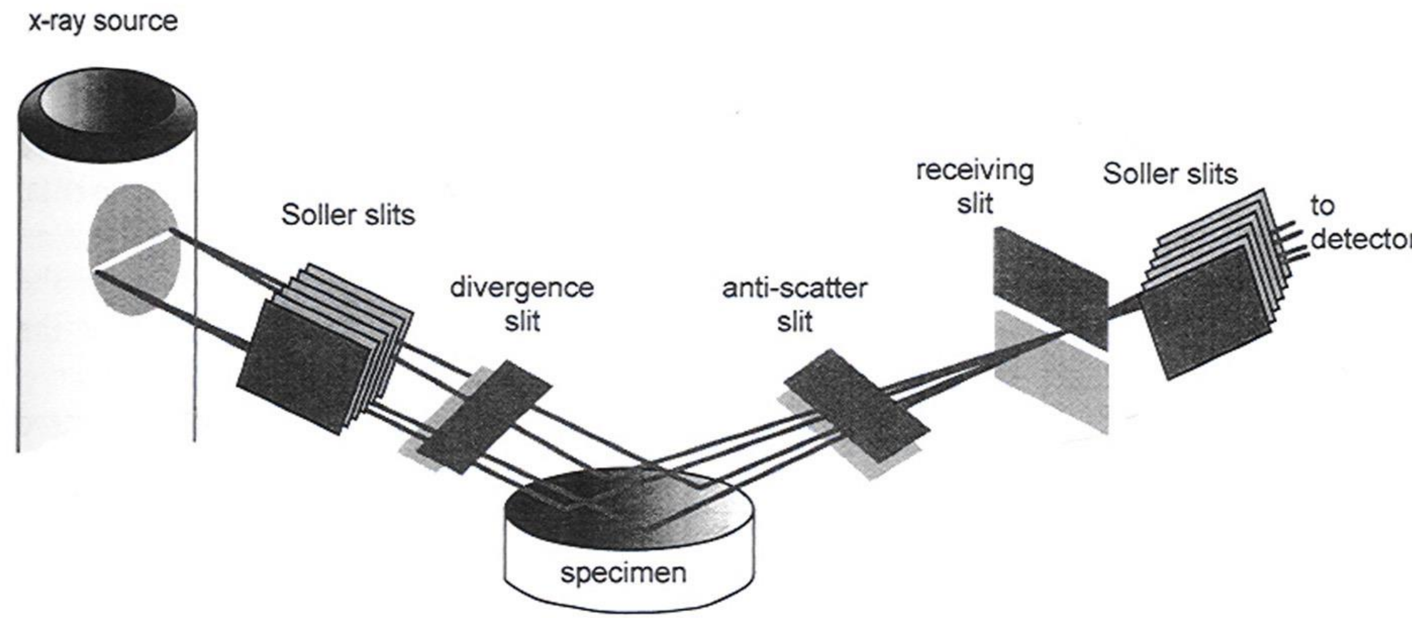
So the choice of divergence slit is critical, especially at low angles.

Instrumentation

D. Optics

2. Various Slits

<u>Antiscatter slits</u> – reduces background radiation.



Instrumentation

D. Optics

<u>Antiscatter slits</u> – 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.

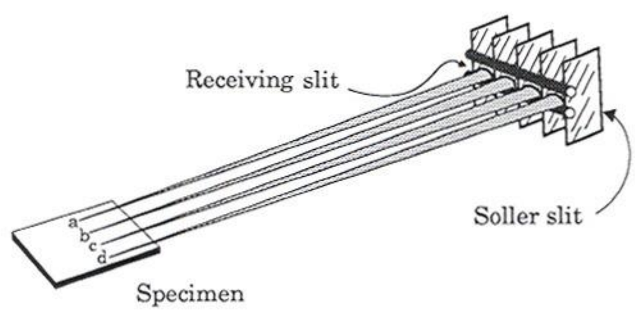
Instrumentation

D. Optics

2. Various Slits

<u>Receiving slit</u> – defines the width of the diffracted beam.

