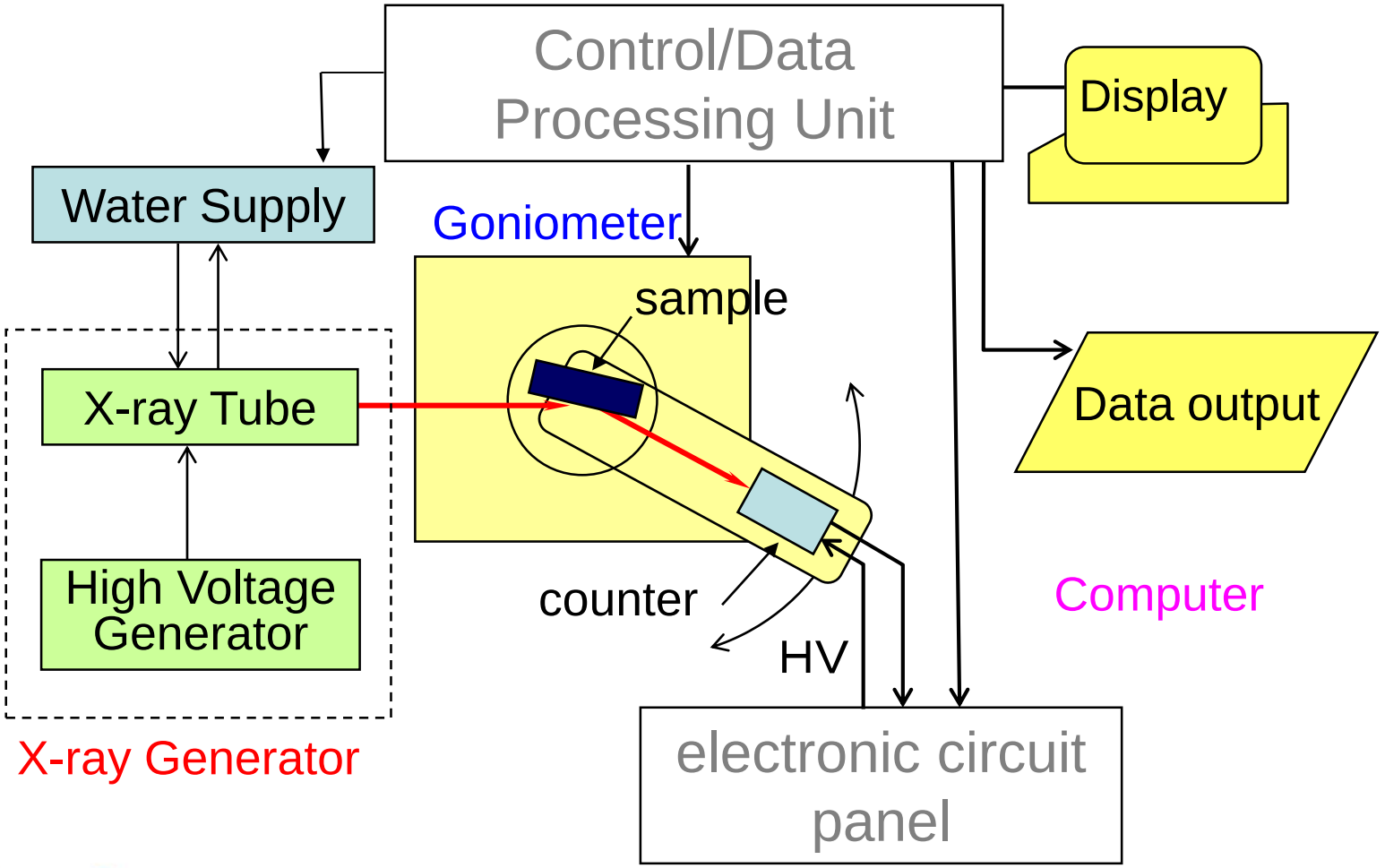
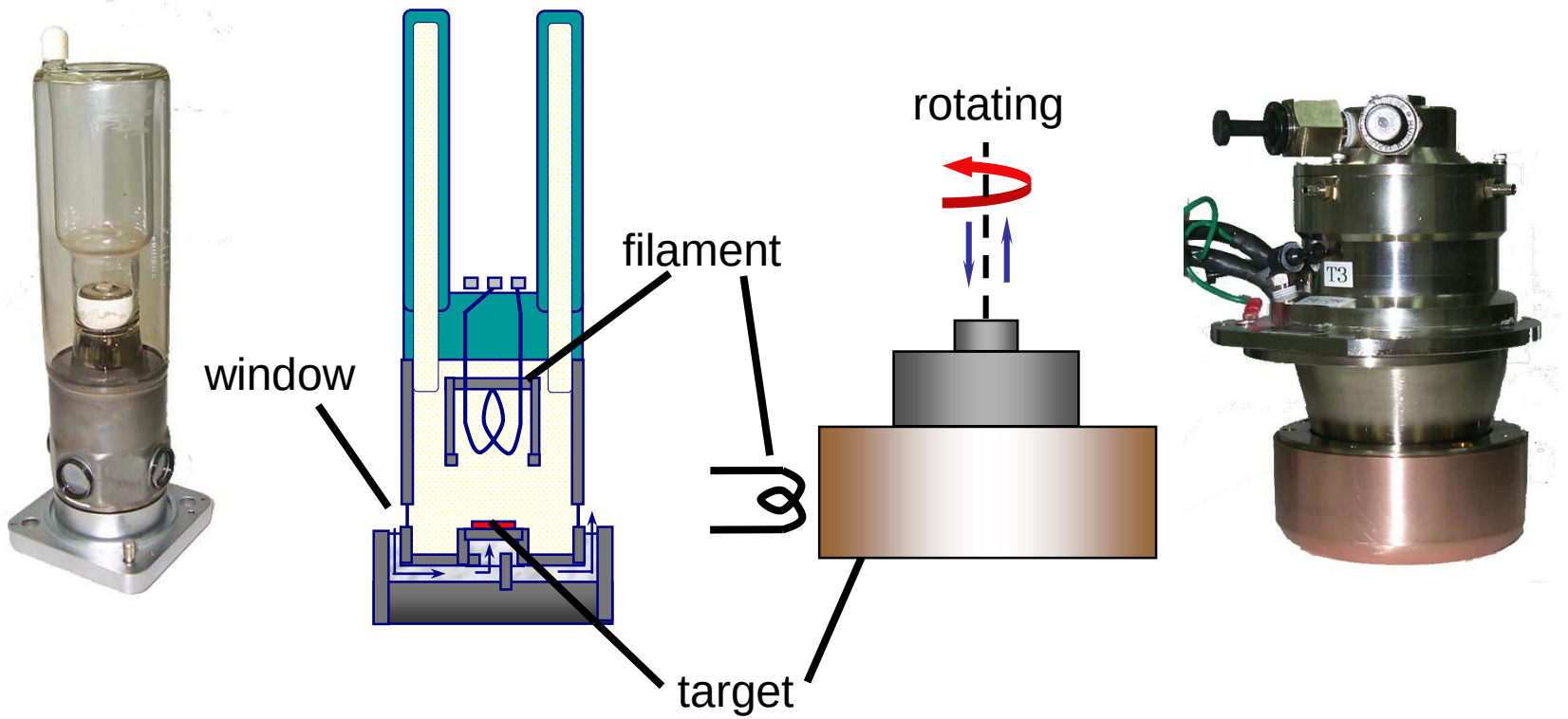
X-ray Diffractometer

Instrument


Control/Data
Processing Unit
Display
Water Supply
Goniometer
sample
X-ray Tube
Data output
High Voltage
Generator
counter
Computer
HV
X-ray Generator
electronic circuit
panel

