POWDER X-RAY DIFFRACTION
III – POWDER DIFFRACTOMETRY

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Outline of the course

1. – SOURCE OF X-RAYS

1.1. – X-ray tube

1.2. – White radiation

1.3. – Characteristic lines

1.4. – Take-off angle

2. - DETECTION OF X-RAYS

3. – SAMPLING

4. – SIZE OF THE IRRADIATED AREA

5. - DIFFRACTOMETER

6. - CORRECTIONS

7. – PEAK PROFILE ANALYSIS

8. – DATA TREATMENT

1.1. – X-ray tube

Electrons are emitted from a heated tungsten filament (thermoelectronic effect)
They are accelerated by a high potential difference ➔ high speed
They hit a target (anode, W, Cu, Mo, Co, Cr) ➔ strong deceleration

➔ emission of electromagnetic waves in all directions
2 or 4 circular beryllium windows

Operating conditions
Filament current: 3 A
Electronic current: 30 mA
High voltage: 40 kV
Power: 1200 W

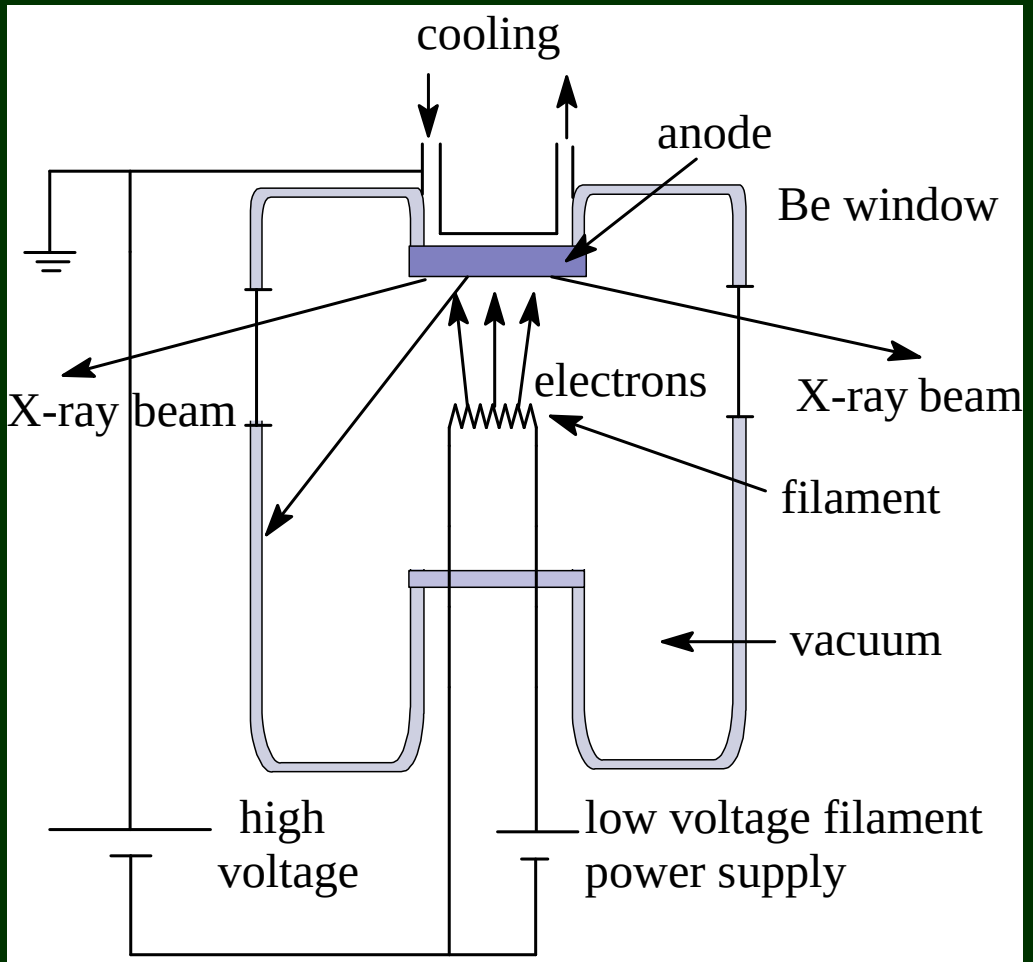


Figure 1. Scheme of a X-ray tube

1.1. – X-ray tube

Plot of the intensity of the emitted beam versus the wavelength

Main features:
- sharp cut-off
- continuous radiations (white radiation)
- very intense and narrow peaks

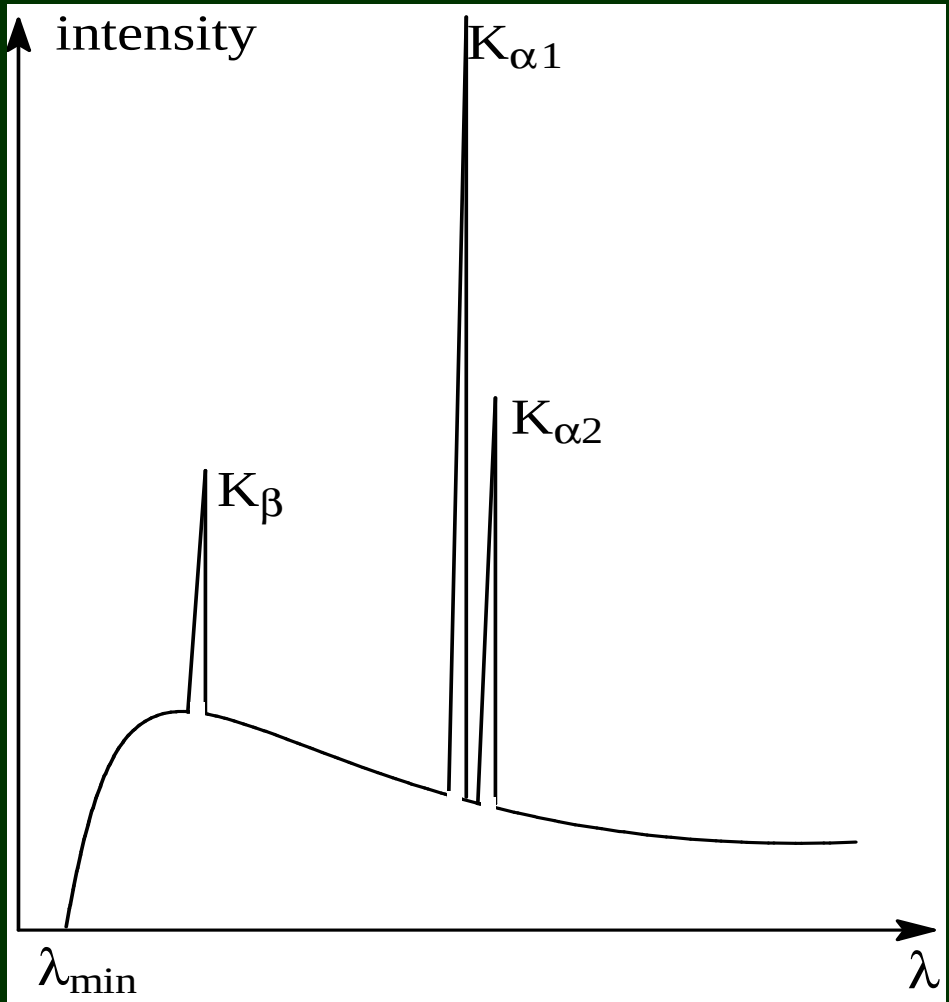


Figure 2. Intensity of the beam versus the wavelength

1.2. – White radiation

The radiation corresponds to the emission of electromagnetic waves linked to the sudden deceleration of the electrons when they hit the target

