



Marianne Liebi- Material Science at Large Scale Facilities

# X-ray Fluorescence Spectroscopy (XRF)

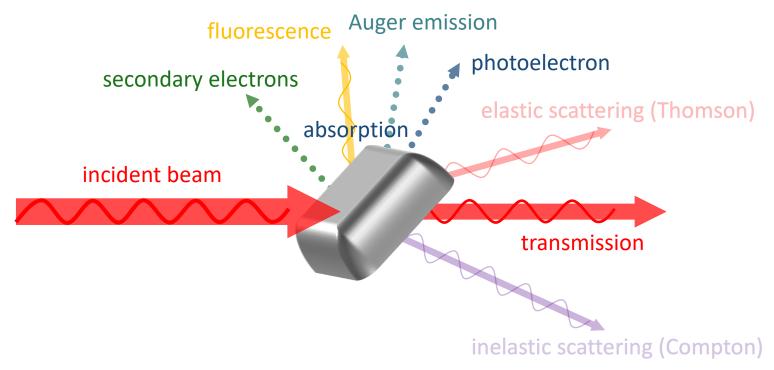
**EPFL Master Course 2024 MSE435** 



09.09.24	Introduction, sources, beamlines, detectors	Steven Van Petegem
16.09.24	Holiday	
23.09.24	Excursion to PSI	Steven Van Petegem / Marianne Liebi
30.09.24	Interaction with matter	Steven Van Petegem
07.10.24	Fluorescence	Marianne Liebi
14.10.24	Diffraction I	Steven Van Petegem
21.10.24	Break	
28.10.24	Small angle x-ray scattering	Marianne Liebi
04.11.24	Diffraction II / Magnetic scattering	Steven Van Petegem
11.11.24	XANES/EXAFS	Marianne Liebi
18.11.24	Phase contrast / Tomography	Steven Van Petegem
25.11.24	Coherent imaging	Marianne Liebi
02.12.24	Neutron imaging	Steven Van Petegem
09.12.24	PEEM/Muon	Steven Van Petegem
16.12.24	Case study presentations	Steven Van Petegem / Marianne Liebi



## Interaction of X-ray with matter





## Spectroscopy

- Spectroscopic methods: measure the response of a system as a function of energy
- The energy that is scanned may be that of the incidient beam (photon, electron, neutron,..) or the energy of the outgoing particles (photons in X-rax fluorescence, electrons in X-ray photo electron spectroscopy)
- Often combined with spatial resolution (imaging): Microspectroscopies and spectromicrsocopies

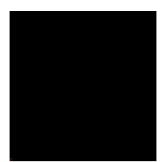


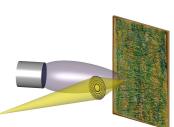
## Microspectroscopies and spectromicroscopies

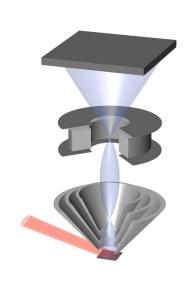
Microspectroscopies: record energy spectra by scanning a focused incidient beam over the sample

Spectromicroscopies: changes of a full-field image as a function of polarization or energy

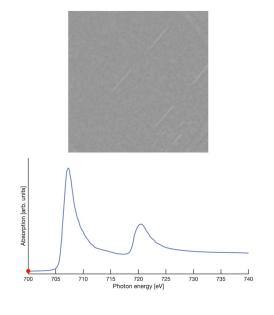








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Scanning XRF

J. Dik et al., Anal. Chem. 80 (2008) 6436

Photoemission electron microscopy

A. Fraile Rodríguez et al., J. Phys. D **43** (2010) 474006



# **EPFL** Overview of spectroscopy techniques

Technique	Abbreviation	Applications	
X-ray absorption near-edge spectroscopy	XANES	Local chemistry, absorbate structure/orientation, oxidation state, coordination, spin state	
Photoemission electron microscopy	PEEM	Magnetic structures (ferro-, ferri-, antiferromagnetisms). Variant of XANES	
Scanning transmission x-ray microscopy	STXM Variations of XAS	Polymer physics, thin films, segregation, morphology. Variant of XANES	
Extended x-ray absorption fine structure	EXAFS	Local structure in disordered ("real") systems, trace element detection, chemical dynamics, catalysis	
X-ray fluorescence	XRF	Geochemistry, archaeology, forensic science, cultural artifacts/heritage, biology	
Resonant inelastic x-ray scattering	RIXS	Electronic structure (charge, orbital, spin), materials science	
Angle-resolved photoelectron spectroscopy (also consider the direction of incoming and outgoing beam)	not covered in this course	Electronic structure, surface and interface science	
X-ray photoelectron spectroscopy (measurements of directly ejected electrons, information of core or valence state from which the electrons orginated)	XPS  MSE435 - Marianne Liebi	Chemistry, surface/absorbate structure, interface chemistry	