Sealed tube and rotating anode X-ray tube

- Sealed X-ray tube
  - **1-3 kW**
- Rotating anode
  - **9-18kW**



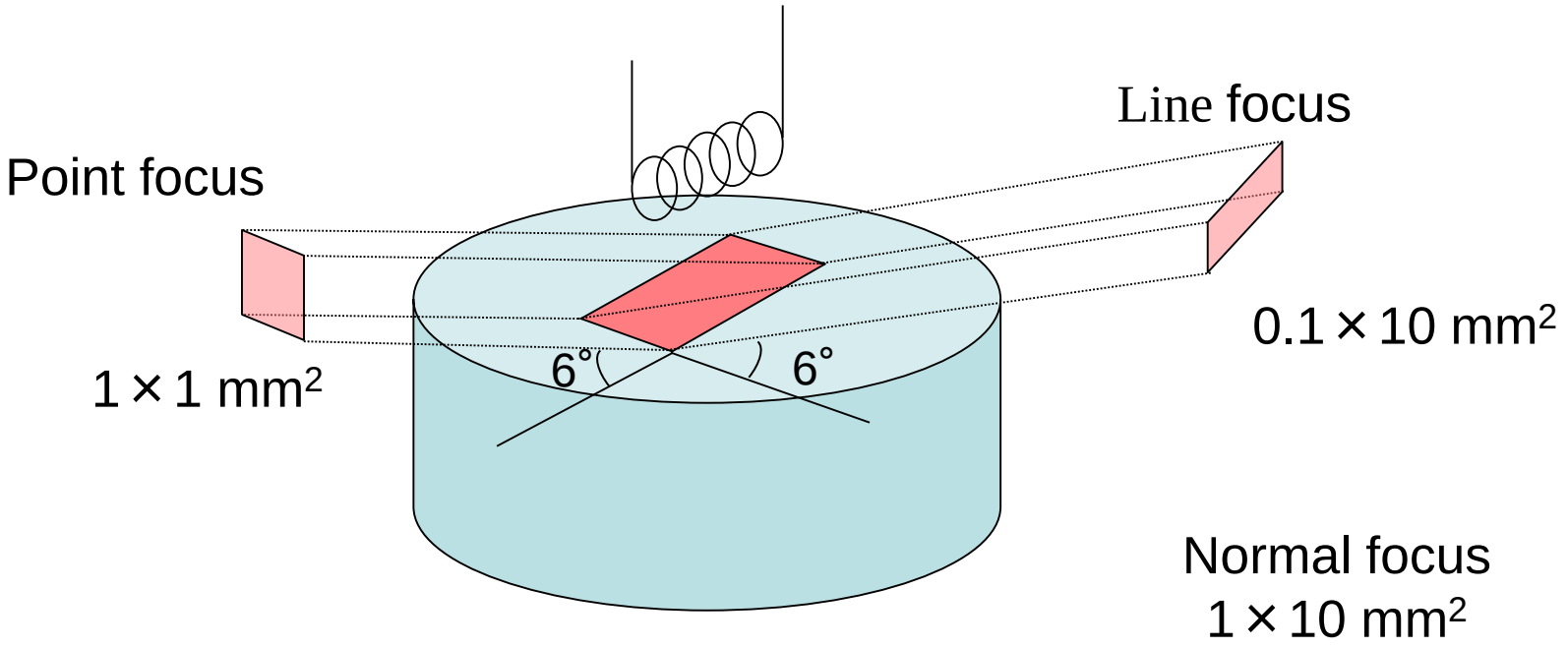
Excitation voltage

- Intensity ratio $K\alpha_1 : K\alpha_2 : K\beta = 100 : 50 : 20$
  - $K\alpha_1$ radiation is usually used for X-ray diffraction

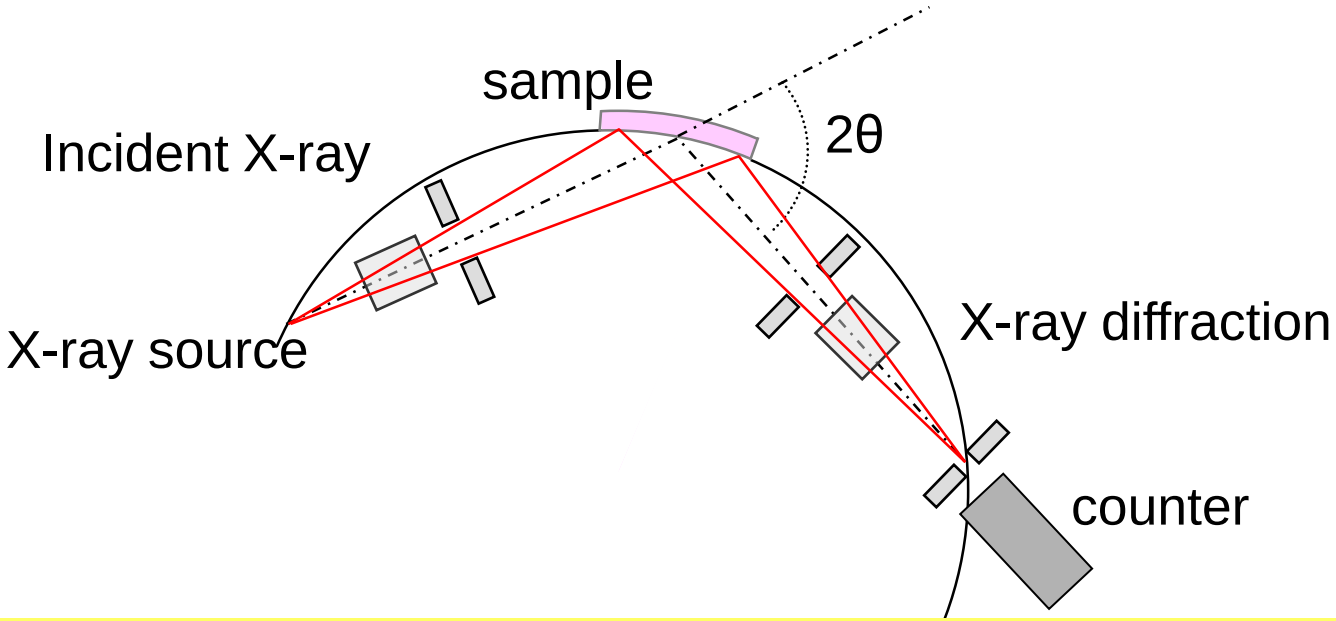
Target		Wavelength (Å)			excitation voltage (keV)
material	No.	$K\alpha_2$	$K\alpha_1$	$K\beta$	
Cr	24	2.294	2.260	2.085	6.0
Fe	26	1.940	1.936	1.757	7.1
Co	27	1.793	1.789	1.621	7.7
Cu	**29**	**1.544**	**1.541**	**1.392**	**8.9**
Mo	42	0.714	0.709	0.632	20.0
Ag	47	0.564	0.559	0.497	25.5
W	74	0.219	0.209	0.184	69.3

X-ray take off angle

- Take off angle is generally set to six degrees.
- There are two types of focal spots, a line focus and a point focus, depending on the take off direction.

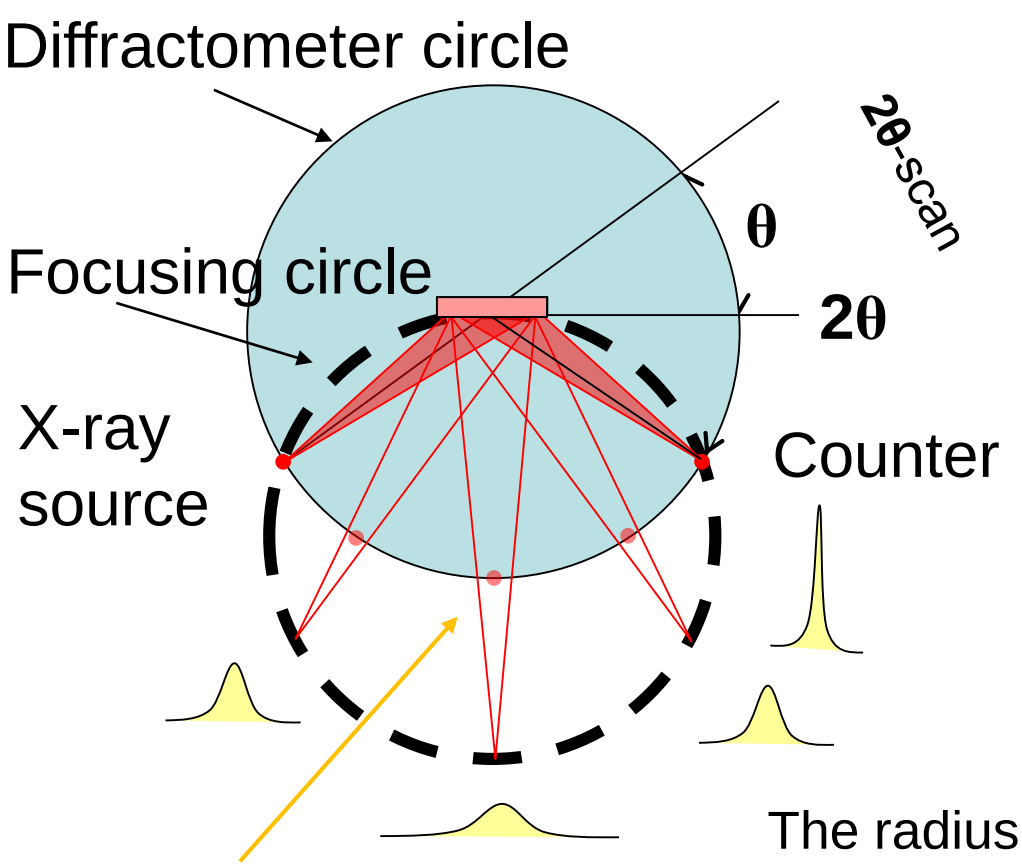


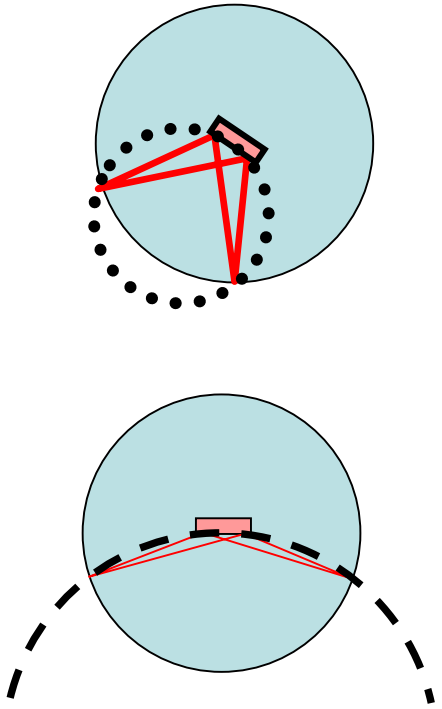
Principle of Focusing method



- The X-ray source, the sample, and the receiving slit must be on the focusing circle.
- The sample must be equidistant from the source and the receiving slit.
- The 2θ-θ scanning mechanism is needed.

