

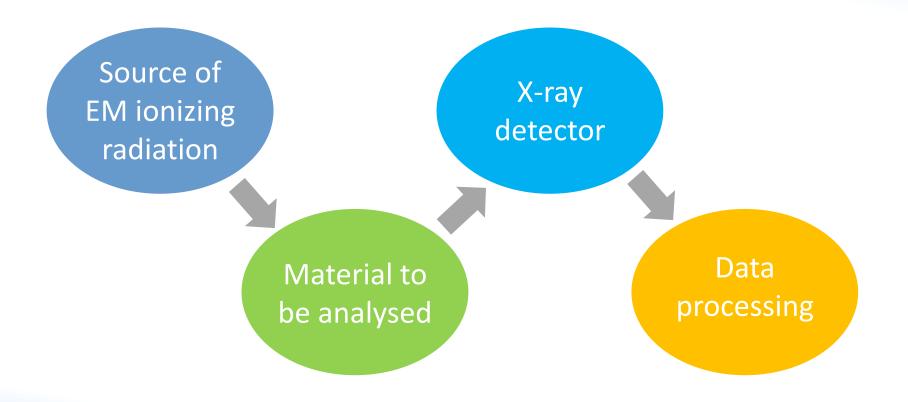
XRF techniques for materials and life sciences

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International Atomic Energy Agency

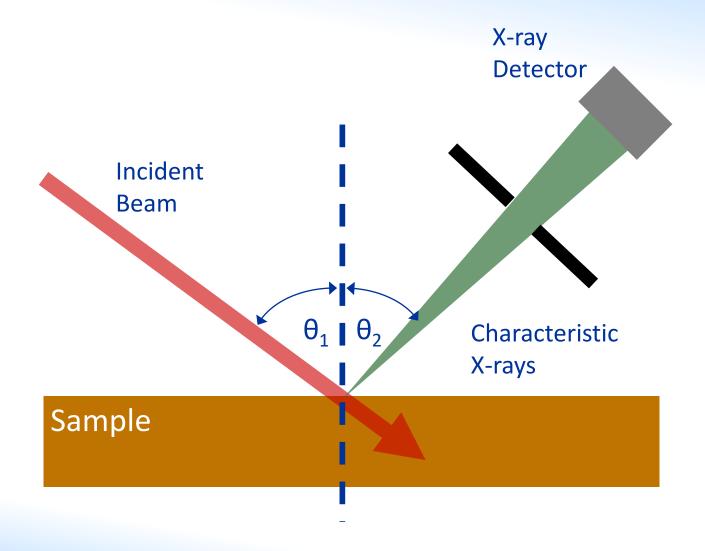
☐ Elements in XRF











■ Sources of ionizing radiation



- Electrons (SEM)
- Charged particles (accelerators)
- Radioisotopes (α, γ, X-rays)
- X-ray Tubes
- Synchrotron radiation

☐ Interaction of X-rays with matter



X-rays can interact with the atoms of the material in two different ways:

• <u>Photoelectric effect</u>: Primary X-ray radiation can ionise atoms of the material. The X-ray is absorbed in this process

Scattering:

- ✓ Elastic/Coherent scattering (Rayleigh): no energy loss after collision with electrons. The Rayleigh effect is present when electrons are strongly bound (inner atomic electrons)
- ✓ Inelastic/Incoherent scattering (Compton): energy loss after collision with electrons. The Compton effect is present when electrons are loosely bound (outer, less bound electrons)

Photoelectric effect

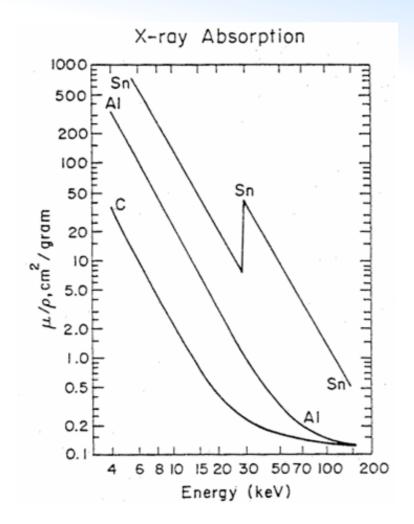


Photoelectric effect: Primary X-ray radiation can ionise atoms of the material to be analysed

Cross section of the PE depends strongly on Z of the material and on the energy of the primary X-ray

$$\sigma_{Ph} \propto \frac{Z^n}{E_X^{3.5}}$$
 $n = 3 \div 4$

To maximize the ionization probability, the energy of the primary X-ray should be higher than the binding energy but as close as possible to it



☐ X-Ray Fluorescence



Incident photon
Energy E_0 should be adequate to ionize the atomic bound electrons $\rightarrow E_0 \ge inner shell$

Fluorescence X-ray emission is **isotropic**

binding energy

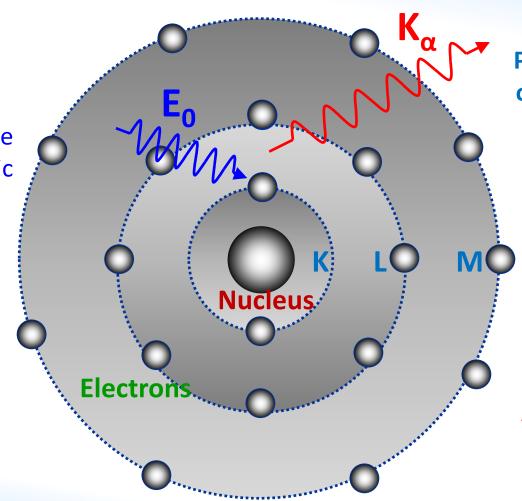


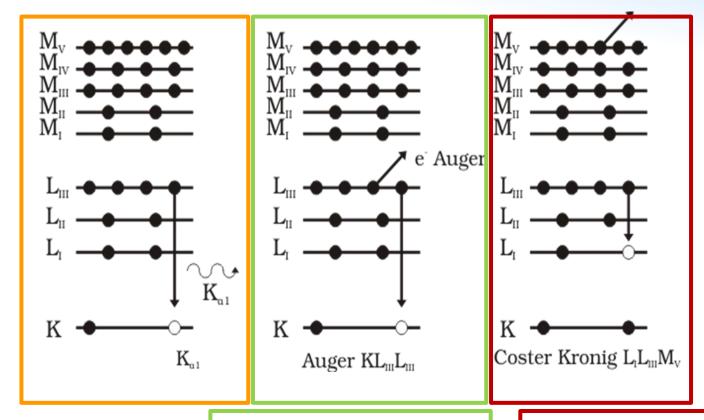
Photo-Ionization of atomic bound electrons (K, L, M) (Photoelectric absorption)

Electronic transition and emission of element characteristic

→ characteristic fluorescence radiation

□ De-excitation: Fluorescence/Auger





Emission of characteristic X-ray

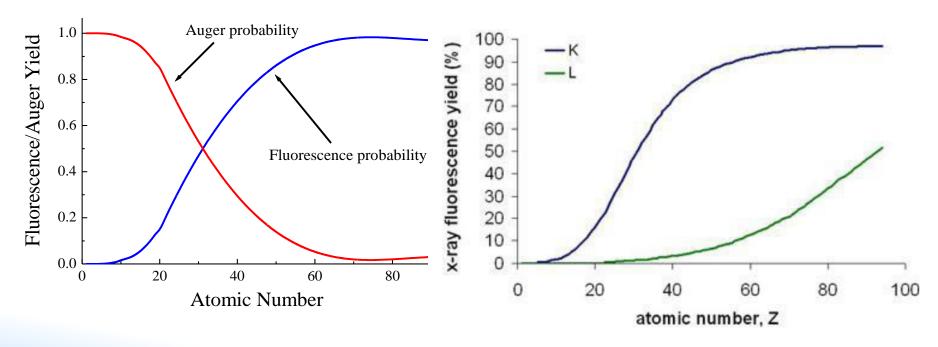
Emission of electron (vacancy filled by electron from different shell)

Emission of electron (vacancy filled by electron from the same shell)

☐ Fluorescence yield



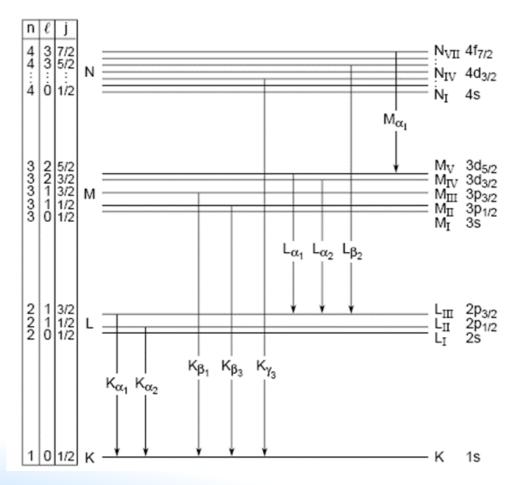
The fluorescence yield is given by the ratio of the emitted fluorescence photons over the number of the created holes. The competing process is the emission of Auger electrons as the atom returns to its ground state