- X-ray absorption spectroscopies (XAS) are concerned with the change in response of a system as a function of the incident photon energy and as such can only be performed at synchrotrons. In general, an electron is excited to either an unoccupied, bound, valence state, or is completely ejected from the electrostatic influence of its parent atom. This state can then relax via emission of a photon, be scattered elastically or inelastically by neighbouring atoms, or may be radiationless, leading to the ejection of photoelectrons, Auger electrons, and a cascade of lowenergy secondary electrons. As such, x-ray absorption spectroscopies probe the unoccupied density of states of the system
- In contrast, **x-ray photoelectron spectroscopies (XPS**) involve the collection and measurement of the energies of directly ejected electrons, yielding information about the core or valence state from which the electrons originated.



# **EPFL** Overview of spectroscopy techniques

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## Overview of spectroscopy techniques

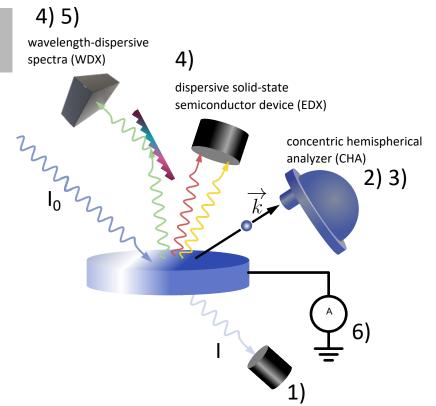
Technique		Abbreviation	
X-ray absorption near-edge spectroscopy	XANES		<b>✓</b>
Photoemission electron microscopy	PEEM	Variations of XAS	<b>✓</b>
Scanning transmission x-ray microscopy	STXM	UI AAS	<b>✓</b>
Extended x-ray absorption fine structure	EXAFS	J	<b>✓</b>
X-ray fluorescence	XRF		
Resonant inelastic x-ray scattering	RIXS		<b>✓</b>
Angle-resolved photoelectron spectroscopy	ARPES	not covered in this course	( < )
X-ray photoelectron spectroscopy	XPS MS	435 - Marianne Liebi	( ✓ )

scanning the incident photon energy → only possible at synchrotrons!

XRF use a constant incident photon energy → can also be performed on a lab source



## Detection methods



#### Form of detection

- 1) Transmitted x-radiation
- 2) Emitted photoelectrons

  Also as function of  $\overrightarrow{k}$
- 3) Auger electrons
- 4) Emitted fluorescence
- 5) Inelastically scattered x-radiation
- 6) Secondary electrons/total electron yield
- Not spectrally resolved
- Used as a measure of absorption strength

Spectrally resolved

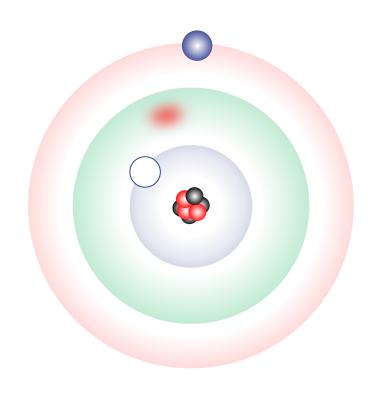


## **EPFL** Overview of spectroscopy techniques

Technique	Abbreviatio	1	Scanned $h\nu_{in}$ ?	Detection methods
X-ray absorption near-edge spectroscopy	XANES		<b>√</b>	1, 2, 4, 6
Photoemission electron microscopy	PEEM	_ Variations	<b>√</b>	6
Scanning transmission x-ray microscopy	STXM	of XAS	<b>√</b>	1, 3
Extended x-ray absorption fine structure	EXAFS	J	<b>√</b>	1, 2, 4, 6
X-ray fluorescence	XRF			4
Resonant inelastic x-ray scattering	RIXS		V	5
Angle-resolved photoelectron spectroscopy	ARPES	not covered in this course	( ✓ )	2
X-ray photoelectron spectroscopy	XPS MS	£435 - Marianne Liebi	( ✓ )	2, 3