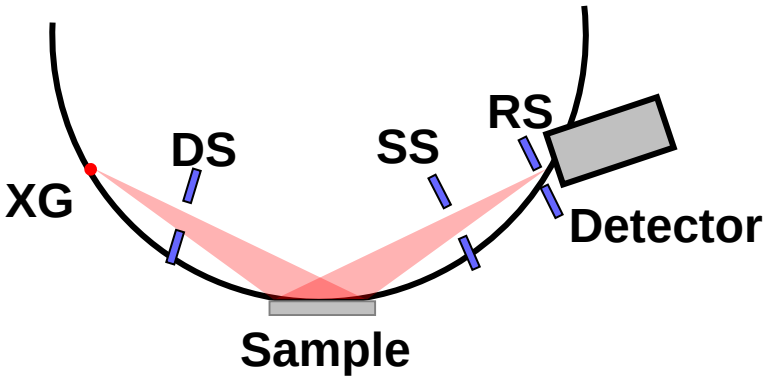
The conditions for the focusing method

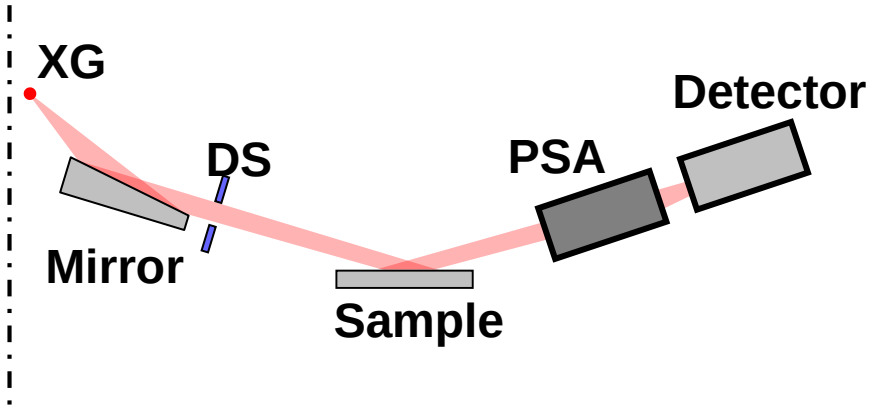




The radius of focusing circle changes depending on the diffraction angle

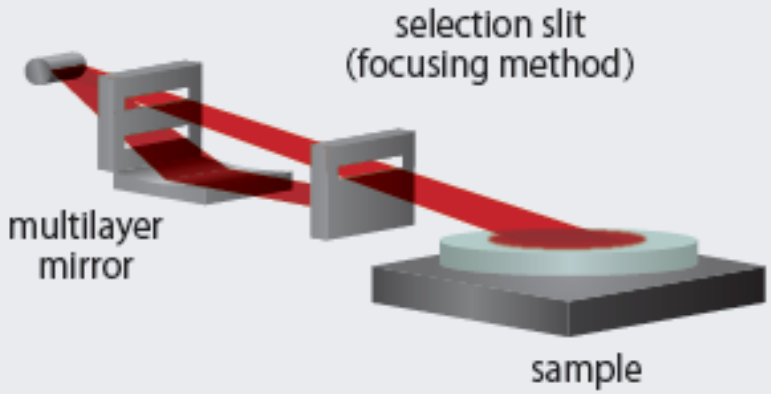
Focusing (BB) vs. Parallel Beam (PB)



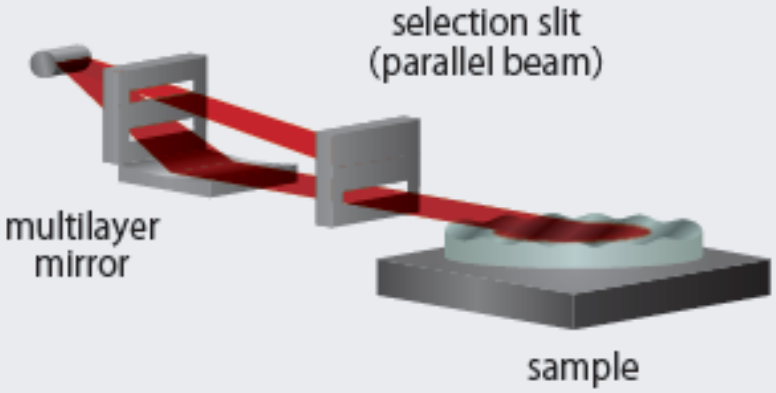


Cause of systematic errors	Non-flat sample	Axial divergence
	Axial divergence	
	Sample absorption	
	Sample displacement	
Calibration	Internal (preferred)	External
Intensity	High	Medium
Good for	Indentification of trace phases	Analysis of a sample with curvature/rough surface Structure refinement In-situ measurements

Bragg-Brentano focusing method



Parallel beam method



Systematic errors

Caused by

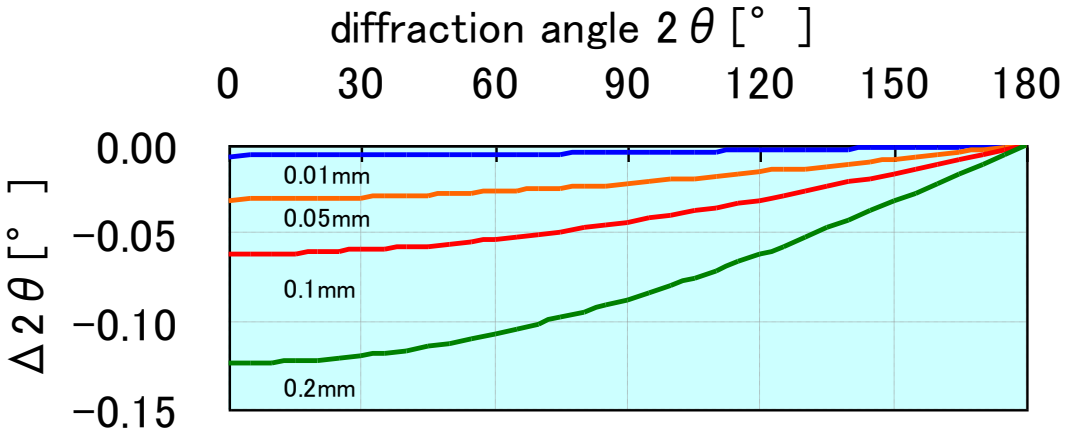
- Horizontal scattering (flat specimen error) (sample should be slightly bended, not flat)
  - gives larger effect on low angle side
- Absorption effect and sample displacement, sample transparency
  - gives large effect on the low angle side
- Axial divergence（umbrella effect）
  - 2θ＜90° ：broadens toward the low-angle side
  - 2θ＞90° ：broadens toward the high-angle side
- Instrument misalignment
  - gives the same shift to each peak on 2theta

Sample Displacement

An angle error occurs when the sample surface is not at the center of the goniometer, so called 2theta offset.

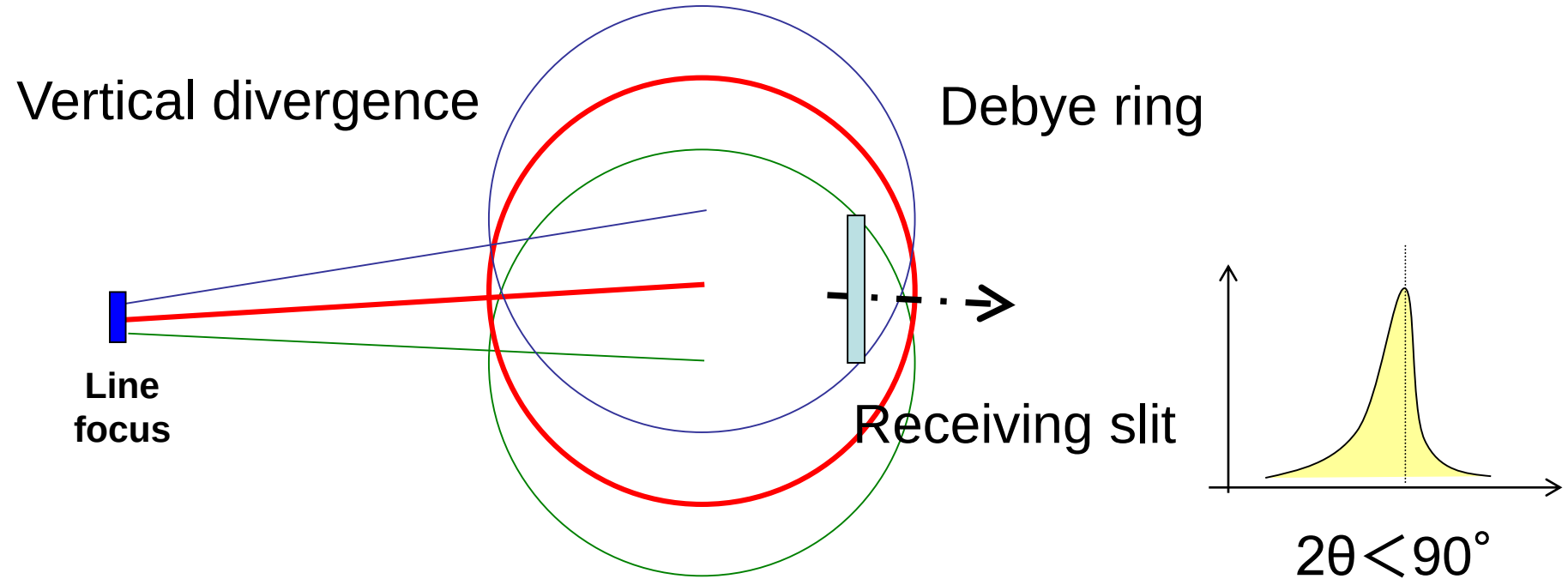
$$\Delta 2\theta(\text{Radian}) = -2 \cdot S \cos\theta / R$$