For low Z the Auger electron emission is dominant

■ Emission of characteristic X-rays





The emission of characteristic X-ray lines follows allowed electronic transitions between specific subshells

Each element has a unique set of emission lines

Siegbahn/IUPAC notation:

$$\mathbf{K}_{\alpha}$$
: $\mathbf{K} - \mathbf{L}_2 + \mathbf{K} - \mathbf{L}_3$

$$K_{\beta}$$
: K-M₂ + K-M₃

$$L_{\alpha}$$
: $L_3 - M_4 + L_3 - M_5$

$$L_{\beta 1}$$
: L_2 - M_4

$$L_{\beta 2}$$
: $L_3 - N_5$

☐ X-ray energies



Moseley's law

$$E = h \cdot A \cdot R \cdot (Z - b)^2$$

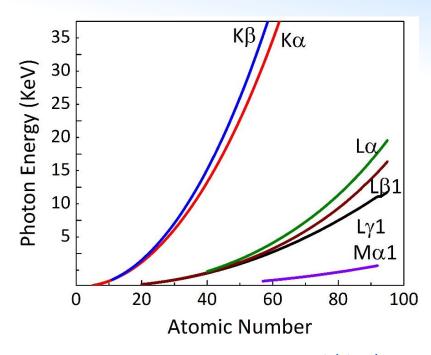
h = Planck constant

R =Rydberg frequency

Z = atomic number

A = 3/4 for K_{α} , 5/36 for L_{α}

b = 1 for K_{α} , 7.4 for L_{α}



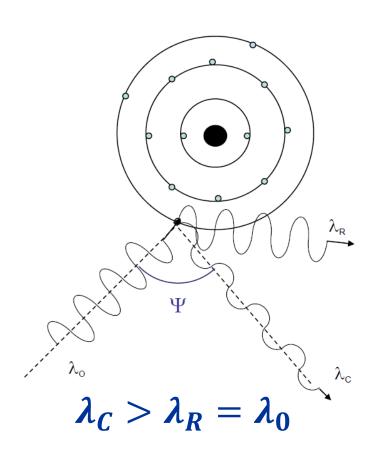
$$\mathbf{K}_{\alpha}$$
 E [eV] ≈ 10.20 · (Z − 1)² $E_{Fe-K\alpha}$ ≈ 6380 eV

L_{\alpha} E [eV] ≈ 1.89 ·
$$(Z - 7.4)^2$$
 $E_{Pb-L\alpha}$ ≈ 10520 eV

X-ray spectroscopy within the energy range $1\div30$ keV offers in principle the possibility to detect all the periodic table elements (Z > 10) through their K, L or even M series of emission lines

☐ X-ray scattering





Elastic/coherent scattering (Rayleigh):

no energy loss after collision with electrons. The Rayleigh effect is present when electrons are strongly bound.

Rayleigh is more intense for high Z (= heavy) matrices

Inelastic/Incoherent scattering (Compton):

energy loss after collision with electrons. The Compton effect is present when electrons are loosely bound.

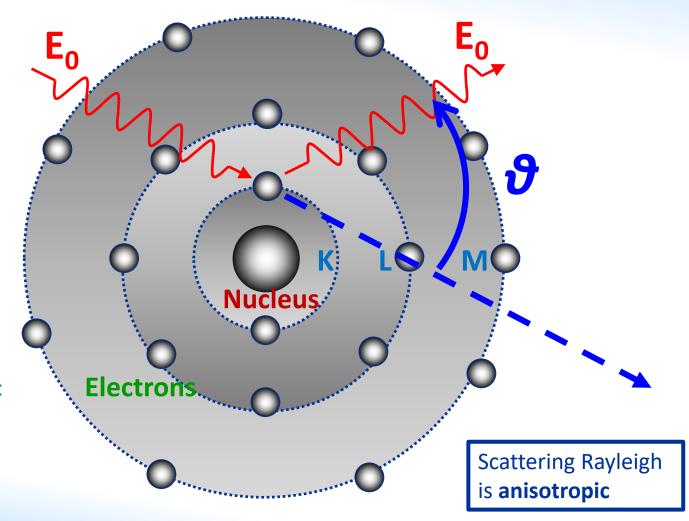
Compton is more intense for low Z (= light) matrices

□ Rayleigh scattering



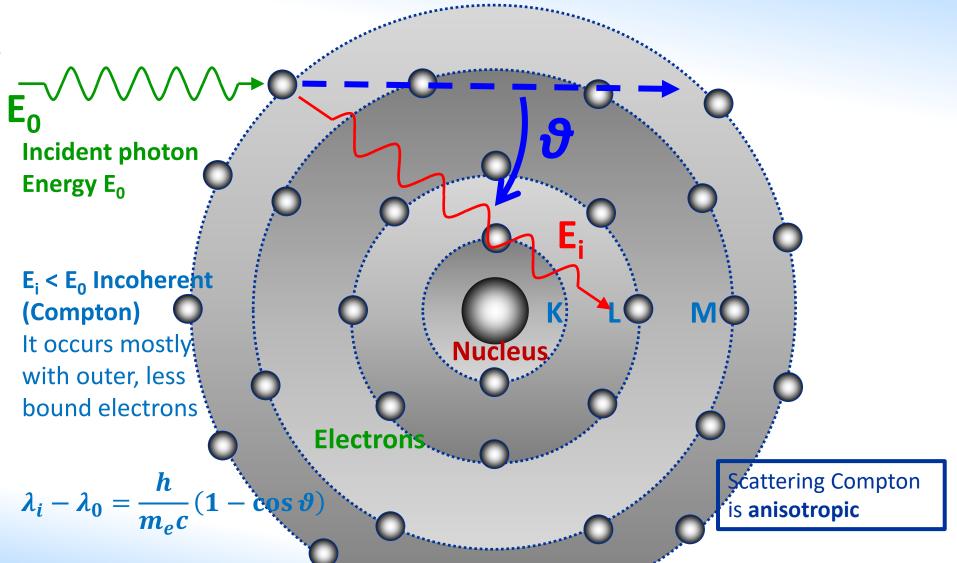
Incident photon Energy E₀

 $E_i = E_0$: Coherent (Rayleigh)
It occurs mostly with inner atomic electrons



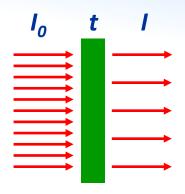
Compton scattering





\Box Linear attenuation coefficient μ





Attenuation of photons by a thin layer of thickness dt is described by

$$dI = I \cdot \mu \cdot dt$$

where I is the number of photons per unit area and unit time (photon flux) of which dI are attenuated while penetrating the layer of a material characterized by the (total, linear) attenuation coefficient μ . This is equivalent to

$$I = I_0 \cdot e^{-\mu \cdot t}$$

I and I_0 are the photon fluxes behind and in front of the absorber, respectively, and t is the thickness. μ is a function not only of the material (atomic number Z) but also of the photon energy E

\square Mass attenuation coefficient μ_m



$$\mu = \mu_m \cdot \rho$$

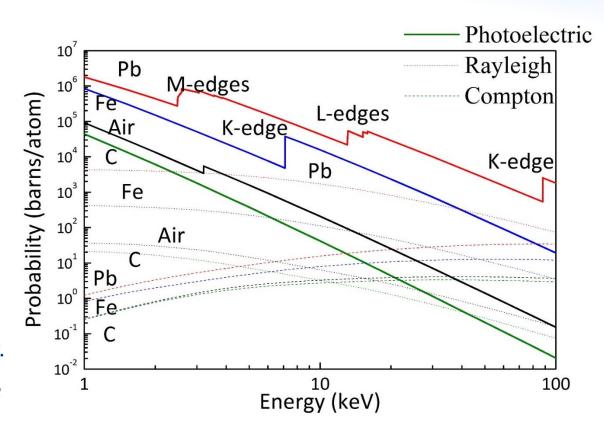
the total mass attenuation coefficient μ_m doesn't depend on the density ρ of the material. The coefficient μ_m summarizes all

The coefficient μ_m summarizes all possible photon interactions

$$\mu_m = \tau_m + \sigma_m$$

where τ_m describes the photo absorption and $\sigma_m = \sigma_{coh} + \sigma_{inc}$ are the contributions by coherent and incoherent scattering, respectively.

