The Tao Of X-Ray Analytical Systems

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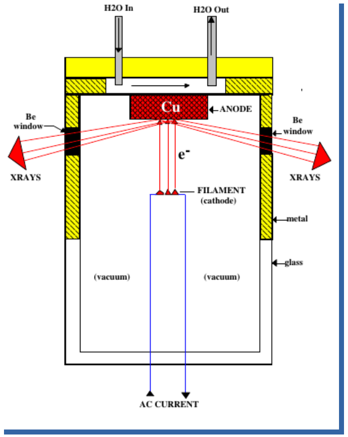
1869

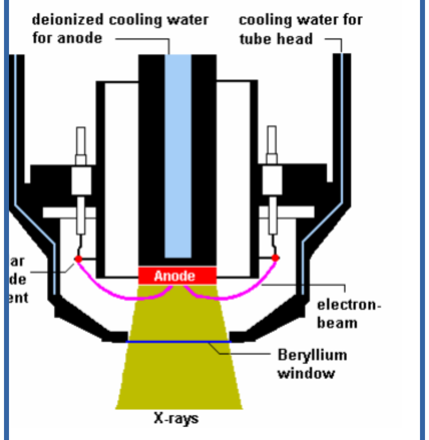
One (and only one) slide about philosophy

- Lao Tzu (Old Master) wrote “Tao Te Ching“ (“The Book of the Tao and Its Power”)
- The masculine principle (Yang) - associated with strength, activity, light, hardness, and the energy of the day.
- The feminine principle (Yin) - associated with softness, receptiveness, darkness, gentleness, and the energy of the night.
- These two opposites are interdependent and complementary. Together, they represent the dynamic balance and harmony – Tao.

	XRD	XRF
Coherent scattering of X-rays	Useful signal	Noise
X-Ray florescence	Noise	Useful signal
Quality results	Crystal Lattice (Distances between atom planes)	Type of atoms
Quantitative results	Compound concentrations	Atoms concentrations
Type of measurement	Absolute	Comparative

XRD/XRF tubes





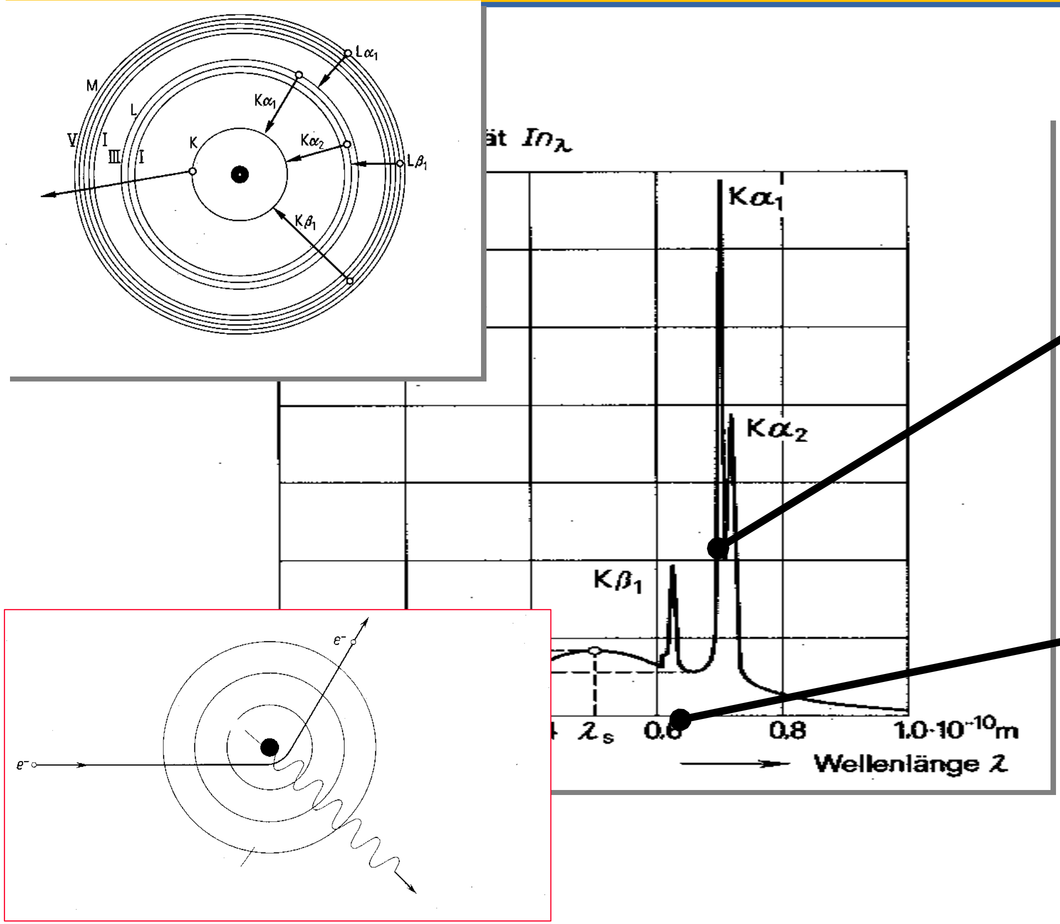
XRD Side windows

- Point focus (A line from orthogonal window)
- Anode on GND
- Cathode with -kV
- Water cooling (tape water)

XRF End window tube

- Large surface focus (30mm)
- Anode with +kV
- Cathode on GND
- Water cooling (deionized water)

X-ray tubes spectra



<u>XRD:</u> line spectra, $K_{\alpha,\beta}$ shells recombination.

