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Introduction to XRD instrumental function

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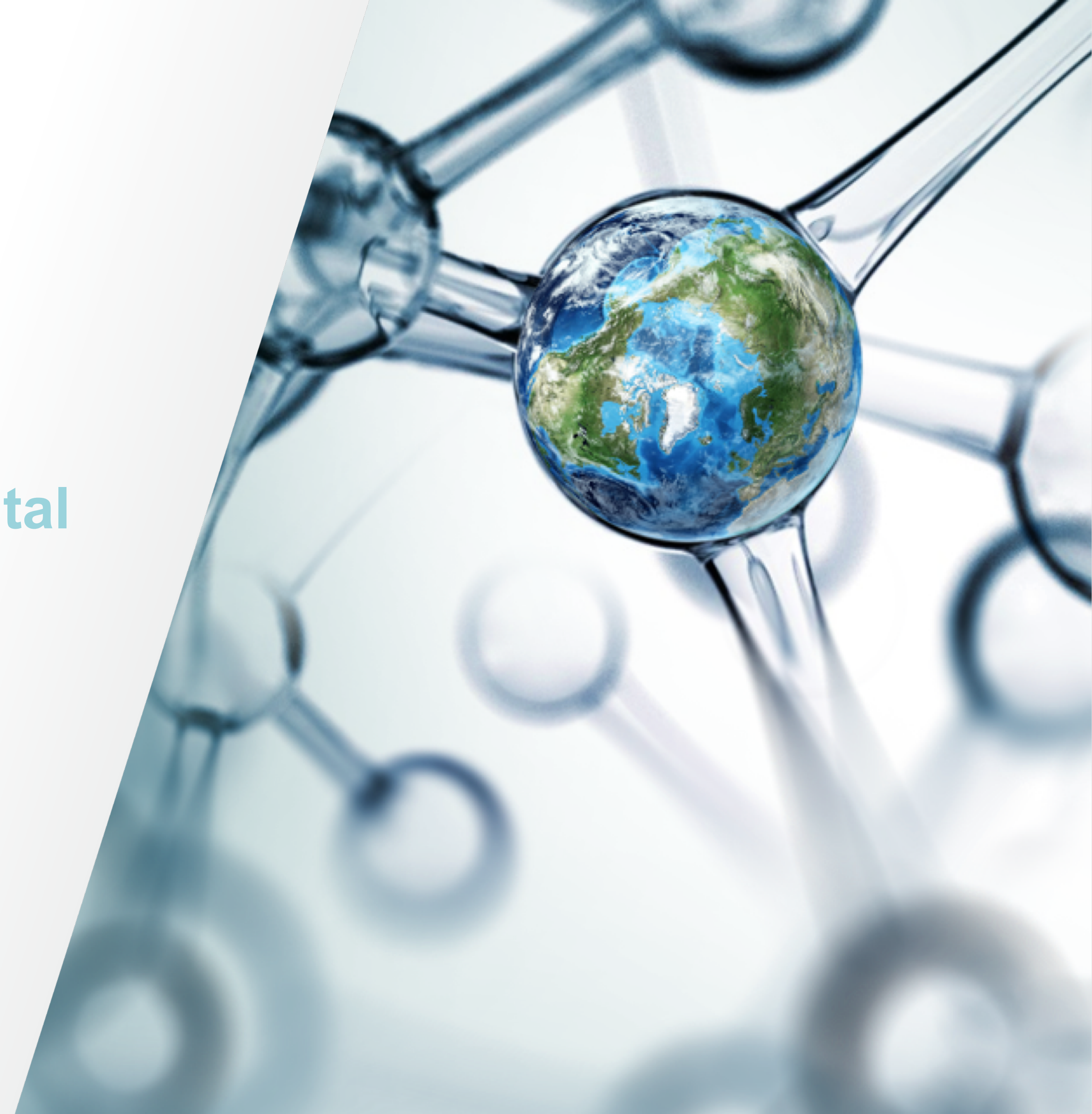
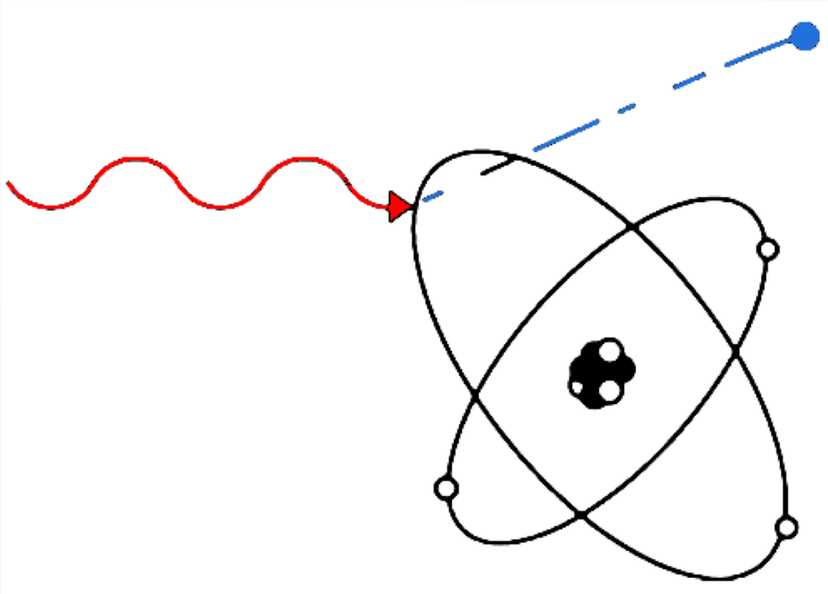
5-Jul-21



The world leader in serving science

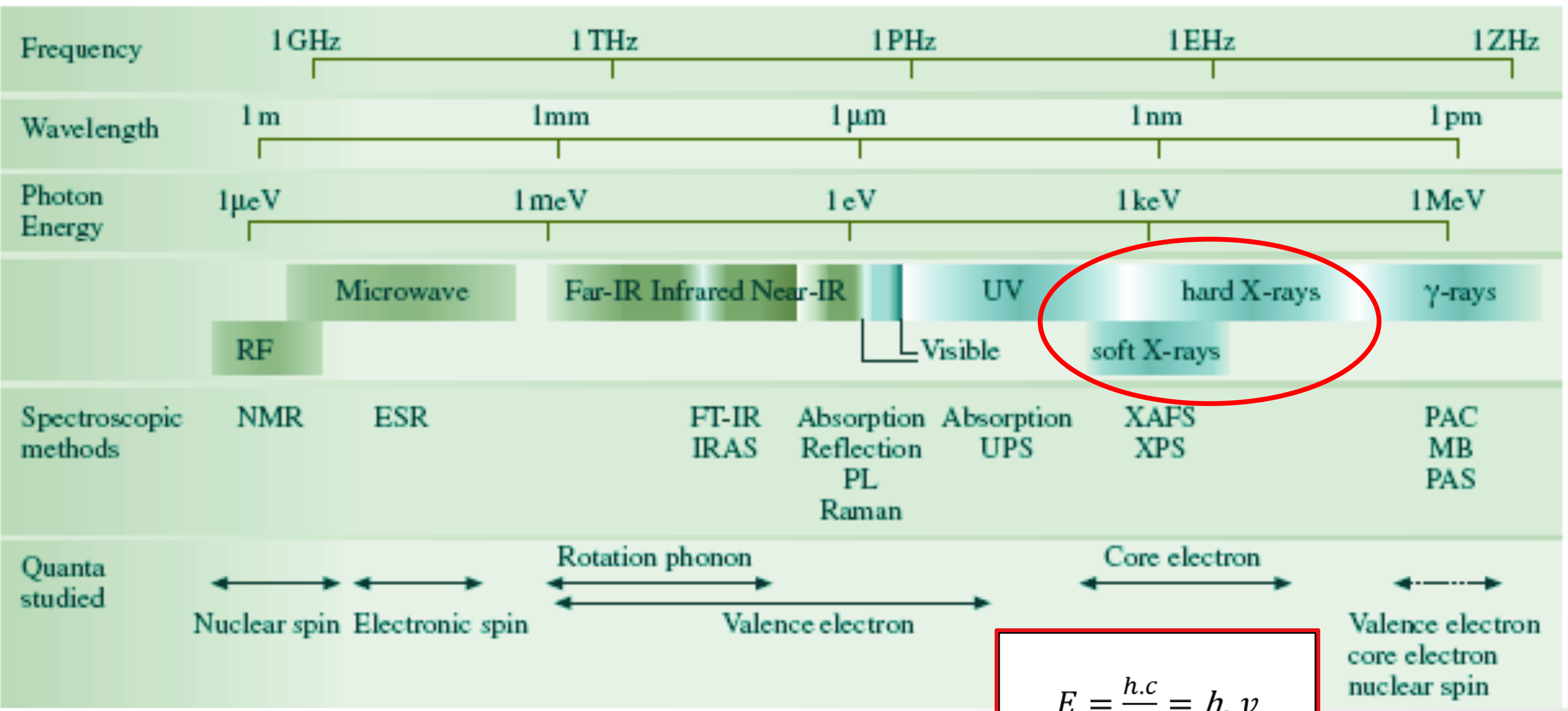
Wave-matter interaction

When a photon does encounter an atomic particle, it transfers energy to the particle. The energy may be reemitted back the way it came (reflected), scattered in a different direction or transmitted forward into the material.



Wave-matter interaction

The energy of photons used for optical spectroscopic measurements of various quanta

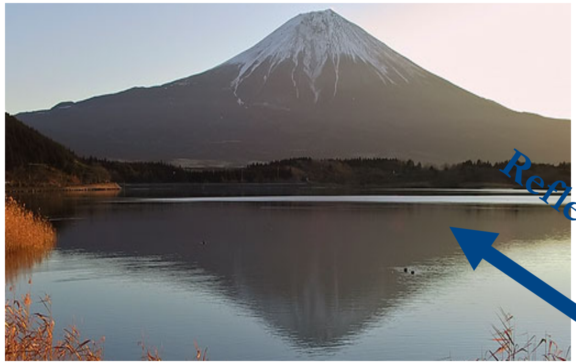


$$E = \frac{h.c}{\lambda} = h.\nu$$

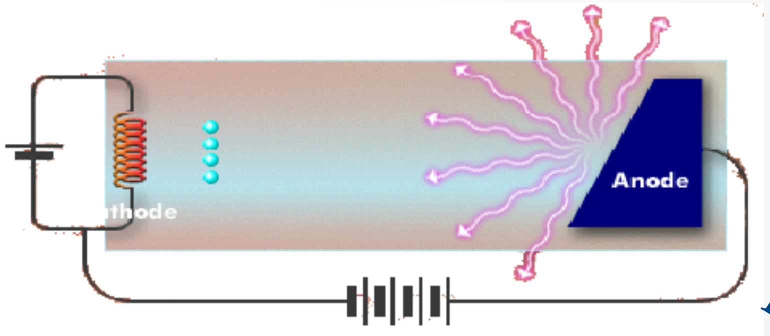
EHz : exahertz (10^{18}) - ZHz : zettahertz (10^{21}) - YHz : yottahertz (10^{24})

Wave-matter interaction

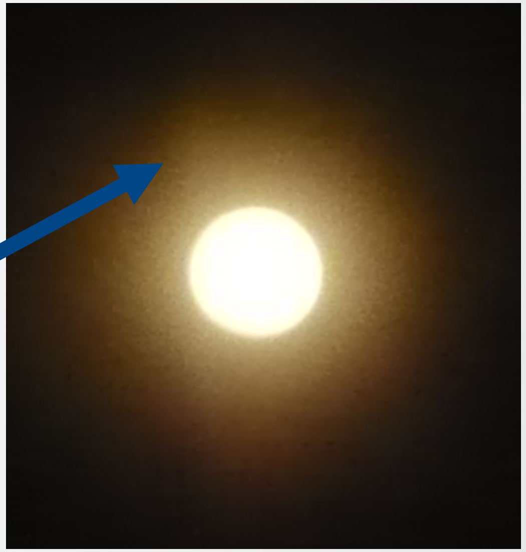
X-rays Production : classically by excitation of external electronic level with electron beam