Both kinds of scattering contribute much less than the photo absorption to the total μ_m



Mass attenuation coefficient μ_m



the mass attenuation coefficient of a material that is <u>composed of</u> <u>several elements</u>, with weight fractions w_i , is

$$\mu_m = \sum_i w_i \cdot \mu_m^i$$

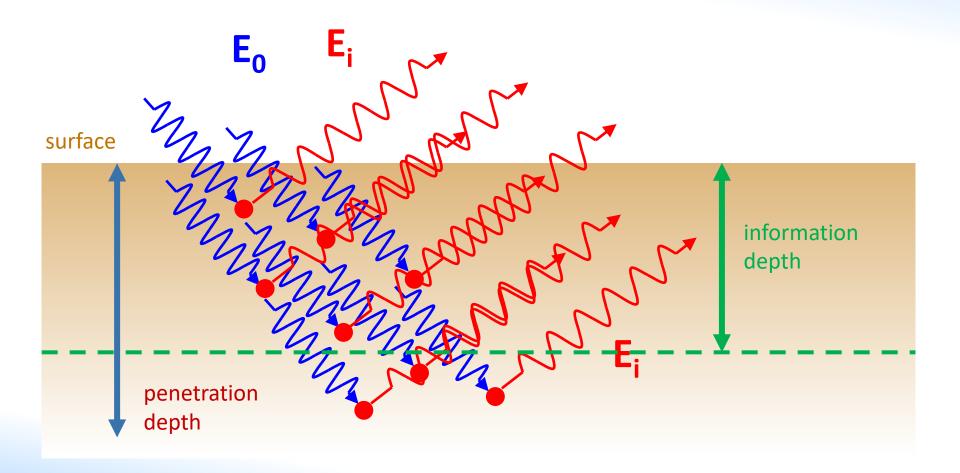
Use of mass attenuation coefficients suggests replacing the thickness by the **area-related mass** m = M/A (mass M per unit area A) and rewriting the attenuation law as

$$I = I_0 \cdot e^{-\mu_m \cdot m}$$

$$t \cdot \rho = M/A$$
, in grams/cm²

Penetration and information depth



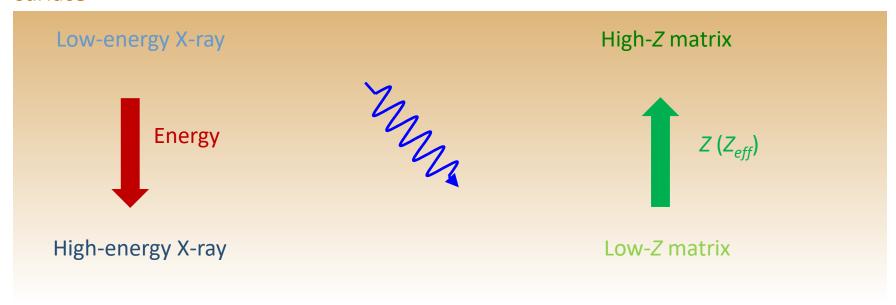


Penetration and information depth



Penetration and information (analytical) depth depend on the energy of the X-ray and on the matrix:

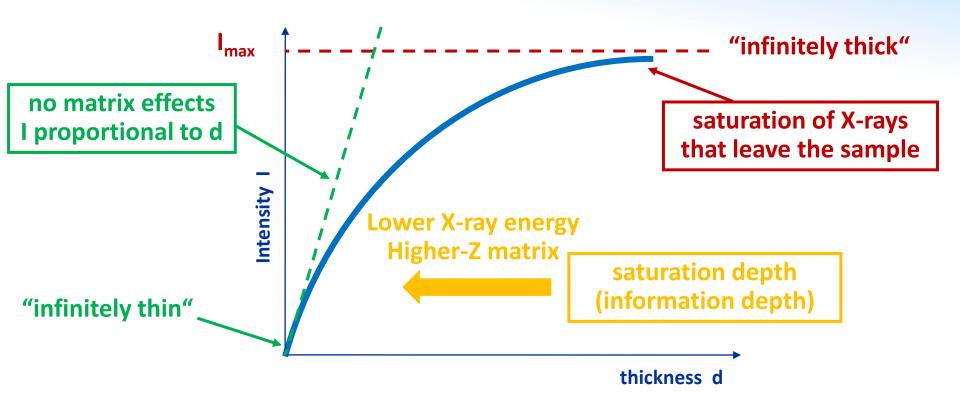
surface



- Surface treatment is extremely important for heavy matrices
- Information thickness is essential for light matrices

☐ Influence of sample thickness





Increasing the thickness of the sample above the information depth will not increase the signal but only the scattering of the primary radiation

Analytical depths in different matrices

Different elements exhibit different Information thicknesses (99%), depending on their characteristic X-ray energy and on the overall matrix

Line	Energy	Graphite	Glass	Iron	Lead
Cd K _{α1}	23,17 keV	14,46 cm	8,20 mm	0,70 mm	77,30 μm
Mo K _{α1}	17,48	6,06	3,60	0,31	36,70
Cu K α1	8,05	5,51 mm	0,38	36,40 μm	20,00
Ni K _{α1}	7,48	4,39	0,31	29,80	16,60
Fe K _{α1}	6,40	2,72	0,20	*164,00	11,10
Cr K _{α1}	5,41	1,62	0,12	104,00	7,23
S K α1	2,31	116,00 μm	14,80 μm	10,10	4,83
Mg K _{α1}	1,25	20,00	7,08	1,92	1,13
FK _{α1}	0,68	3,70	1,71	0,36	0,26
Ν Κ α1	0,39	0,83	1,11	0,08	0,07
C K α1	0,28	*13,60	0,42	0,03	0,03
B K α1	0,18	4,19	0,13	0,01	0,01

$$E_{KC} = 0.2842$$

 $E_{KFe} = 7.112$

Detectors

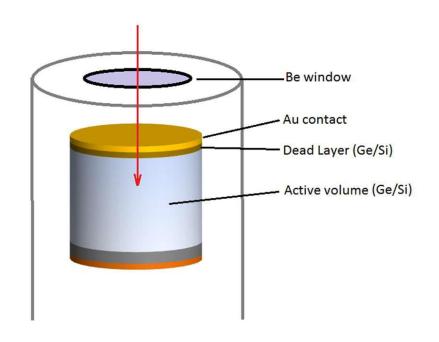


- Proportional Counters
- Scintillation Detectors
- Si(Li)
- LEGe
- PIN Diode
- SDD
- CCD, CMOS cameras
- CZT, other

Semiconductor detectors



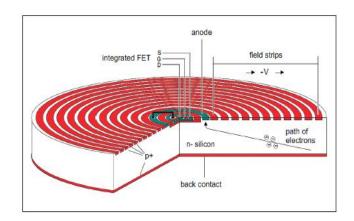
- X-rays produce electron-hole pairs, whose number is proportional to the energy of the radiation (average energy to produce an electron/hole pair is 3.6eV for Si and 2.9eV for Ge)
- Electrons and holes are collected from the depleted active region to the electrodes, where they result in a pulse that can be further amplified and finally measured
- This pulse carries information about the energy of the original incident radiation. The number of such pulses per unit time also gives information about the intensity of the radiation



☐ Silicon Drift Detectors - SDD



The charge is drifted from a large area into a small read-out node with low capacitance, independent of the active area of the sensor. Thus, the serial noise decreases, and shorter shaping time can be used. For SDDs faster counting is enabled and higher leakage current can be accepted, drastically reducing the need for cooling.