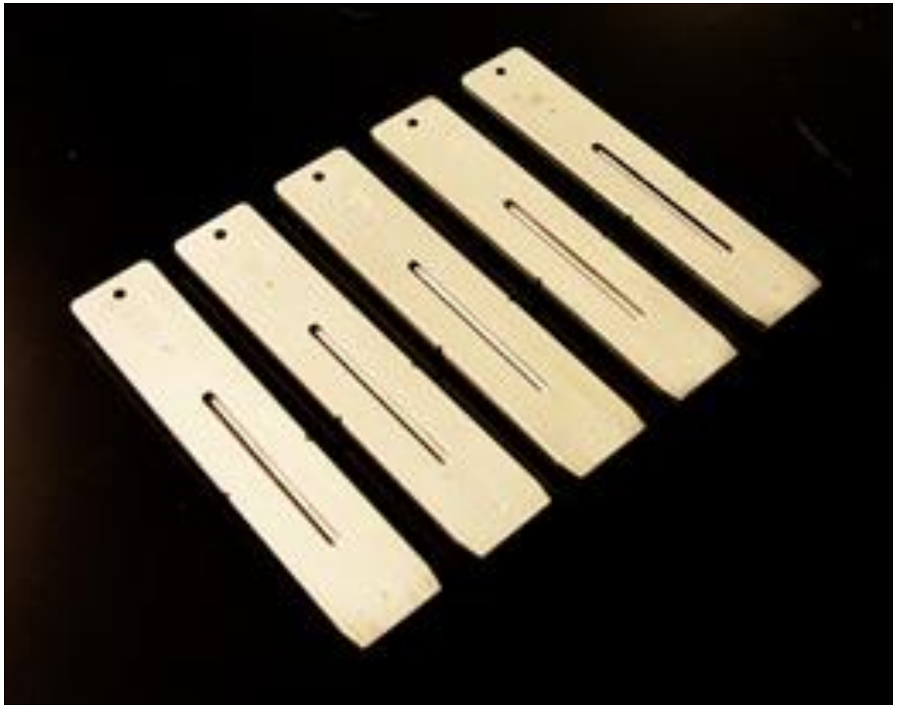
The receiving slit size can be varied, and has a dramatic effect on the peak shape and intensity.



Instrumentation

D. Optics

Receiving slits



Instrumentation

D. Optics

2. Various Slits

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

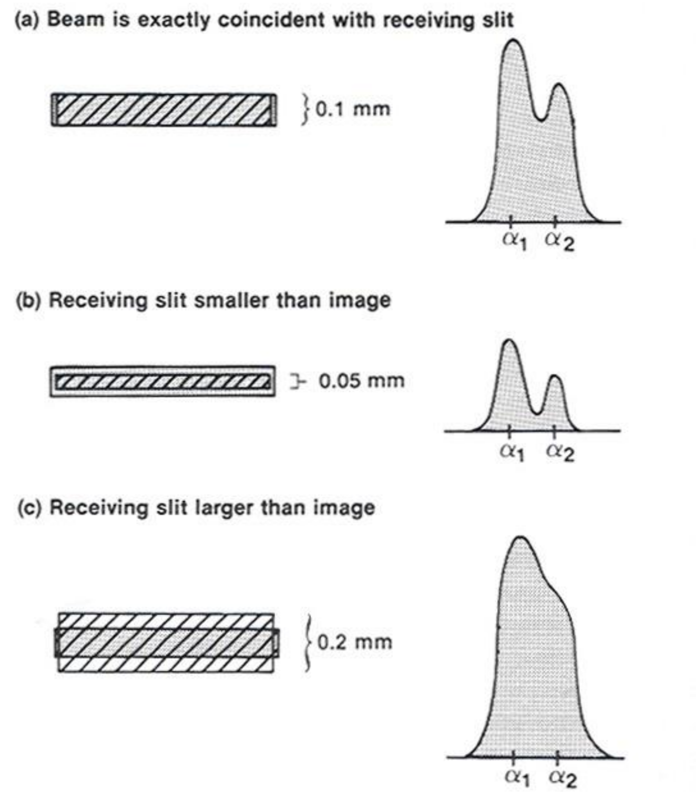
D. Optics

2. Various Slits

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.



Instrumentation

D. Optics

2. Various Slits

<u>Detector slit</u> **- 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

D. Optics

3. 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.

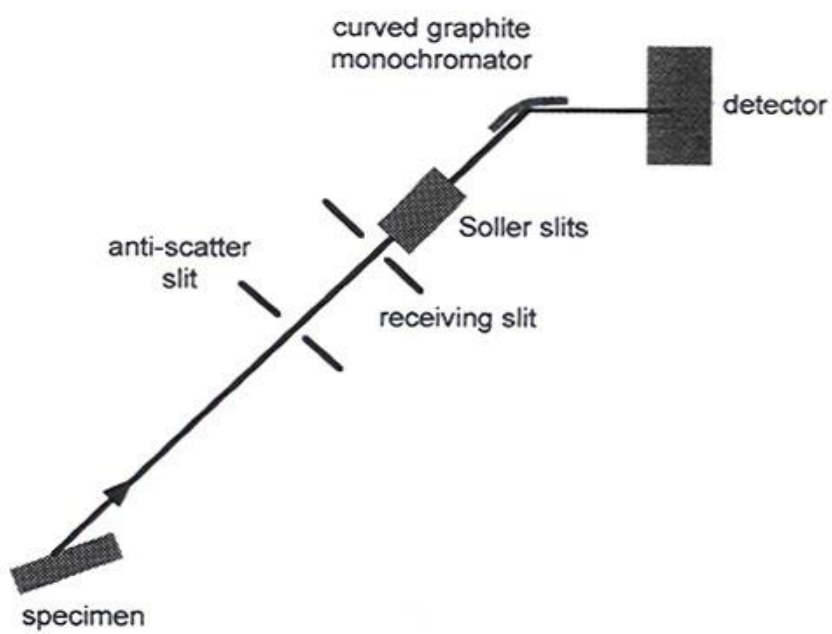
Plane crystal monochromators are used in camera work, while curve (bent) crystal monochromators are used in powder diffractometers.