## Photoelectrons and fluorescence



Photoelectron

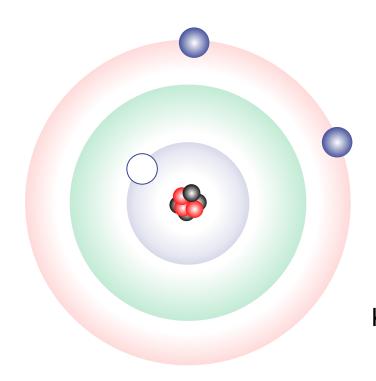
$$KE = hv_{in} - E_B$$

 $hv_{in} > hv_{out}$ 

$$hv_{out} = E_{B,1} - E_{B,2}$$



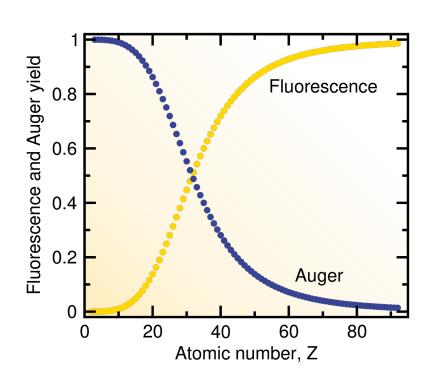
# Auger electrons



Auger-electron KE independent of hv



## Fluorescence or Auger?

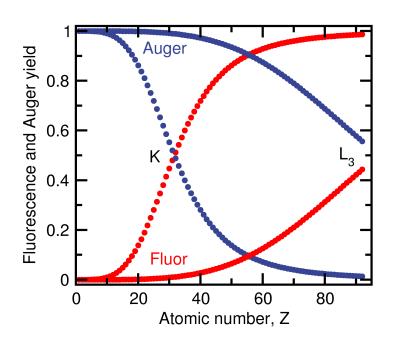


$$p_{\rm fl} \propto (h\nu)^3$$

$$Y_K = \frac{Z^4}{10^6 + Z^4}$$



## Fluorescence or Auger?



#### Fluorescence

Spontaneous process, determined by "Einstein-A coefficient" A<sub>21</sub>

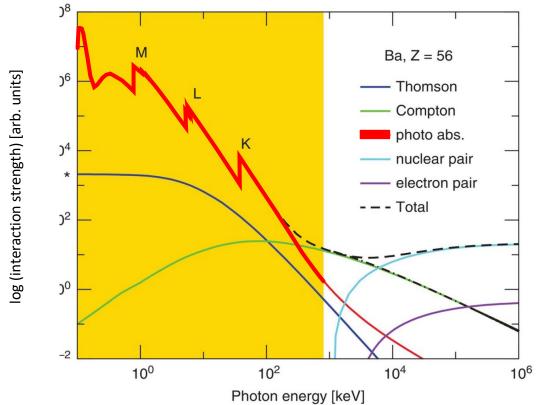
$$A_{21} \propto hn^3$$

Dominates for relaxation to empty K-states in high-Z elements

$$Y_{K,L_3} = \frac{Z^4}{A_{K,L_3} + Z^4}$$
$$A_K \approx 10^6 \qquad A_{L_3} \approx 9 \times 10^7$$



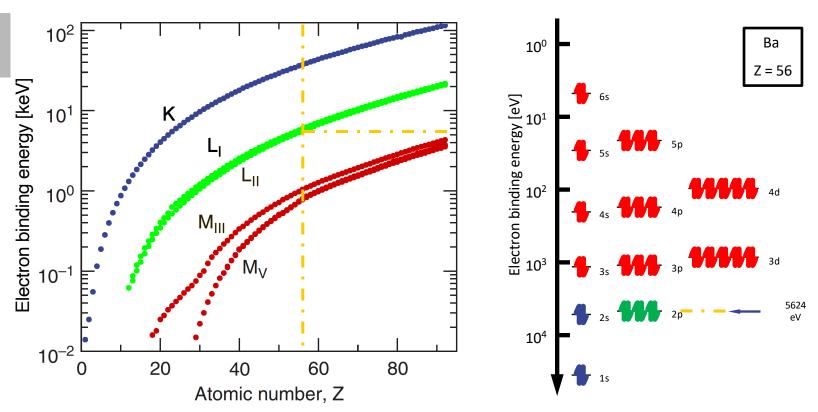
## Interaction strengths of photo absorption



absorption cross-section varies approximitely as the third power of the photon energy, interrupted by step-like increases in absorption as the photon energy matches the ionization potential of an occupied electron state in the atom.