- Energy resolution ~ 125 140 eV (Mn-Ka)
- Input capability ~ 10⁶ photons/sec

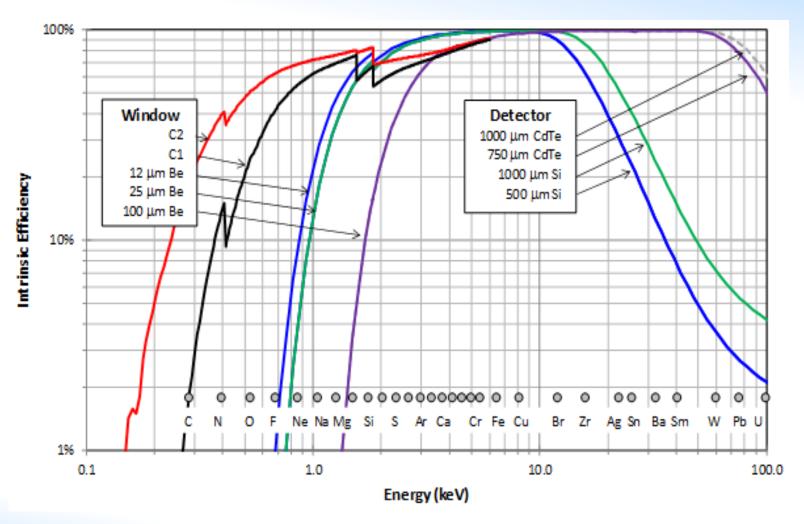
https://tools.thermofisher.com/content/sfs/brochures/TN52342 E 0512M SiliconDrift H.pdf



Detector photograph reproduced from https://www.rayspec.co.uk/x-ray-detectors/silicondrift-detectors/xrf/

Efficiencies of different detectors



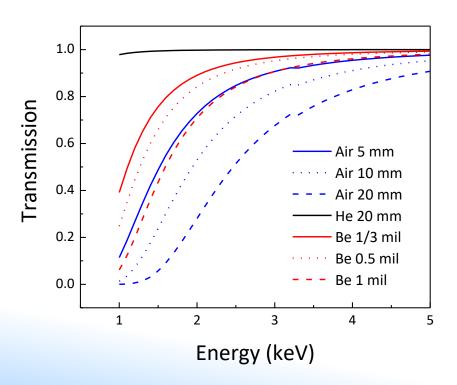


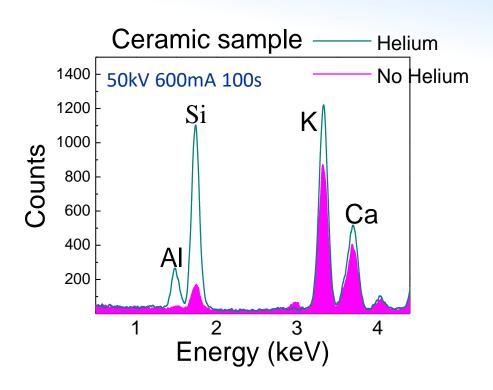
Comparison of different detector's efficiency from AMPTEK https://www.amptek.com/products/x-ray-detectors/fastsdd-x-ray-detectorsfor-xrf-eds/fastsdd-silicon-drift-detector

"Light" elements (Na, Mg, Al, Si)



Vacuum atmosphere or **He flushing** is required in the x-rays path between sample and detector

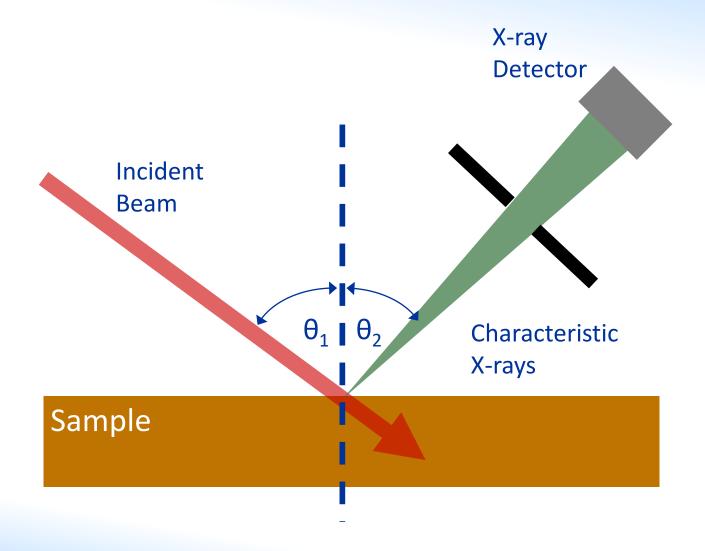




The improvement in the intensity of Al-K and Si-K characteristic X-ray lines is significant, 22 and 7.3 times respectively

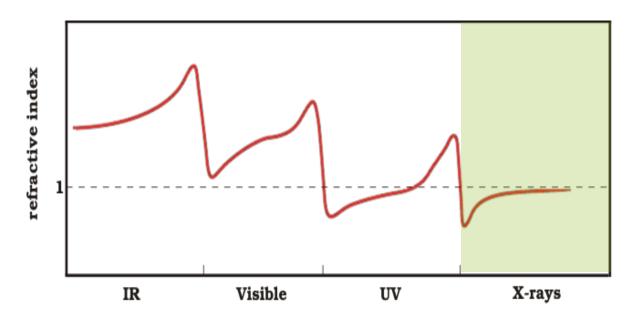








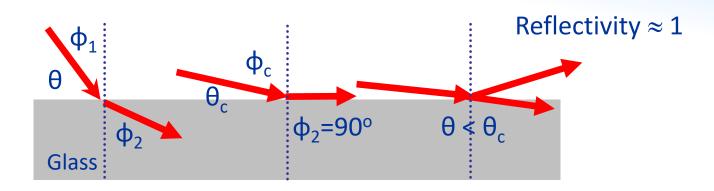
Refractive index:
$$n = \frac{c}{u_p}$$



$$n=1-\delta+i\beta$$
 $\beta=$ Attenuation term $\delta=$ Phase term

☐ X-ray total reflection





Snell Law
$$\frac{\sin\phi_2}{\sin\phi_1} = \frac{1}{n}$$
 \Rightarrow $\sin\phi_2 = \frac{\sin\phi_1}{n}$ \Rightarrow $\phi_2 > \phi_1$ $n \approx 1 - \delta$

$$\vartheta_{crit} = \sqrt{2\delta}$$
 $\vartheta_{crit}(deg) \approx \frac{1.651}{E(keV)} \sqrt{\frac{Z}{A}} \rho(\frac{g}{cm^3})$

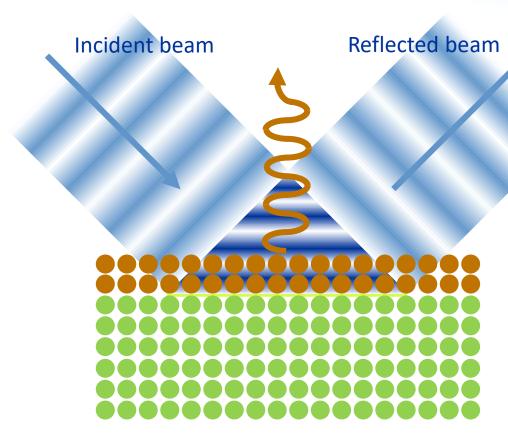
Z: Atomic number

A: Atomic mass

ρ: Density

☐ X-ray Standing Wave





Formation of X-ray Standing Wave (XSW) at grazing incident/exit angle

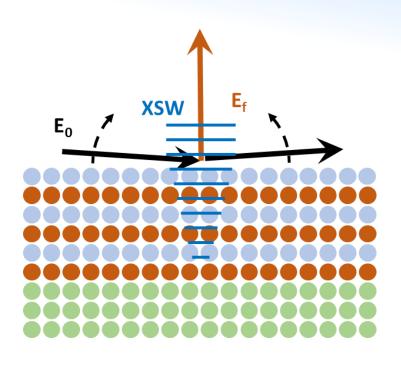
Electric Field Modulations above the surface

The X-ray fluorescence intensity from the sample depends on the varying field intensity of the XSW field within the sample

GIXRF and XRR



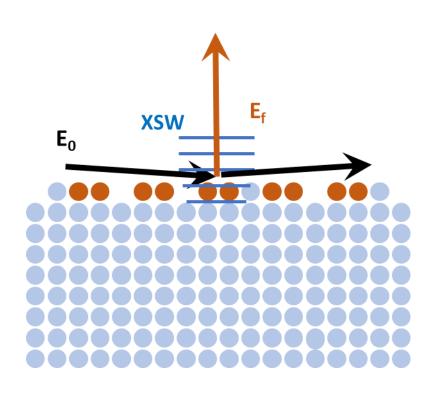
By varying continuously the grazing incident angle through and few times above the critical angle for TR, the recorded XRF intensity profiles (Grazing Incidence-XRF analysis) have the potential to provide information on structural and compositional properties of thin films, such as the layer composition, sequence, thicknesses and densities, interface roughness, in depth elemental gradients of matrix elements or dopants in semiconductors, characterization of nano-particles deposited on flat surfaces, etc



A more accurate and robust reconstruction of these thin film properties requires the synergy or even the simultaneous fitting of GI-XRF with X-ray reflectometry (XRR) data

■ Total reflection X-ray Fluorescence





TXRF is essentially an energy dispersive XRF technique arranged in a special geometry.

Due to this configuration, the measured spectral background in TXRF is less than in conventional XRF. This reduction results in increased signal to noise ratio.

TXRF is a surface elemental analysis technique often used for the ultra-trace analysis of particles, residues, and impurities on smooth surfaces.