Instrumentation

D. Optics

3. 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.

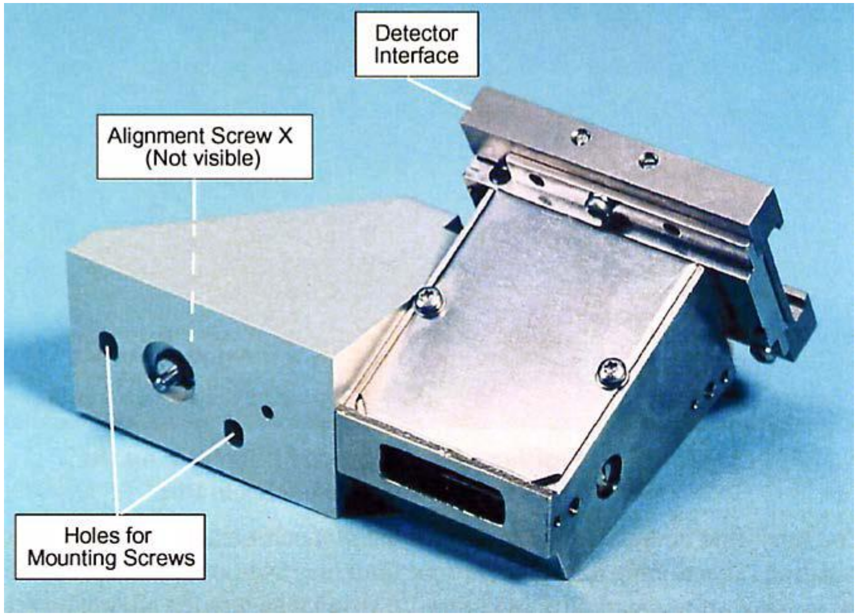


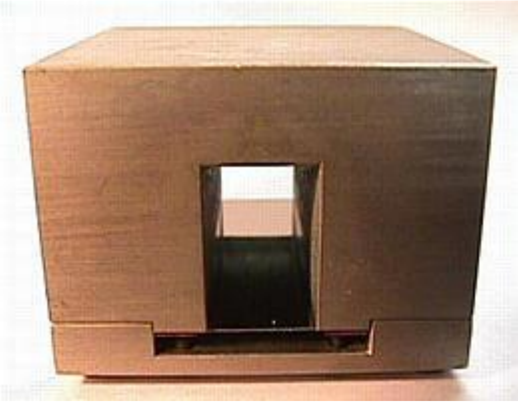
Instrumentation

D. 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) pyrolitic graphite crystal.





Instrumentation

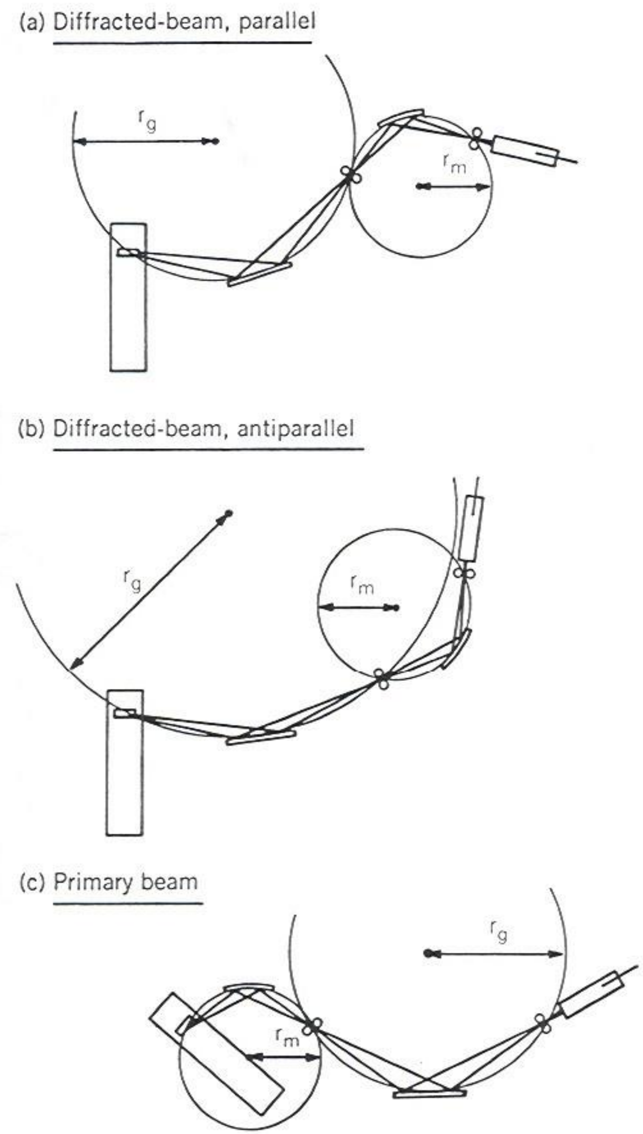
D. Optics

3. Monochromators

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

r_g – radius of the goniometer circle.

r_m – radius of the monochromator circle.



Instrumentation

D. Optics

3. Monochromators

The antiparallel puts the lowest torque on the detector arm.

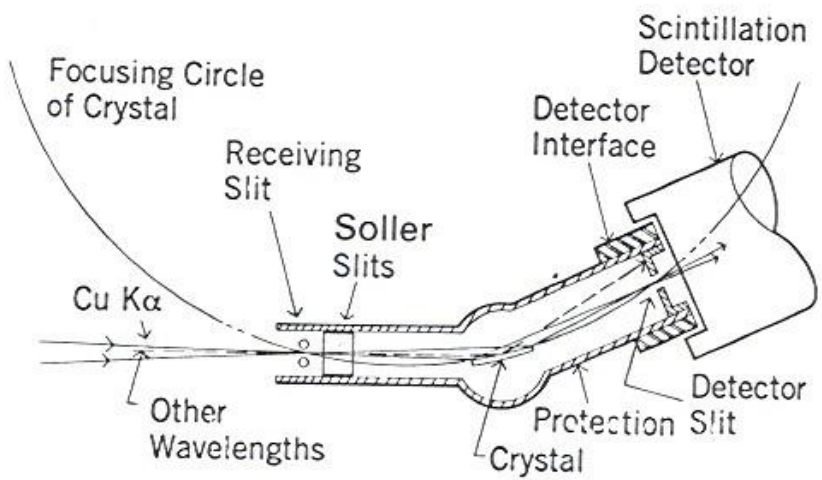