HV settings policy:

$V = 5 * E_{k\alpha}$

$I = I_{max}$

<u>Example for Cuk$_{\alpha}$</u>

V = 5*8kV = 40kV
40mA < I < 55 mA
70% to save tubes

<u>XRF:</u> continuous spectra (Bremsstrahlung), accelerated electrons in anode material.

HV settings policy:

$V = V_{max}$ or lower to excite light elements more efficiently

$I = I_{max}$ or lower

Xrays - Particles or Waves

Planck Formula

$$E.\lambda = h.c$$

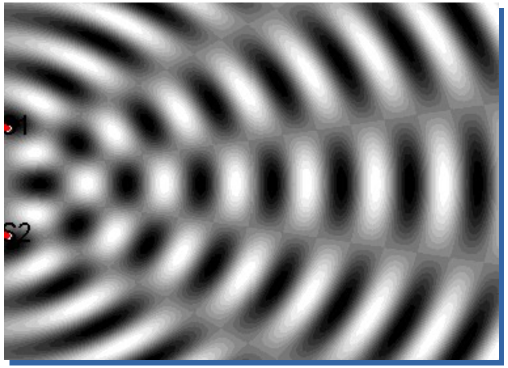
E - energy
λ – wavelength
c – speed of light
h – Planck constant

$$E\ \lambda = 1.2\ [kV.nm]$$

Or

$$E\ \lambda = 12\ [kV.A^o]$$

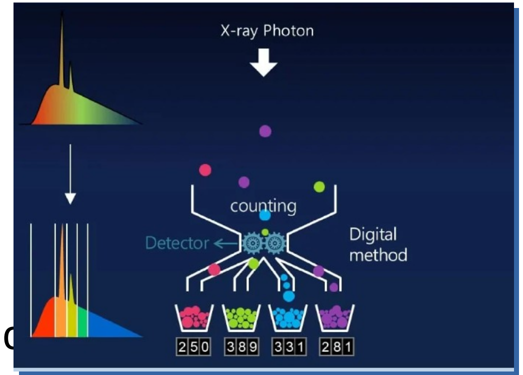
X-ray tube: characteristic spectra ($K_{\alpha,\beta}$) - particles
Continues spectra – waves



Diffraction: waves

Wave Dispersive X-ray Fluorescence - WDXRF

X-Ray Diffraction - XRD

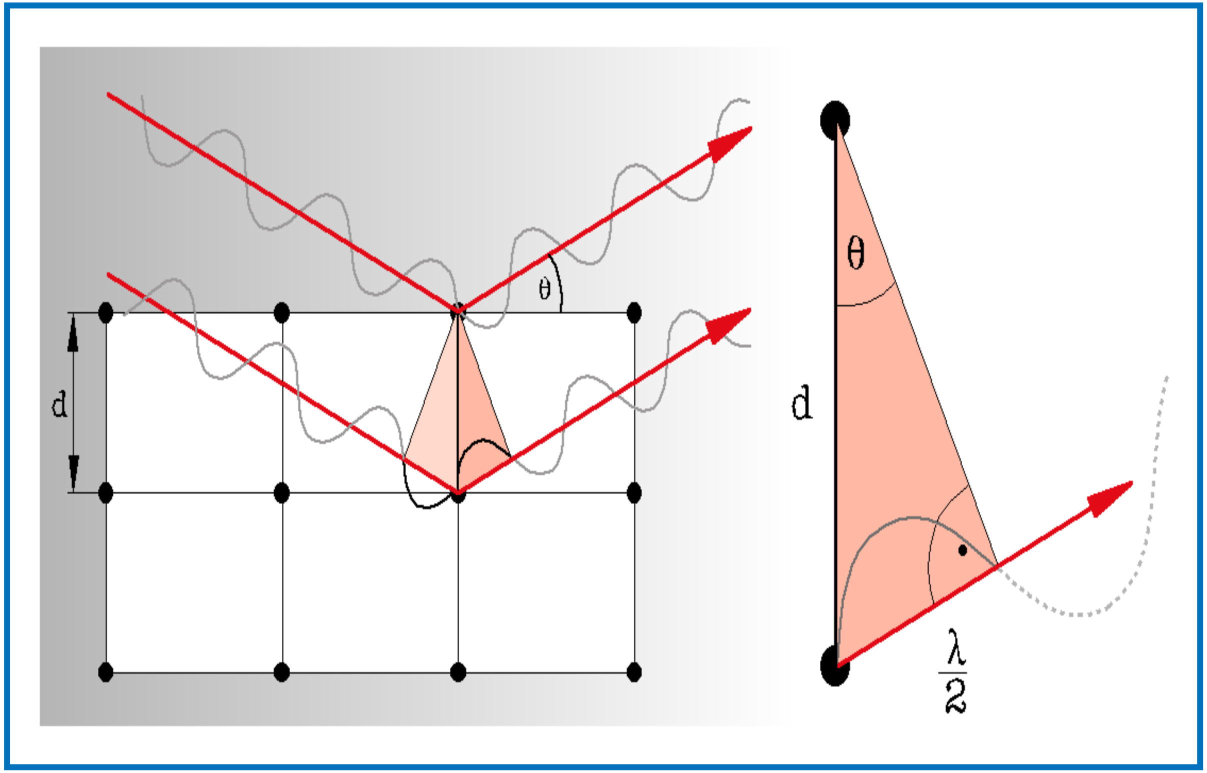


Registration: particles

Energy Dispersive X-ray Florescence – EDXRF

But photon counting detectors in XRD and WDXRD to

Bragg's Law



Bragg's Law:

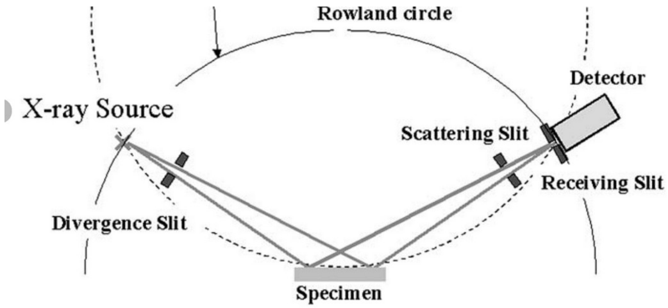
Conditions to have maximum:

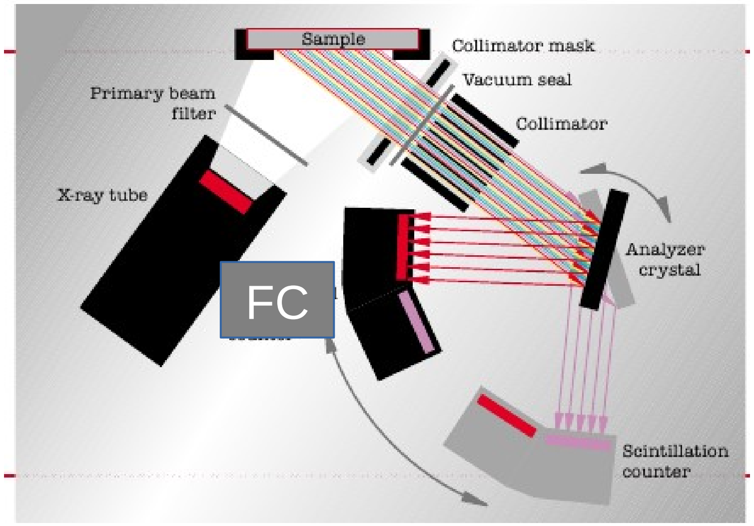
$n\lambda = 2d \sin\theta$

XRD: known **λ, d=?**

WDXRF: known **d, λ=?**
(but a monocrystal have to be used)

Goniometers





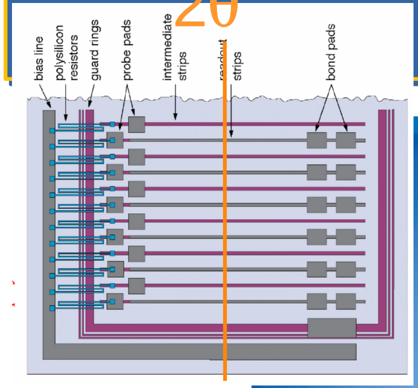
<u>XRD</u> Bragg-Bretano Geometry

- Point(line) focus x-ray source
- Divergent incident beam
- 3 Slits
- Diffraction from powder sample
- <u>Receiving(detector) slit = slower element in the system.</u>
- Distance Source to Sample = Sample Receiving Slit
- X-Ray Source angle = Detector angle = θ

<u>WD-XRF</u> Parallel Geometry

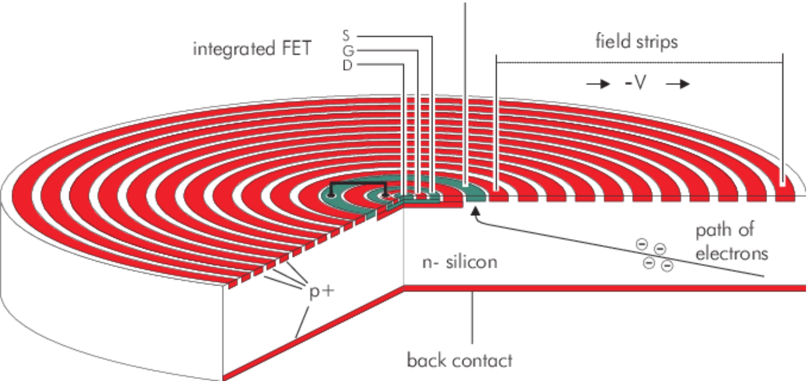
- Large spot (to 34mm) x-ray source
- Parallel incidence beam
- 2 sollers/collimators
- Diffraction from an analyzer monocrystal
- Distances are differed (detectors with collimators)
- But X-Ray Source angle = Detector angle = θ

Modern Detectors



XRD Silicon Strip Detector(SSD)

- A position sensitive solid state detector
- Every strip is equivalent of a detector slit
- 0.04º – 0.01º strip dimensions in deg.
- Efficiency > 90%
- Resolution 20% to 8%(Cu_{Kb}-Cu_{Ka})/Cu_{Ka} = 11%)
  Without $Cu_{K\beta}$ filter 2*I