Reflection

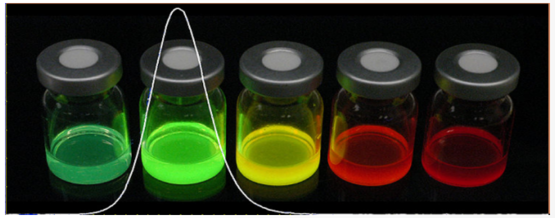


Diffusion



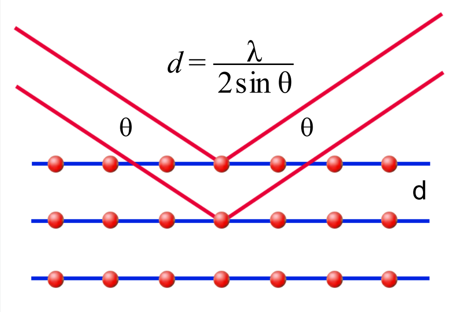
Absorption

fluorescence

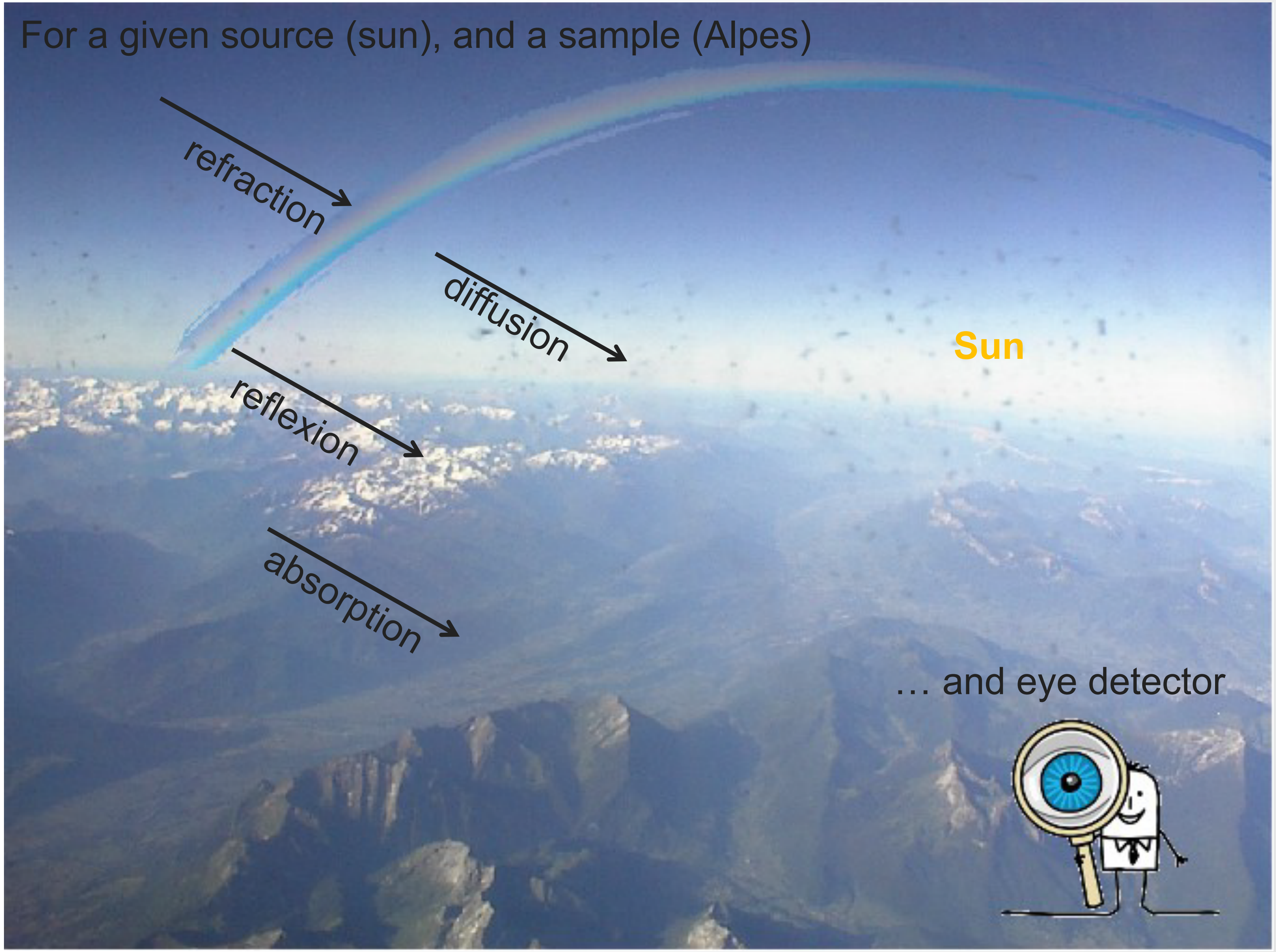


Diffraction

Bragg's law



Wave-matter interaction



Instrumentations using radiation for material analysis need to be optimized :
- source characteristics
- detection characteristics
- sample environment
- mechanical design

Wave-matter interaction

We can propose instruments for this expertize:

- X-ray diffraction : phase analysis, identification and quantification of phase
- X-ray diffusion (SAXS) : nanoparticles morphology
- X-ray fluorescence : elemental analysis
- X-ray imaging : image of X-ray absorption
- X-ray reflection : nanometric coating analysis

Focus on X-ray diffraction

Wave-matter interaction

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Which material is able to diffract ?

Anything which has a structure at the nanometric scale, with enough contrast.

Structure : ordering at the atomic scale
Then, mostly crystallized material in bulk or powder but even in liquid cristals or in smoke

Contrast : X-ray interacts with electronic level
Then, heavy atoms => high contrast

Instrument

Instrument is designed for the need we are looking for. It allows to measure and quantify physical parameters (length, weight, power, energy, time…)

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X-ray diffraction setup

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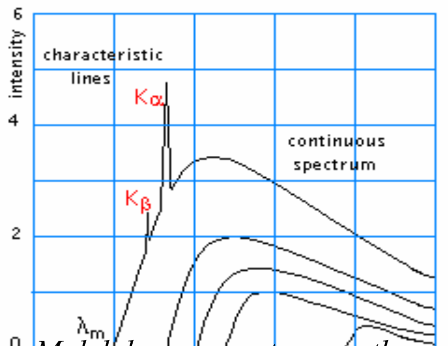
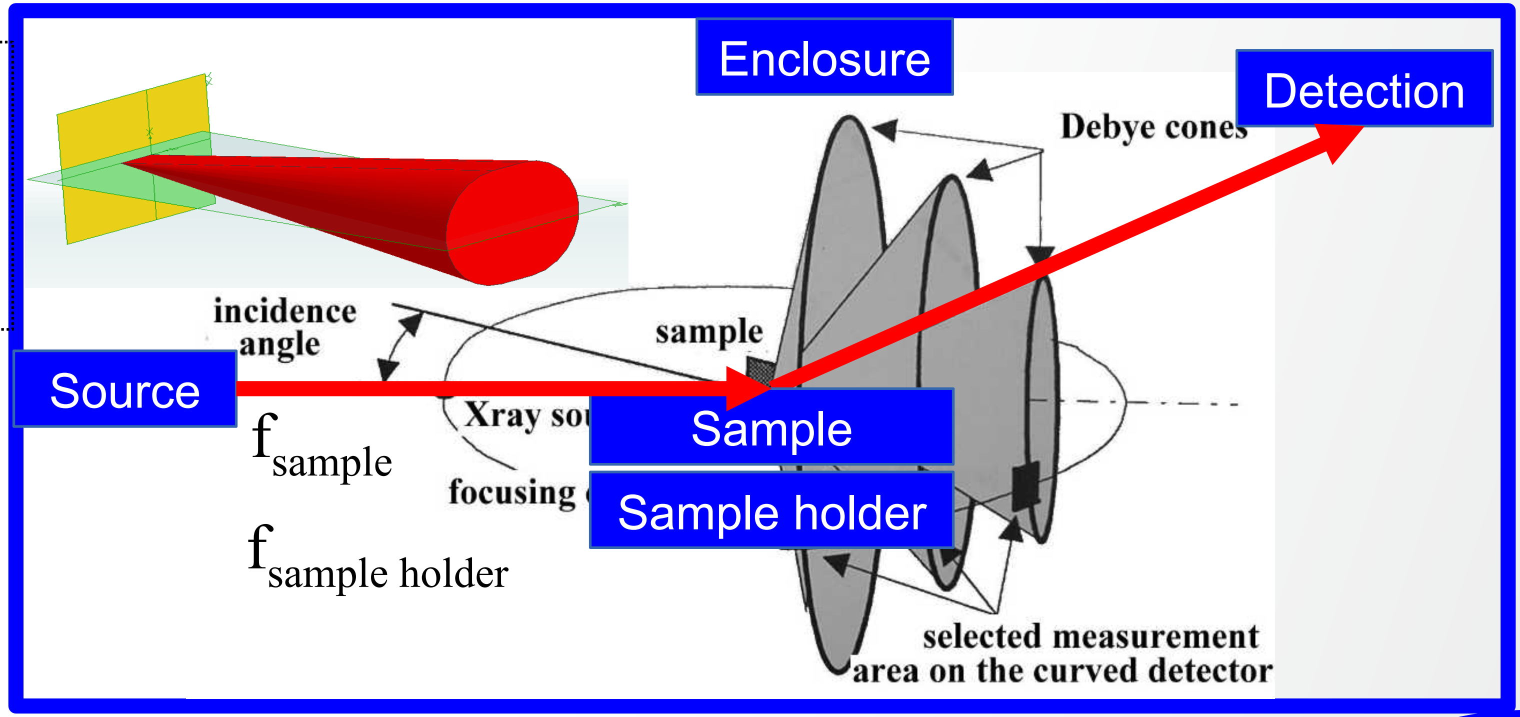
Instrument using a wave for probing matter is defined by several functions :

A light emission characterized by :

- a spectral range
- a solid angle
- intensity
- dimension and shape of the source



Molybdenum spectrum vs the applied voltage



A detector is characterized by :

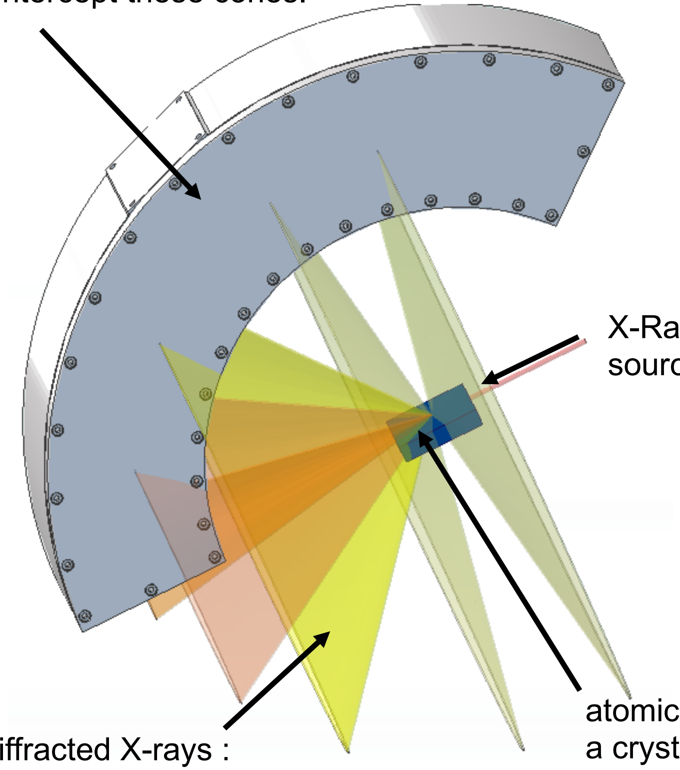
- spacial resolution
- dynamic range
- energy resolution
- dimension

$f_{operator}$

Most instruments using radiation corresponds to this scheme :
XRD – XRF- FTIR- Raman-UV …

X-ray diffraction

“Phenomenon in which the atoms of a crystal, by virtue of their uniform spacing, cause an interference pattern of the waves in an incident beam of X-rays. The crystal's atomic planes act on the X-rays in the same way a uniformly ruled grating acts on a beam of light (see polarization). The interference pattern is specific to each substance and gives information on the structure of the atoms or molecules in the crystal. “



Considering a monochromatic and (quasi) parallel X-ray beam hitting a crystallized material. X-rays are able to diffract on the sample. Diffraction is represented by concentric cones (Debye cones), where the center is the sample. The axis of cones is the direction of the primary beam. The solid angle is called (4.theta). There is a relationship between theta and the periodicity of the material, the Bragg law :

$$\lambda = 2d_{hkl} \sin(\theta_{hkl})$$

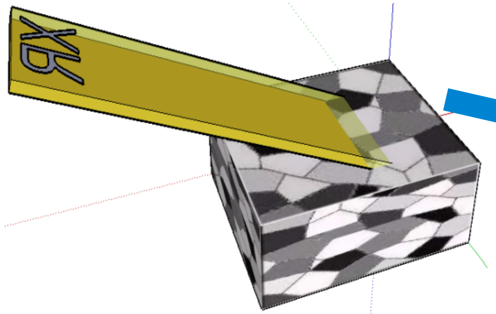
λ = X-ray wavelength

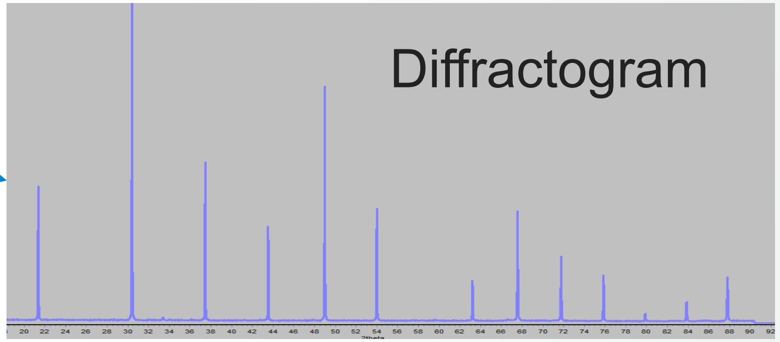
d_{hkl} , the periodicity of atomic planes in the (hkl) direction,

θ_{hkl}, the deviation angle

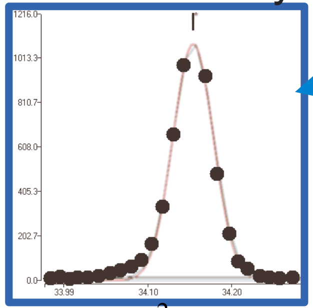
In other words, X-ray diffraction allows to identify the phase of a given material, when it is crystallized.

Information obtained by XRD





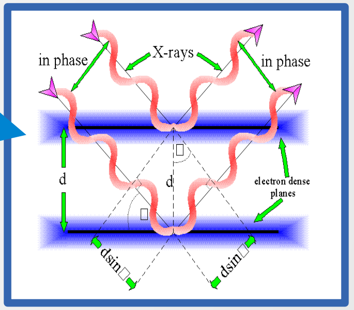
Peak intensity/shape



$$I = I_0 . P . L . F^2 . m . A . e^{-2M} . \frac{1}{V^2}$$

Overall analysis of peaks shape, position and intensity and background function

Peak position



$$\lambda = 2d_{hkl} \sin(\theta_{hkl})$$

What is the composition?	Phase identification
and how much?	Phases quantification
what is the crystallite size and morphology?	Particles size,
Is-there any constrains inside crystallite?	micro strains
Or in the overall sample?	Stress analysis
Is there an organization at the crystallite scale?	Preferred oritentation (powder) or texture (bulk)
And can we quantify a distribution? Pole figures,	ODF
Structure, organization of electronic density levels :	cell parameters, valence, atomic occupation, ...
What is the structural modification of my sample vs physical parameters (P, T...)?	dilatation, phase transition
Structural anisotropy :	stress, texture, thin film characterization ...