Independent of the nature of the target

Kinetic energy of one electron E_C

$$E_C = mv^2/2 = eV$$

m = mass of the electron

v = speed of the electron

e = charge of the electron

V = voltage

Kinetic energy is converted into radiation

Energy hν and heat Q

$$E_C = h\nu + Q$$

maximum photon energy when Q = 0

$$E_C = h\nu_{max} = hc/\lambda_{min} = eV$$

➔ $\lambda_{min} = hc/eV$

for V = 40 kV ➔ $\lambda_{min} = 0.31$ Å

for

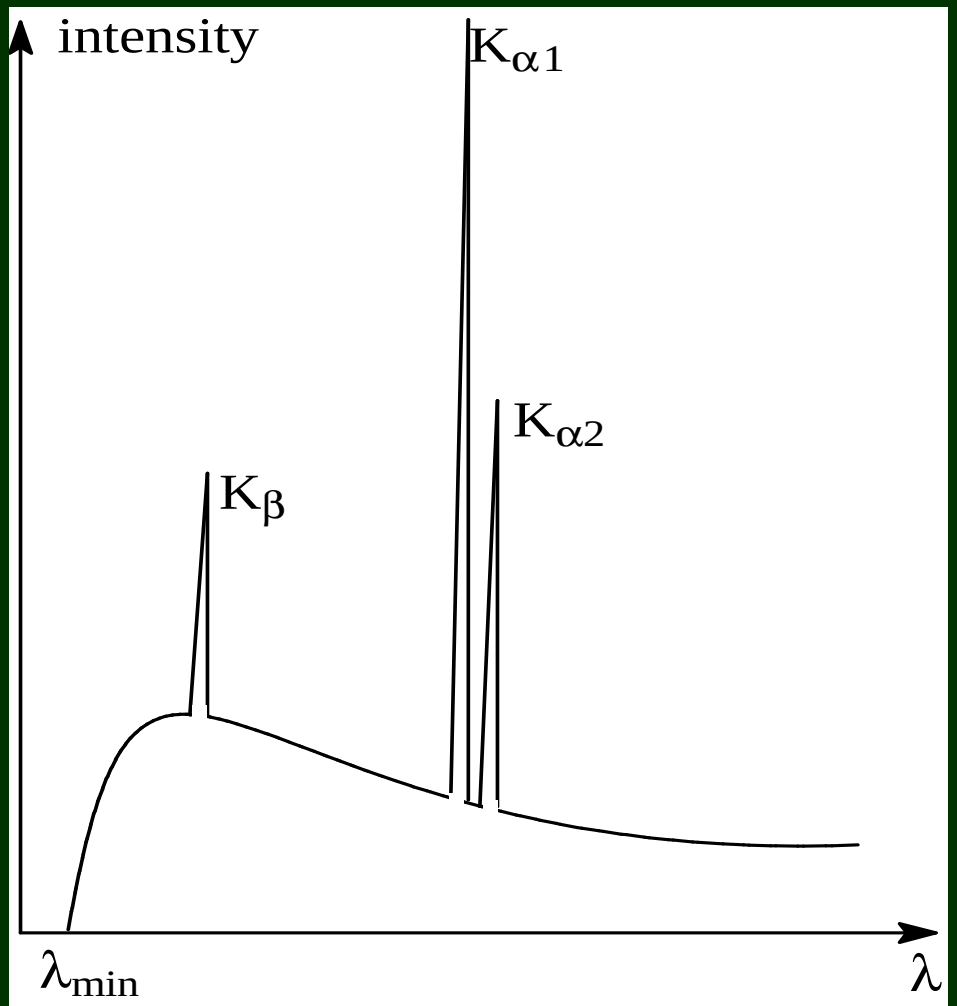


Figure 2. Intensity of the beam versus the wavelength

1.2. – White radiation

Yield $h\nu/E_C \sim 0.5\ \%$ very low

The most part of kinetic energy is transformed into heat

➔ the temperature of the target increases ➔ need to cool the target with water

Maximum of the white radiation for about $1.5\ \lambda_{min}$

Power of commercially available X-ray tube: 300 to 2700 W

How to increase the power:

- rotating anode up to 10 000 W
- synchrotron radiation

1.3. – Characteristic lines

Depends on the nature of the target

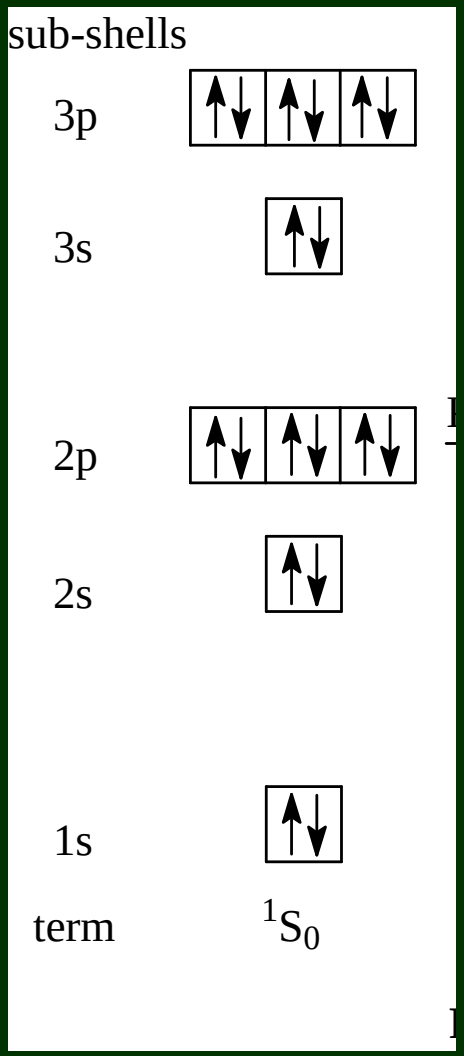
➔ quantum origin: electronic transition in the core levels of the target atoms

➔ core electrons are ejected ➔ atom in an higher energy state

➔ relaxation process to a lower energy state with simultaneous emission of photon