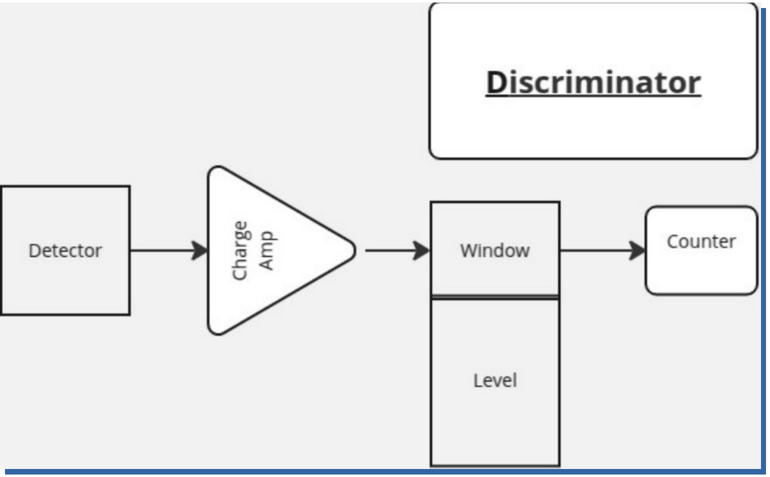


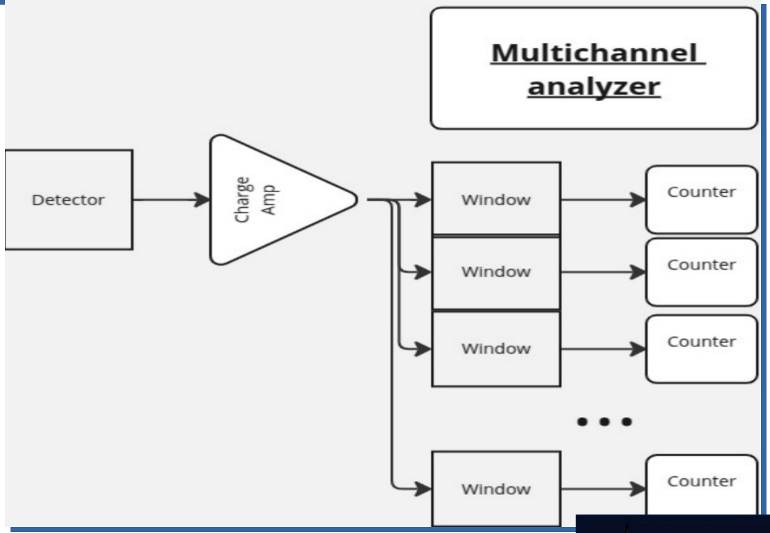
EDXRF Silicon Drift Detectors (SDD)

- Electrons drift to the central area due to the field strips.(with red)
- An integrated FET in the center with very low C
- Works from NaK_{α}
- built-in electric cooling
- 130-140 eV @ 5.9 keV MnK_{α} . Ext. 2%

C1U1 = C2dU2, if C1<<C2, U1 >> U2

Detector Electronics



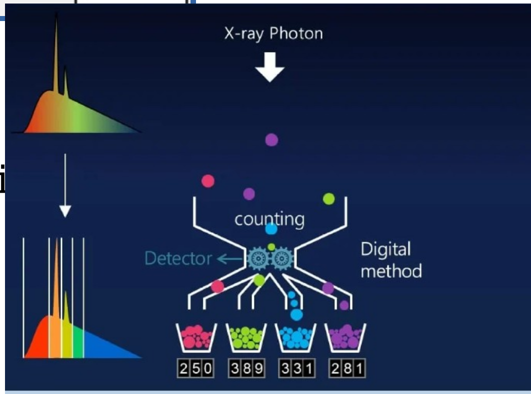


<u>XRD,WDXRF</u>

1. Detector
2. Pulse Shape Preamplifier
3. Discriminator
4. Counter

<u>EDXRF</u>

1. Detector
2. Pulse Shape Preamplifi
3. Multichannel Analyzer



Critical Sample Thickness

Klenk, M.; Schenker, O.; Probst, U.; Bucher, E. X-ray fluorescence measurements of thin film chalcopyrite solar cells. Sol. Energy Mater. Sol. Cells 1999

$$I_r = C_r * K_r / \mu_r (1 - \exp(-\mu_r * \rho * d)) \quad (1)$$

When $d \to \infty$ then $I_r = C_r * K_r / \mu_r$ (2)

When $d \to 0$ then $I_r = C_r * K_r * \rho * d$

$\rho * d * S = m_r$ **or**

$$Ir = m_r / S * K_r \quad (3)$$

Where:

I_r[CPS]	r-element intensity
C_r[%]	r-element concentration in the sample
K_r	Constant depending of various properties of the spectrometer, tube, HV settings and depends on other elements in the sample.
μ_r[cm^2/g]	The mass absorption coefficient depends on other element in the sample.
ρ [g/cm^3]	Density of the sample
d[cm]	Sample thickness
m_r [g]	Mass of element r
S [cm^2]	Irradiated surface

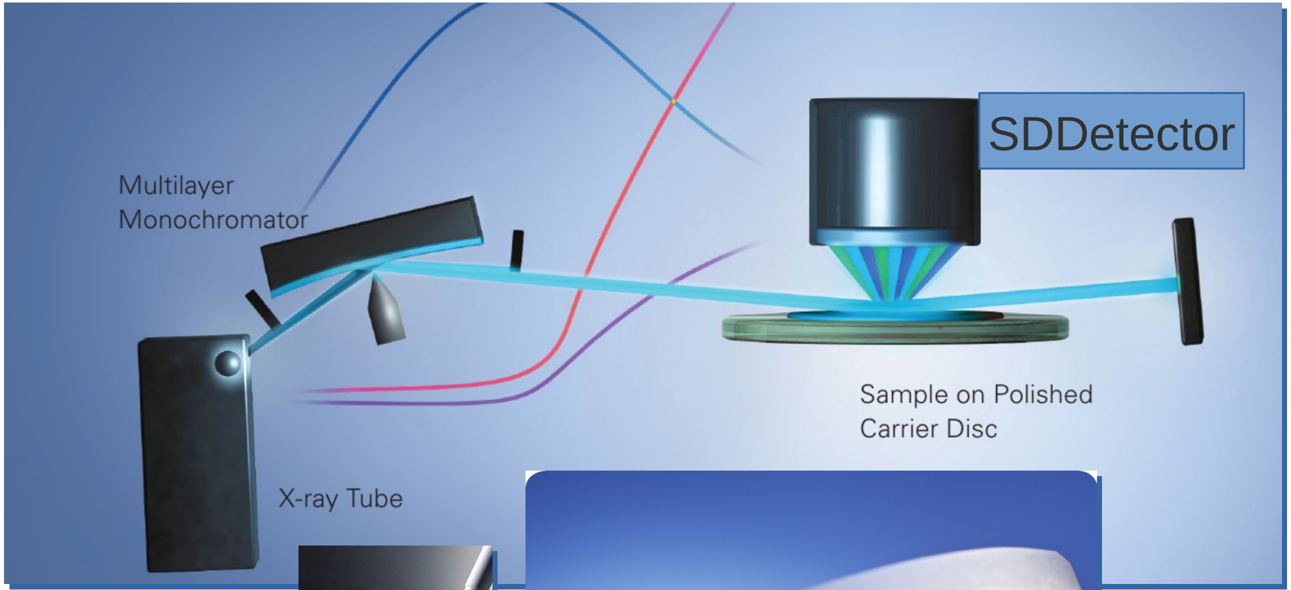
A sample is considered infinite when its thickness is much greater than the critical depth – the layer that generates 99% of the XRF signal.