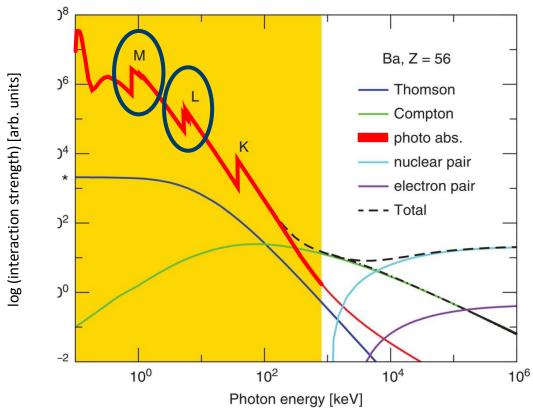
## Electron binding energies of the elements

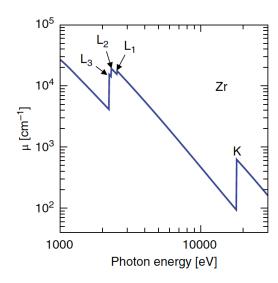


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## Interaction strengths of x-rays with matter

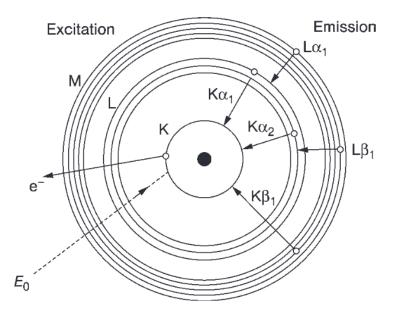




all absorption edges except the K-edges exhibit three or more more "sub-edges"



## X-ray fluorescence emission lines



**Figure 1.** Scheme of X-ray fluorescence: an electron in the K shell is ejected from the atom by an incident photon of energy  $E_0$  (dashed line). The vacancy is filled by an electron from the L shell and K X rays are emitted, in competition with Auger electrons

Fitton, G. (2014). X-ray fluorescence spectrometry., 87–115. https://doi.org/10.1007/978-3-030-58292-0\_240014 **Theoretically**, when K shells are excited, four lines are emitted by each element:  $K_{\alpha 1}$ ,  $K_{\alpha 2}$ ,  $K_{\beta 1}$ , and  $K_{\beta 2}$ . When L shells are excited, nine lines are emitted by each element, i.e.,  $L_{\alpha 1}$ ,  $L_{\alpha 2}$ ,  $L_{\beta 1}$ ,  $L_{\beta 2}$ ,  $L_{\beta 3}$ ,  $L_{\gamma 1}$ ,  $L_{\gamma 3}$ ,  $L_{\lambda}$ , and  $L_{\eta}$ . When M-shells are excited, four lines are emitted, i.e.  $M_{\alpha 1}$ ,  $M_{\alpha 2}$ ,  $M_{\beta}$ , and  $M_{\gamma}$ .

From a **practical point** of view, and because of the finite energy the line combinations  $L_{\alpha 1}-L_{\alpha 2}$  and  $L_{\beta 1}-L_{\beta 2}$   $-L_{\beta 3}$  approximately coincide in a unique larger peak, and the same happens for the pairs  $K_{\alpha 1}-K_{\alpha 2}$  and  $K_{\beta 1}-K_{\beta 2}$ , at least for elements with atomic number up to about Z =50. The K lines are therefore identified by two lines  $\textbf{K}_{\alpha}$  and  $\textbf{K}_{\beta}$ , and L lines by six lines  $\textbf{L}_{\alpha}$ ,  $\textbf{L}_{\beta}$ ,  $L_{\gamma 1}$ ,  $L_{\gamma 3}$ ,  $L_{\lambda}$ , and  $L_{\eta}$ , of which only the first two are of high intensity.

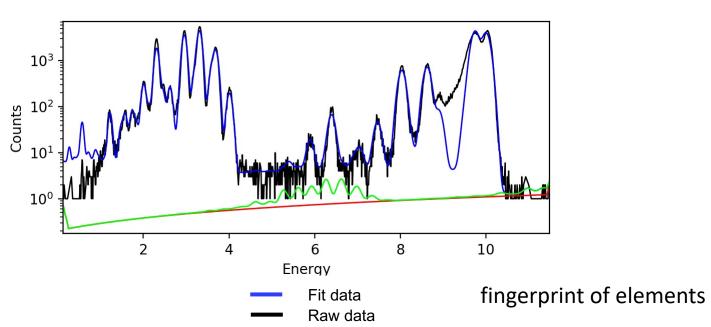
 $M_{\alpha 1}$  ,  $M_{\alpha 2}$  ,  $M_{\beta}$ , and  $M_{\gamma}$  always coincide in an unique peak, and M lines, detected as a single line, are in any case only visible for heavy elements.