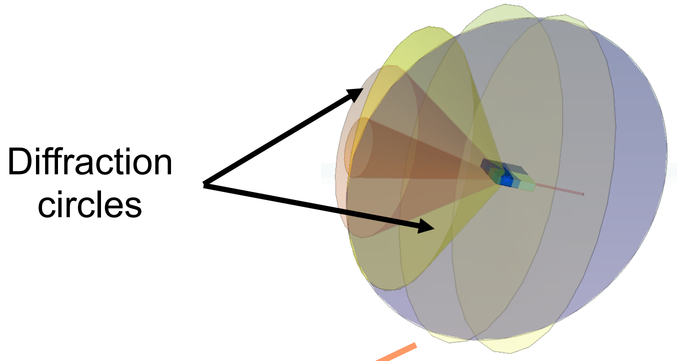
Powder vs crystal

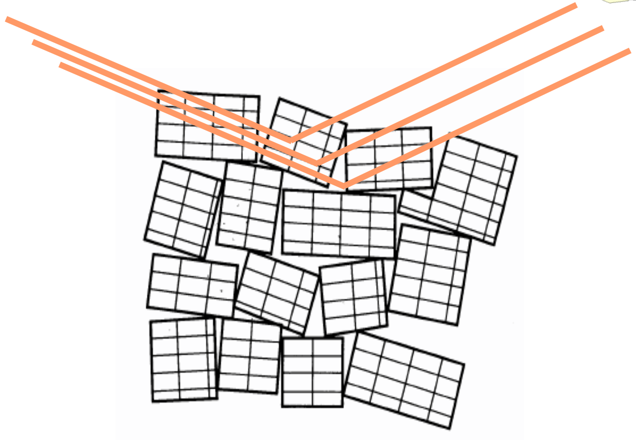
Powder sample :

- **Large number of grains probed by X-rays**
- Grains are small according to beam size (20µm)
- Each grain is able to diffract according to its orientation

=> several diffracted beam for a fixed sample orientation

Diffraction plane intercepts all diffraction cones





Possible with ARL EQUINOX

Not possible with ARL EQUINOX

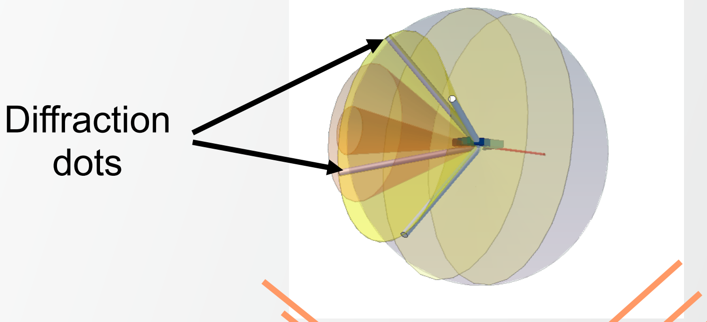
Single cristal :

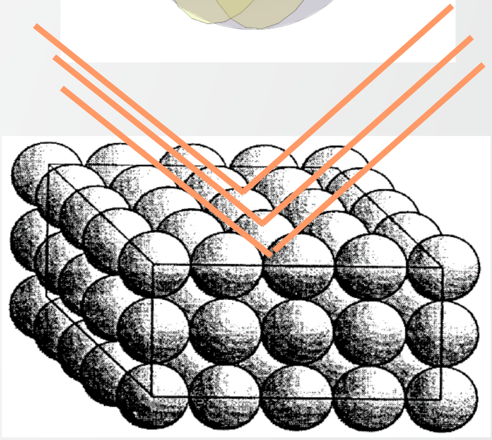
- **1 unique grain probed by X-rays**
- 1 unique diffacted signal for a given orientation of cristal

=> only possibilities to record several diffracted beam

- Moving cristal by using a goniometer and monochromatic beam
- Not moving cristal, but using a polychromatic beam

→ Laue method (consult us to define the instrument)



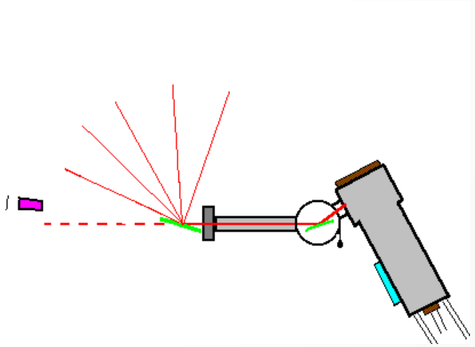


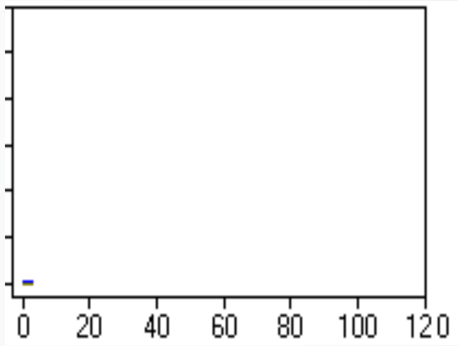
Function X-ray detection

0D Detection :

Acquisition is done Stepwise

2θ and statistics are time dependent



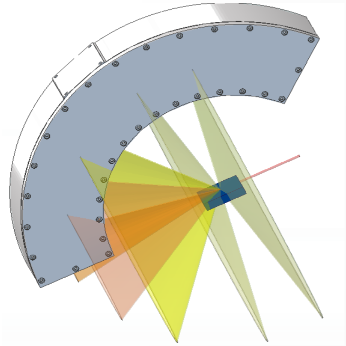


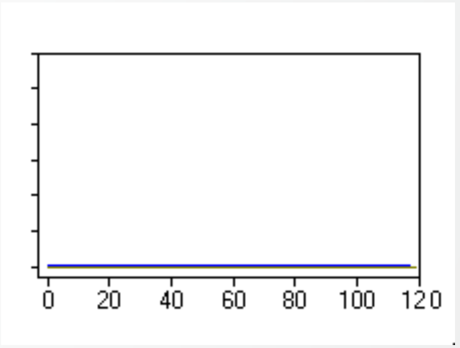
Bragg-Brentano geometry

1D Detection :

Acquisition is done in snapshots

Statistics is time dependent





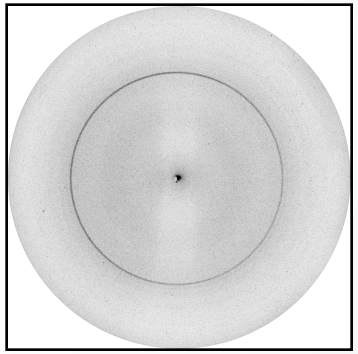
asymetric geometry

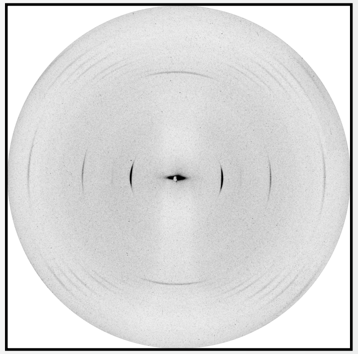
2D Detection :

Acquisition is done in snapshots

Statistics is time dependent

Texture information but point beam required

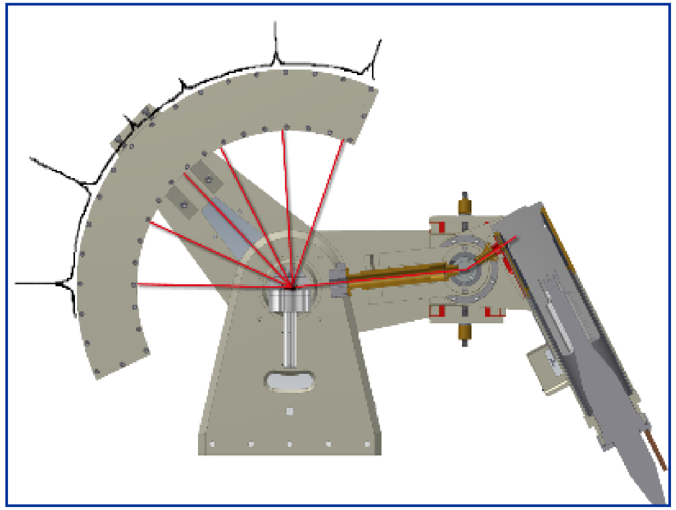




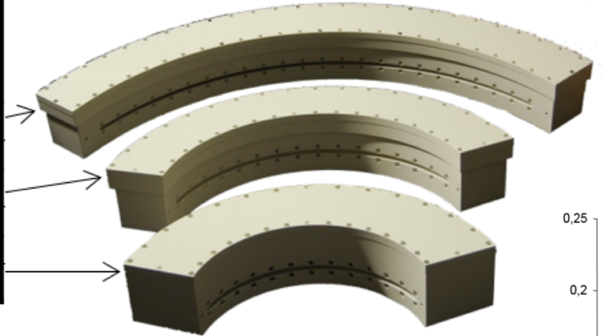
Function X-ray detection

We are the only ones to offer this kind of detector

It is a real time XRD system based on a curved detector



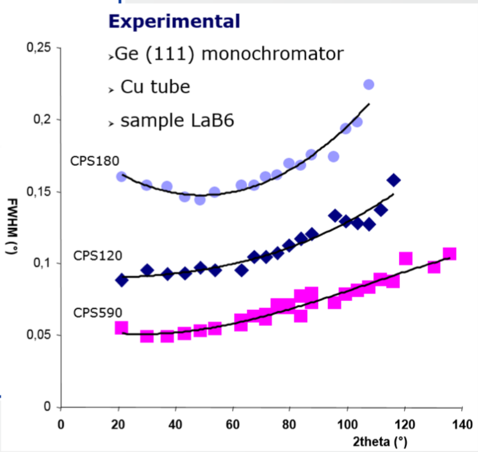
Version	Detection angular range	Curvature (mm)
CPS 590	90° 2θ	R = 500
CPS 120	120° 2θ	R = 250
CPS 180	110° 2θ	R = 180



Maximum information in minimum time

Analysis speed & resolution

No maintenance

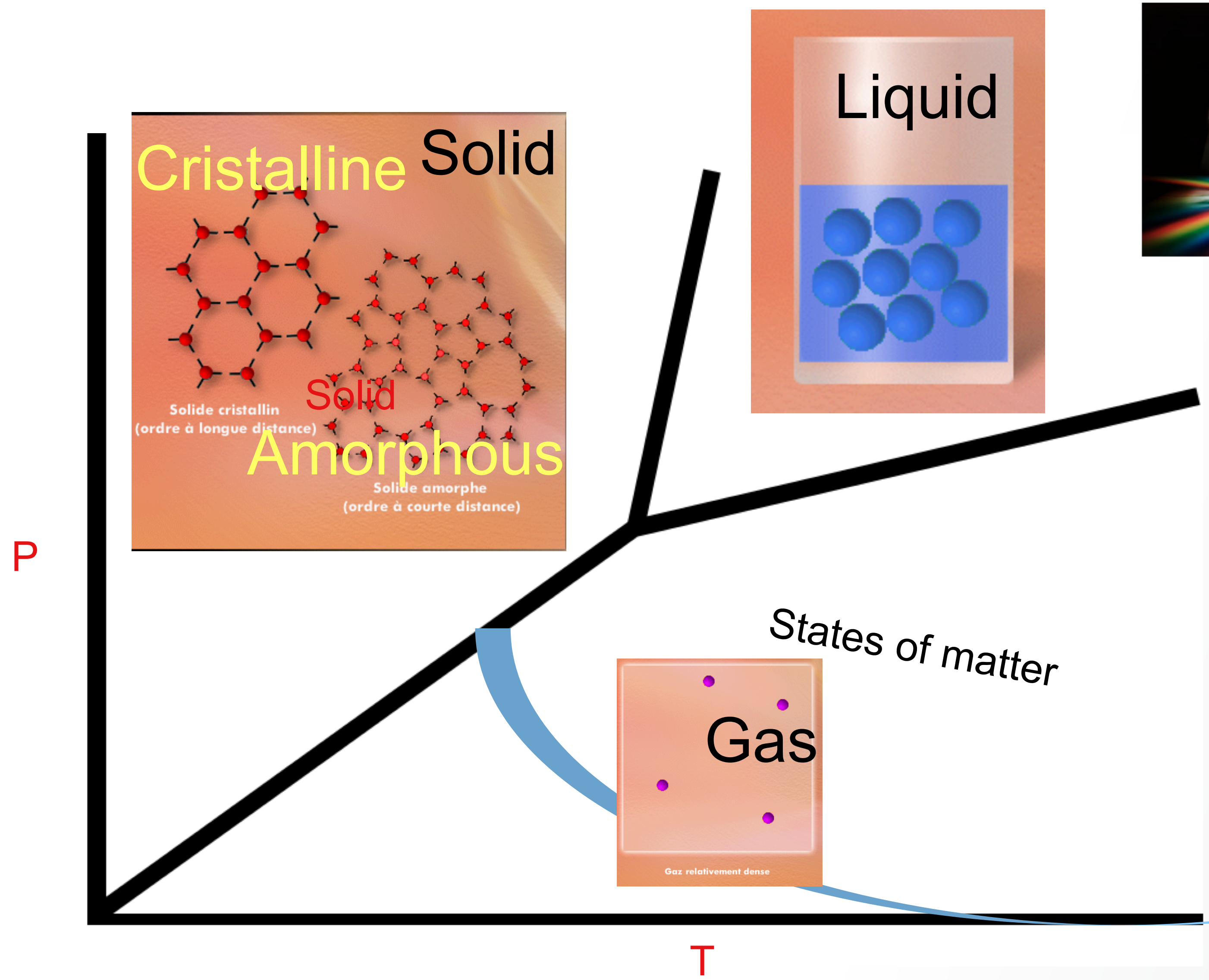


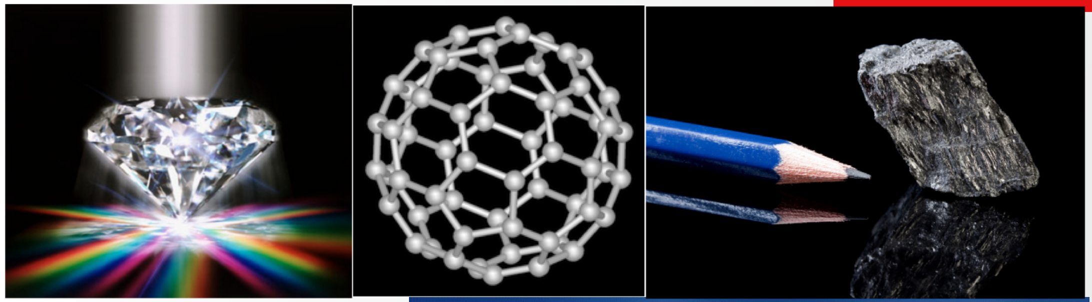
Curved detectors principle

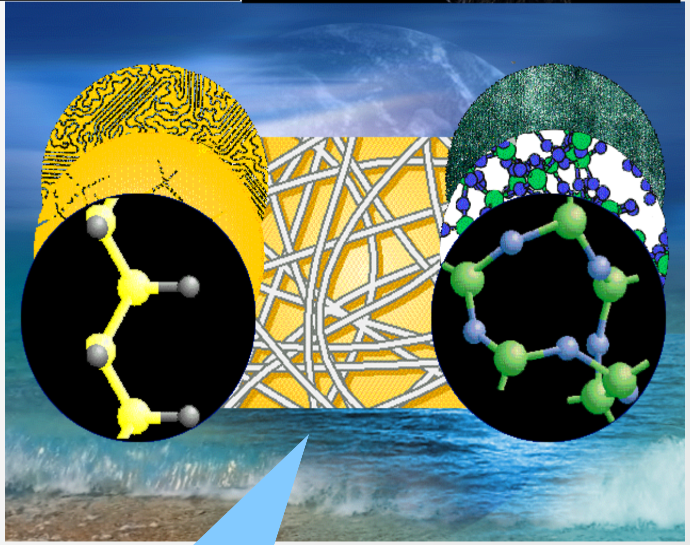
The EQUINOX diffractometers use the curved detectors principle, namely real time acquisition across a wide acquisition range.