See figure

1.3. – Characteristic lines



1.3. – Characteristic lines

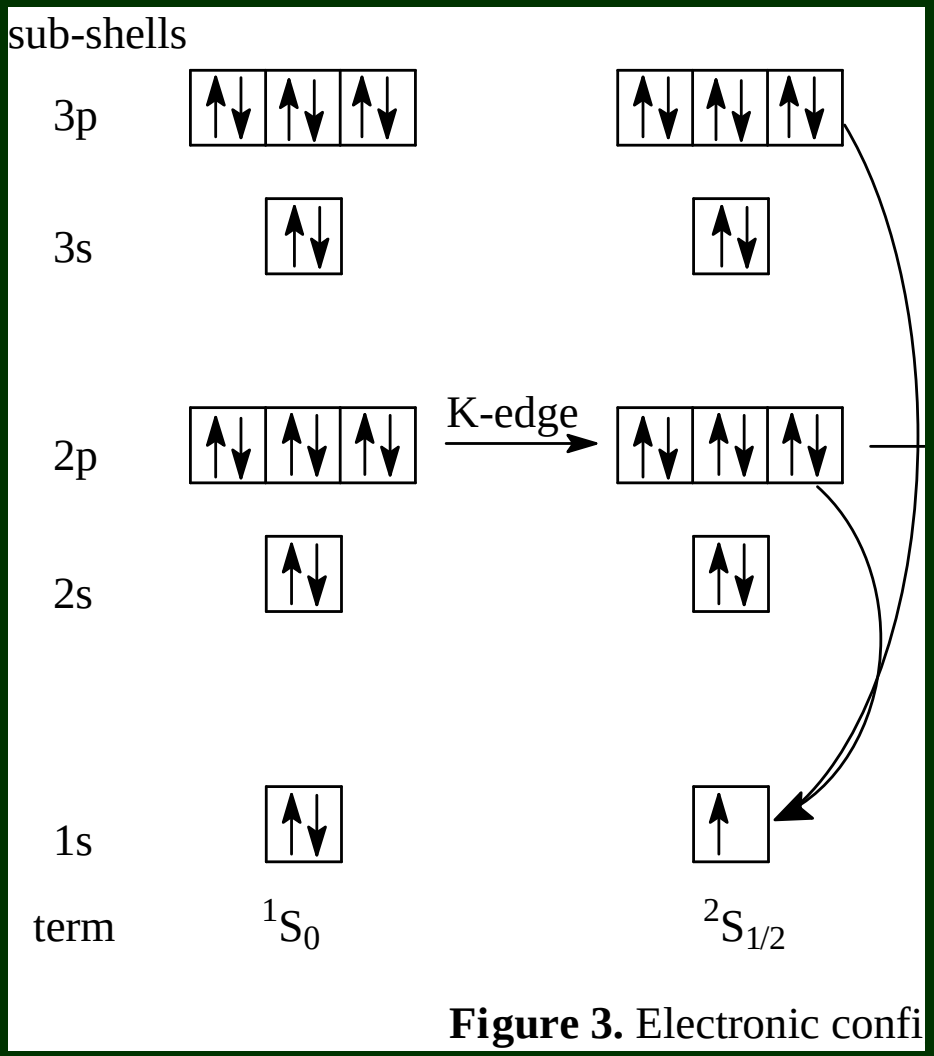


Figure 3. Electronic confi

1.3. – Characteristic lines

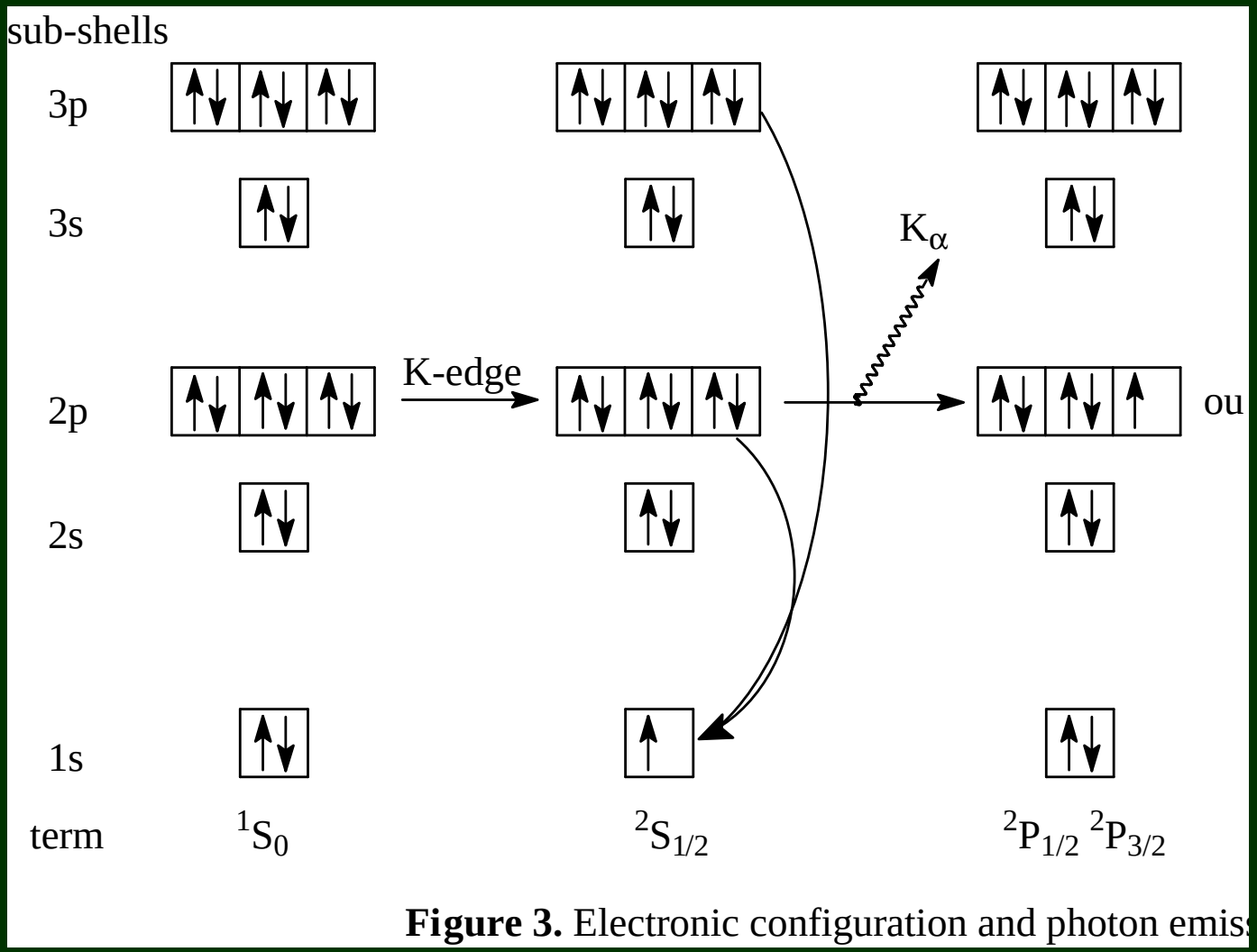


Figure 3. Electronic configuration and photon emiss

1.3. – Characteristic lines

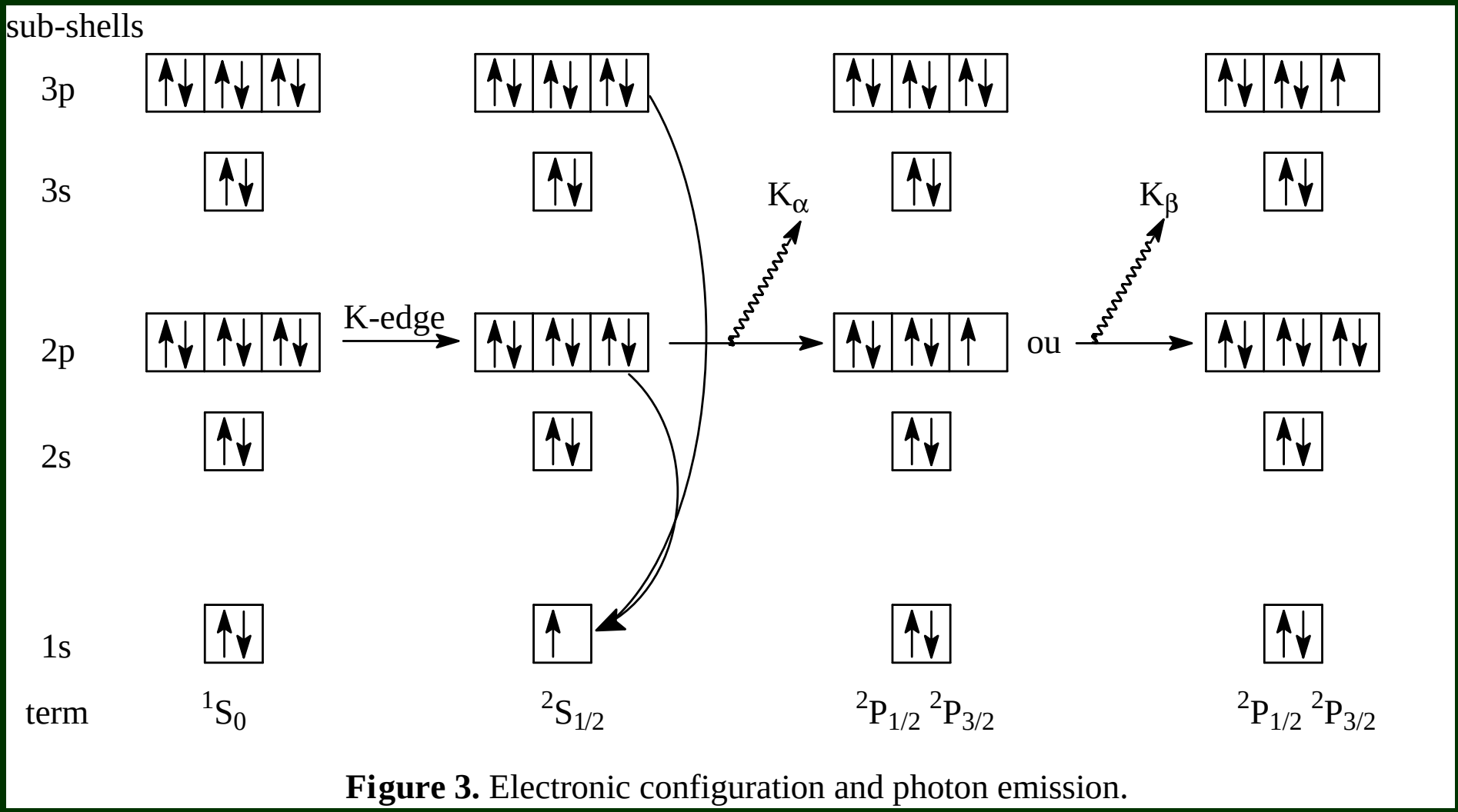


Figure 3. Electronic configuration and photon emission.

1.3. – Characteristic lines

From these electron configurations, we have the following possible transitions:

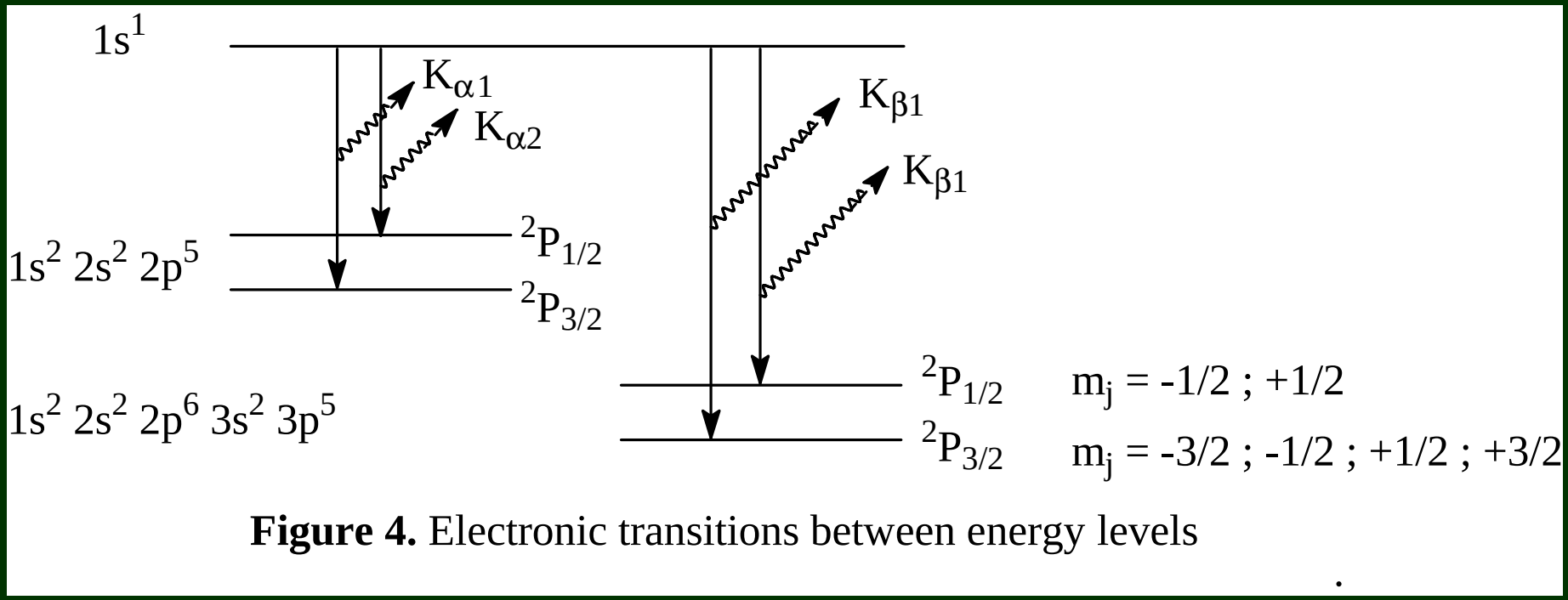


Figure 4. Electronic transitions between energy levels

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$\lambda(K_{\alpha 1}) < \lambda(K_{\alpha 2})$ $\qquad$ $\lambda(K_{\beta}) < \lambda(K_{\alpha})$