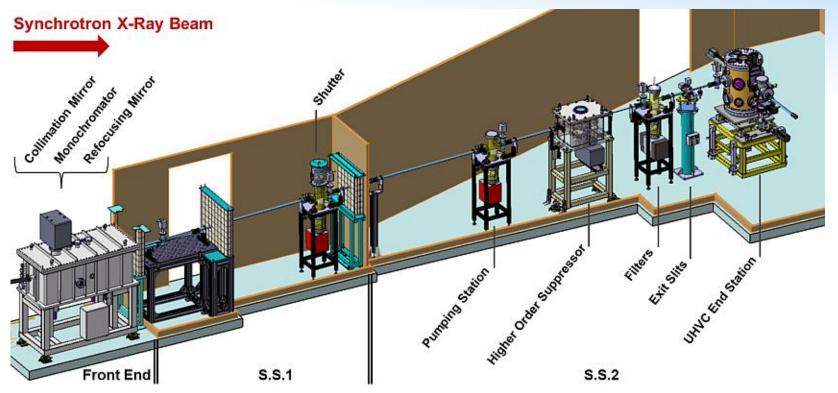
The joint IAEA-Elettra XRF beamline at Elettra Sincrotrone Trieste





Optical layout



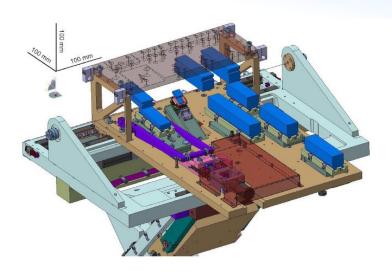


Source	Bending magnet		
Flux	10 ¹⁰ ph/s (at 5 keV for 2.0 GeV, at 10 keV for 2.4 GeV) (Si 111)		
Spot size	250 x 100 (H x V) μm ²		
Beam divergence	< 0.15 mrad (at exit slits)		

Werner Jark, Diane Eichert, Lars Luehl, Alessandro Gambitta, *Optimisation of a compact optical system for the beam transport at the x-ray fluorescence beamline at Elettra for experiments with small spots*, Proc. SPIE 9207, Advances in X-Ray/EUV Optics and Components IX, 92070G, 2014; doi: 10.1117/12.2063009

■ The monochromator at XRF





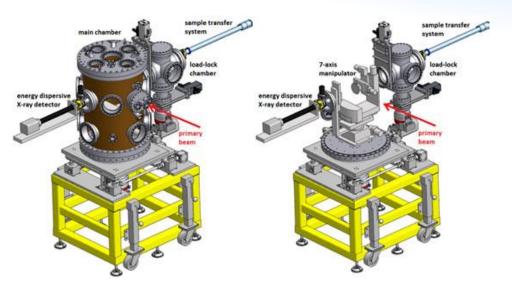


Optics type	E range (keV)	E resolution (△E)	
Si(111)	3.6 - 14	~ 1 eV at 7 keV	
InSb(111)	2.0 – 3.8	~ 1eV at 2.2 keV	
ML: High E (RuB ₄ C)	4.0 – 14.0	~ 55 eV at 1 keV ~ 180 eV at 14 keV	
ML: Medium E (NiC)	1.5 – 8.0		
ML: Low E (RuB ₄ C)	0.7 – 1.8	100 CV Ut 14 RCV	

Werner Jark et al., Proc. SPIE 9207, Advances in X-Ray/EUV Optics and Components IX, 92070G, 2014; doi: 10.1117/12.2063009

■ IAEAXspe endstation



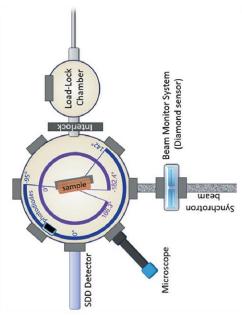




The IAEA end-station is based on a prototype design by Physikalisch - Technische Bundesanstalt (PTB, Berlin) and Technical University of Berlin (TUB)

Available detectors:

- Diamond detector for I₀
- SDD detector for XRF (different variants) and XAS (in fluorescence geometry)
- Photodiodes for XAS in transmission geometry
- Photodiodes with 100 and 200μm slits and SDD for XRR



Andreas G. Karydas et al., J. Synchrotron Rad. (2018). 25, 189–203

□ 7-Axis Manipulator



Sample arm

- 3 linear stages (X, Y, Z)
- 2 goniometers (Theta, Phi)

Photodiodes arm:

- 1 linear stages (diode)
- 1 goniometer (2Theta)

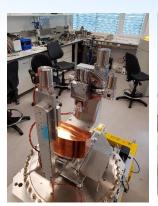


Ultra Thin Window (UTW) Bruker Silicon
 Drift detector (30 mm², FWHM 131 eV @
 Mn-Ka), Si photodiodes

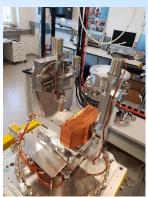
Full step resolution

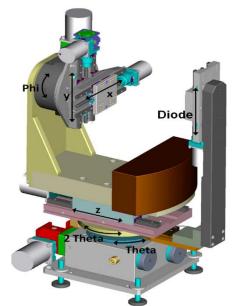
Linear axes: Diode, X, Y, Z (0.005mm, 0.005mm, 0.0005mm, 0.01mm)

Goniometers: Theta, 2theta, phi (0.001°, 0.001°, 0.005°)





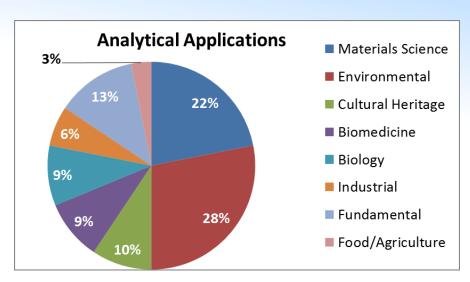


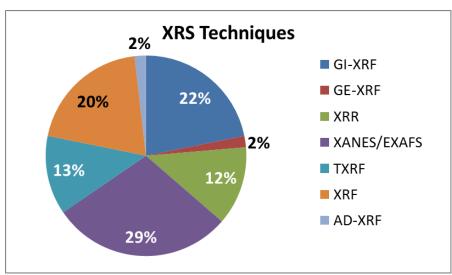


■ IAEA Coordinated Research Project



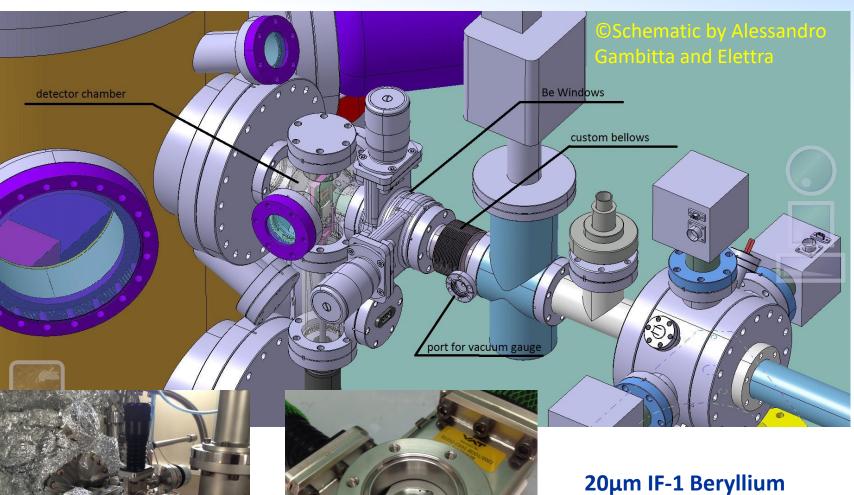
- Materials Science: Structured materials for energy storage and conversion technologies
- Nanomedicine Biosensing technologies
- **Environmental monitoring** (air particulate matter, water)
- Biological: Elemental distribution/ speciation on plant organ (leaves, roots, shoots, seeds, etc.)
- Cultural Heritage –preventive conservation
- Food products security Authenticity
- Determination of X-Ray Fundamental Parameters





non-UHV compatible samples

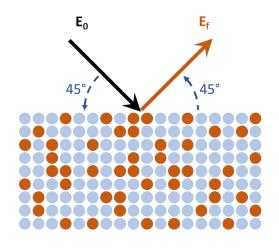




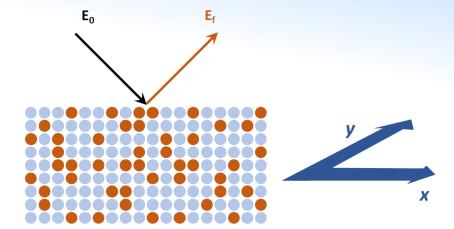
20µm IF-1 Beryllium Luxel Corporation

☐ Geometries and techniques









micro - XRF

Elemental characterization

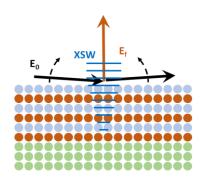
Mapping



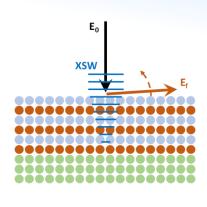
X-ray Absorption Spectroscopy (on hot spots)