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## X-ray fluorescence (XRF)

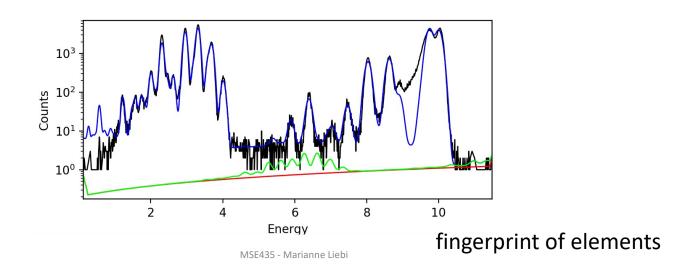
X-ray fluorescence spectrum (measured with 10 keV X-rays)



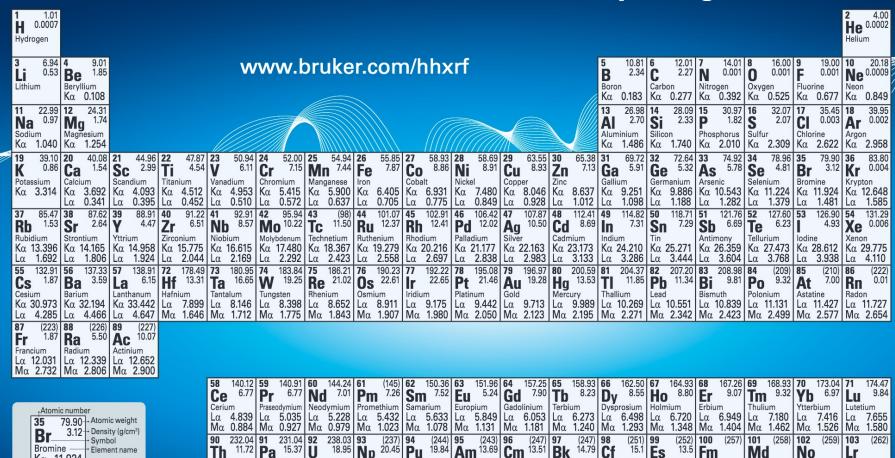


## X-ray fluorescence spectrum

 A set of X lines for each detectable element present in the analyzed object (in the form of K and/or L and/or M X rays; energy and intensity of these lines depend on the composition of the object).



## Periodic Table of Elements and X-ray Energies



Neptunium Plutonium Americium Curium

Berkelium

Californium Einsteinium

Fermium

Protactinium Uranium

Lα 12.968 Lα 13.291 Lα 13.614 Lα 13.946 Lα 14.282 Lα 14.620 Μα 2.996 Μα 3.082 Μα 3.171 Μα 3.250 Μα 3.339 Μα 3.438

Energy (keV)

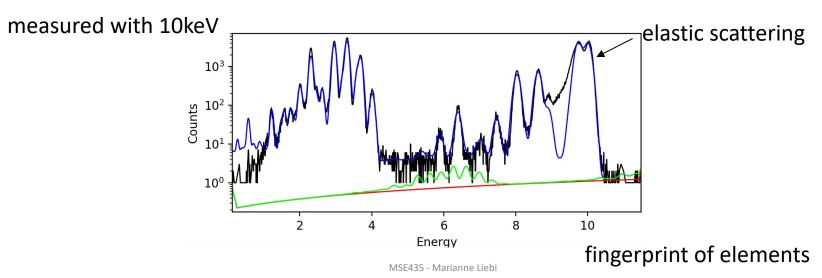
Spectral line

1.481



## X-ray fluorescence spectrum

- A set of X lines for each detectable element present in the analyzed object (in the form of K and/or L and/or M X rays; energy and intensity of these lines depend on the composition of the object).
- A continuous contribution due to Compton and elastic scattering of incident radiation (depending on the excitation source and on the sample).



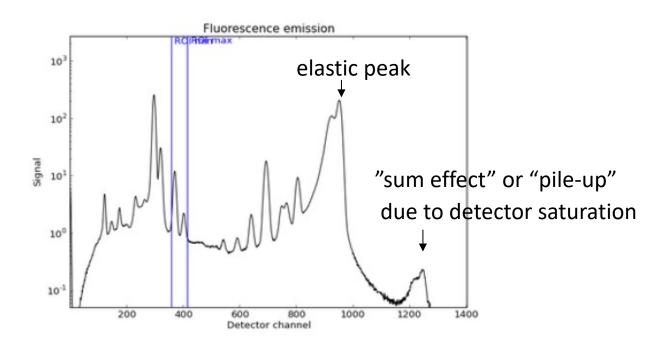


## X-ray fluorescence spectrum

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- A continuous contribution due to Compton and elastic scattering of incident radiation (depending on the excitation source and on the sample).
- Lines due to possible "escape" of incident lines in the detector (photoelectric effect of photon in the detector)
- Lines due to possible "sum" effects in the detector (two photons proscessed within the resolution time).
- Possible lines due to elements in some way irradiated by incident and/or secondary radiation present, for example, in the source shielding or in the source and/or detector collimators and filters.
- Argon K-X line due to photoelectric effect in air (ca. 0.9% argon).