$I(K_{\alpha 1}) / I(K_{\alpha 2}) = 2$ $\qquad$ $I(K_{\beta}) / I(K_{\alpha}) = 0.35$

$\lambda(K_{\alpha 1}) = 1.54060$ $\qquad$ $\lambda(K_{\alpha 2}) = 1.54439$ Å

average value $\lambda(K_{\alpha}) = 1.54186$ Å $\qquad$ $\lambda(K_{\beta}) = 1.39222$ Å

1.4. – Take-off angle

Angle τ between the plane defined by the target and the X-ray beam crossing the window.
Mean value: 6 ° to 12 °

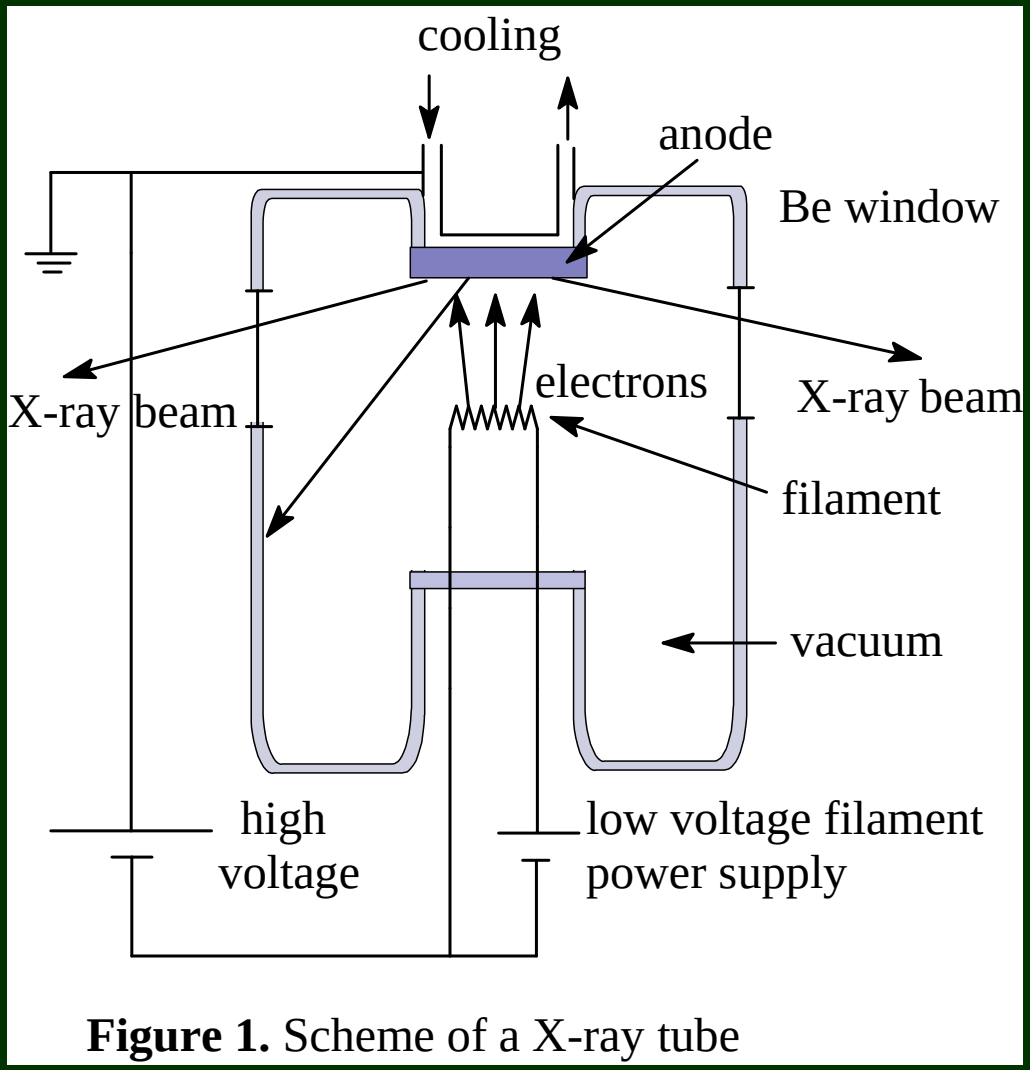
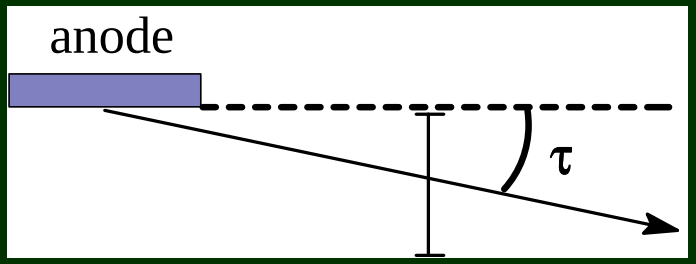


Figure 1. Scheme of a X-ray tube



Outline of the course

1. – SOURCE OF X-RAYS

2. - DETECTION OF X-RAYS

2.1. - Proportional scintillation detector

2.2. – Linear detector

2.3. – Counting statistics

2.4. – Standard deviation and intensity

2.5. – Stability of the X-ray source

3. – SAMPLING

4. – SIZE OF THE IRRADIATED AREA

5. - DIFFRACTOMETER

6. - CORRECTIONS

7. – PEAK PROFILE ANALYSIS

8. – DATA TREATMENT

2.1. - Proportional scintillation detector

2.2. – Linear detector

See figures

2.3. – Counting statistics

Gaussian statistics

$$\rho = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{x - M}{\sigma} \right)^2 \right]$$

with ρ : frequency for a measurement
M : mean value
σ : standard déviation

Probability to have the value in the range $M \pm \alpha\sigma$:

68 % for $\alpha = 1$
95 % for $\alpha = 2$
99 % for $\alpha = 2.6$

2.3. – Counting statistics

For a counting: $\sigma = \sqrt{N}$

If we repeat the measurement n times: $\sigma = \frac{\sqrt{N}}{\sqrt{n}}$

How to define the best strategy for a given powder?