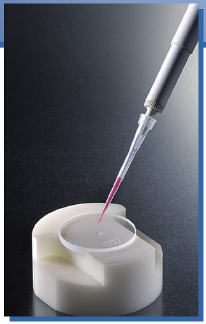
XRF is a comparative method – it works best when the sample closely matches the chemistry of the references.

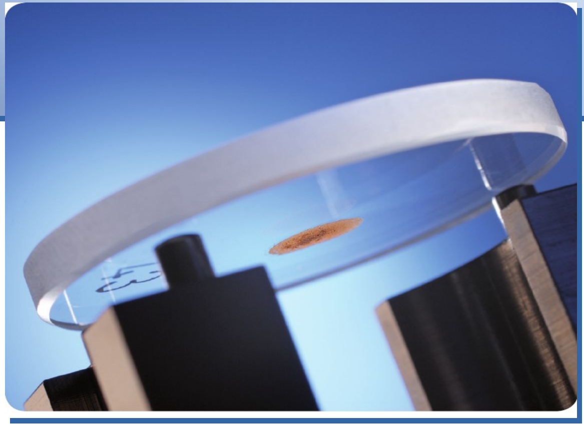
For broader comparisons, mathematical alpha corrections are used to model matrix effects.

Alternatively, fused beads turn the sample into an effectively infinite thin layer, minimizing these effects from the start..

TRXRF







For element r, when d->0

$Kr = I_{o\lambda}(V,I) * P_{\lambda r}$ - Monochromator

$$\mathbf{Ir = m_r/S * Kr = m_r/S * I_0 * P_{\lambda r}}$$

Ir [CPS] Fluorescent yeld
I_0 [CPS]. Initial intensity
m_r/S [g/mm^2] Irradiated surface density
$P_{\lambda r}$ [mm2/g] or $\mu_{\lambda r}$[cm^2/g](Tab.in NIST)

1. Thin film = no absorption in other elements in the sample(simple and linear calculations)

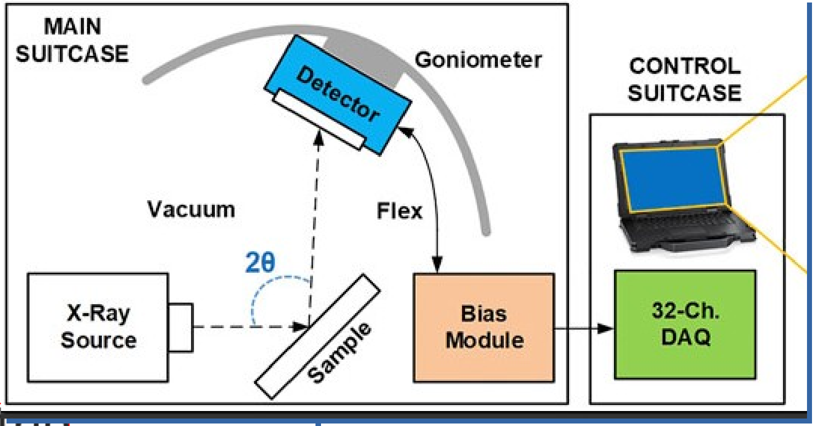
2. Momochromator = $\mu_{\lambda r}$[cm^2/g](Tab.in NIST)

3. Grazing incidence to the substrate = Total reflection = Low background + No Air absorption = LLD ppm to 0. ppm

An Italian Story…

Carminati Marco , Borghi Giacomo.. ,32-Channel silicon strip detection module for combined X-ray fluorescence spectroscopy and X-ray diffractometry analysis, Frontiers in Physics 2022 vol10

DOI=10.3389/fphy.2022.910089



- 32 silicon strip detector,
- 32 channel CUBE low noise charge integrator.
- Thermoelectric cooling module -10 C^{o}
- 32 channel 16bit DAC with 62.5 MSpS
- Better than 200 eV at 5.9 keV
- A goniometer with a radius of 15 cm
- Moderate vacuum (10 mbar)
- Mo tube operated at 50 W power

32-Channel silicon strip detection module for combined X-ray fluorescence spectroscopy and X-ray diffractometry analysis