S: displacement, R goniometer radius



Umbrella effect

The umbrella effect is caused by vertical divergence of the incident X-ray, which makes the profile asymmetric



Slit selection

slit	size	resolution	intensity	position
divergence slit	wide	lower	higher	incident side
	narrow	higher	lower	
scattering slit	wide	lower	higher	receiving side
	narrow	higher	lower	
receiving slit	wide	lower	higher	receiving side
	narrow	higher	lower	

See the following website for the calculation of the ideal slit size:

http://www.ccp14.ac.uk/ccp/web-mirrors/krumm/html/xray/vcc.html

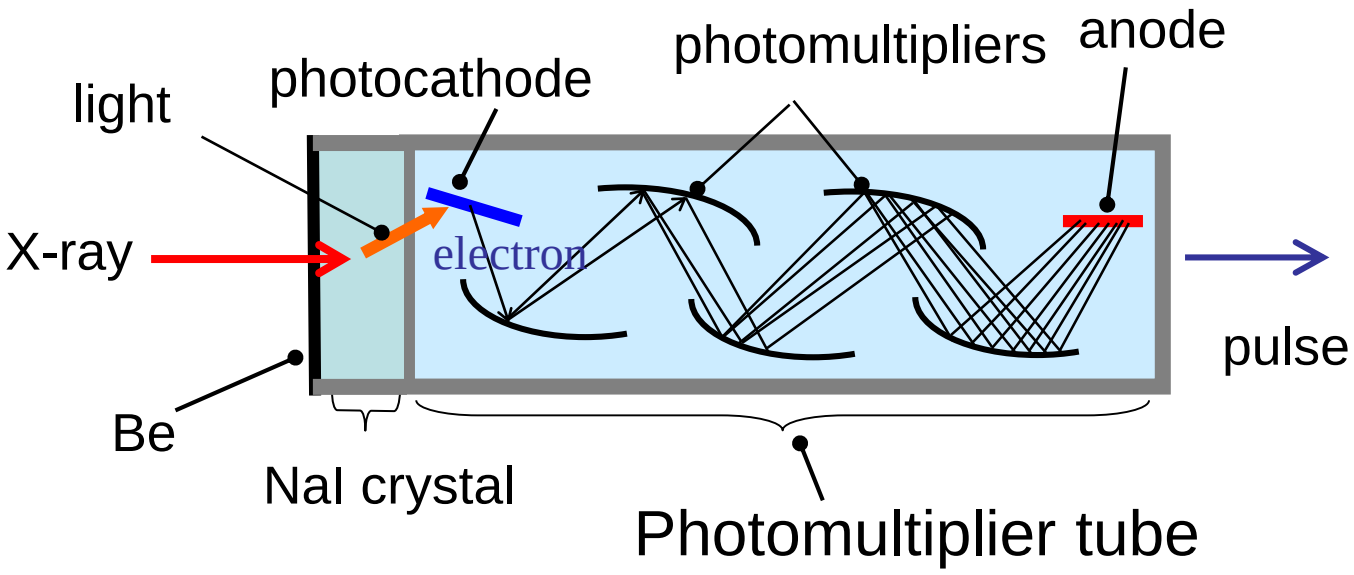
Counters

Interactions between X-rays and some materials are used to detect diffracted X-rays

Ionization effect	Position Sensitive Proportional Counter
	Solid State Detector
Scintillation effect	Scintillation Counter
	Imaging Plate
Photosensitivity	Photofilm

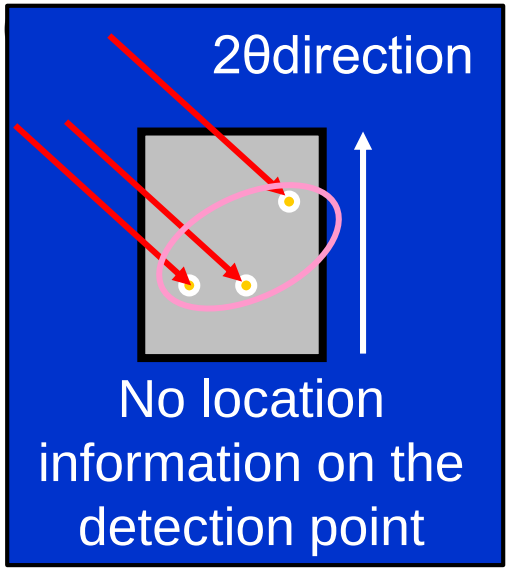
Scintillation counter (0D)

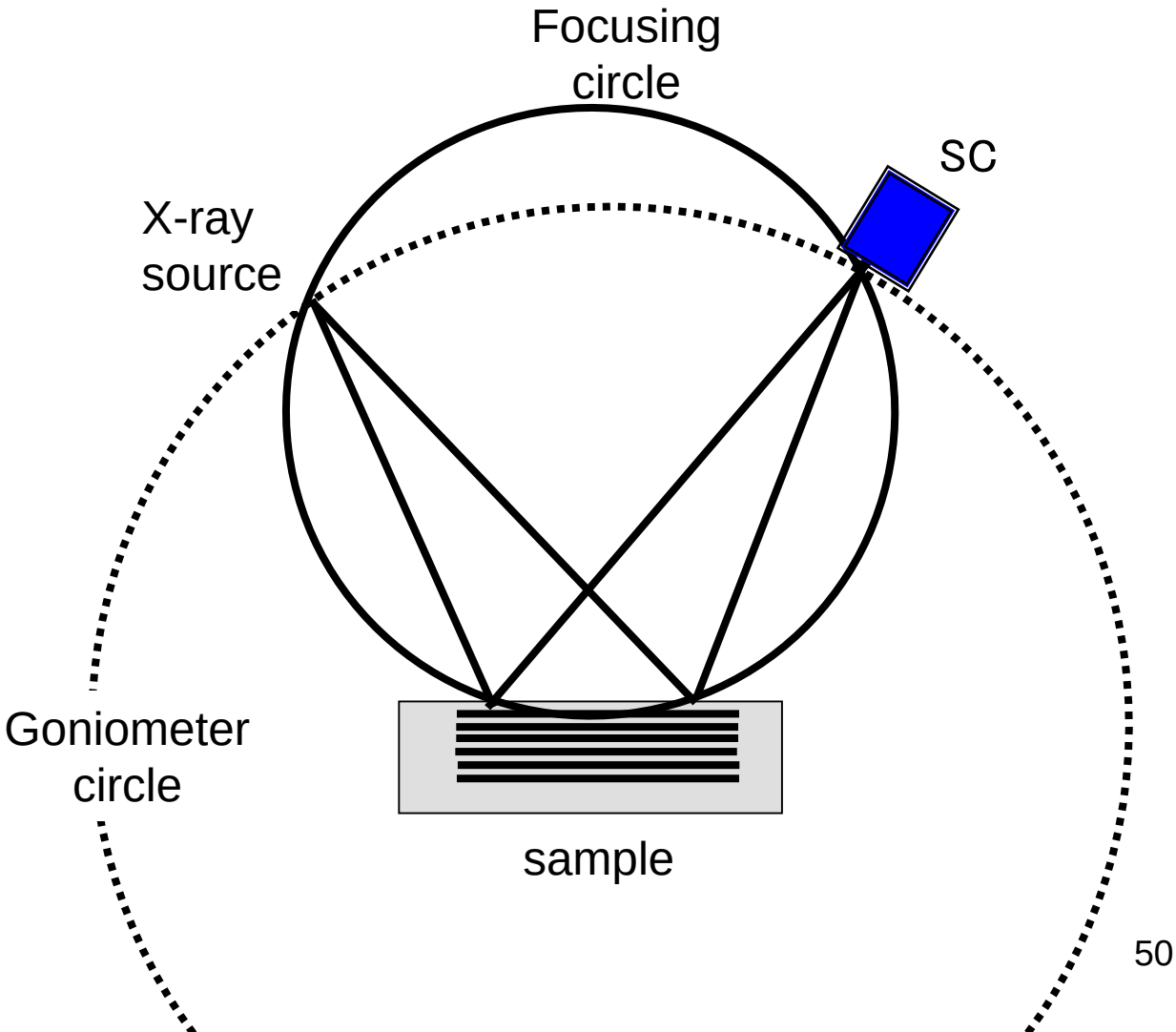
This counter uses a luminescent material called the scintillator to detect X-rays



Scintillation counter (0D)