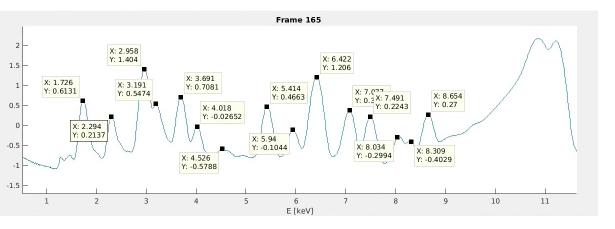


## X-ray fluorescence (XRF)





## XRF: a first qualitative analysis

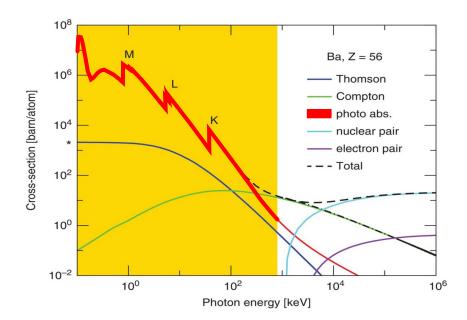


- 1.7 : Si, embedding material or detector?
- 2.3: S
- 2.95 Ar from air
- 3.2 Ar from air
- 3.69 & 4 Ca
- 4.5 very weak
- 5.4& 5.94 Cr
- 6.4 7.05 Fe
- 7.49 Ni
- 8.03 & 8.3 Cu
- 8.65 Zn



## XRF at Labsource vs. Synchrotron

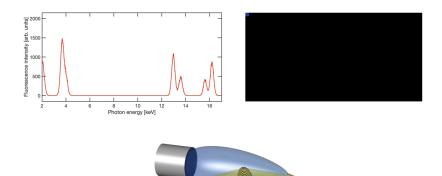
- XRF can be done on lab sources or at synchrotrons
- not monochromatic X-ray beam: adds background noise
- X-ray energy has to be higher than the excitation energy of the probed element
- for a specific element to increase sensitivity: largest cross-section just above the edge





## XRF at Labsource vs. Synchrotron

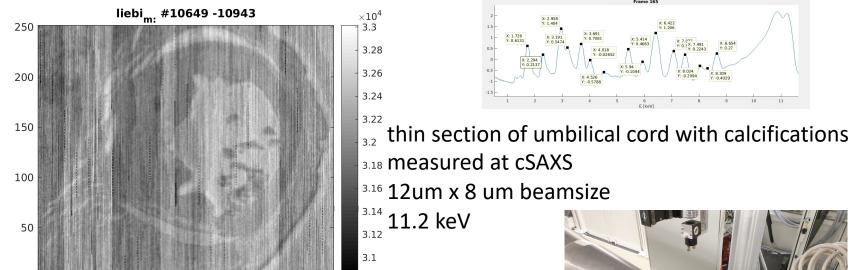
- XRF can be done on lab sources or at synchrotrons
- not monochromatic X-ray beam: adds background noise
- X-ray energy has to be higher than the excitation energy of the probed element
- for a specific element to increase sensitivity: largest cross-section just above the edge
- high flux and small beam → high spatial resolution and high sensitivity (ppm)



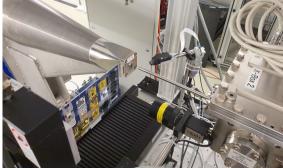
scanning XRF: Microspectroscopy



## XRF measurement at cSAXS



transmission signal (and top-up of SLS!)





- PyMCA
   developed at ESRF, free to use
   Guide/Tutorial and downloads at: <a href="http://pymca.sourceforge.net/">http://pymca.sourceforge.net/</a>
   more simplified and straight forward guide at NanoMAX webpage:
   <a href="https://www.maxiv.lu.se/beamlines-accelerators/beamlines/nanomax/user-information/experimental-station/data-access-and-processing/">https://www.maxiv.lu.se/beamlines-accelerators/beamlines/nanomax/user-information/experimental-station/data-access-and-processing/</a>
- estimates background and removes escape peaks, sum effects, scattering
- Least-squares fitting of fluorescence peaks (Gaussian)
- Quantifies are under the element specific peaks
  - without standard → mostly qualitative comparison within and between elements
  - with standard → estimation of concentration possible and quantitative comparison between elements (for thin samples)