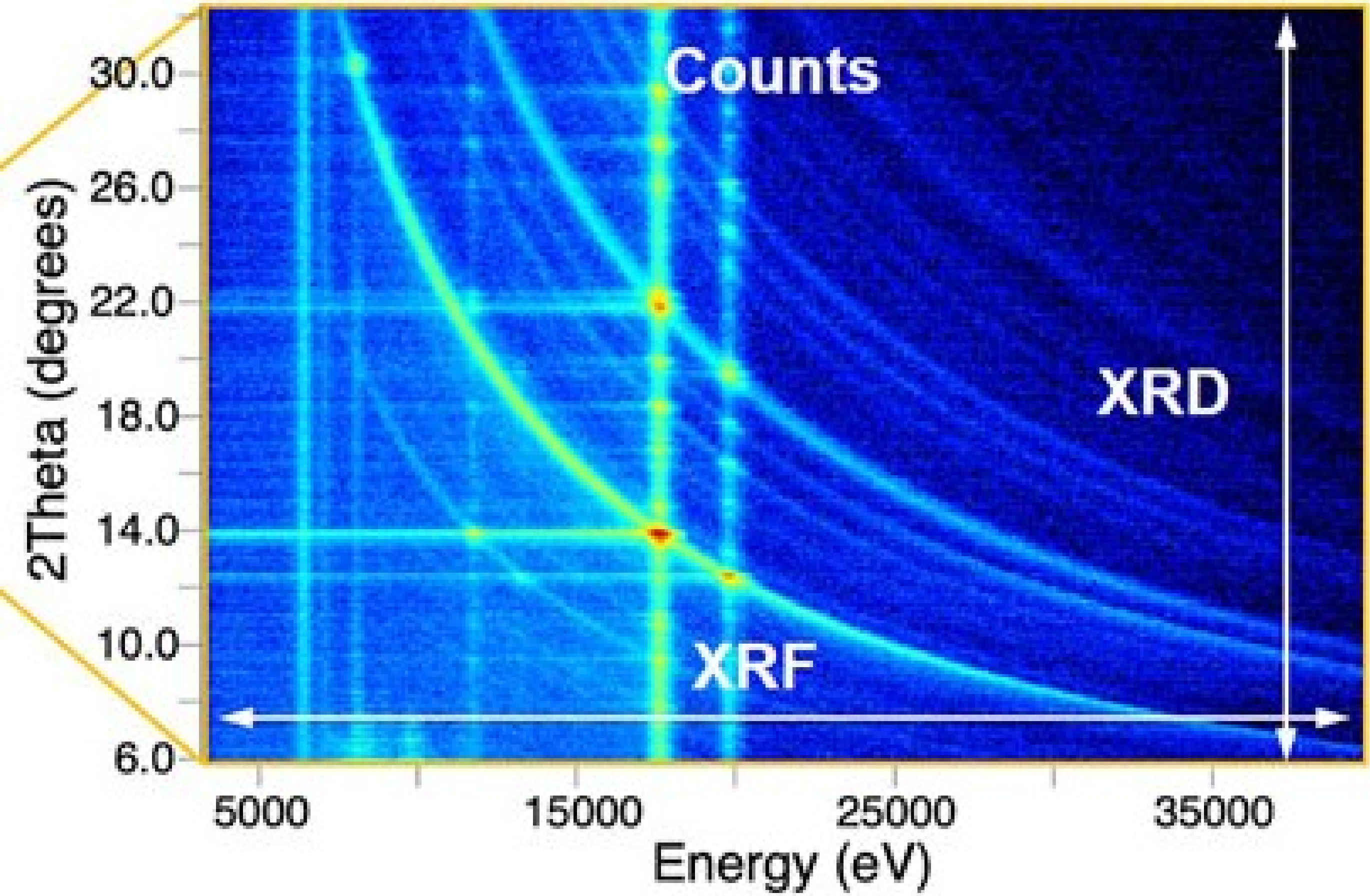
Marco Carminati[1,2]*, Giacomo Borghi[3], Evgeny Demenev[3], Matteo Gugiatti[1,2], Giancarlo Pepponi[3], Michele Crivellari[3], Francesco Ficorella[3], Sabina Ronchin[3], Nicola Zorzi[3], Evgeny Borovin[4], Luca Lutterotti[4] and Carlo Fiorini[1,2]

[1]DEIB, Politecnico di Milano, Milano, Italy, [2]INFN Sezione di Milano, Milano, Italy, [3]Fondazione Bruno Kessler (FBK), Trento, Italy, [4]Università di Trento, Trento, Italy

Color Diffraction

Or

Angularly Distributed Fluorescence



$CaCO_3 + FeSO_4$

https://plotdigitizer.com/app

MoKα = 17.48kEv MoKβ=19.61keV

Continuous spectra diffraction

6.56 - FeKα = 6,40keV +0.16

7.24 - FeKβ = 7,08keV +0.18

8.23 - CuKα = 8,05keV +0.18

11.81 – BrKα =11.92keV -0.11

< 4.5 kV

CaKα = 3.69keV CaKβ = 4.01keV

SKα = 2.32keV SKβ = 2.46keV

Conclusions

XRD and XRF are fundamentally different techniques – one sees structure, the other sees composition – yet they share common roots in X-ray physics.

Still, human imagination knows no limits – and hybrid systems like TRXRF prove that diffraction and fluorescence can work together, delivering absolute results from a spectrometer built like a XRD machine.