☐ Grazing angle geometries

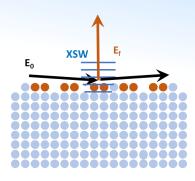




Grazing Incident - XRF

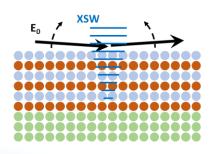


Grazing Emission - XRF



Total reflection - XRF





X-Ray Reflectometry

Depth profiling measurements

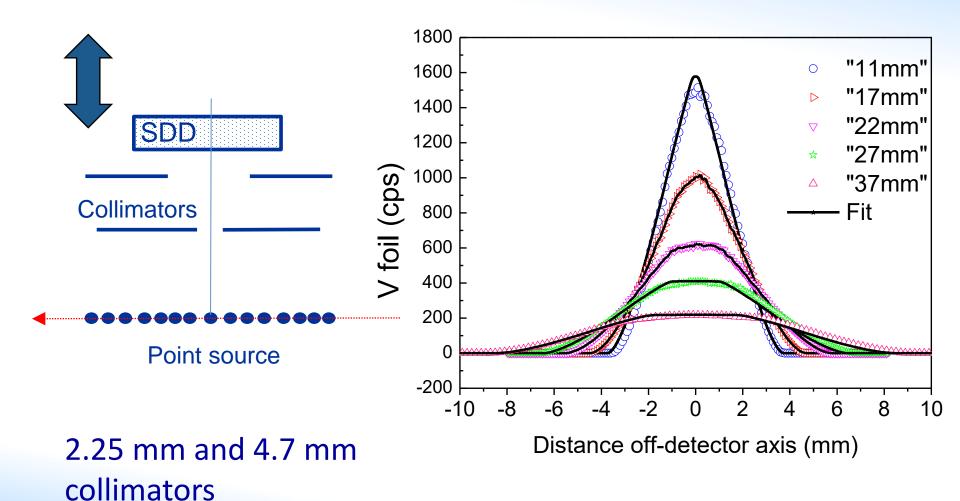
Trace element analysis
Surface contamination



X-ray Absorption Spectroscopy (in TXRF geometry)

☐ GIXRF Geometry aspects

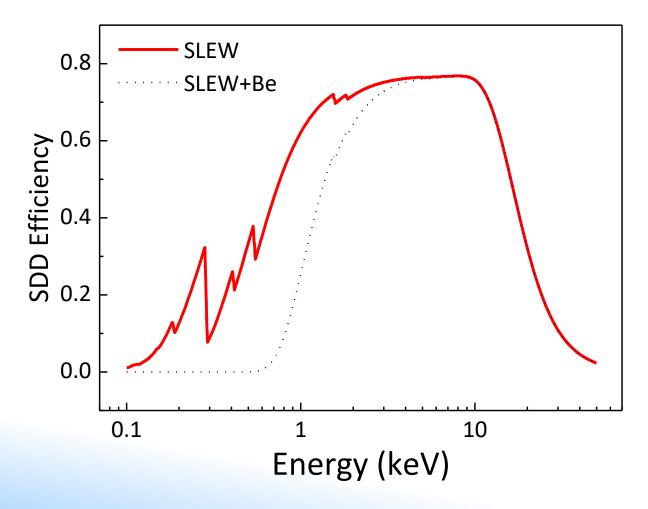




■ SDD analysis modes (UTW/Be+UTW)



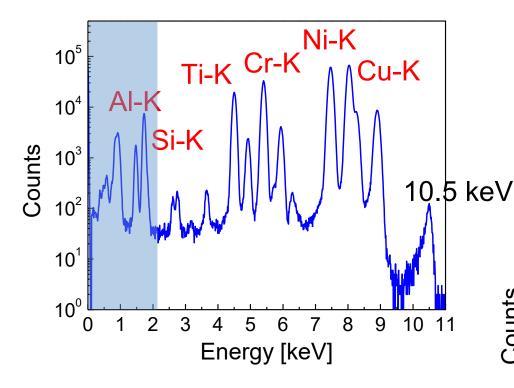
X-ray detector efficiency



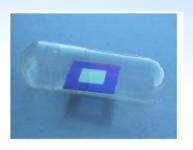
Elemental XRF sensitivities



10 mins measurement, 2.4 GeV mode

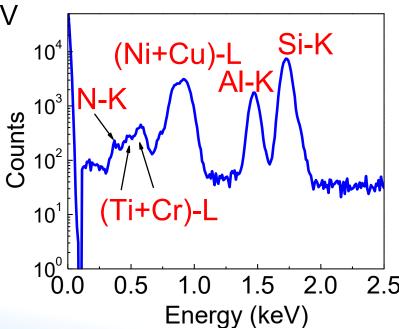


Beam dimensions @ 10.5 keV 260 um (H) 110 um(V)



AXO Dresden

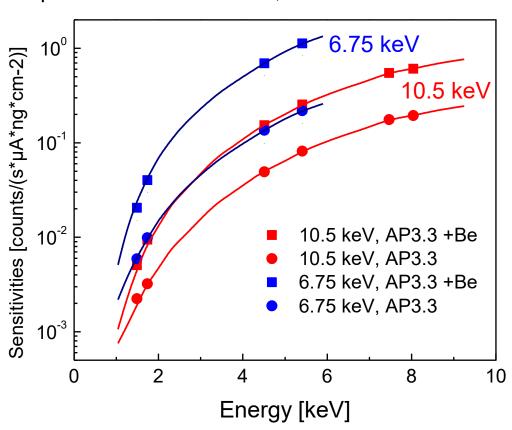
Cr/Al/Ni/Cu/Ti/Si₃N₄ 200 nm, each layer about 10 ug/cm²

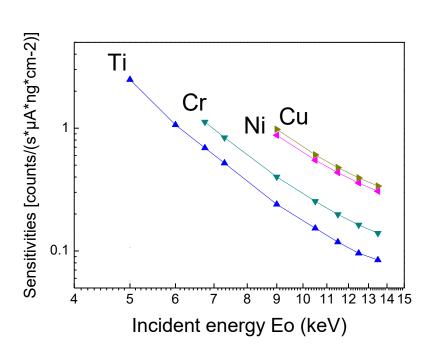


☐ Elemental sensitivities, Exp. vs MC



Experimental Sensitivities, XMI-MSIM MC calculations



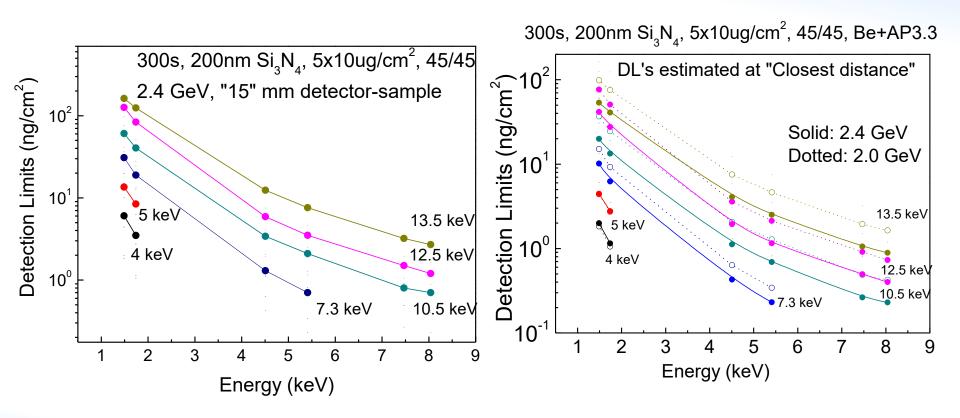


Sensitivities: counts/(s*µA*ng*cm⁻²)