- No motorization required during the acquisition (no wear, accuracy)
- Asymmetric acquisition mode: for a single θ sample incidence you can see all diffraction peaks on the detector

Function matter







whatever the state,
XRD allows to evidence and measure structural parameters in matter

Instrumental function for XRD

- Instrumental function is governed by all components of the XRD instrument :
- - source characteristics
- - optics and collimation
- - detection device
- - sample environment

- XRD components should be compatible to each other
  - Example : 1D optic is not recommended with a 2D detector (equatorial aberration)

- The good knowledge of the instrumental function allows to estimate as well the quality of the result
- Example : absorption correction or LP correction are not the same in Bragg Brentano or in Debye Scherrer

- The instrument must be adapted to the requested measurement
- Example : performing transmission measurement with Bragg-Brentano XRD is not appropriate

- Instrumental conditions must be correctly chosen (reproducibility of results)
- Example : choose of the appropriate wavelength vs sample

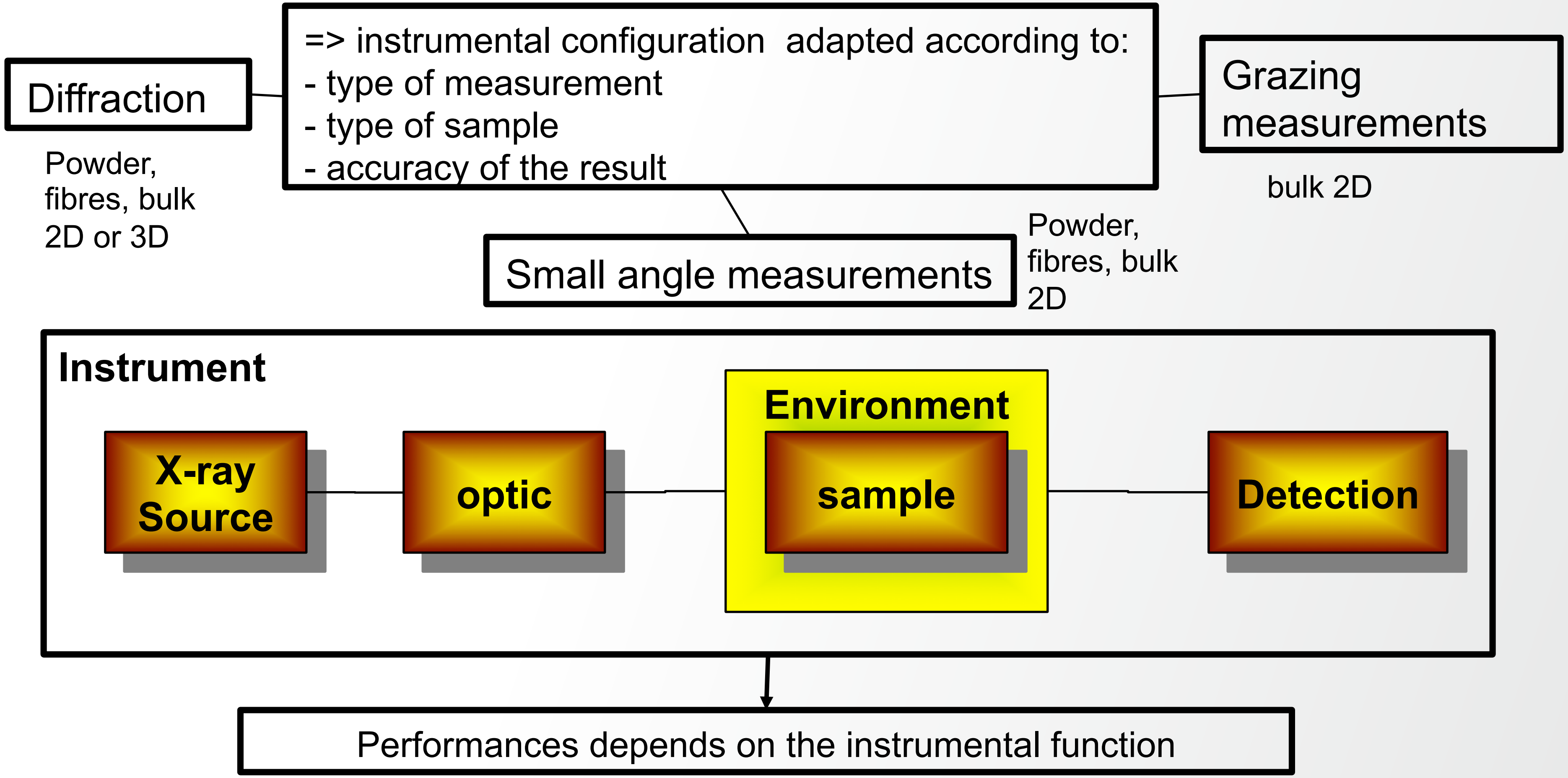
- Use of appropriate standards

Example : in reflection, eccentricity is influenced by transparency. Using standard with same absorption can correct this

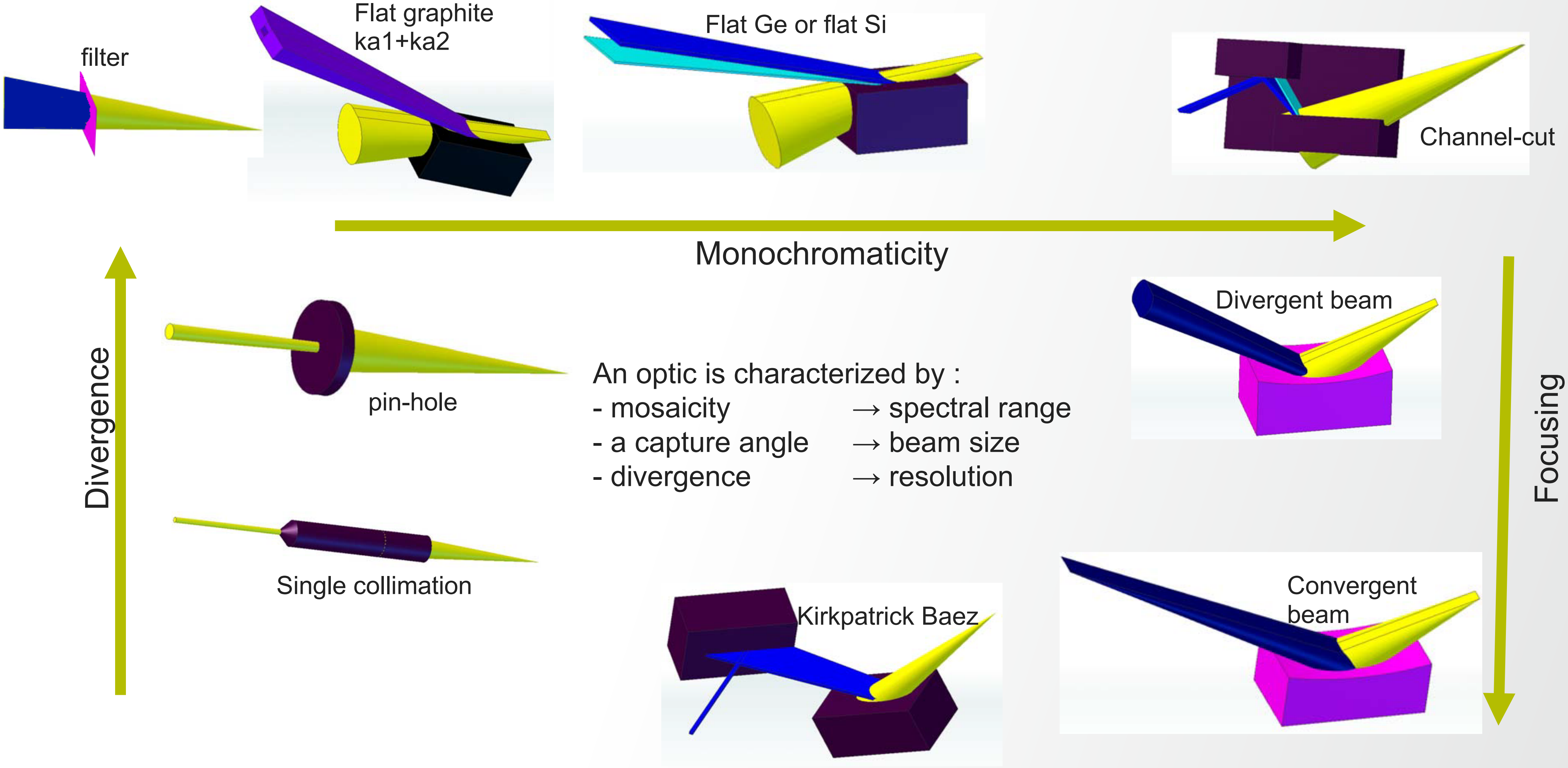
Instrumental function for XRD

Elastic coherent interaction :
reflectometrie : investigation on thin film for measuring thickness, roughness and density
diffraction : investigation on phases
absorption : imaging and radiography.

Incoherent elastic interaction :
diffusion by a rough surface or cristalline defects.



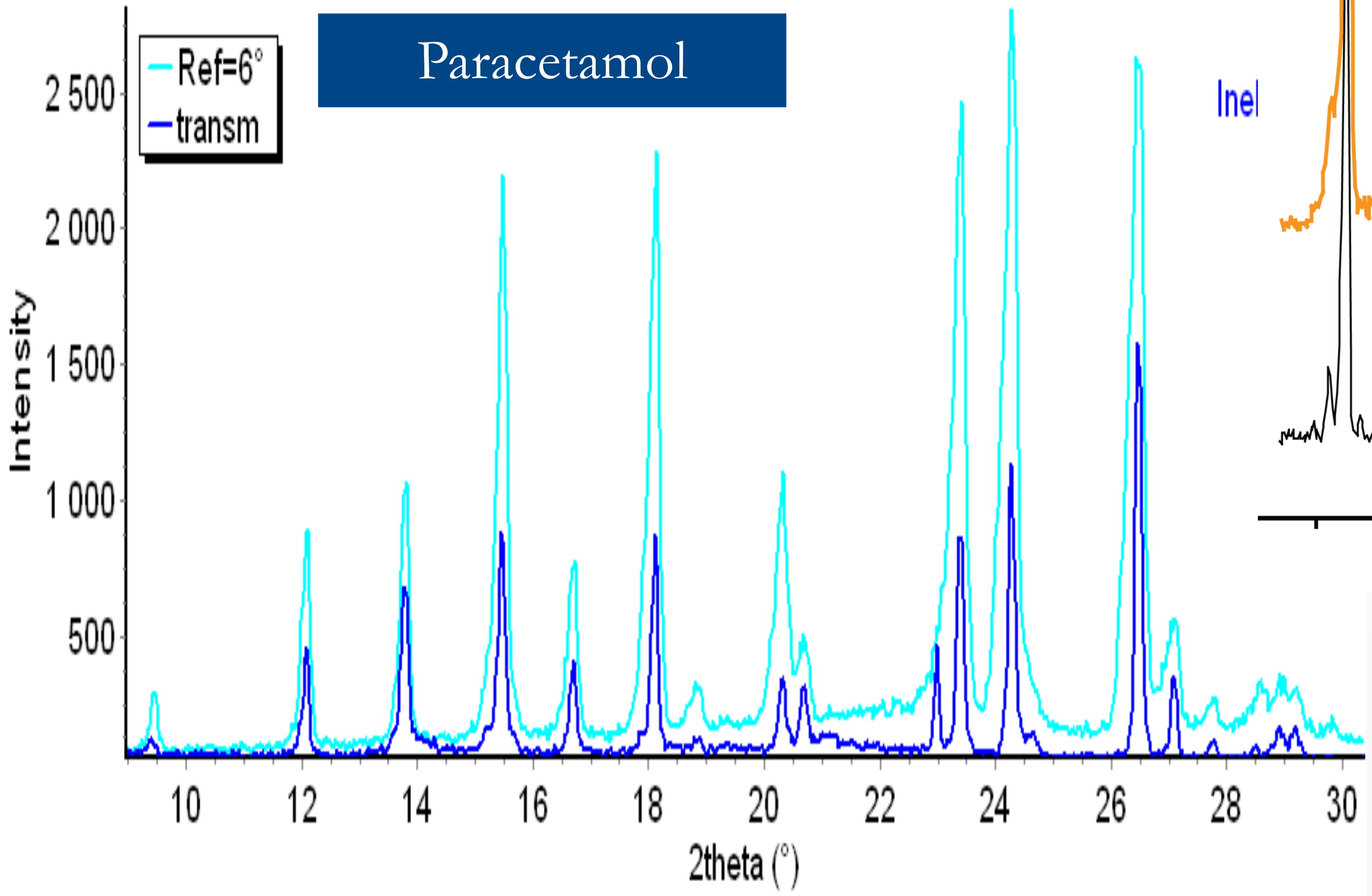
Instrumental function for XRD – beam characteristics