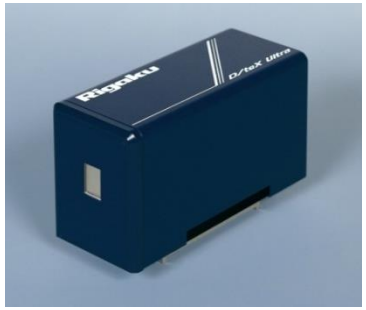
Scintillation Counter



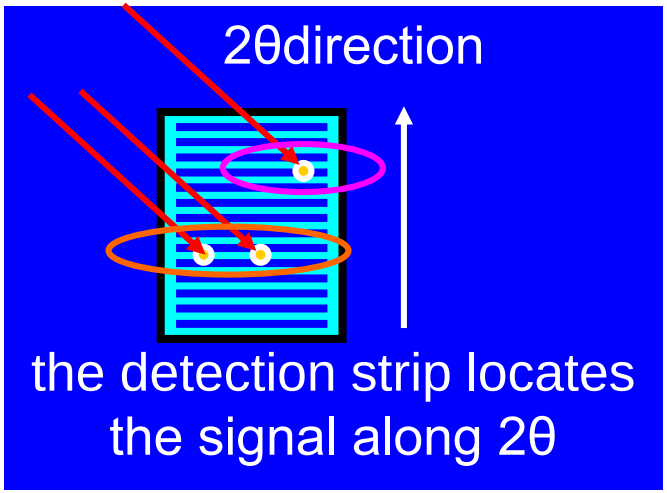


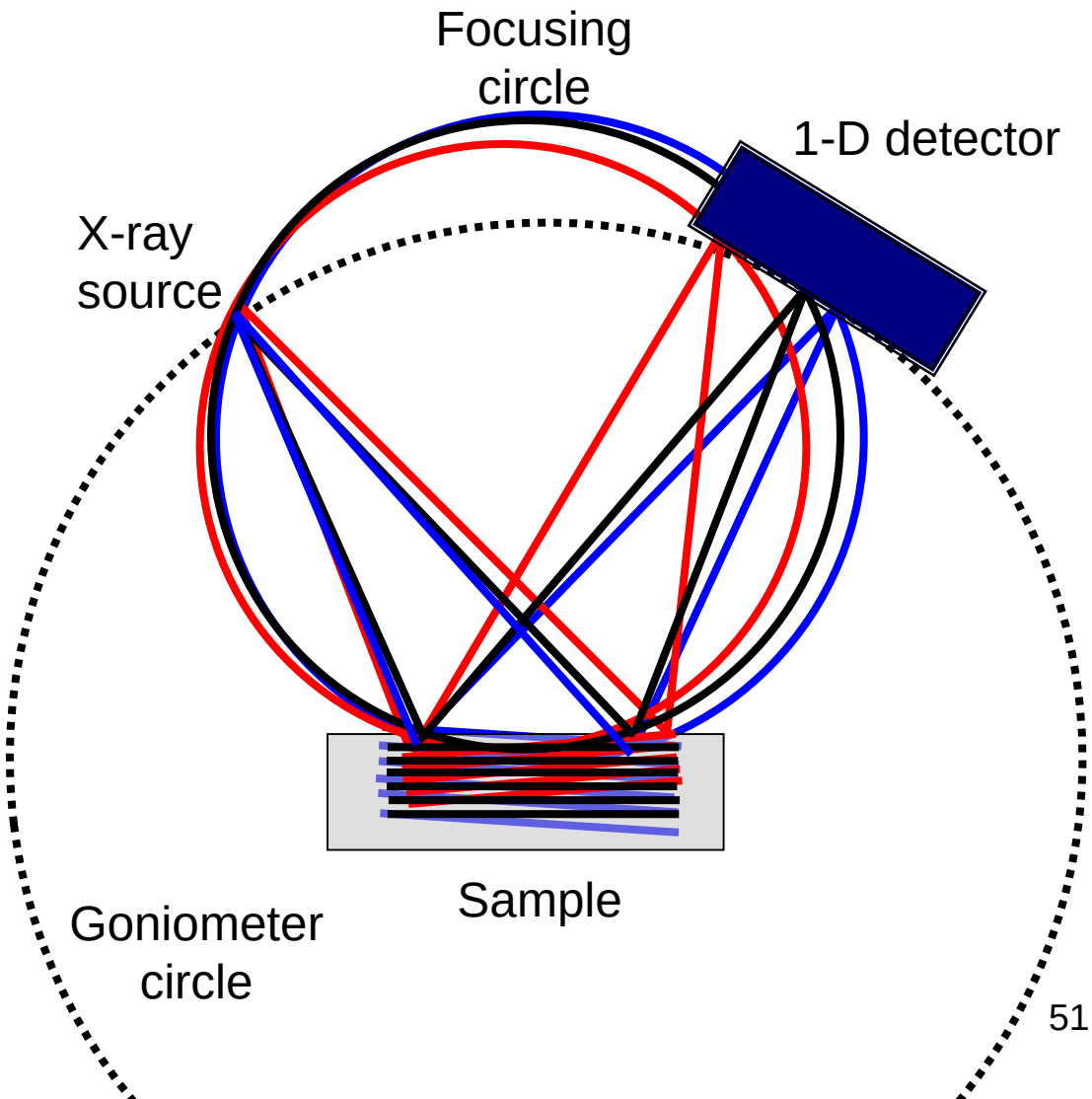
Rigaku

1D-Silicon Strip Detector



high speed 1-dimensional detector D/teX Ultra





XRF suppression mode for D/teX Ultra

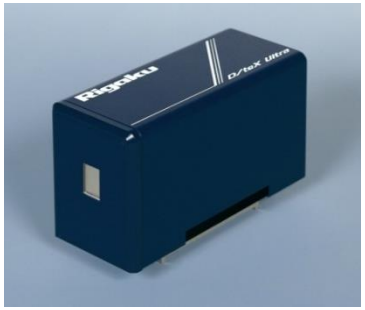
The energy discrimination baseline and window for the D/teX XRF reduction mode can be calculated easily using the following equation:

Calculation:

- $baseline_{XRF}$ = (baseline + upper-end)/2 -1
- $window_{XRF}$ = upper-end – $baseline_{XRF}$

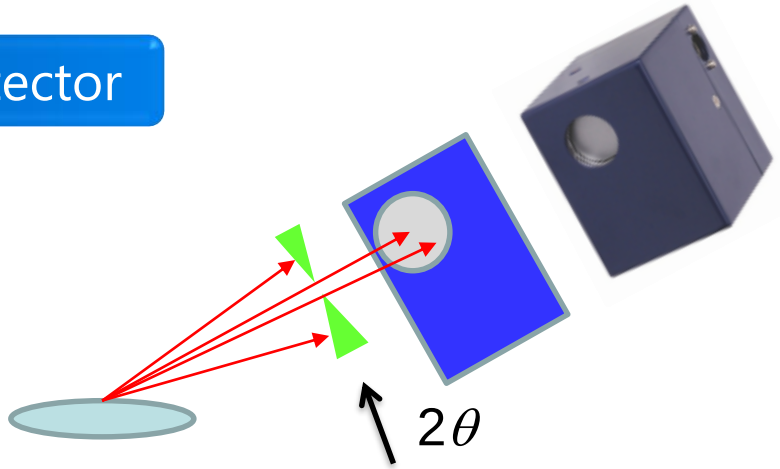
Example:

- baseline 38, window 16 → upper-end 54
- $baseline_{XRF}$ = (38+54)/2 – 1 = 46 – 1 = 45
- $window_{XRF}$ = 54 - 45 = 9