Detection limits from thin sample



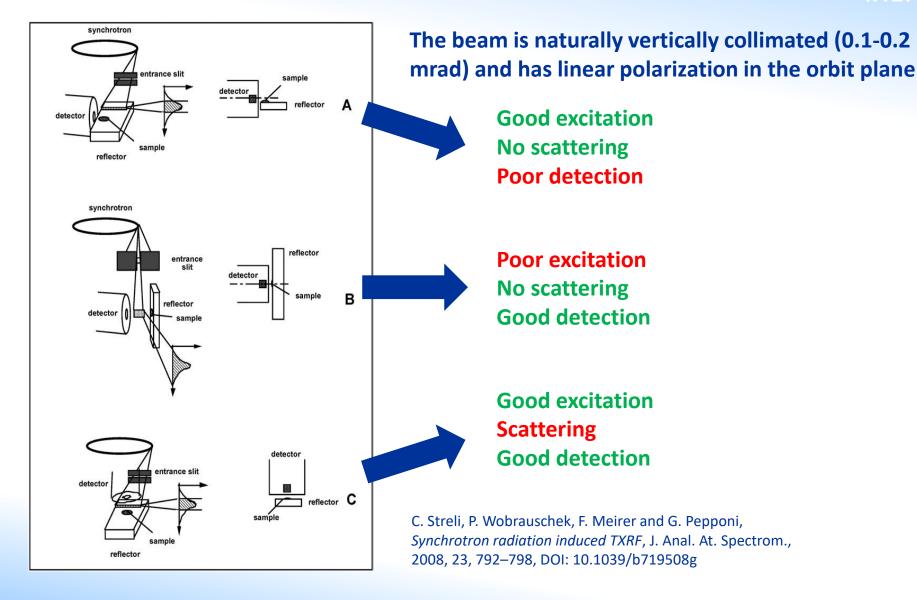
Si₃N₄ 200 nm membrane, with 10ug/cm² of Cr/Al/Ni/Cu/Ti



Detection limits (Al - Cu): 2 - 0.2 ng/cm²

Detector geometry for TXRF



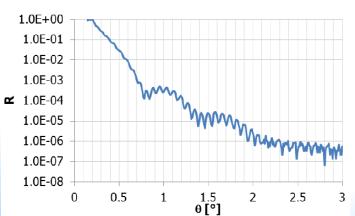


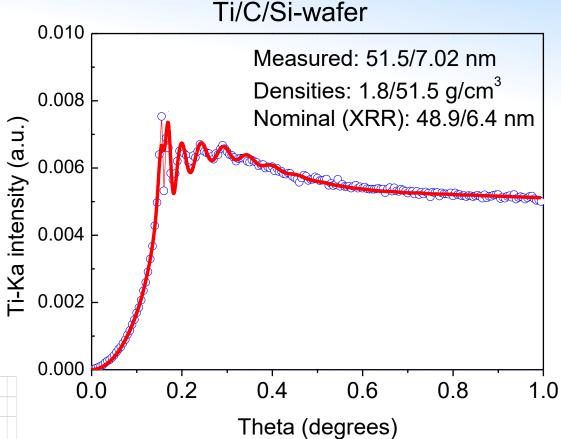
☐ GIXRF: C/Ti double layer



Prepared and characterized by AXO Dresden





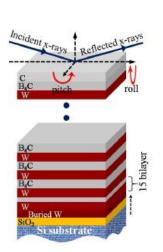


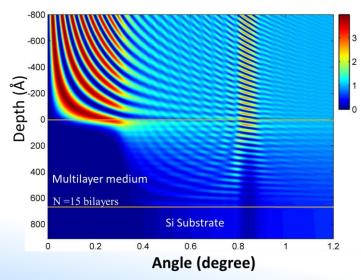
	Fit	Nominal
Ti (nm)	7.0	6.4
C (nm)	51.5	48.9

■ W/B₄C multilayered (x15) thin film

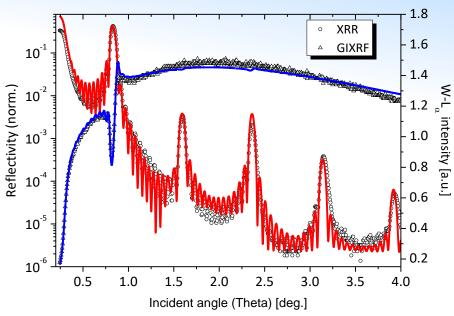


Multilayered sample, prepared by the Ramanna Center for Advanced Technology, Indore, India





Electric Field Intensity (Normalized)



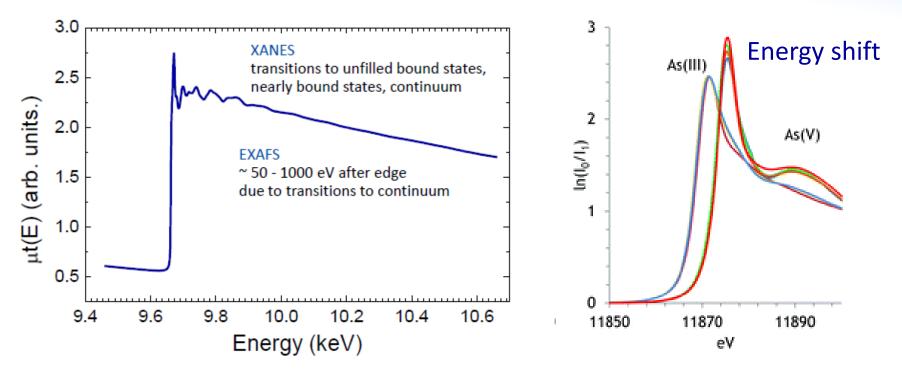
		'B ₄ C'/'W' multilayer		
Layer Material	Periodicity	Thickness (nm)	Roughness (nm)	Density (g/cm³)
B_4C	14	1.9 ± 0.1	0.2 ± 0.1	2.10 ± 0.2
W	14	2.4 ± 0.2	0.3 ± 0.1	16.0 ± 0.2
B_4C	1	2.1 ± 0.6	0.45 ± 0.2	2.3 ± 0.2
W	1	3.6 ± 0.3	0.55 ± 0.2	15.5 ± 1.0
SiO ₂	1	2.0 ± 0.3	0.5 ± 0.2	2.0 ± 0.3

good agreement with previous analyses performed at the BL-16 beamline of Indus II

X-ray Absorption Spectroscopy



XANES: local site symmetry, oxidation state, orbital occupancy EXAFS: local structure (bond distance, number and type of neighbors)



Fine structure is affected by energy and density of electronic states and transition probabilities

Extended fine structure presents oscillated pattern due to constructive and destructive interferences of the outgoing photo-e wave with neighbor atoms.

Zn speciation in fractionated APM



9-stage Maytype cascade impactor

Sampling of size fractionated aerosol, down to 0.07um size 20-3200 L of air

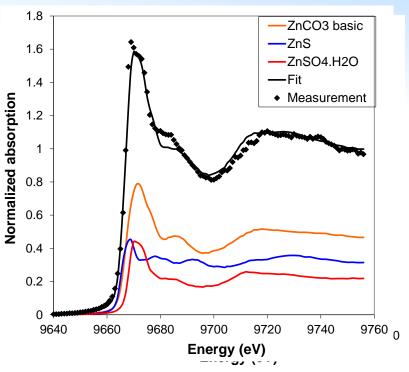


Deposited particles form a stripe of 200-500 µm width on the 20x20 mm² Si wafer



Sample geometry well suited to SR-TXRF-XANES investigations!

J. Osan, Environmental Physics Department, Centre for Energy Research, Budapest, Hungary



Samplete PBksd lipheng (Hrv.) in gaby (). 6. 1454-0.3 µm, Zurceoteetit: 7439g ng/3m 62884 ng con 220 mm stripp)

38%/ZnSO4,,492%/ZnSs,222%/Znninngetass*

Main คองแจะ ! เขา คาการู tarpainted wood

^{*}Self-absorption correction as described in: Osán J et al., Spectrochim Acta Part B 65 (2010) 1008-1013

Aerosols from 3D metal printing

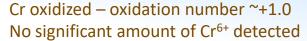


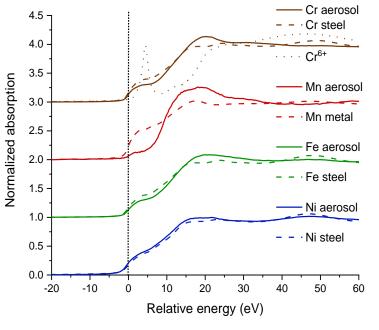


Figure courtesy: Attila Nagy, Wigner FK, Budapest, Hungary

Most of emitted aerosol particles are in the ultrafine range

XANES: Elettra XRF and XAFS beamlines





Mn mostly oxidized – oxidation number ~+2.3

Fe slightly oxidized – oxidation number ~+0.7

Ni mostly metallic – oxidation number ~+0.1

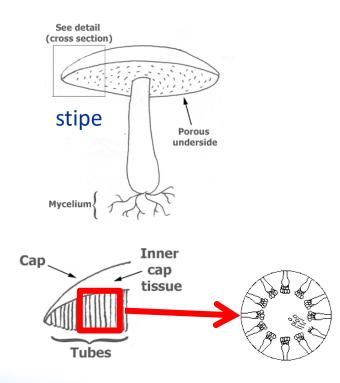
Oxidation number increases with decreasing particle diameter – important for estimation of health effects