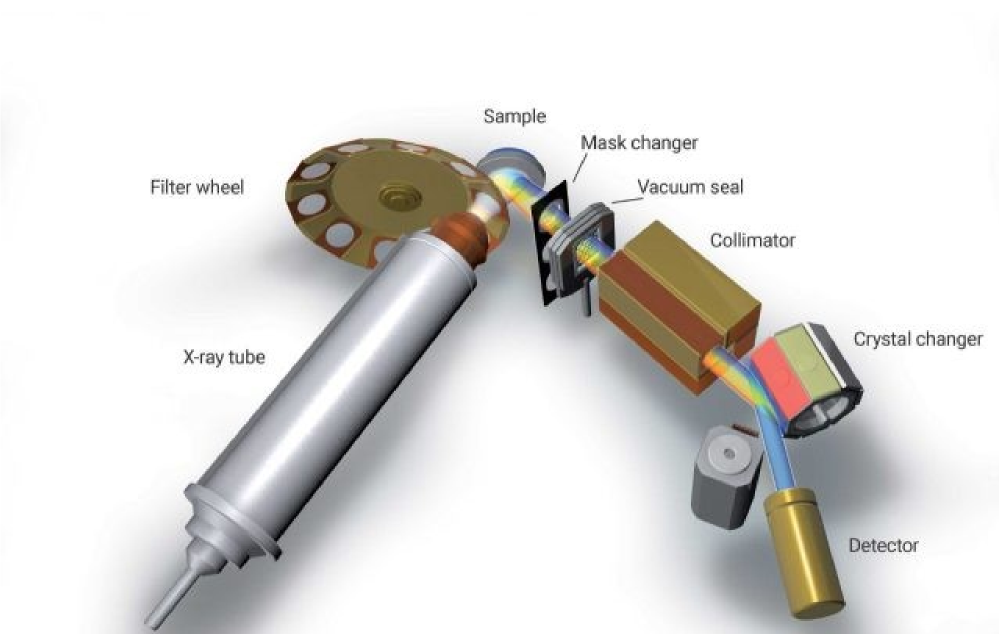
Looking ahead, I believe that within the next decade, we may see the rise of color diffraction systems – a breakthrough that could redefine the entire X-ray analytics landscape.

Thanks for attention!
The End

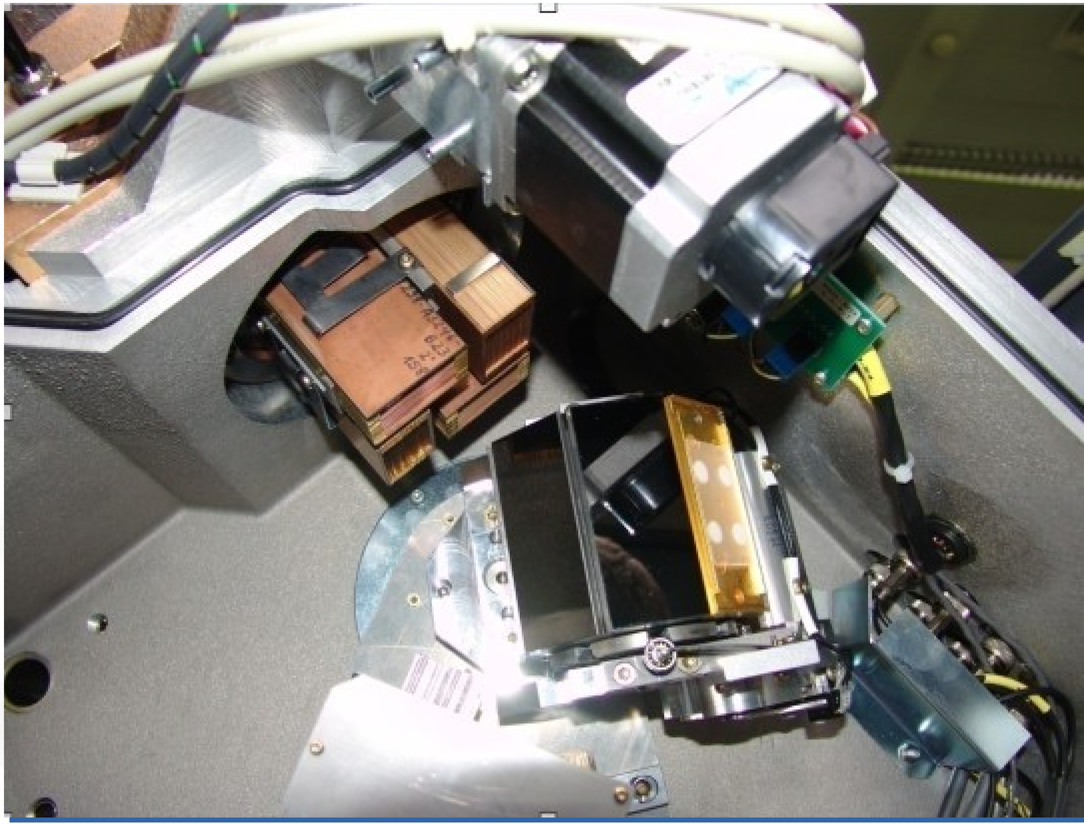
Detectors Table

	Resolution	Efficiency	• keV Range
Scintillation Detector	51%-3.0keV@5.9kV	95%	>CuKα
Gas Filled Proportional Counter	17%-1.0keV@5.9kV	30-35%	BKα to FeKα
XRD Silicon Strip Detector(SSD)	20% to 8% @5.9kV	>90%	**>FeKα**
EDXRF Silicon Drift Detectors (SDD)	2%-130eV@5.9keV	>90%	>NaKα
WDXRF	0.08%- 5eV@5.9keV	< 5%	BKα