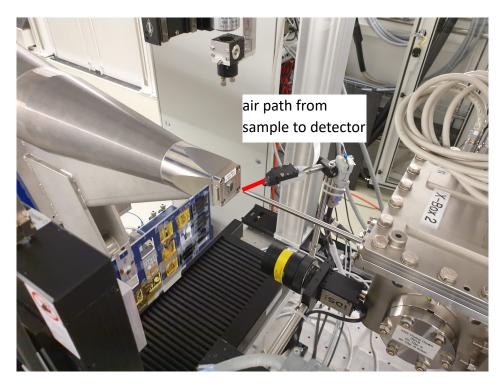


## Quantification

- To analyze samples quantitatively an X-ray fluorescence reference standard is normally used. A typical standard is a thin film sample, where several elements have been deposited on a very thing silicon nitride window.
- for example AXO Dresden: <a href="http://www.axo-dresden.de/mainframe\_reference.htm">http://www.axo-dresden.de/mainframe\_reference.htm</a>
- The calibration measurement must be done with the same conditions as the samples were measured; the same photon energy, incidence angle, exit angle, distance to detector, surrounding of the sample area, etc. Calibration should be measured right before or after the sample measurement.
- Main problem for quantification is self-absorbance, in particular for heterogenous samples



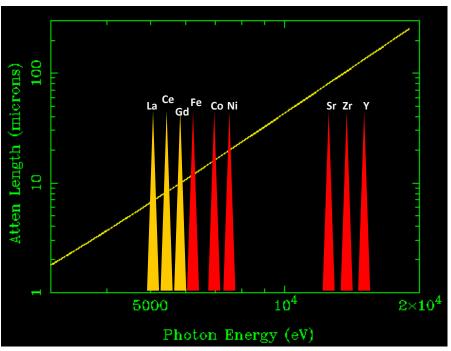
## Absorbance in air and self-absorbance



- air path: aborbance of lowerenergy lines → measurement in vacuum is beneficial
- self-absorbance within the sample: quantification of thicker samples is very complicated (in particular for hetereogenous samples)
- for lower energies only the last layer probed → different resolution and sensitivity for different elements!



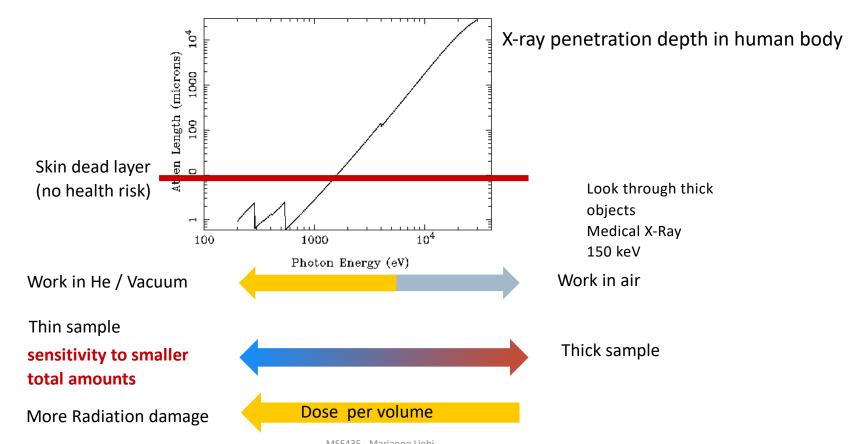
What elements we want to see? What sample size?



Solid Oxide Fuel/Electrolyzer Cell



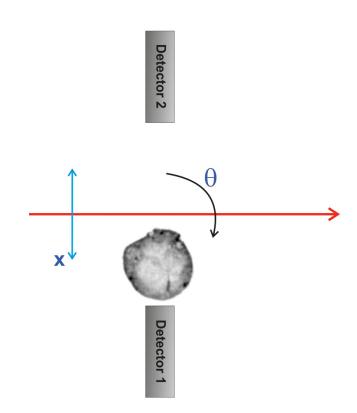
## X-ray Penetration depth in human body



Images Wilhelm Röntgen., Public domain, via Wikimedia Commons, By OpenStax College: Elements of the Human Body-01.jpg, CC BY 3.0, https://commons.wikimedia.org/w/index.php?curid=46182835

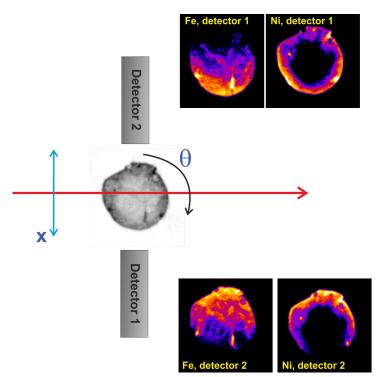


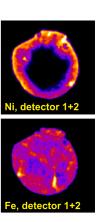
# μXRF scanning tomography





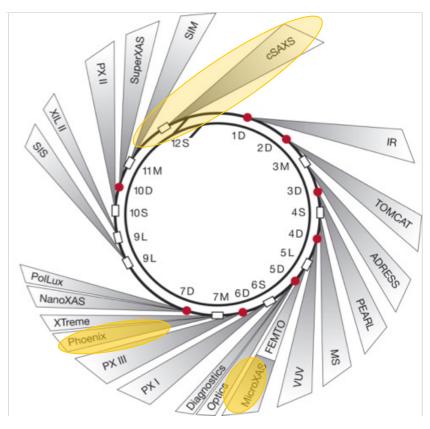
## μXRF scanning tomography: self-aborbance