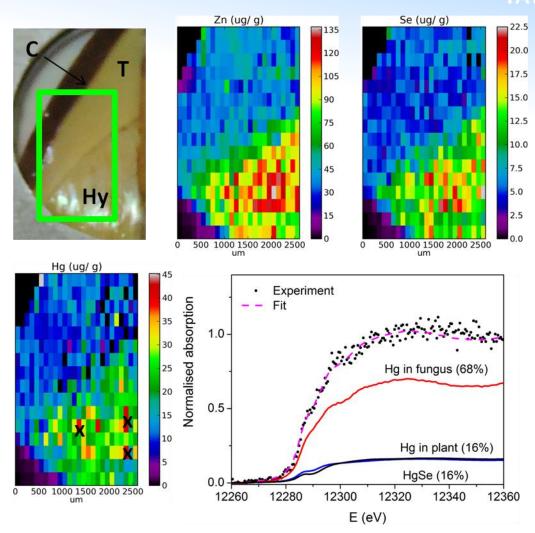
S. Kugler et al., Spectrochim. Acta Part B 2021, 177, 106110

Se and Hg in edible mushrooms



K. Vogel-Mikuš ¹, P. Kump², I. Arčon³
¹ Biotechnical faculty, University of Ljubljana, ²Jozef Stefan Institute,
³ University of Nova Gorica





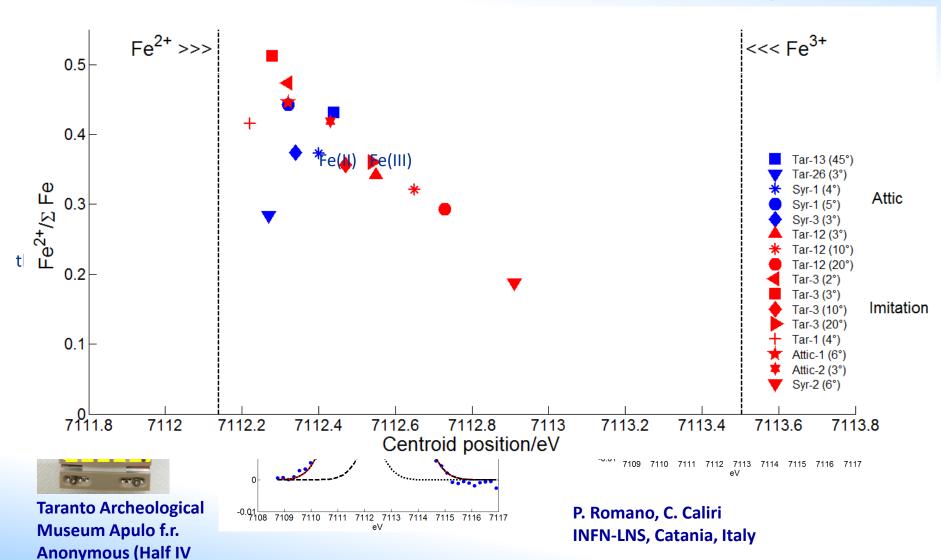
Hg is bound to tetra-cysteine proteins (metallothioneins). These proteins are digested by enzyms in the stomach and Hg is released and absorbed in our body.

☐ GI-XANES on Black Glaze

cent. b.C.)



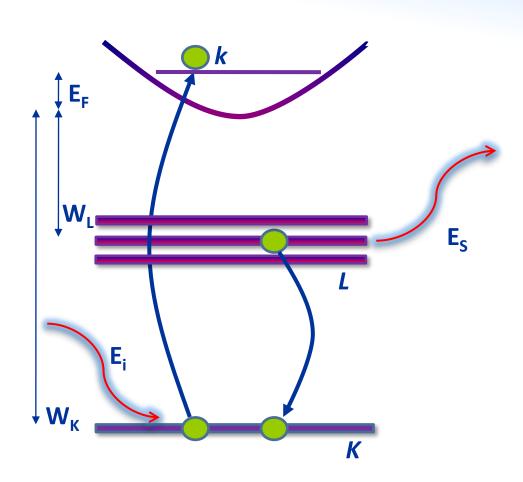
Fe-based decorations of Ancient ceramics manufactured in South Italy



School on Synchrotron Light Sources and their Applications, 15-26 January 2024

Resonant inelastic X-ray scattering

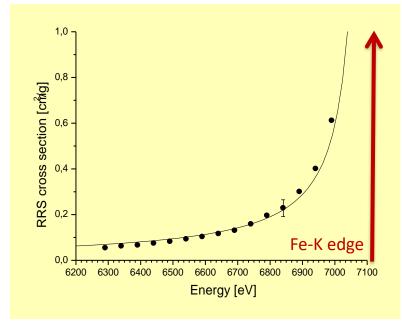




$$E_S = E_i - \Omega_L - E_F - k$$

Courtesy of J.J. Leani, CONICET, Argentina

 E_S = emitted photon energy E_i = incident photon energy $\Omega_{K/L}$ = K/L binding energy E_F = Fermi energy k = photoelectron energy



Measured KL-RIXS cross section for Fe (points) and a non-linear fitting to an expression with the functional form of the theoretical cross section (solid line)

■ Elemental speciation in contaminated water by TR-RIXS

The toxicity and mobility of metal species varies with oxidation state and chemical environment

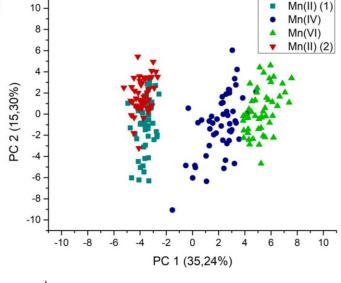
The analyzed samples consisted of droplets dried on silicon wafers. The solutions consisted of the different compounds diluted in distilled water (to 1 % by mass concentration).

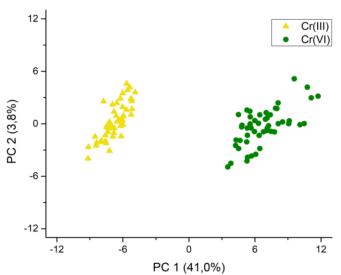
- Two chromium compounds, CrCl3 (+III), K2CrO4 (+VI),
- Four manganese species MnCl2.(H2O) (+II), KMnO4 (+VI), Mn(H2PO2)2 (+II) and MnO2 (+IV) were studied.

Incident photons energy was set 10 eV below the K-edge binding energy, i.e. 6529 eV (Mn) and 5979 eV (Cr), under TXRF conditions.

50 spectra of each sample acquired (5 min each). A PCA procedure was performed over the selected energies (RIXS peaks).







■ Analysis of gold samples

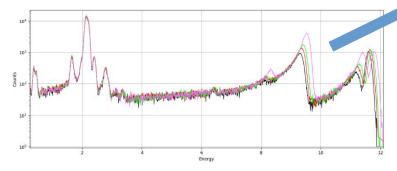


Absorption edges of Pt and Au

	Pt	Au
Z	78	79
L1 (keV)	13.88	14.353
L2 (keV)	13.273	13.734
L3 (keV)	11.564	11.919

Pt La: 9.44 keV

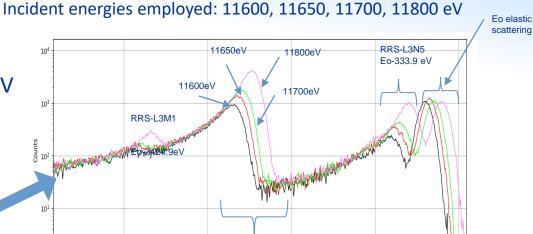
Synchrotron XRF spectra of pure (99.99%) thick (thickness 25 μm) gold samples

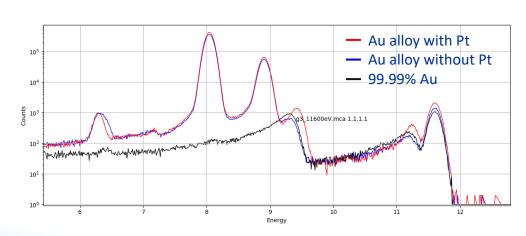


Eo=11600 eV @Elettra

Pure gold spectrum vs. Gold alloy with 0.15% Pt (Au:65.56%, Cu:25.21%, Ag:9.08%) and vs. a different certified alloy of similar composition without Pt

11600 eV > Pt(U L3)=11564 eV





RRS-L3M4,5=Eo-M4,M5



Thanks for your attention!

Alessandro Migliori a.migliori@iaea.org

https://nucleus-new.iaea.org/sites/nuclear-instrumentation/Pages/Home.aspx

https://www.elettra.trieste.it/lightsources/elettra/elettra-beamlines/microfluorescence/x-ray-fluorescence.html