2.4. – Standard deviation and intensity: Statistical background

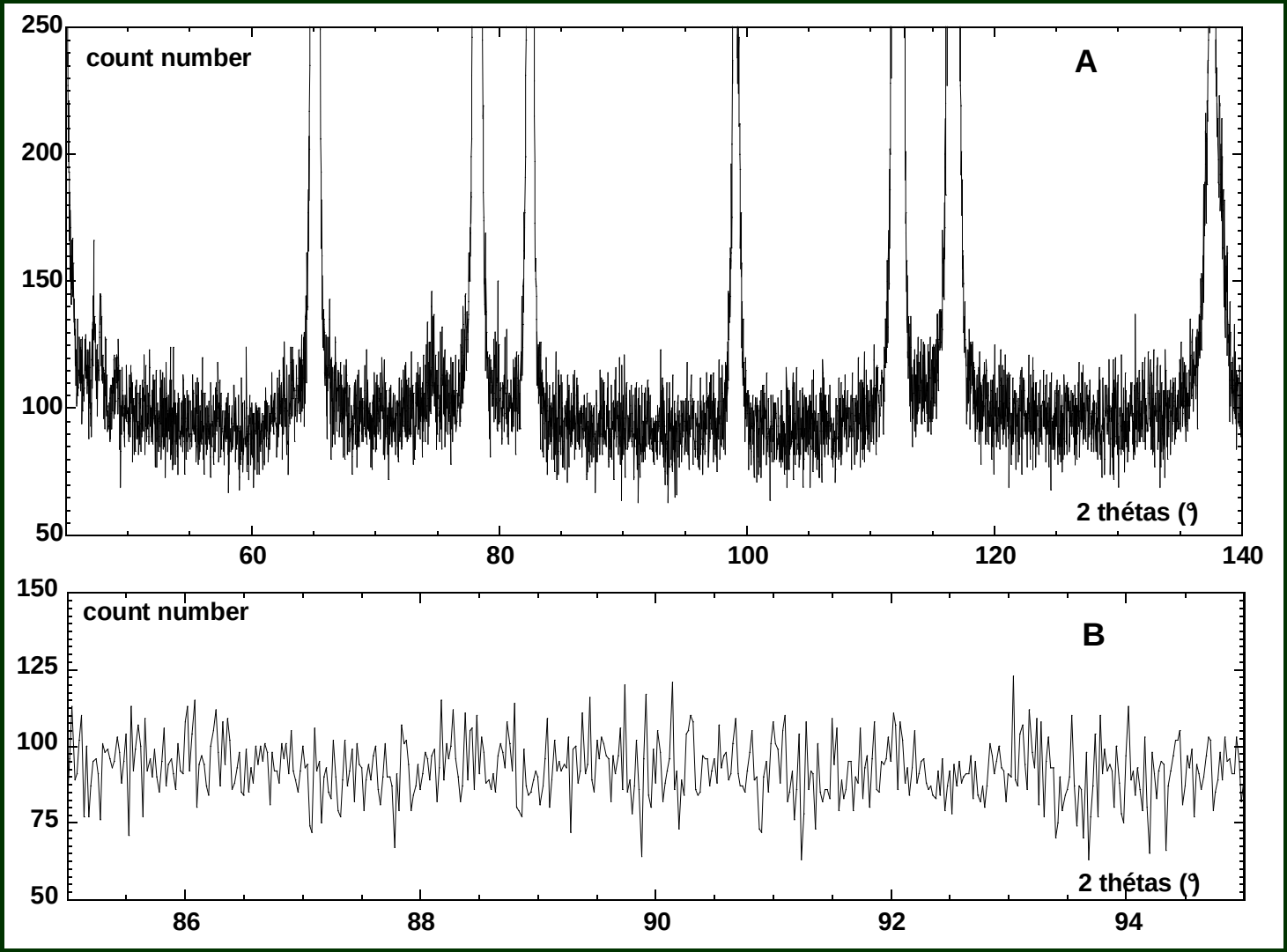


Figure 5. Background analysis. A) XRD plot of Al sample-holder in the range 45 to 140 ° 2 θ. B) enlargement of the range 85 to 95 ° 2 θ. Step 0.02 ° ; dwell time 1 s ; slit aperture 1 °.

2.4. – Standard deviation and intensity: Statistical background

Use statistic functions to determine the level of statistical noise in the background.
Exp. data for Al for different 2θ ranges between diffraction peaks (see previous figures).
For these ranges the mean count level is approximately 100 and we expect a statistical standard deviation of the order of $100^{1/2}$ that is about 10. The results are as follows:

2 θ range	50 to 60 °	85 to 95 °	100 to 110 °	120 to 135 °
Point number	501	501	501	751
Minimum	67	63	64	68
Maximum	124	123	122	137
Mean	94.24	92.51	92.90	97.11
Exp. std deviation	9.91	9.85	9.78	10.07
$(mean)^{1/2}$	9.71	9.62	9.64	9.85

➔ Very good agreement between experimental value and calculated value $(mean)^{1/2}$

2.5. – Stability of the X-ray source

Due to fluctuations of the X-ray tube
For a given count number, the fluctuations will increase the standard deviation

Stability parameter h
We want $hN << \sigma(N) = N^{1/2}$

Assumption $h \sim 10^{-3}$ for a good stability

For $N = 10^6$ counts ➔ $\sigma(N) \sim 10^3$
➔ $hN \sim 10^3$ same magnitude order
➔ influence of fluctuations and risk of saturation of the detector

For $N = 10^4$ counts ➔ $\sigma(N) \sim 10^2$
➔ $hN \sim 10^1 << \sigma(N)$

➔ it is not useful to make a measurement for a long time
➔ possibility of systematic errors due to aging of the tube

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1. – SOURCE OF X-RAYS
2. - DETECTION OF X-RAYS
3. – SAMPLING
3.1. – Sample preparation
3.2. – Different sample holders
4. – SIZE OF THE IRRADIATED AREA
5. - DIFFRACTOMETER
6. - CORRECTIONS
7. – PEAK PROFILE ANALYSIS
8. – DATA TREATMENT

3.1. – Sample preparation

Size of the grain: 5 to 10 μm.

The raw powder has to be milled very carefully in an agate mortar, using a pestle.
This is very important to get a good measurement.

For one grain with a size of 1 mm ➔ how many grains with a size of 10 μm?

➔ 10^6 grains !!

3.2. – Different sample holders

Different types of sample holders

- Plastic
- Glass
- Metal
- Silicon wafer: (511) face

For sample holder with a hole: determine the volume and dimensions of the hole
Weight the mass of the sample.
Then determine the apparent density

Avoid the possibility of preferential orientation of the crystallites

➔ random orientation is the best

➔ the surface has to be well defined: the best is to erase the excess with a razor blade

3.2. – Different sample holders

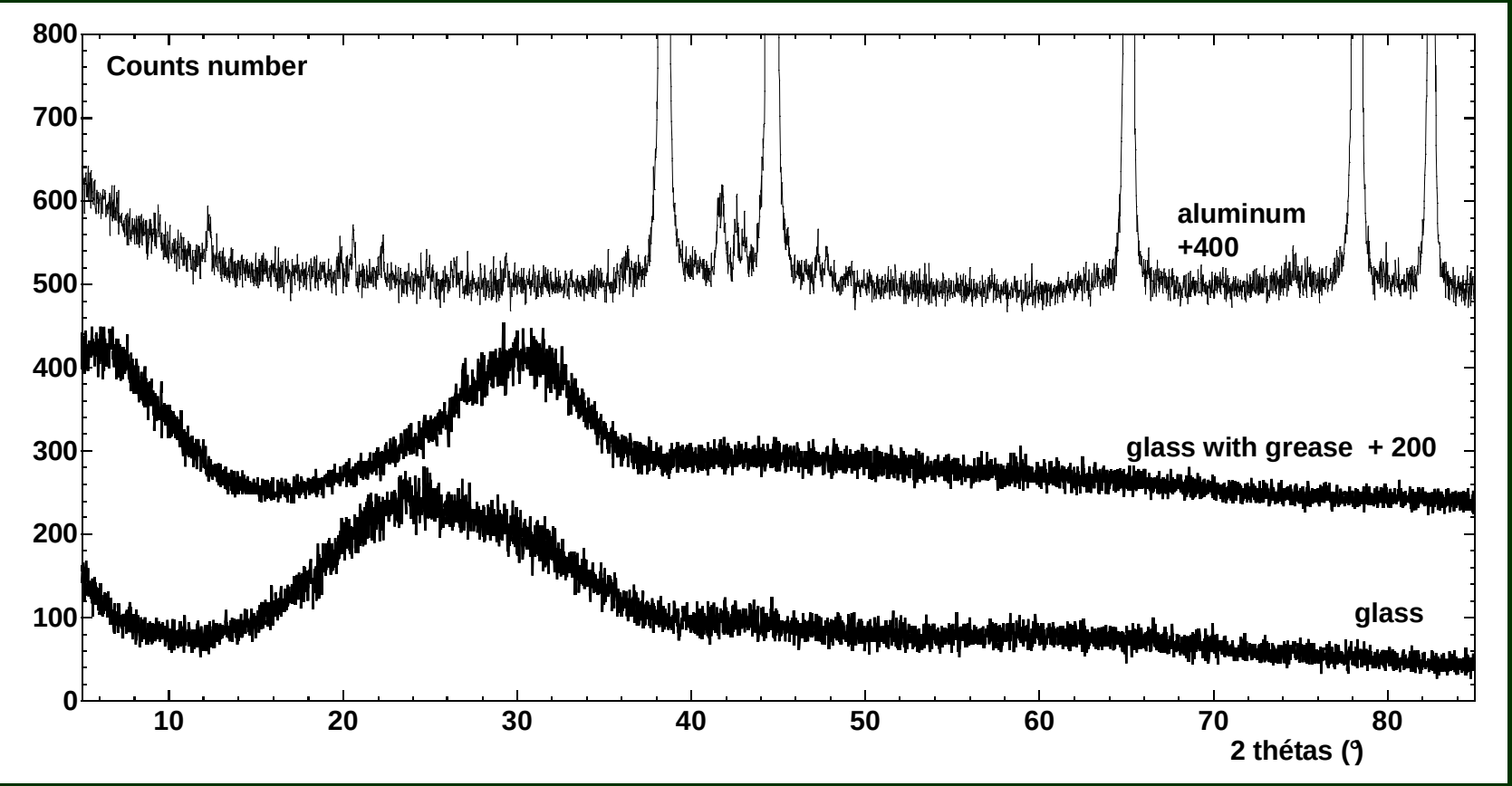
Different sample holders have been measured in the same conditions to determine the level of the corresponding background:

aluminum,

glass,

silicon wafer...

Fig. Aluminum, glass, glass covered by grease. Step 0.02 °, dwell time 1 s, slit aperture 1 °.