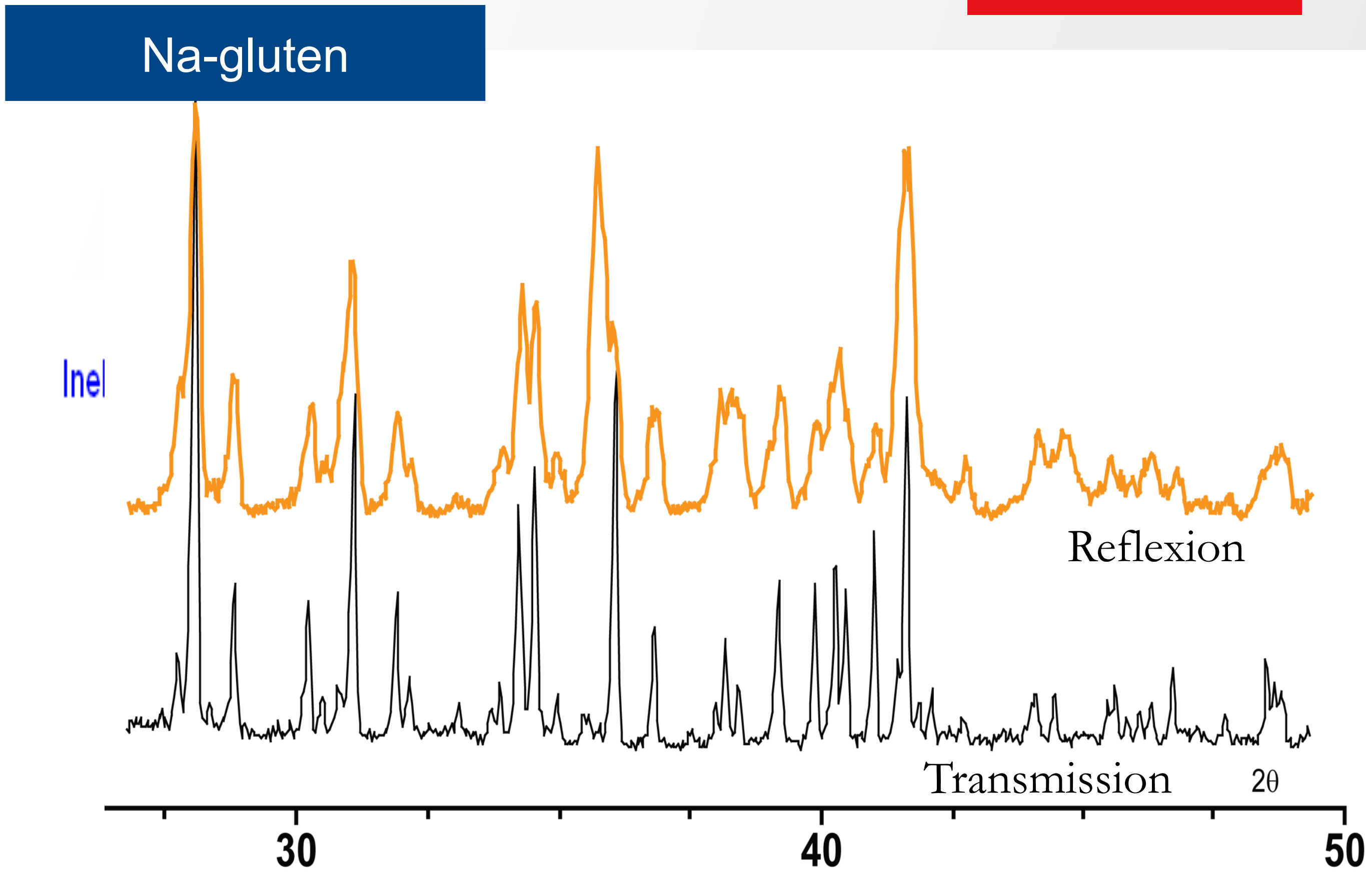


An optic is characterized by :

- mosaicity → spectral range
- a capture angle → beam size
- divergence → resolution

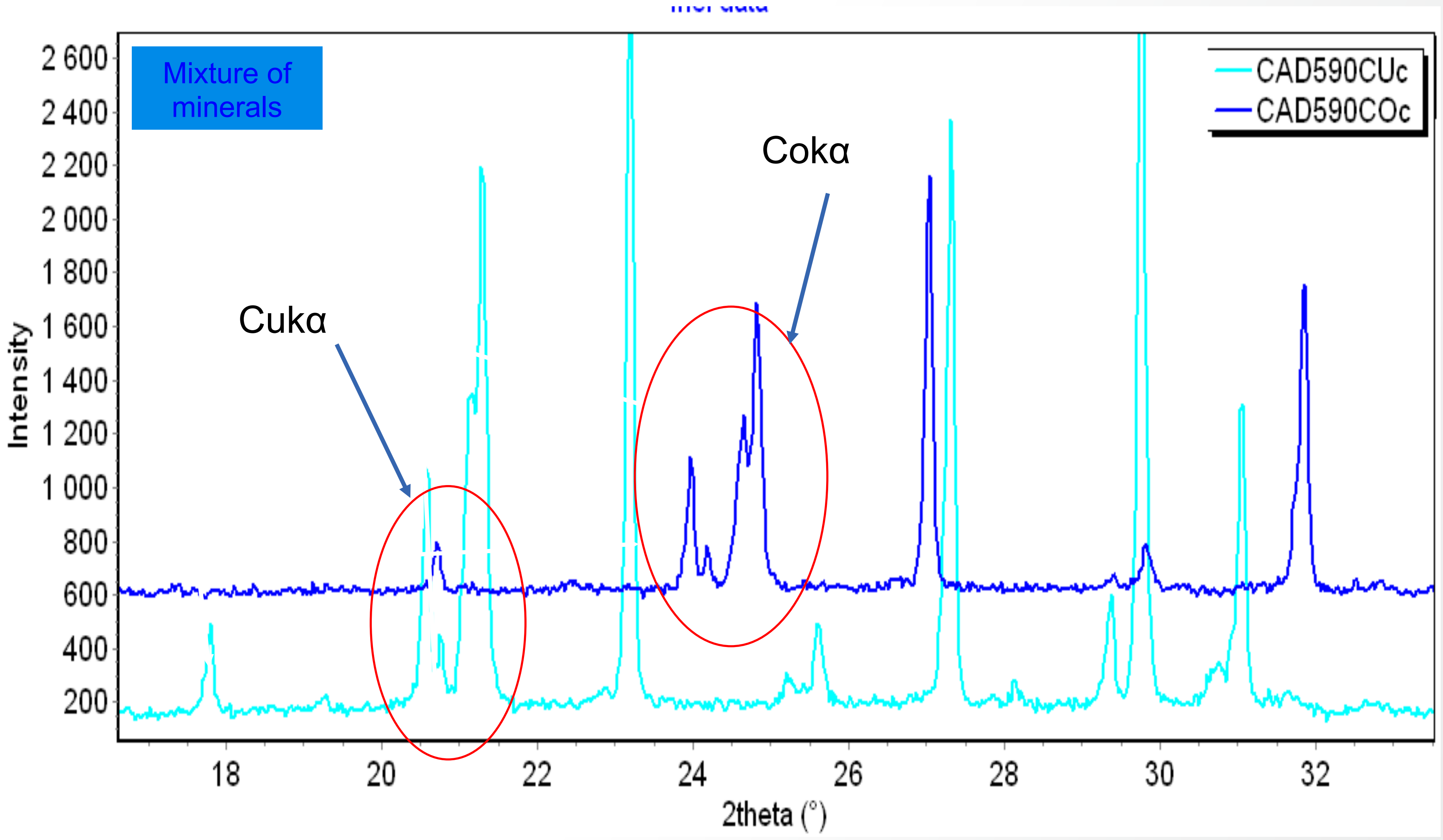
Instrumental function for XRD – effect of sample holder



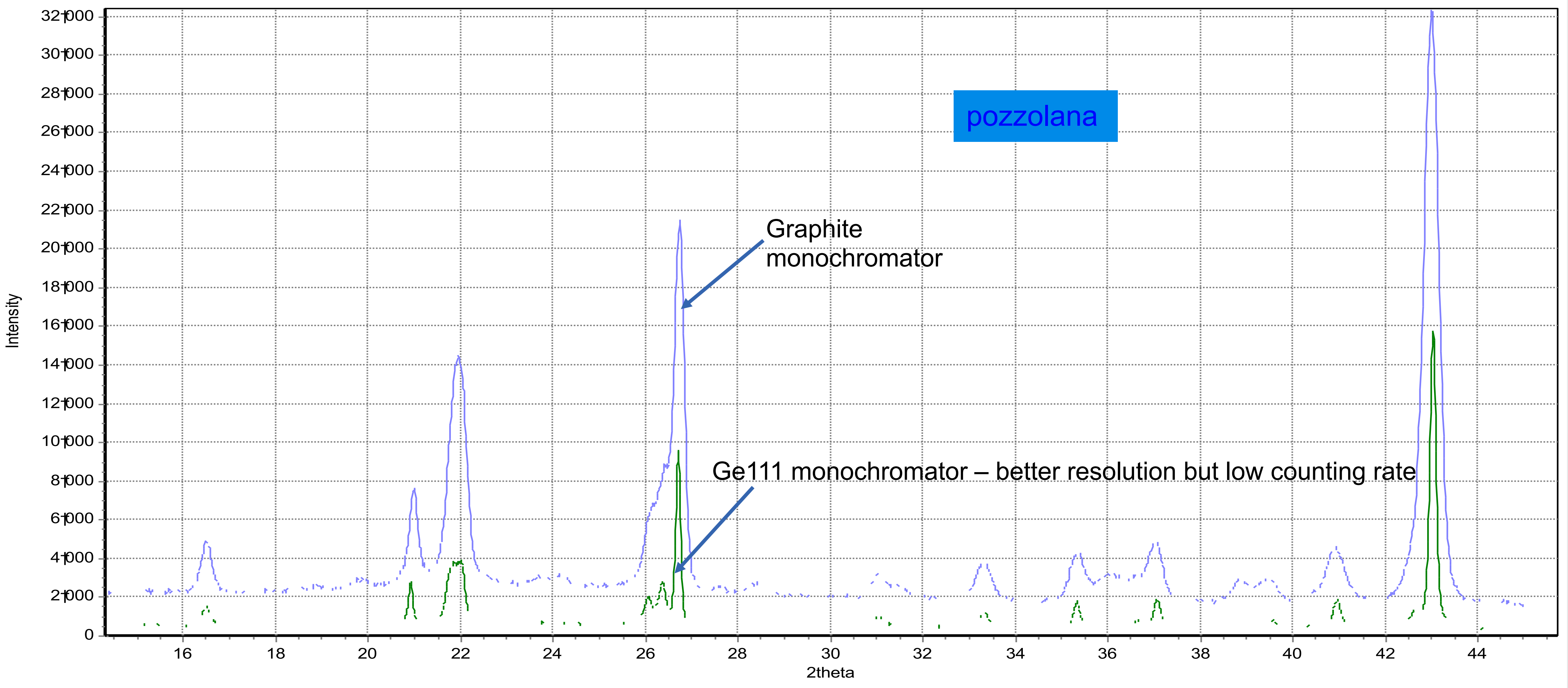


Better resolution in transmission

Instrumental function for XRD – effect of wavelength



Instrumental function for XRD – effect of optic

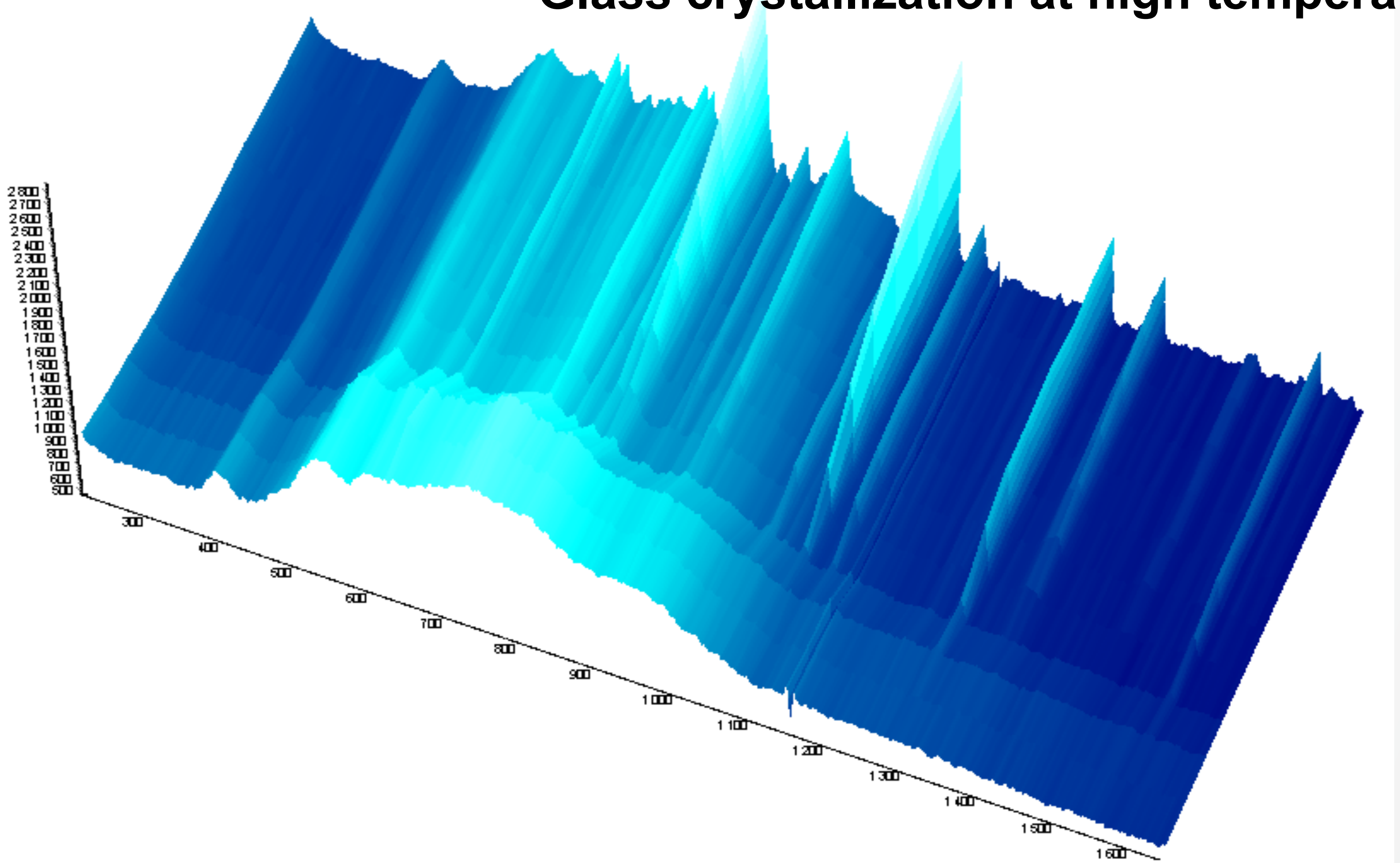


  henry.pilliere @thermofisher.com

Instrumental function for XRD – effect of optic

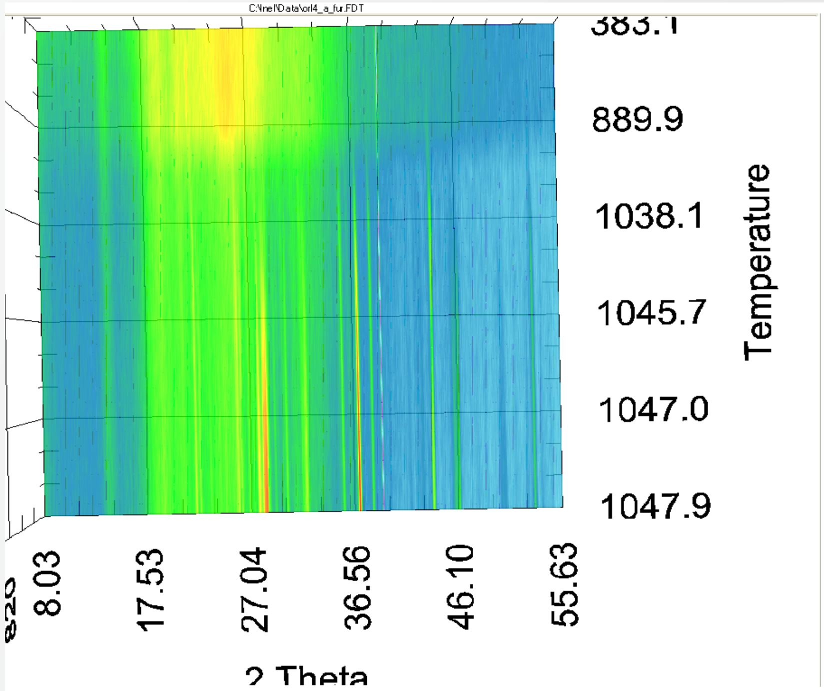
High flux by using elliptical mirror

Glass crystallization at high temperature



CONDITIONS :

power : 38kV – 38mA,
Furnace : FUR1200
acquisition: 3min



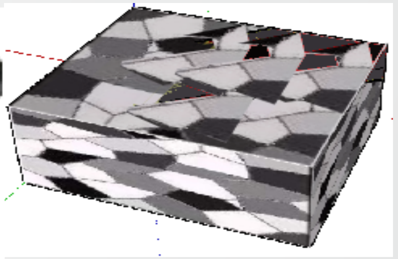
X-ray diffraction setup

Understanding how to get the result

- appropriate instrumental configuration
- appropriate sample conditioning
- appropriate calibrations / corrections