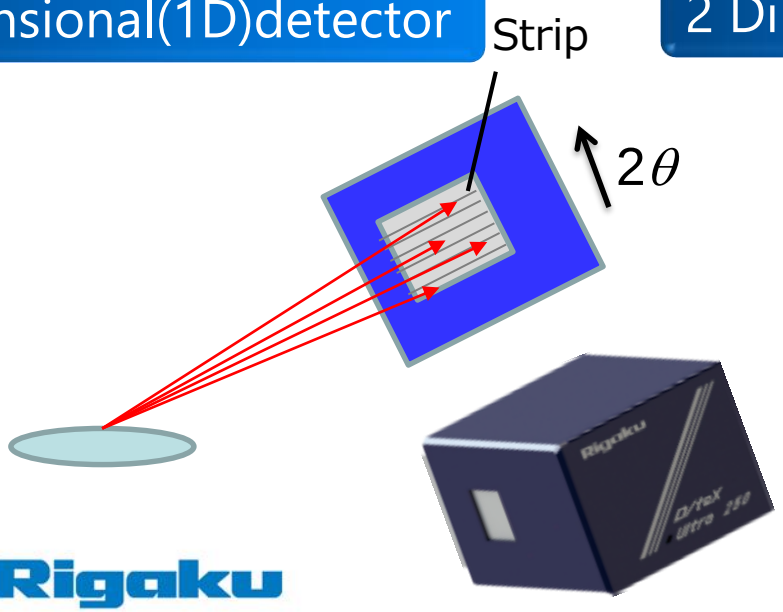


Detector for PXRD Equipment

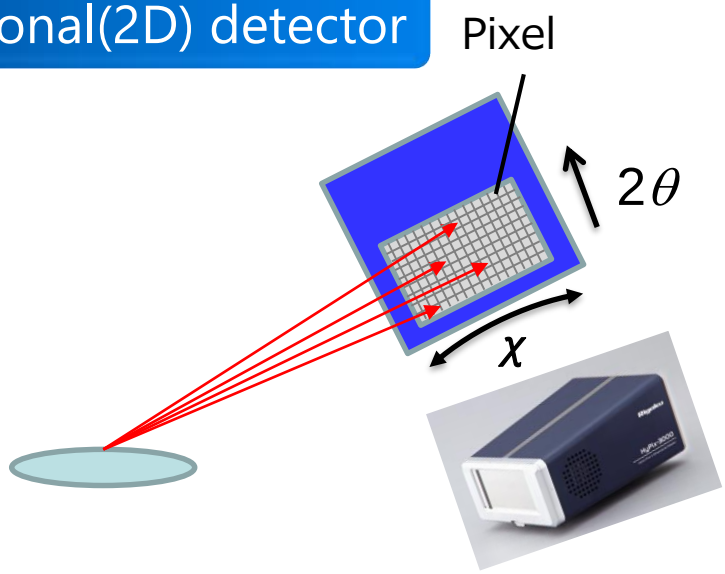
0 Dimensional(0D) detector



1 Dimensional(1D)detector

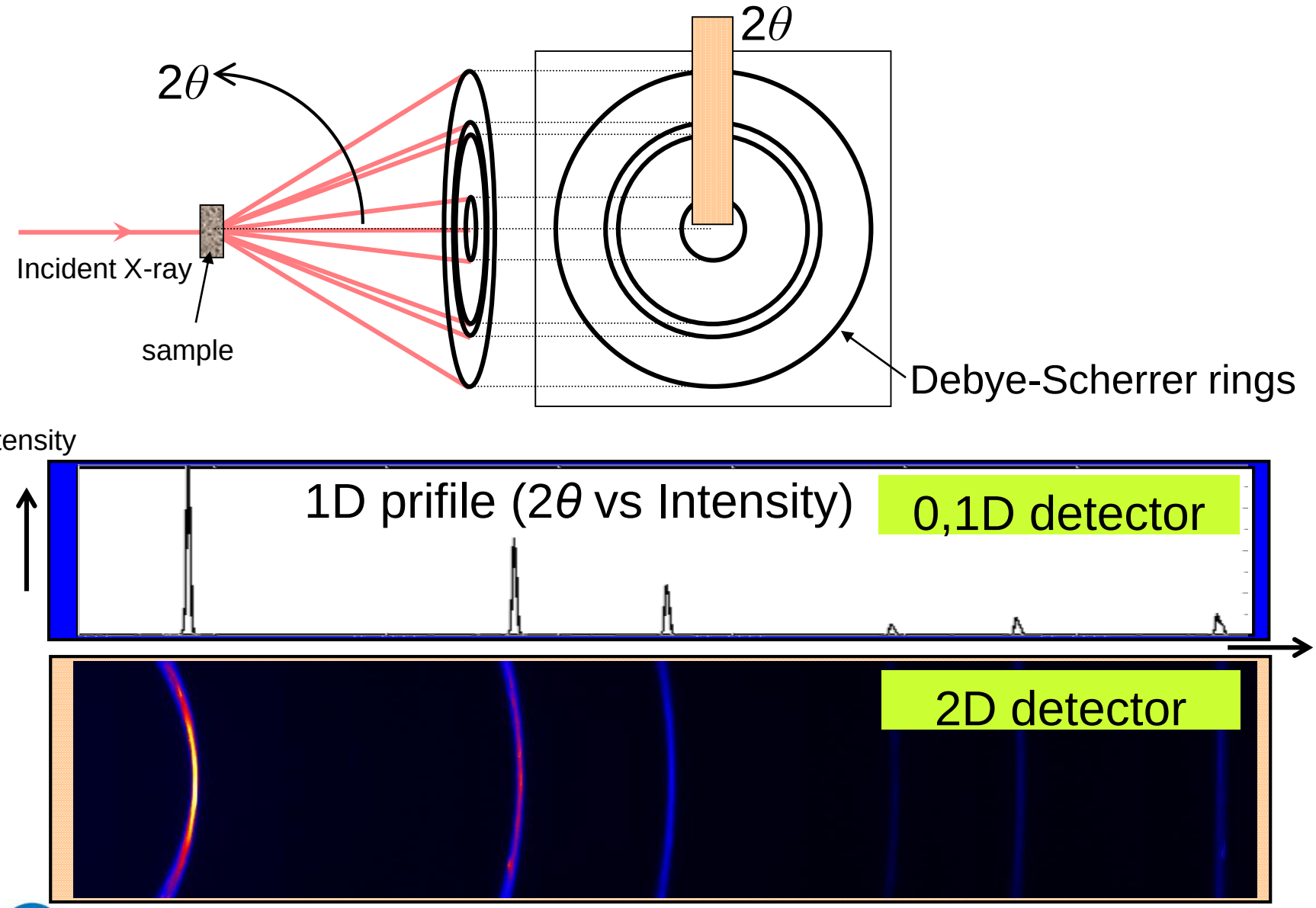


2 Dimensional(2D) detector



Rigaku

Comparison of 0D, 1D and 2D Detector



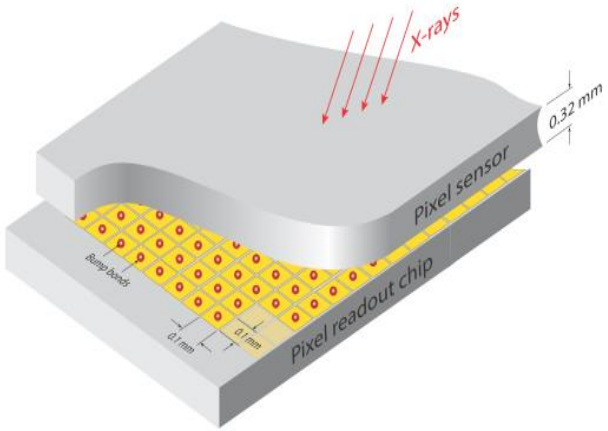
HyPix-3000 – Technical Specifications

0D – 1D – 2D snapshot/TDI mode	
Active area	38.5 x 77.5mm
Pixel size	100um x 100um
Pixel number	298,375
Energy resolution	< 15%(CuKa)
Count rate	> 2Mcps/pixel
Natural count	< 0.1cps/frame
Dead time	3.7 msec (standard mode) 0 msec (zero dead mode)

5 years warranty!

Hybrid multi-dimensional pixel detector

- Ultra-high dynamic range and high sensitivity
- Seamless switching from 2D to 1D and 0D mode with a single detector
- High spatial resolution, direct-detection pixel array detector
- XRF suppression by high and low energy discrimination



- Direct photon counting
  - Efficiency: >99% (Cu, Co)
- 100x100 μm^2 pixel size
  - No point spread function
  - Resolution = pixel size
- “Zero” background

Use to be...

Detector had to be changed
depending on dimension of detector

HyPix-3000 + SmartLab

0D-1D-2D application is done
by single detector

Sample preparation

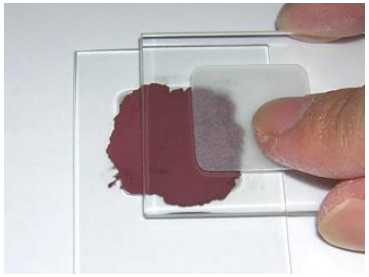
- Aluminum sample holder
- Glass sample holder

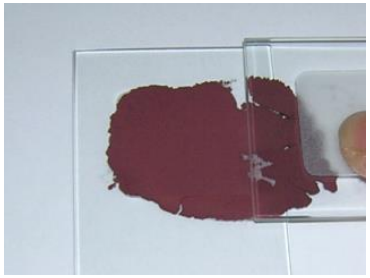
Sample preparation

~ glass sample holder ~

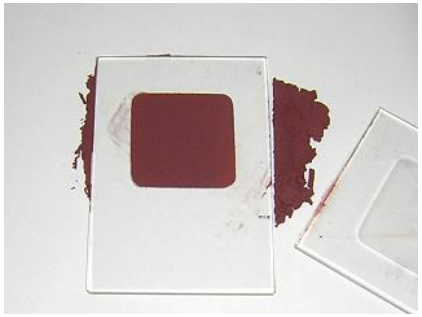
1. Powder sample put in the sample holder