Outline of the course

1. – SOURCE OF X-RAYS
2. - DETECTION OF X-RAYS
3. – SAMPLING
4. – SIZE OF THE IRRADIATED AREA
4.1. – Sample holder
4.2. – Determination of the length L
4.3. – Determination of the width l
5. - DIFFRACTOMETER
6. - CORRECTIONS
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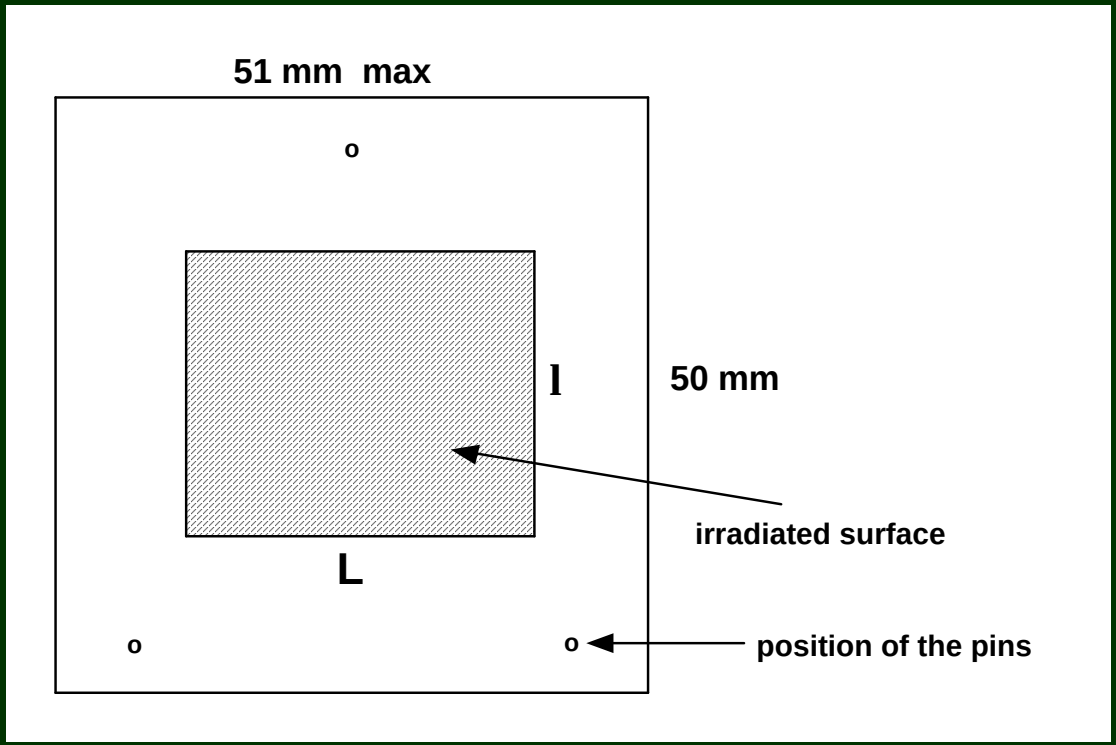
4.1. – Sample holder

Square (50x50 mm) made from plastic, aluminum, glass or single crystal silicon plate (wafer) glued on Al carrier. The hole in the center of the sample holder contains the solid to be examined: cylindrical form with fixed diameter and depth (25x1 mm for routine plastic sample holders) or of parallelepiped form with dimensions specifically defined by the user.

irradiated area must correspond only to the powder and not to the sample holder.
The sample holder is kept in the focal plane by means of pins ot clamp.
The irradiated surface displays a rectangular shape with length L and width l.



4.2. – Determination of the length L

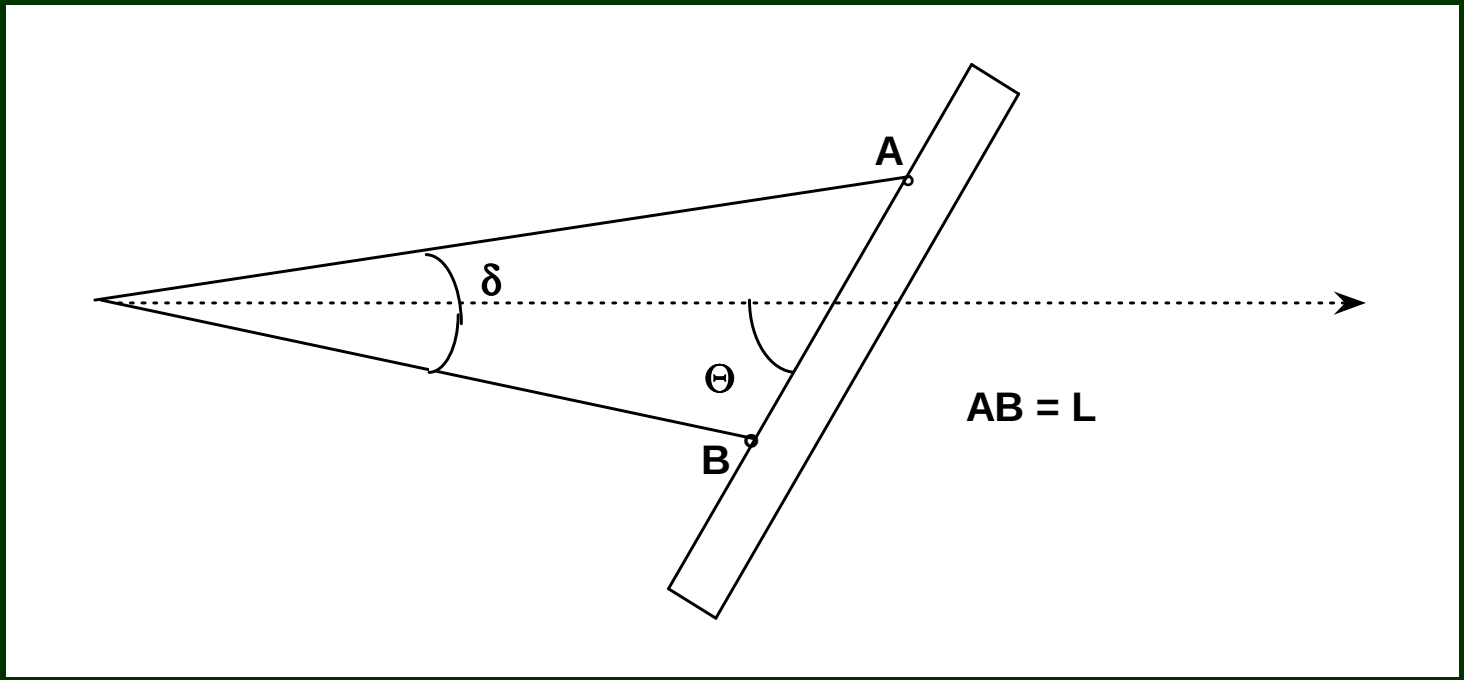
Length **L** depends on δ (aperture slit) and θ angle between sample holder and X-ray beam relation between these values:

$$L = R\delta / \sin\theta$$

R : radius of the goniometer circle

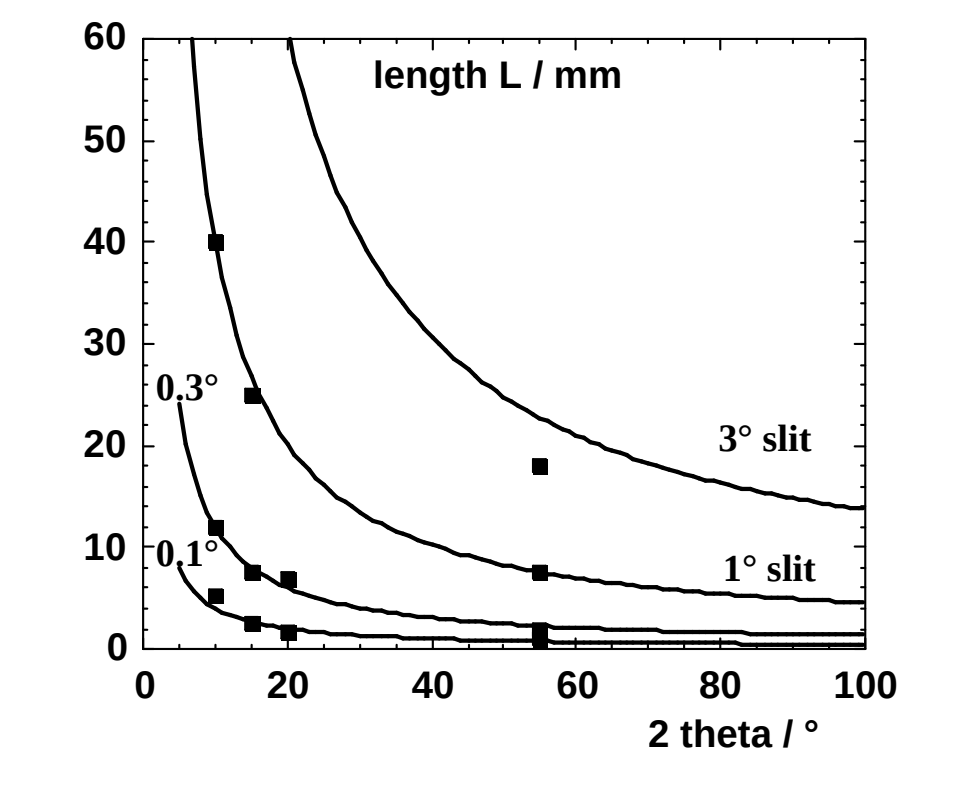
δ : aperture slit in radian

θ : Bragg angle



4.2. – Determination of the length L

The result of this relation is given for different slit aperture angles.



length determined experimentally with a sample holder covered with X-ray fluorescent sheet; visual examination to see the irradiated zone for different slit angle values.
The results (dots) agree well with the calculated curves