		Type of solid	
		Single crystal	polycrystalline
Type of radiation	monochromatic	Rotating crystal Method	Powder XRD
	polychromatic	Laue Method	ED-XRD

Single crystal



Polycristalline material

XRD for polycrystal with monochromatic beam – focusing geometry

Debye Scherrer geometry

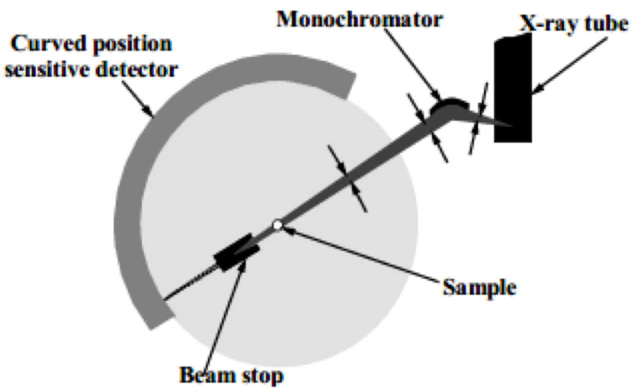


Figure 2.28. *Debye-Scherrer diffractometer equipped with a position sensitive detector*

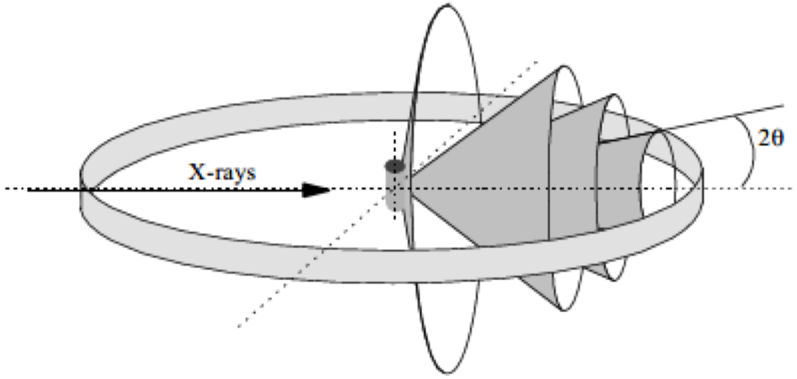


Figure 2.25. *Geometric arrangement of the Debye-Scherrer and Hull diffractometer*

Bragg Brentano geometry

Sample is an optical component!!

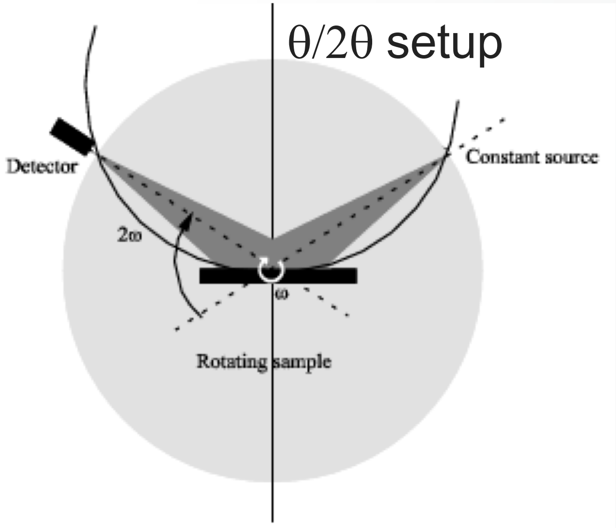


Figure 2.46. *θ-2θ Bragg-Brentano diffractometers*

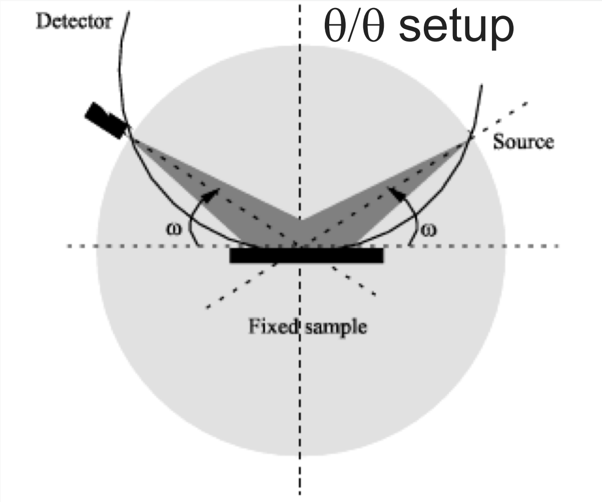


Figure 2.47. *θ-θ Bragg-Brentano diffractometer*

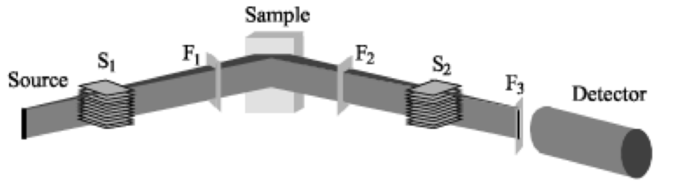


Figure 2.48. *Path of the X-ray beams in a Bragg-Brentano diffractometer*

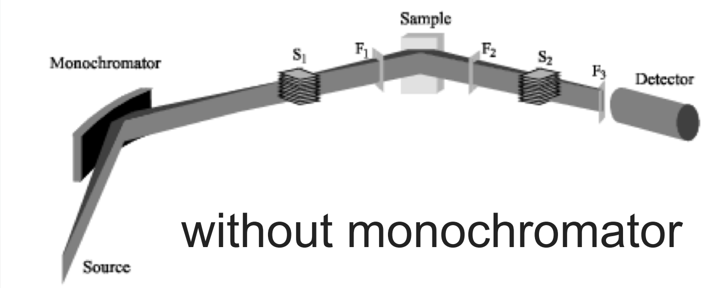


Figure 2.51. *Path of the X-ray beams in a Bragg-Brentano diffractometer equipped with a front monochromator*

From Guinebretière

XRD for polycrystal with monochromatic beam – parallel beam geometry

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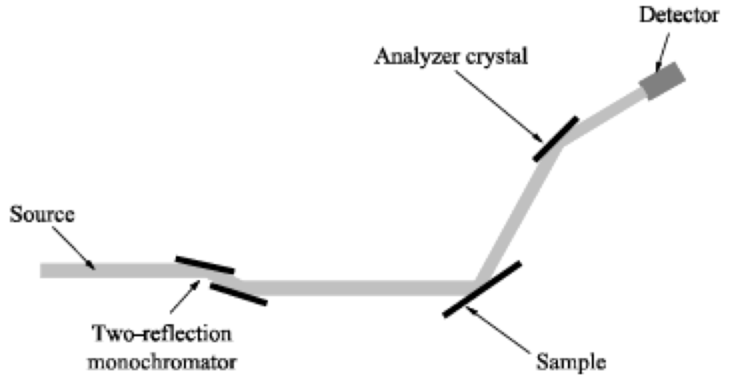
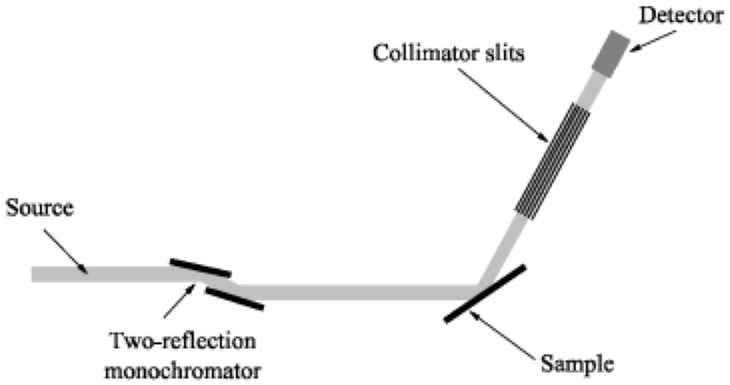
Parallel beam geometry
With flat cristals (1, 2 or 4 bounds)



(a) Use of an analyzer crystal



(b) Use of back collimator slits

Figure 2.54. *Geometrical arrangement of diffractometers for polycrystalline samples using a synchrotron source*

Parallel beam geometry
With parabolic (or elliptic) mirror

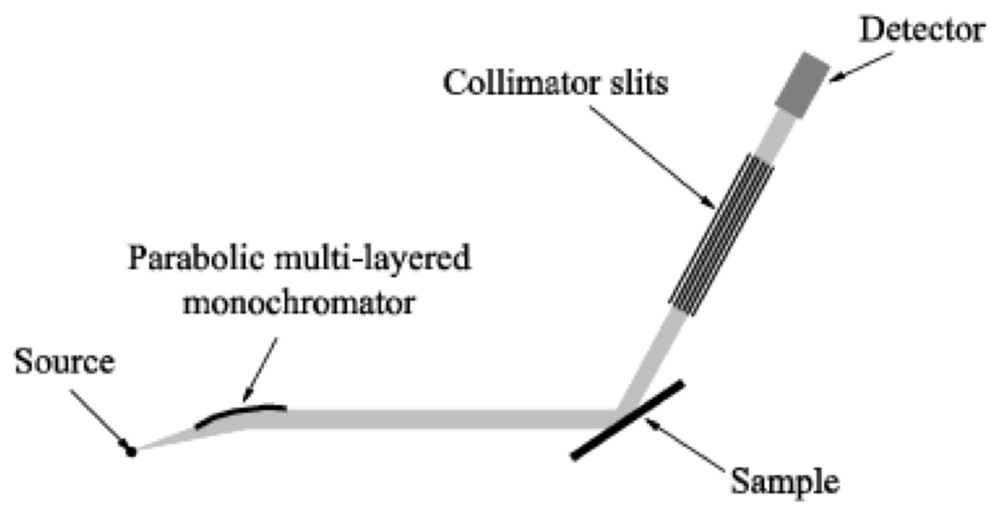


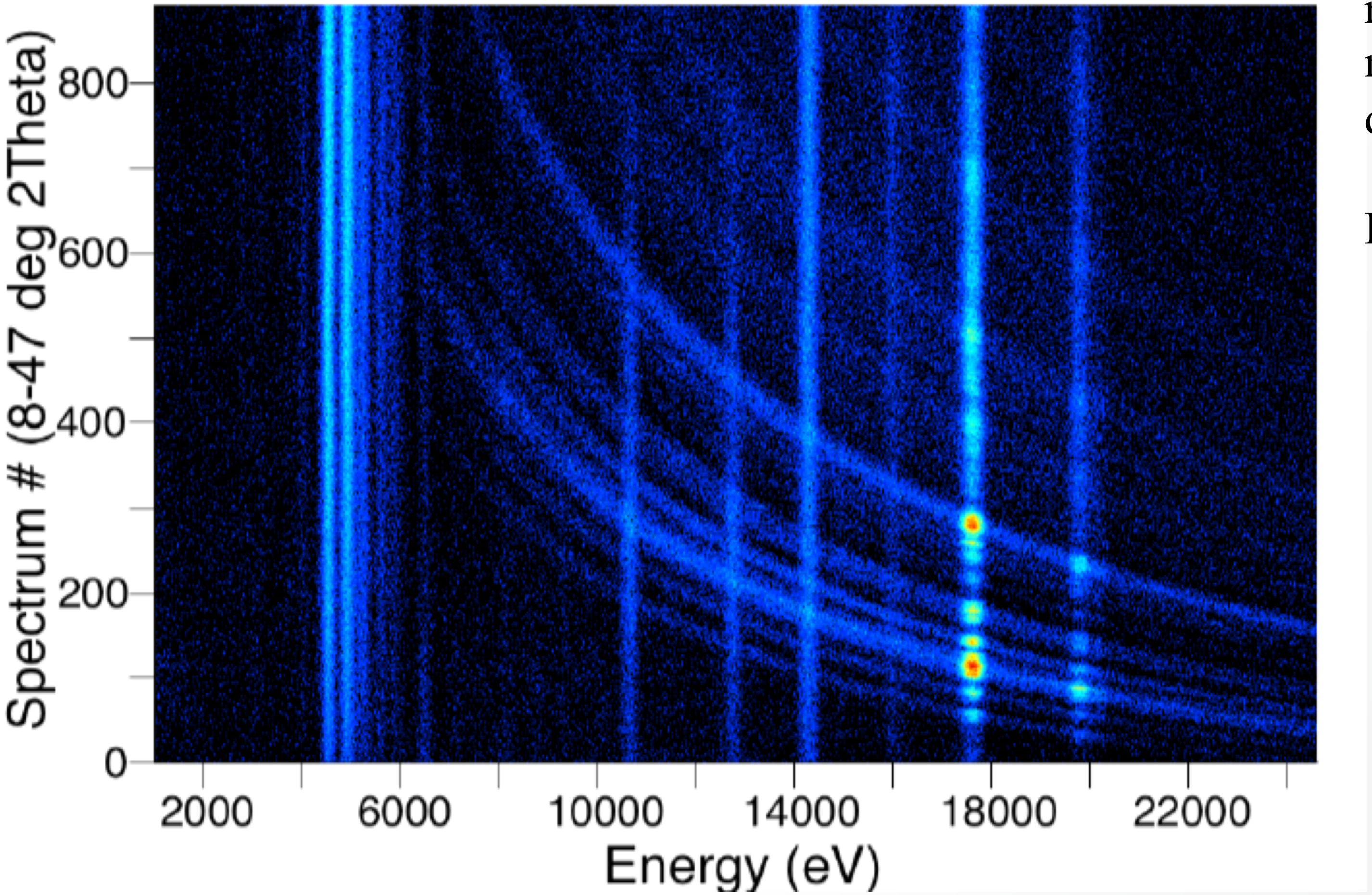
Figure 2.55. *Parallel geometry configuration in the laboratory*