2. Hold a sample with a glass plate.

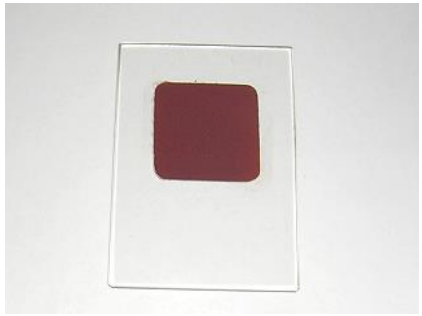




3. Smooth the surface of a sample with the back of a glass plate



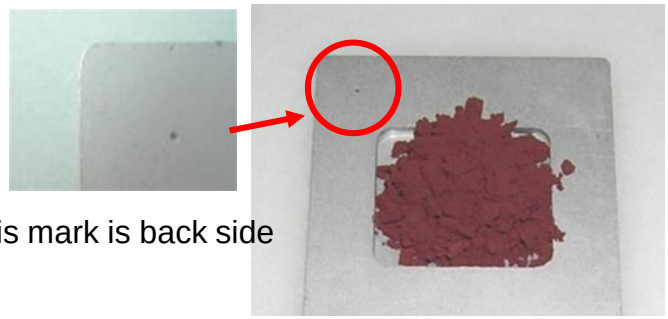
4. Wipe the glass holder with cloth



Sample preparation

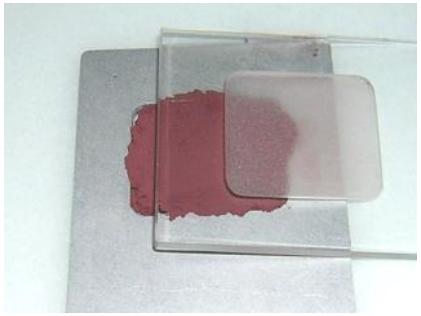
~ aluminum sample holder ~

1. Put a drug packing paper on a glass plate. After that, powder sample put in the sample holder



This mark is back side

2. Hold a sample with a glass plate.

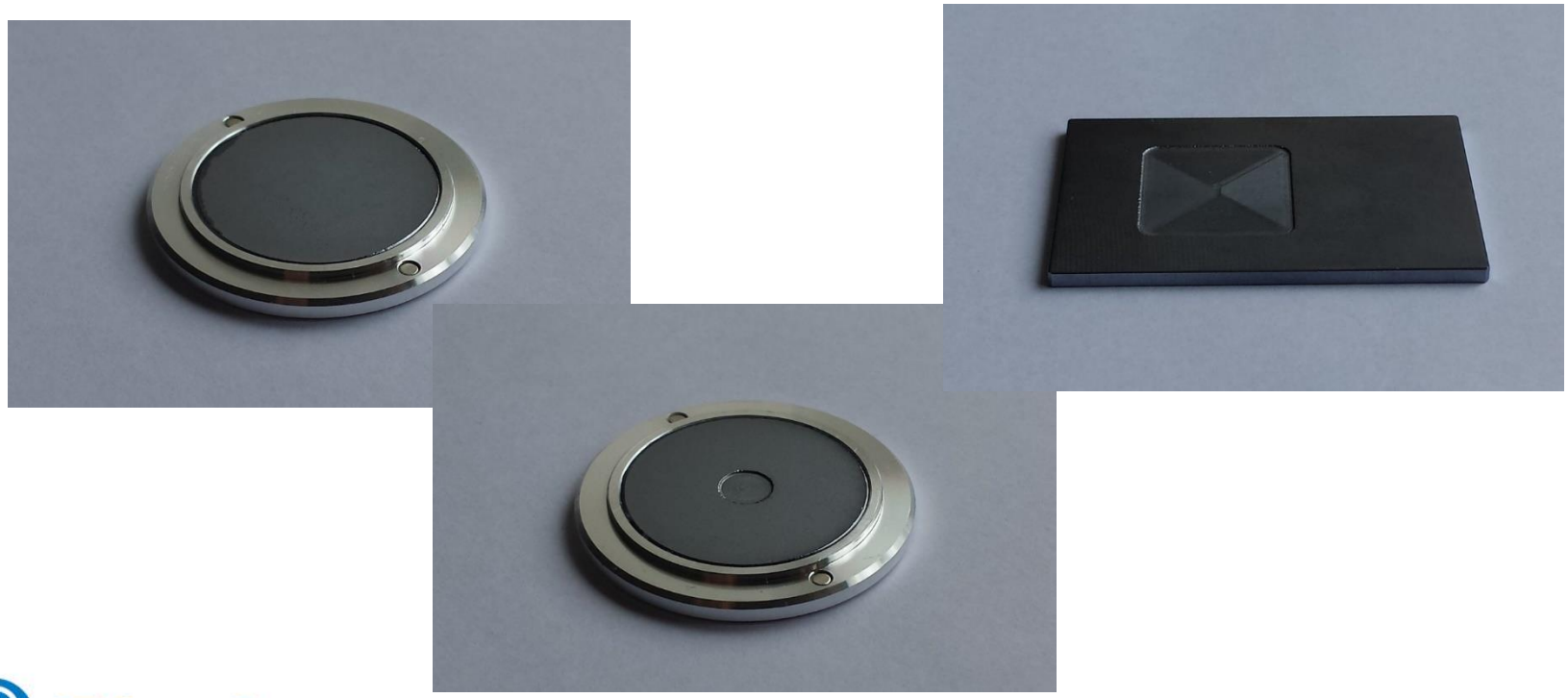


3. Compress a sample by a finger

4. Remove a drug packing paper, turn over the sample.

Zero-background sample holders

- Used for small sample amounts or in order to address transparency effects from weakly absorbing samples
- Available for the standard sample holder and the ASC-6 sample changer

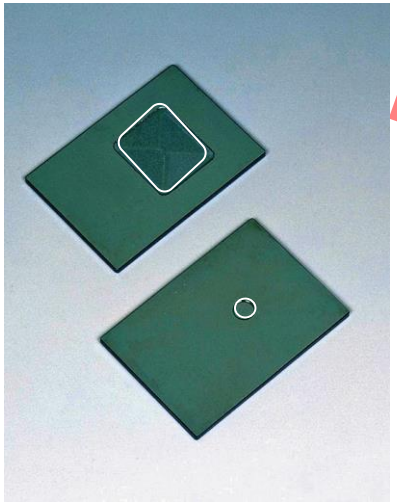


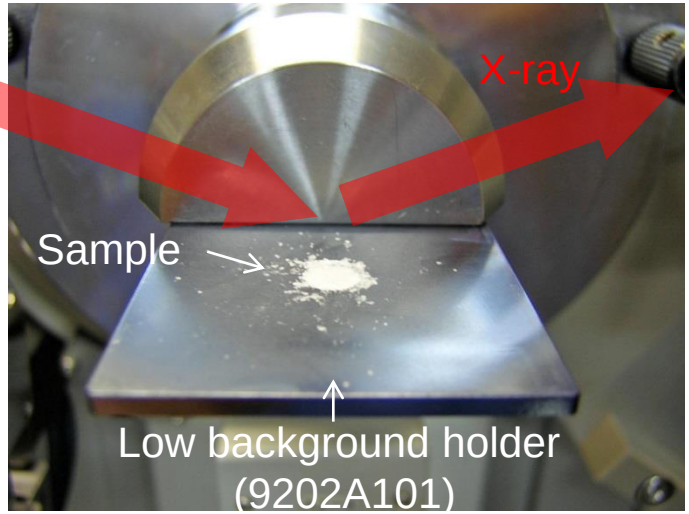
Small sample volume

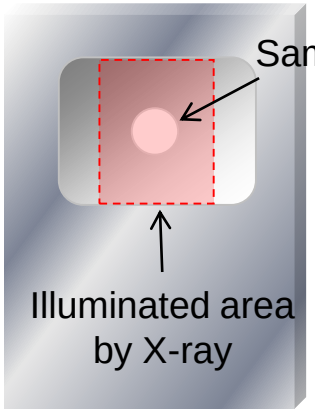
Low-background silicon sample holder

Sample holder made of a silicon single crystal cut in a certain orientation.

It does neither show any diffraction peaks nor halos like glass sample holders.