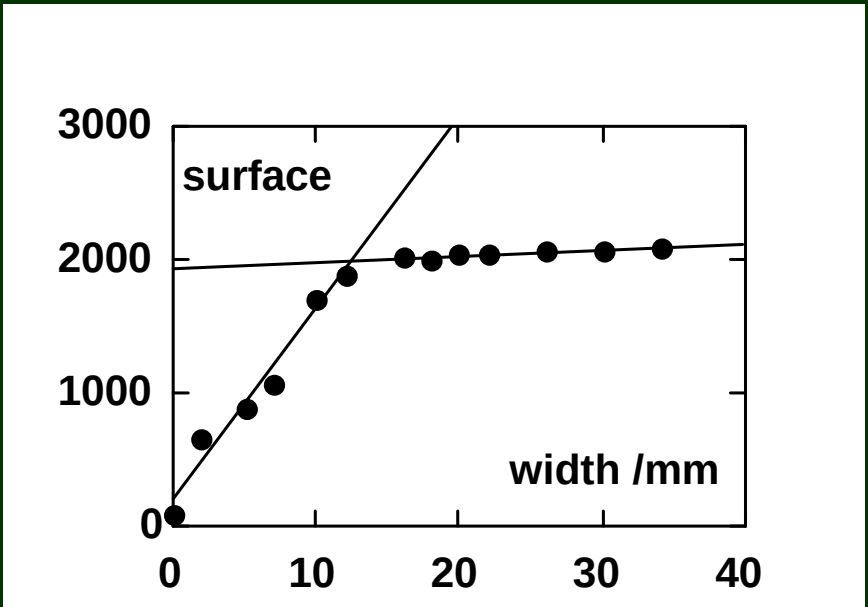
slit angle	0.1 °	0.3 °	1 °
2θ min for L = 20 mm		6 °	20 °
2θ min for L = 10 mm	4 °	12 °	36 °

These values have to be considered as a rough guide before making experiments.

4.3. – Determination of the width l

aluminum sample holder is symmetrically masked by cardboard. The pieces of cardboard have the same dimensions than the sample holder (i.e. 50x50 mm) and display a rectangular hole in the middle with constant length (L = 20 mm) and variable width (l = 0 to 34 mm). The (111) peak of aluminum metal was recorded for each cardboard mask

The results are given in Figure which shows the integrated intensity versus the width l.



The curve displays two ranges :

from 0 to 14 mm with a linear increase of the intensity

above 16 mm with a constant intensity.

➔ useful width 16 - 18 mm.

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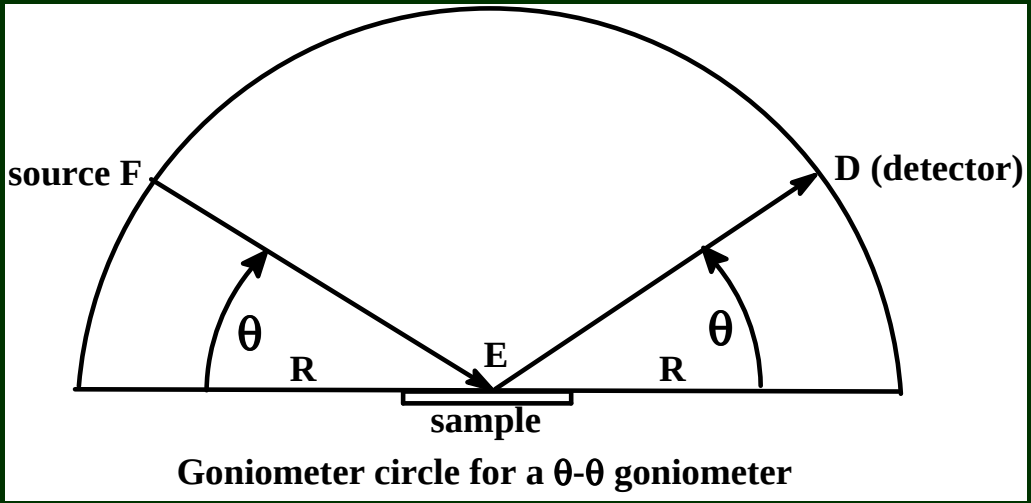
5. – DIFFRACTOMETER
5.1. – Goniometer circle
5.2. – Focusing circle
5.3. – Opening slits
6. - CORRECTIONS
7. – PEAK PROFILE ANALYSIS
8. – DATA TREATMENT

5.1. – Goniometer circle

Bragg-Brentano geometry
Goniometer circle defined by the middle of the sample, the beam focus and the detector

θ-θ goniometer: the sample is fixed and the source and detector are moving.
Radius of the goniometer circle: R (must be known)

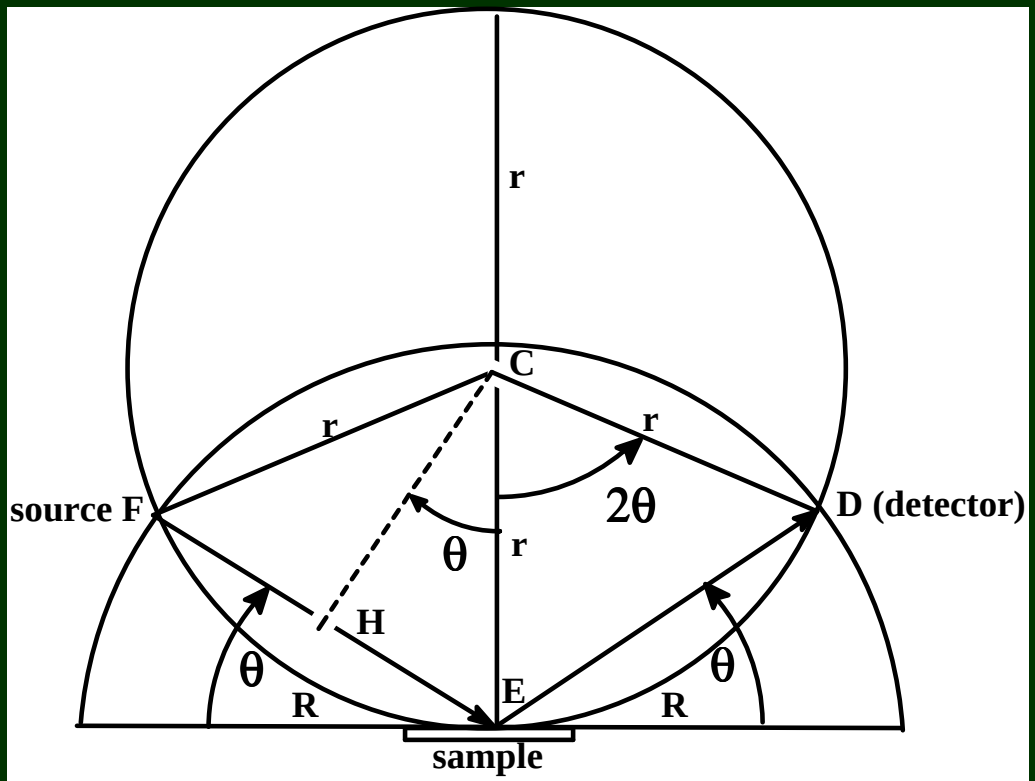
The beam is diverging from the focus and limited by an aperture slit



Goniometer circle for a θ-θ goniometer

5.2. – Focusing circle

Bragg-Brentano geometry
Focusing circle defined by F (source focus), E (sample) and D (detector)
Radius r = R/(2 sinθ)
Depends on the angle θ



definition of the focusing circle with radius r

5.3. – Aperture slits

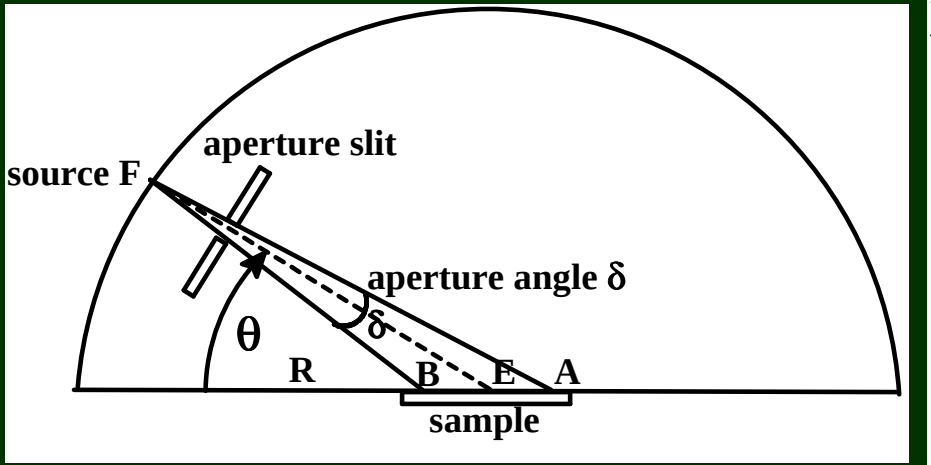
Define the length L of the irradiated area