Case of Equinox; sample can have a fixed incidence (asymetric mode)

XRD for polycrystal with polychromatic beam – parallel beam geometry

1- Structural information are diffracted by all the wavelength
2- Elements are emitting fluorecence signal

Need to have a detector with a **spacial detection**, able to dissociate **energy**



XRD-XRF angle-energy map
(raw data)

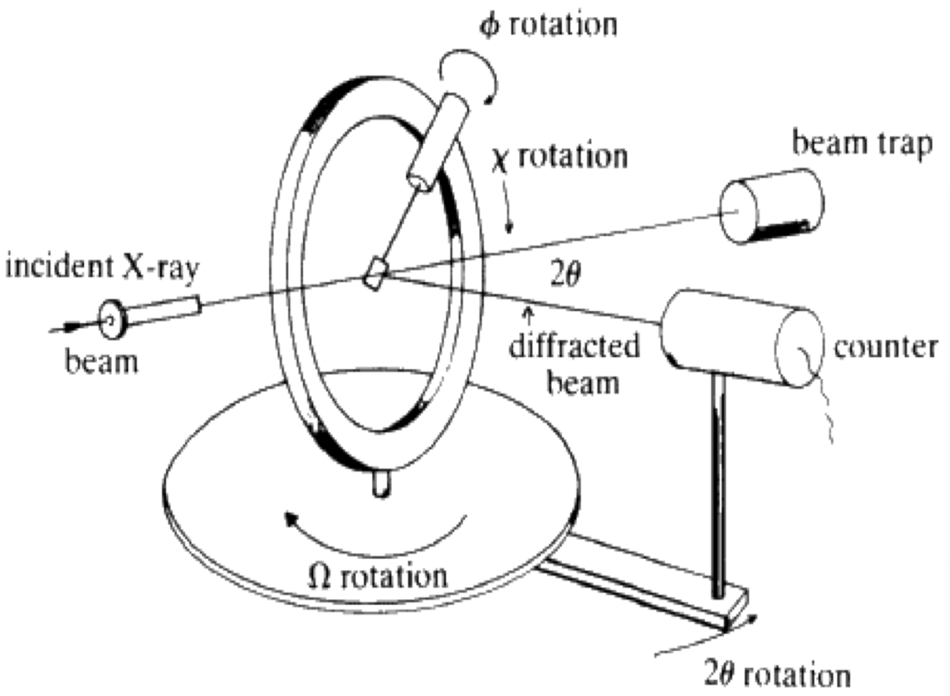
Angle-energy map measured for a $BaSO_4$ rich sample using Mo radiation not monochromatised and scanning the SDD detector from 5 to 47. in 2θ.

Ref. L. Lutterotti, U. Trento

Expected characteristics:
- 50mm Strip detector, composed by 100microns (could be 50?) linear pixel width
- High dynamic per pixel
- Each pixel is able to measure EDX with a resolution better then 180eV
- Light weight and low consumption
- No gas needed
- Real time detector with low dead time
- Possibility to combine several detectors in order to cover a larger intercept of the Debye cones
- Efficiency for energy range from 1keV to 30keV

XRD for single crystal with monochromatic beam – parallel beam geometry

Parallel beam geometry
With flat cristals (1, 2 or 4 bounds)



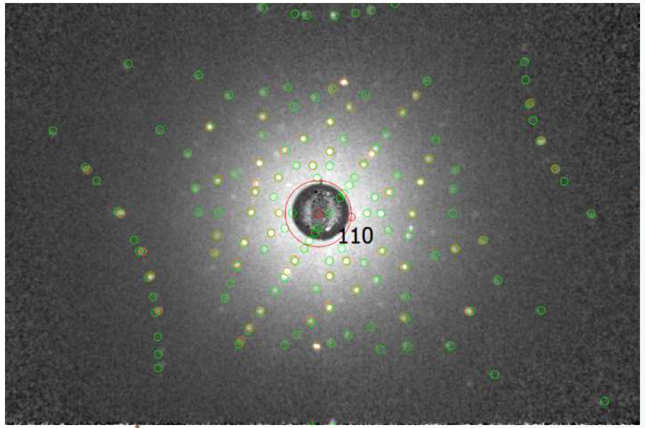
Sample hold by appropriate goniometer
Different type of configuration

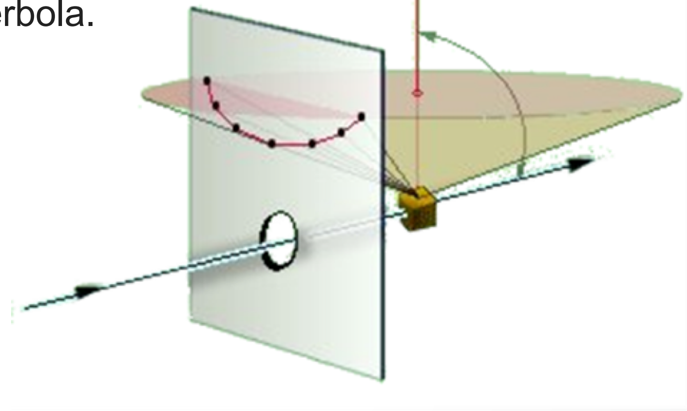
XRD for single cristal with polychromatic beam – parallel beam geometry

The Laue method is mainly used to determine the orientation of large single crystals. White radiation is reflected from, or transmitted through, a fixed crystal.
The diffracted beams form arrays of spots, that lie on curves on the film. The Bragg angle is fixed for every set of planes in the crystal. Each set of planes picks out and diffracts the particular wavelength from the white radiation that satisfies the Bragg law for the values of *d* and θ involved.

Experimental
There are two practical variants of the Laue method, the back-reflection and the transmission Laue method:

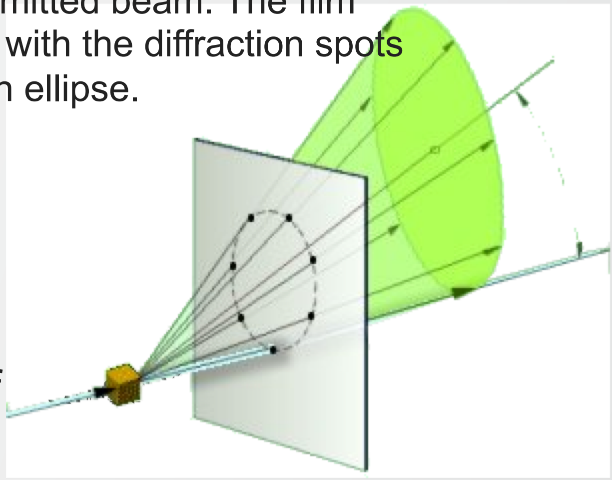
Back-reflection Laue
In the back-reflection method, the film is placed **between** the x-ray source and the crystal. The beams which are diffracted in a crystal. The beams which are diffracted in a backward direction are recorded.
One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an hyperbola.





Transmission Laue
In the transmission Laue method, the film is placed **behind** the crystal to record beams which are transmitted through the crystal.
One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an ellipse.

Case of



Performance in X-ray diffraction

New matter can be complexe

⇒Analytical techniques should be adapted

Performance in accuracy
- New XRD components
- mechanic/electronic performance
- data treatement optimization

Combination of techniques

-XRD, XRF, Raman & IR Spectrometries, environmental
- data treatement optimization

New techniques

-New components (source, detection)
- new configuration
- data treatement optimization

New need to analysed matter : either on line or in situ

⇒Analytical techniques should be adapted

(trans)Portable techniques

-Miniaturization
- automatic software

On line integration

-robustness
- integrated software
- methodology

Automatic expertize

-Expert softwares
- methodology
- statistic analysis of data (data fusion)

Need to build transversal organisation of techniques

database
- creation of a standard

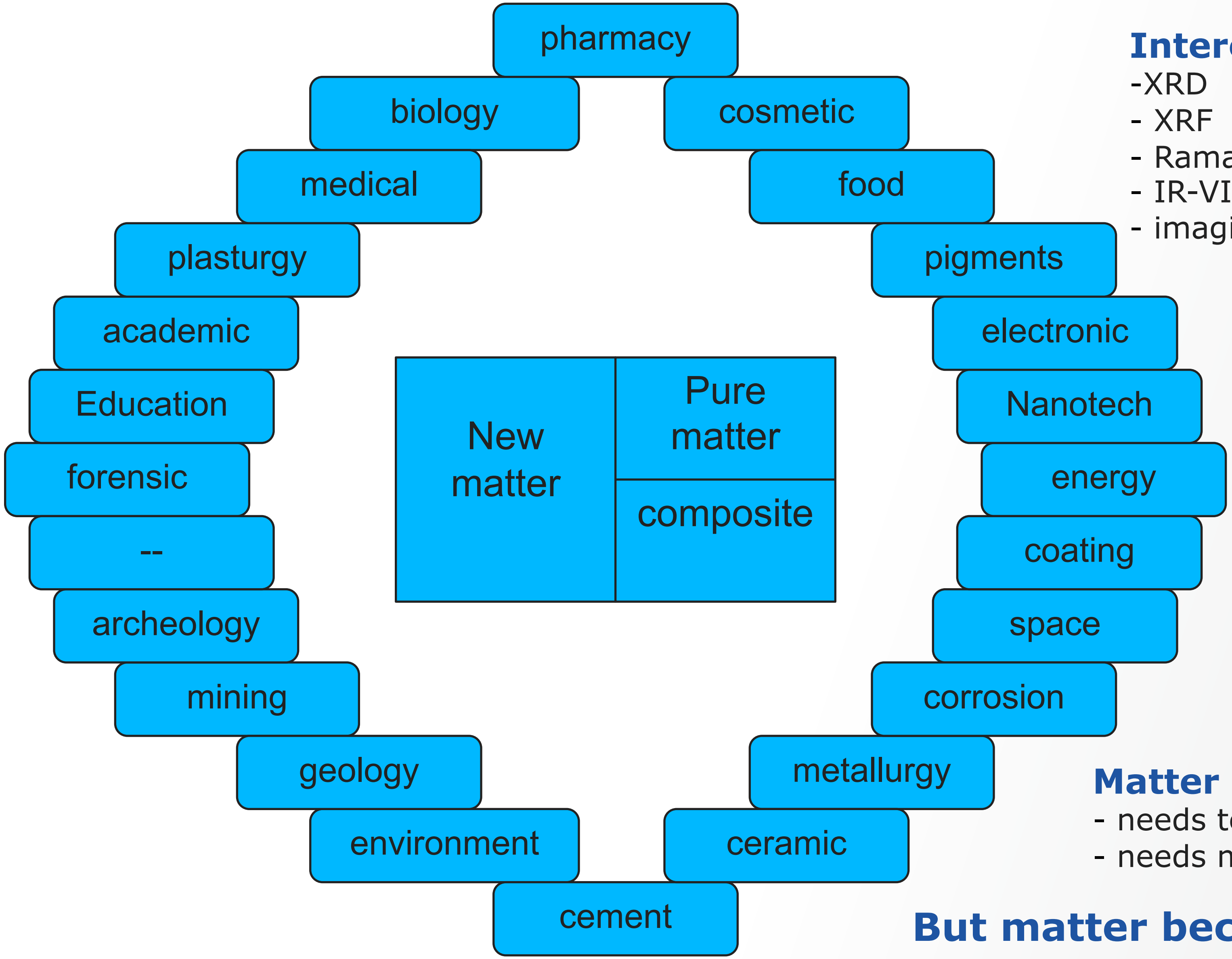
configuration
- standardization of instrumental configuration
- definition of rules for assembling

calibration
- methodology of data calibration

Application fields

Wide domains in material science

Application fields



Interest for using non destructive analytics

-XRD
- XRF
- Raman spectroscopy
- IR-VIS-UV spectroscopy
- imaging (RGB, hyperspectral, radiography …)

Many application fields

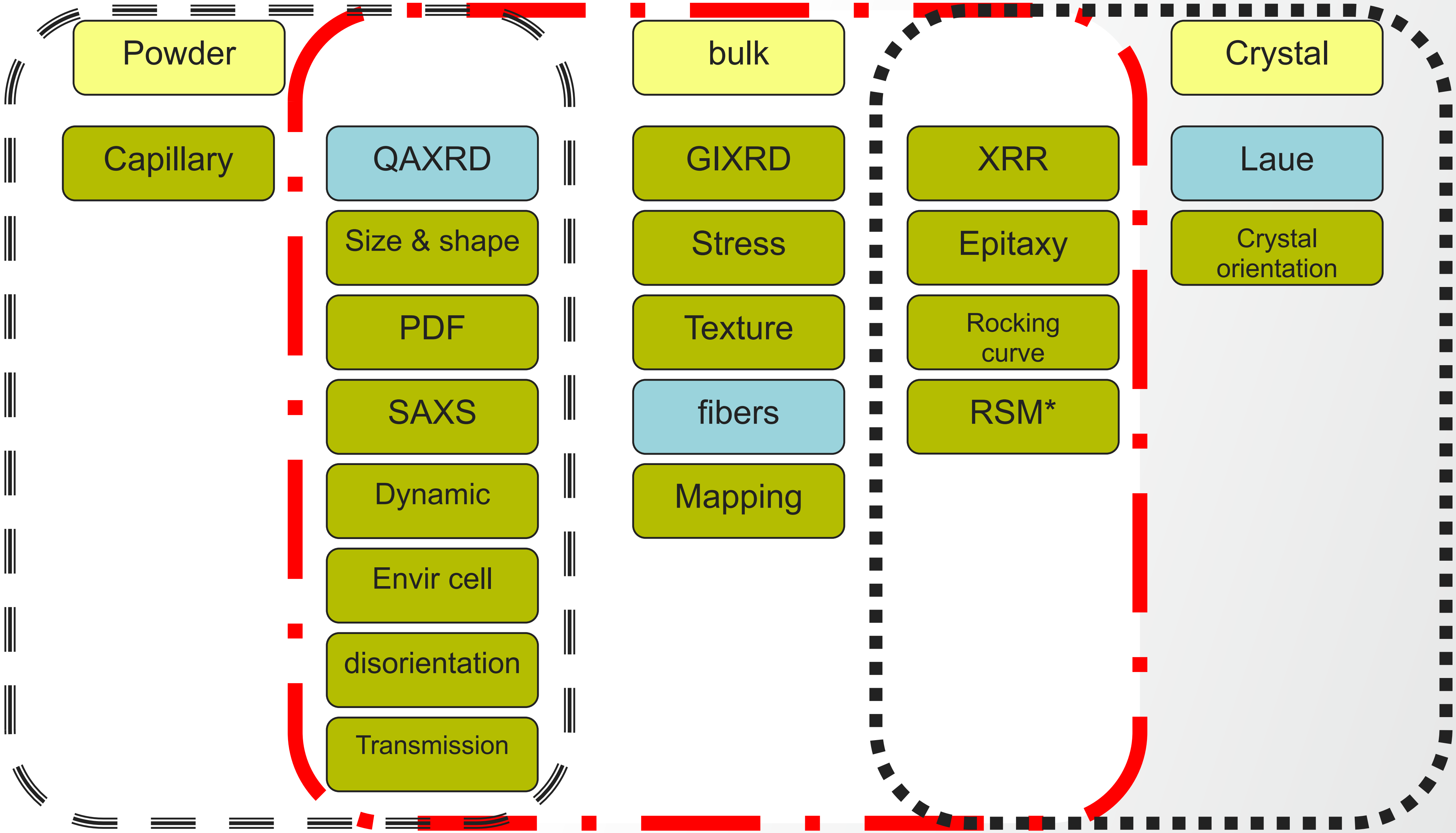
- Academic
- private research
- quality control
- in field analysis

Matter is the center of interest for customer

- needs techniques for characterization
- needs methodology (procedures, norms …)

But matter becomes more complex !