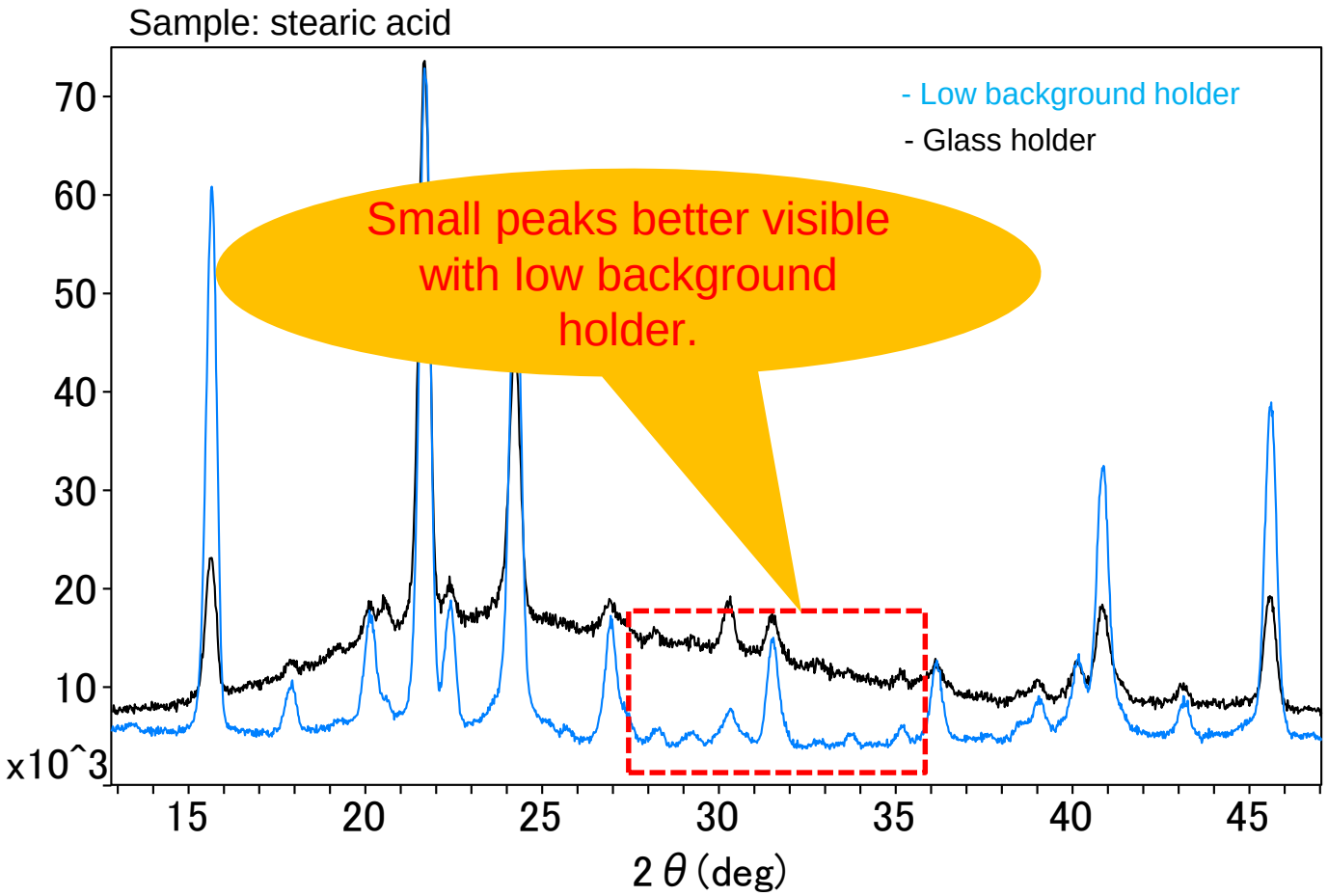






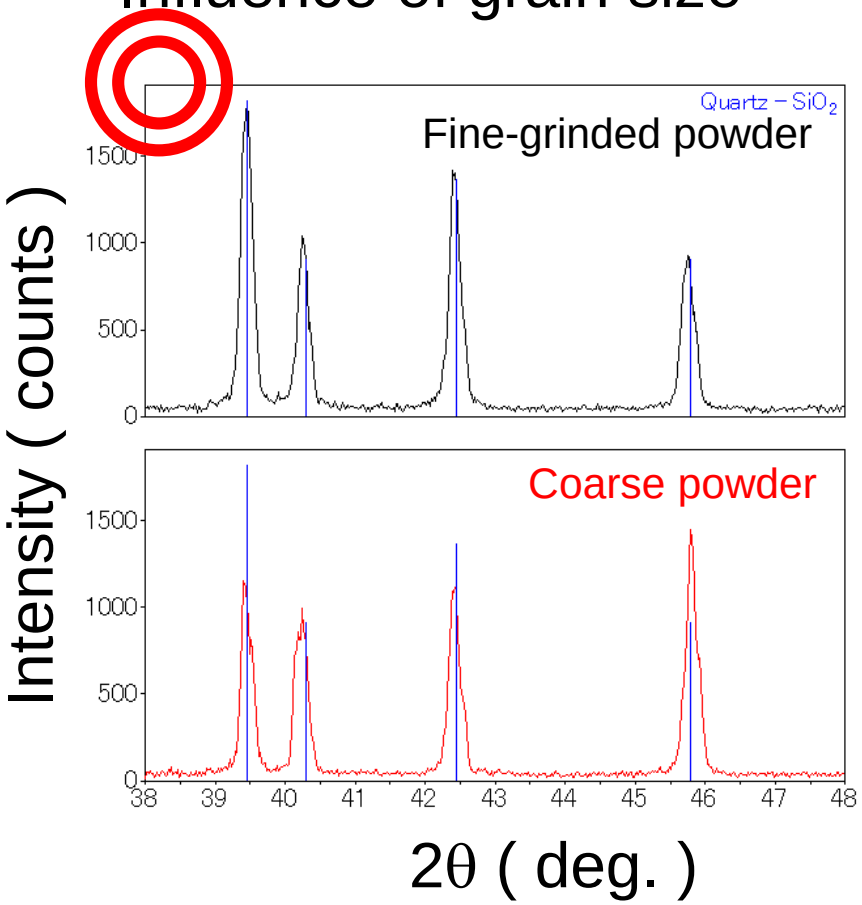
Small sample volume

Low-background silicon sample holder

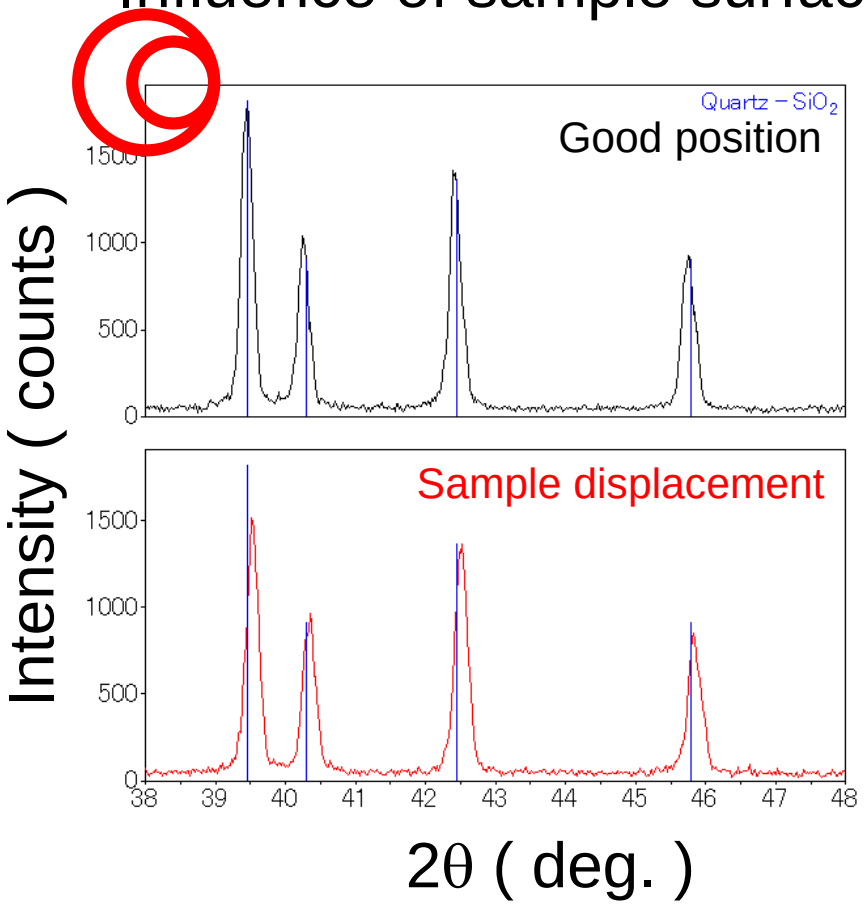


Sample preparation to produce good results

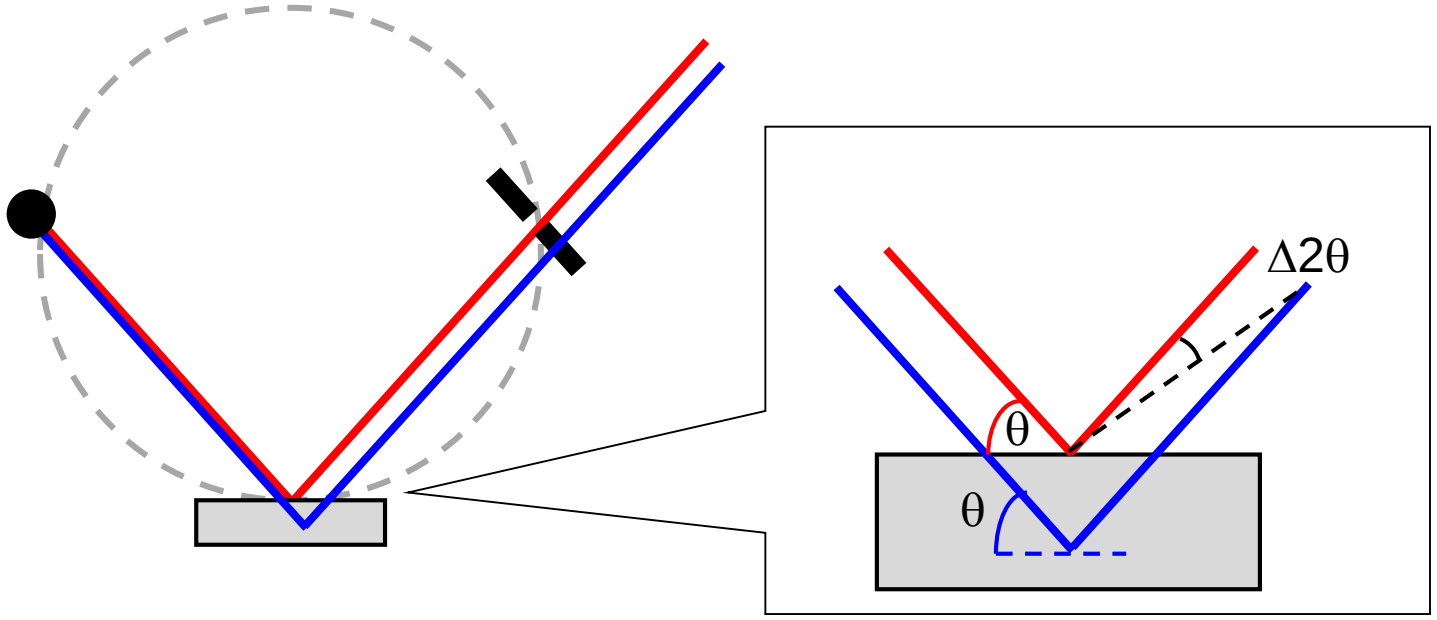
- Influence of grain size



- Influence of sample surface



Peak broadening due to sample transparency



- For materials with weak absorption X-rays penetrate deep into the sample. Thus, diffraction occurs in the sample but with a sort of “sample displacement”. This so-called transparency effect causes peak broadening.
- Simply using a shallower sample holders generates peaks from the sample holder (e.g. Al), thus zero-background sample holders (oriented Silicon single crystals) are needed.