Primary beam monochromator main advantage is the ability to isolate the Kα1 from the Kα2. Disadvantage much more difficult to align.

Instrumentation

D. Optics

3. 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.

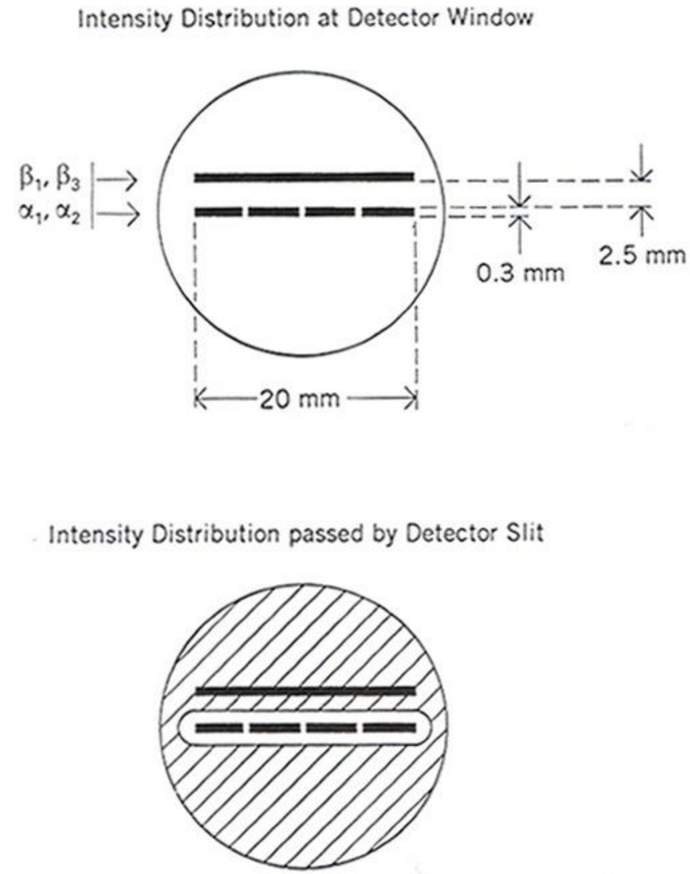


Instrumentation

D. Optics

3. 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.



Instrumentation

D. Optics

3. Monochromators

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

The crystal is oriented to diffract only Kα radiation.

It is pyroltic 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.

Reading Assignment:

Read Chapter 5, 6, and 7 from:

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