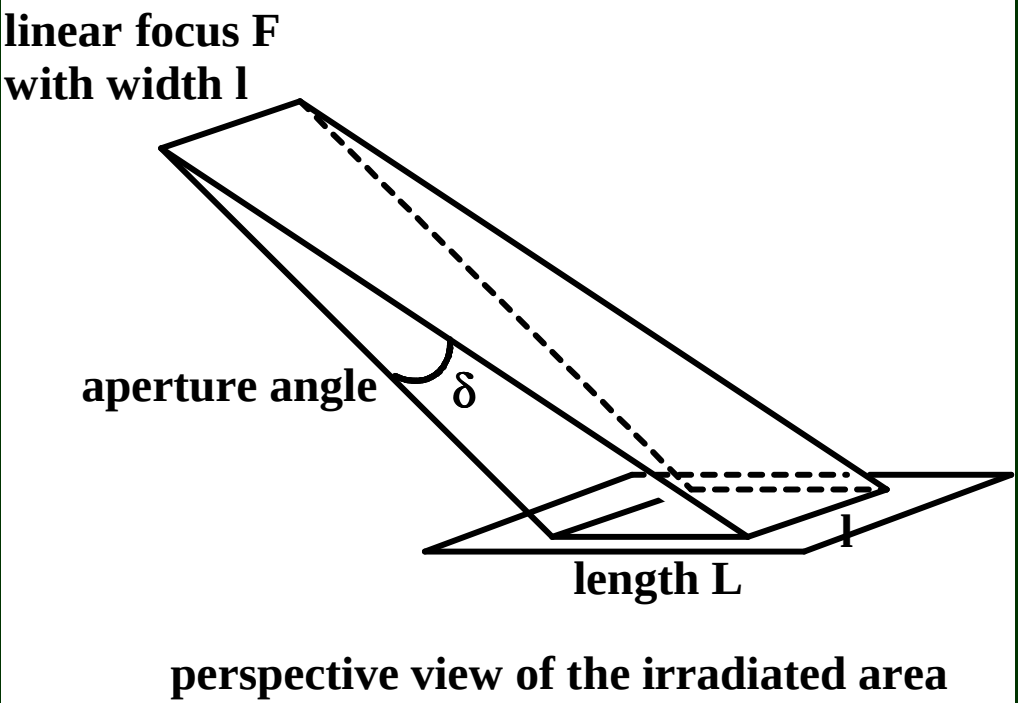
$$L = R\delta / \sin\theta$$

The width l is constant and depends on the X-ray tube and the slits

Fixed slit ➔ L varies

Variable slit ➔ L constant





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5. – DIFFRACTOMETER
6. – CORRECTIONS
6.1. – Zero correction
6.2. – Sample displacement
6.3. – Sample absorption
6.4. – Flatness correction
6.5. – Axial divergence
6.6. – Displacement determination
7. – PEAK PROFILE ANALYSIS
8. – DATA TREATMENT

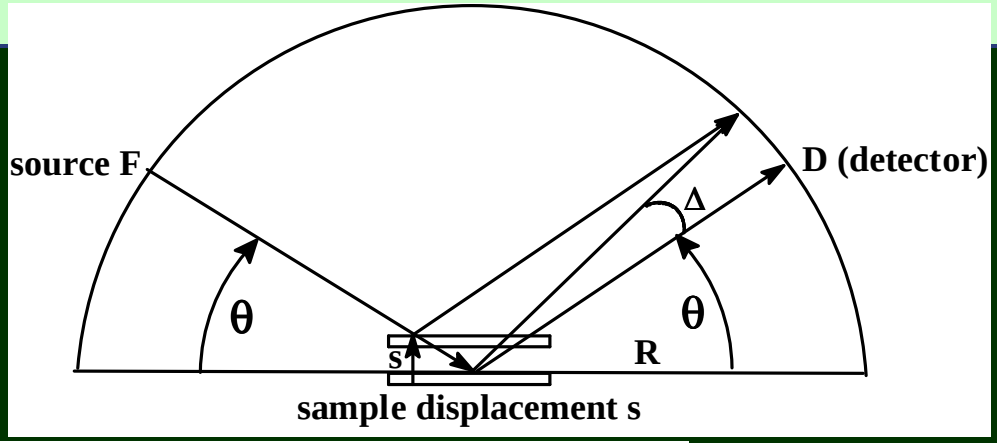
6.1. – Zero correction

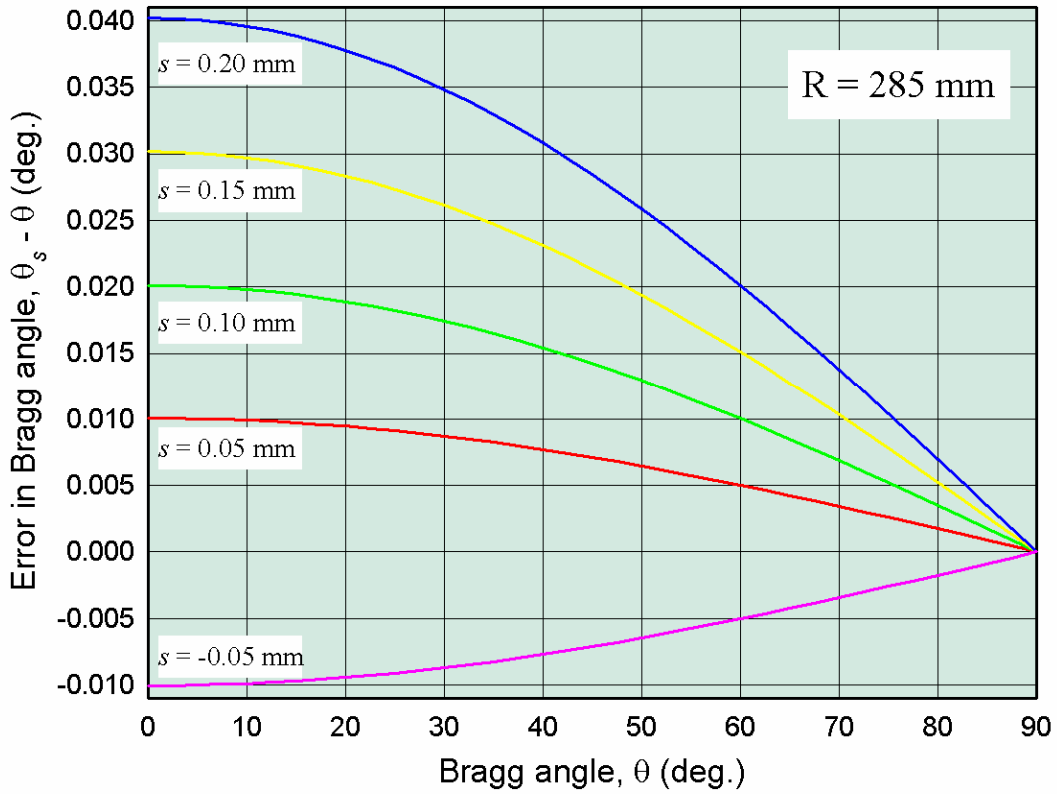
Systematic error due to the alignment of the apparatus
Must be checked regularly and indicated

6.2. – Sample displacement

$\Delta = -\ 2s\ \cos\theta\ /R$ (radian)

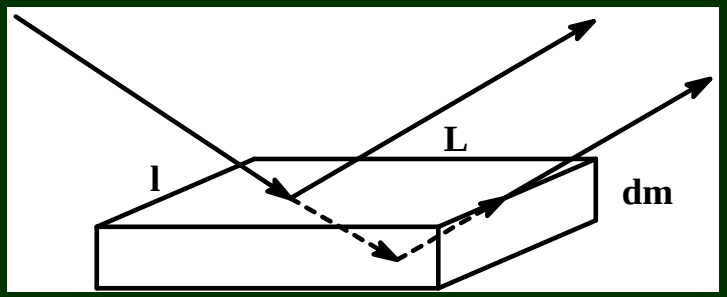
$2\theta_{corrected} = 2\theta_{exp} + 180\Delta/\pi$ (°)



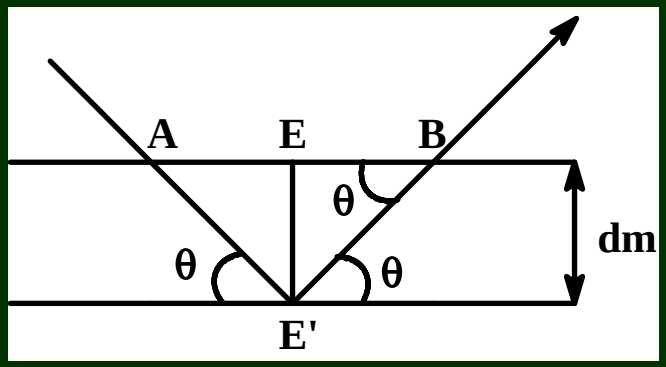


6.3. – Sample absorption

Mean path length of X-rays: $2/\mu$
d_m = mean penetration depth
(depends on the diffraction angle)
Irradiated volume:
V = length * width * depth = L * l * d_m



We have to calculate dm
$2/\mu = AE' + E'B = 2d_m/\sin\theta$
$d_m = \sin\theta/\mu$



Remember $L = R\delta/\sin\theta$
volume $V = R*\delta*l / \mu$ = constant

Two limiting cases:

- μ is large: d_m < thickness t of the powder ➔ displacement s = $d_m/2$
- μ is small: d_m > thickness t of the powder ➔ displacement s = t/2