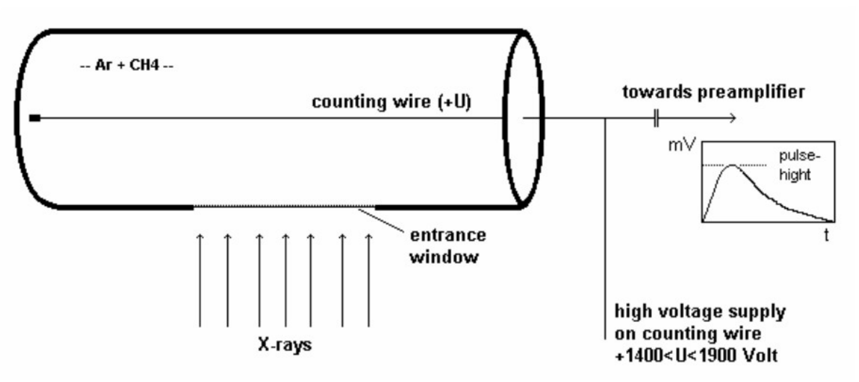
WDXRF Goniometer



Vacuum
Constant Temperature



Classic Detectors



<u>Gas(Ar) Filled Proportional Counter</u>

0.1 – 15keV (B, Na, Mg, Al, Si, K, Ca and Fe)

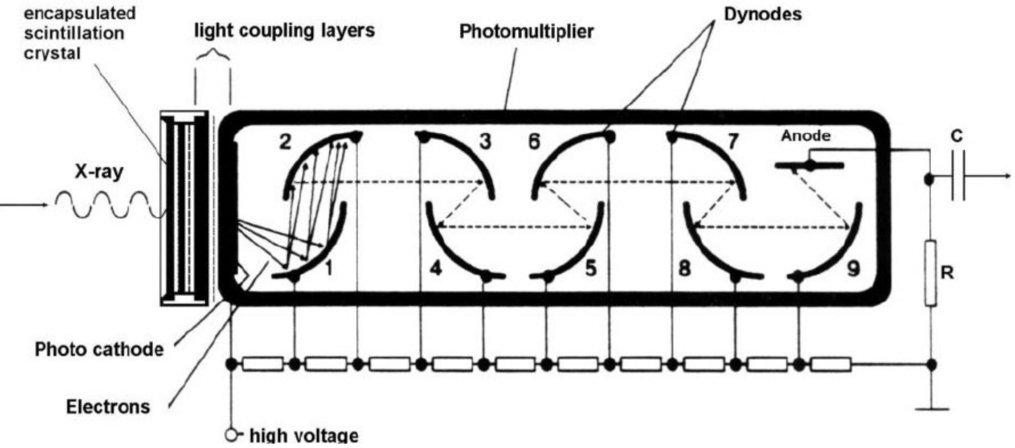
An electron-ion pair, approx. 0.03 keV

Boron (0.185 keV) produces approx. 6 pairs

30-40% efficiency

Res = 1.0keV(17%)@5.9kV

U = 1400-1900V



<u>Scintillation Detector</u>

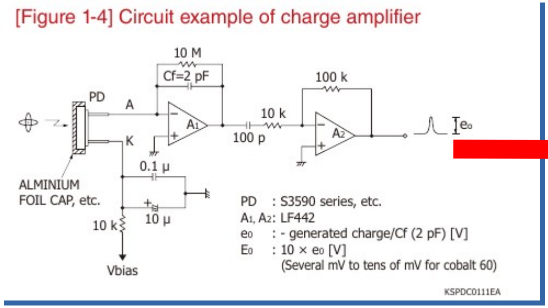
8keV - … (Cu …)

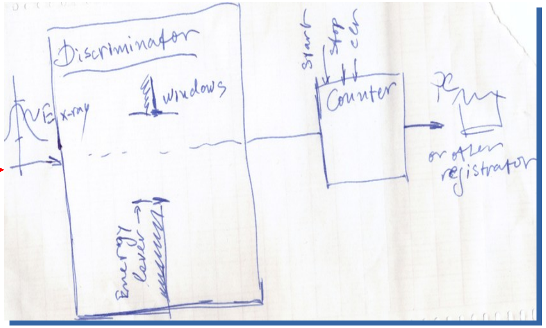
NaI(Tl) 95% efficiency

Res = 3.0keV(51%)@5.9kV

U = 450-700V

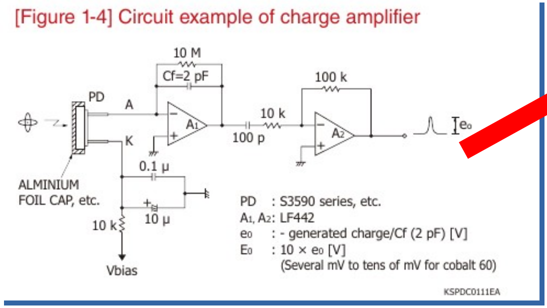
Detector Electronics

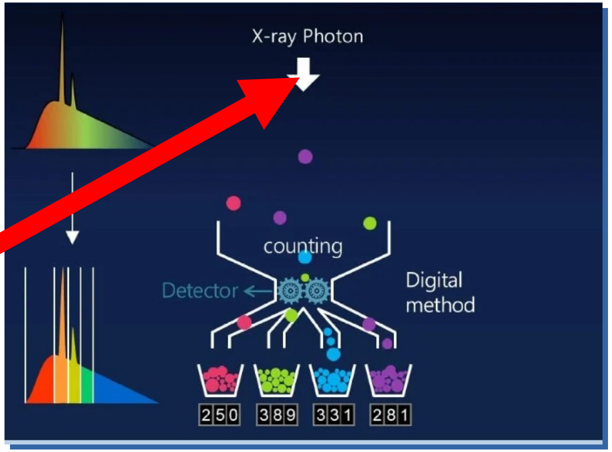




XRD,WDXRF

1. Detector
2. Pulse Shape Preamplifier
3. Discriminator
4. Counter





EDXRF

1. Detector
2. Pulse Shape Preamplifier
   (Usually integrated)

3. Multichannel Analyzer