XRD analytic techniques



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ARL Equinox new design

ARL Equinox 100 in May 2018

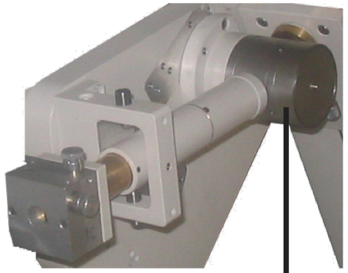
- ARL Equinox 1000 in May 2018

- ARL Equinox 3000 serie in Oct. 2018

- ARL Equinox 5000 serie in Nov. 2018

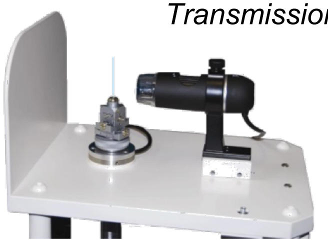
- ARL Equinox LAUE in April 2019

Compliance and industrialization of accessories

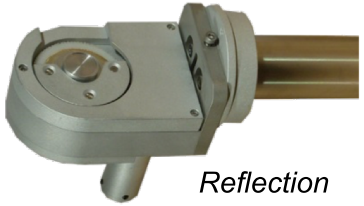


X-Ray optic
Germanium or Graphite monochromator

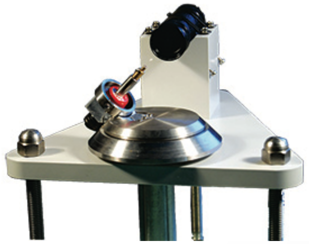
Transmission



Sample holder

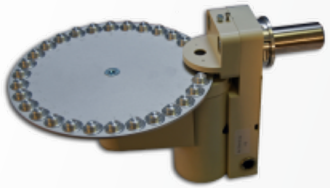


Reflection



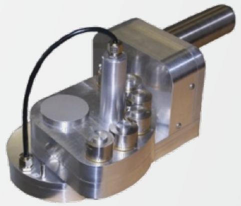
Transmission Powder XRD on a little crystal

Gandolphi chamber

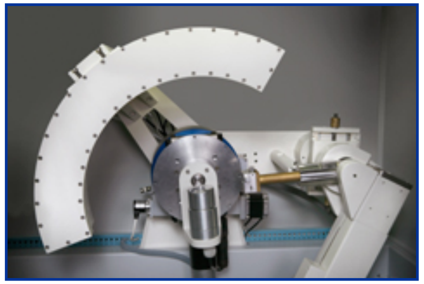


Sample changer
30 positions

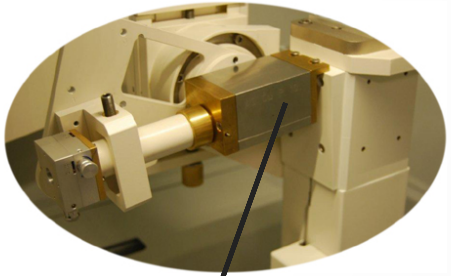
Grazing sample holder



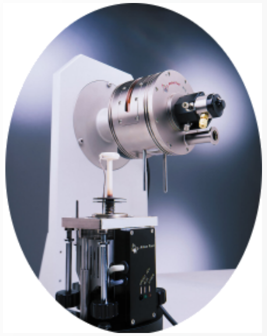
Sample changer
6 positions

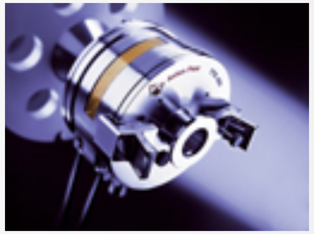


Special thin film attachment
θ/Z motorized



High flux X-Ray optic
X-ray mirror instead of monochromator optic

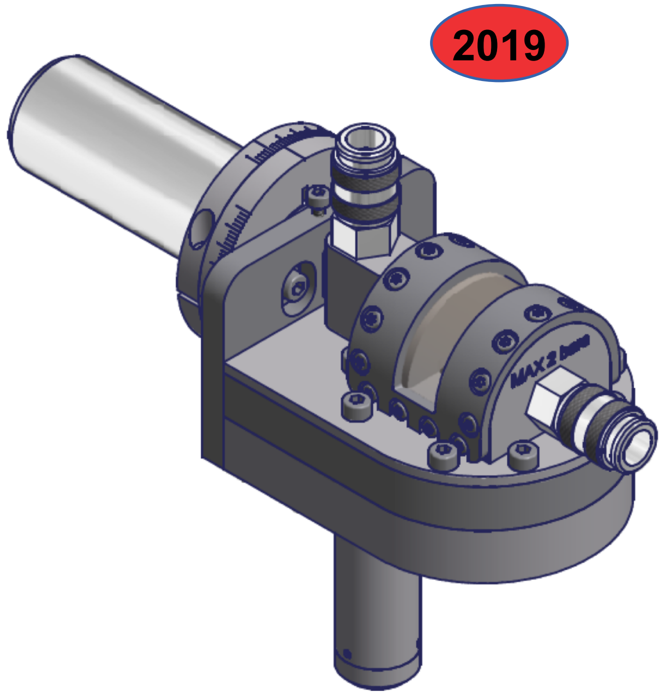




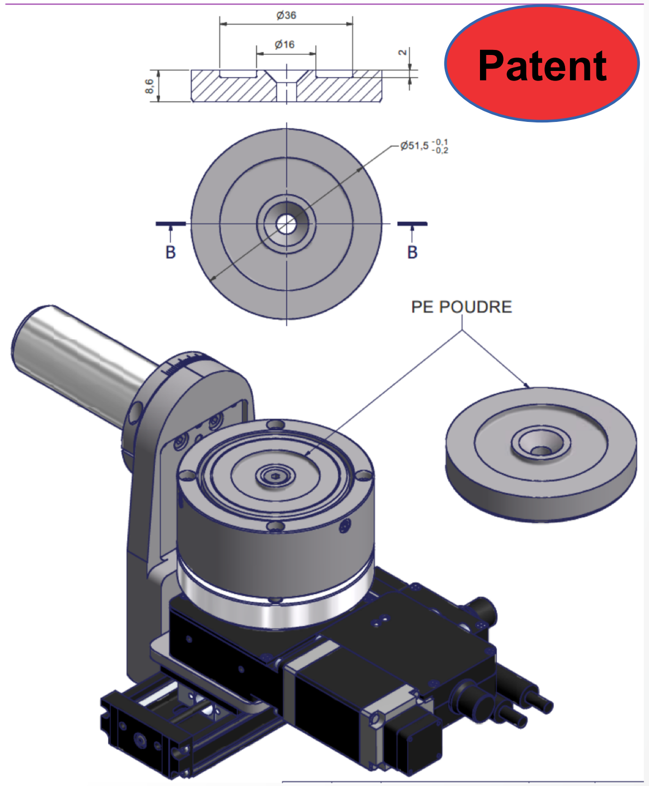
High and low temperature chambers

New Anton Paar furnace
-10°C to +150°C
Ambient to 500°C
Phases transition

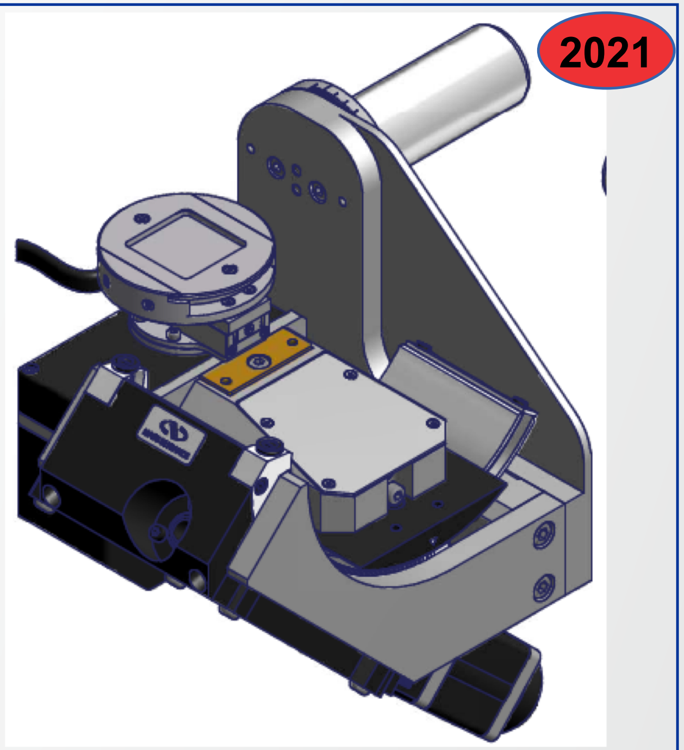
New accessories



SSCA (2019)
For air sensitive samples



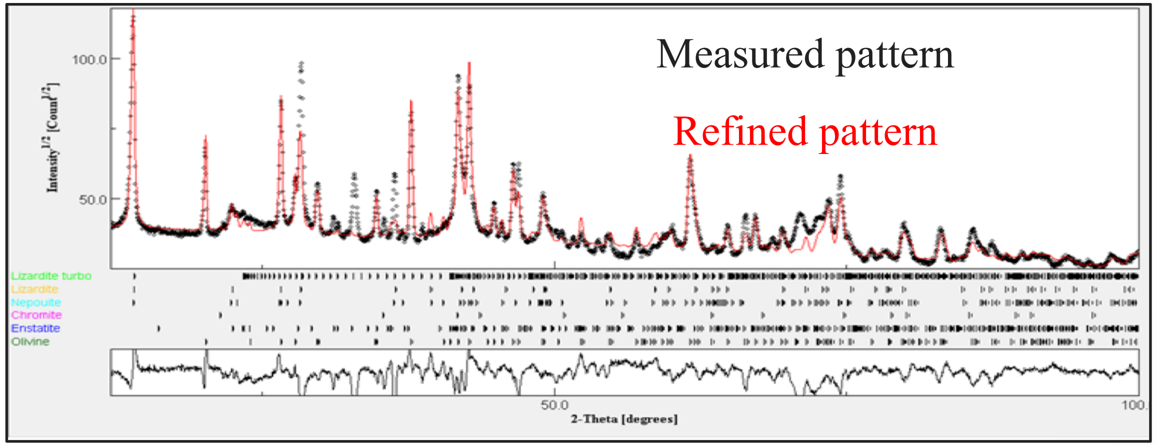
SHC (dec 2020 - patent)
For combined analysis

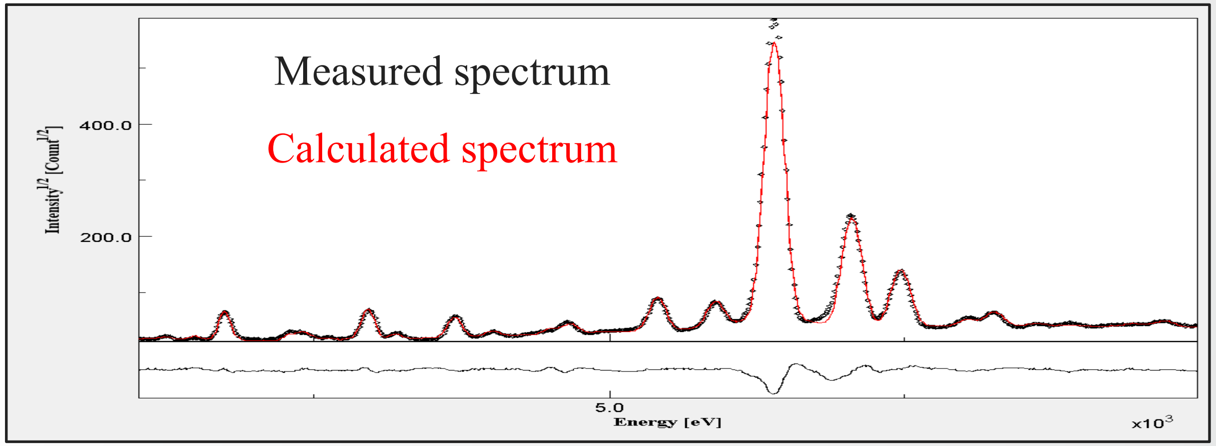


TSSH (June 2021)
For stress/texture analysis

Combined refinement XRD-XRF

Results on powder from Harzburgite H10, using Maud **Rietveld** SW: combined XRD/XRF





phase	Olivine	Lizardite	Lizardite turbostratique	Népouite	Talc	Enstatite	Chromite
Proportion (%)	58,48	15,23	16,48	6,98	0	2,77	0,06

chemical	Mg	Fe	Cr	Si	O	Ca	Cu	Mn	Zn	Ni	Al	Ti
Proportion (%)	15,83	8,35	0,25	18,08	52,74	0,39	0,02	0,14	0,01	0,20	3,28	0,04

chemical	H	Cl	TOTAL
Proportion (%)	0,62	0,06	100,00

Thank you