## XRF @PSI

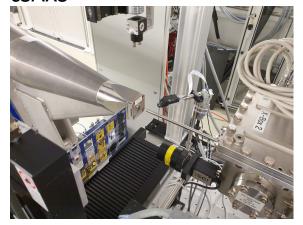


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# SLS beamlines with XRF capabilities

#### cSAXS



#### microXAS



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## PHOENIX beamline

#### XAS in tender energy range

PHOENIX I 0.8-8 keV, DCM, microfocus~ 2.5X 2.5 mm

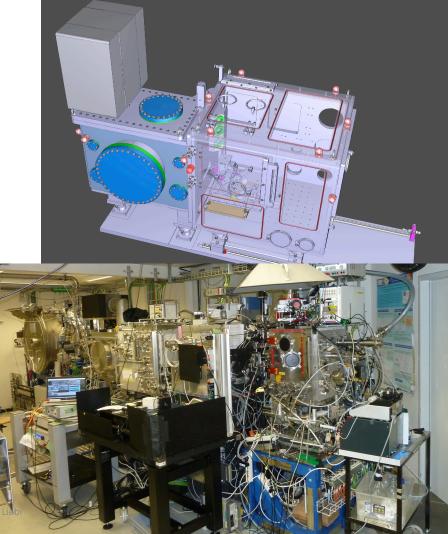
PHOENIX II 0.4-2 keV planar grating, microfocus 4X5 mm

**Scanning fluorescence microscopy** 

**Emission spectroscopy** (2.25-2.8 keV, planned full range 2.05-4.5 keV)

Using KLM-edges, see all elements from O to U

**Topics** Material science, new electronic material, environmental sciences, biology, geology, catalysis, flexibility for *in situ* experiments





## Vacuum endstation of PHONIX beamline



#### **Challenge:**

How to study high vapor pressure materials?

How to study gas-solid interactions?

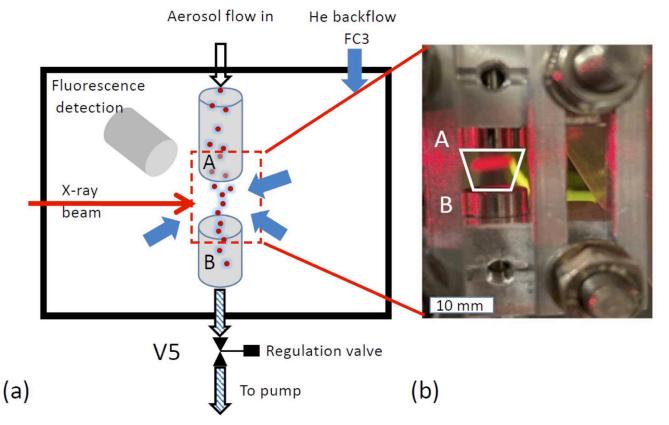
Use cell with window

Cell with silicon nitride window Very stable 1X1 mm 100 nm 1bar

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## Spectroscopy on airborne particles

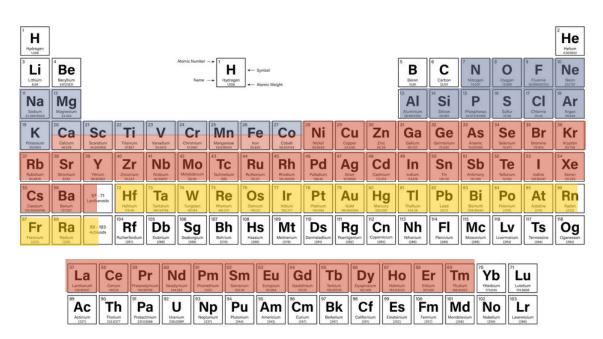




# Accessible edges in for soft and tender x-rays 0.4/8 keV.

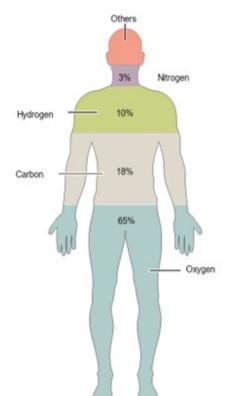
K-edge L-edge M-edge

#### **Periodic Table of the Elements**





## Low-Z elements



Most common materials on earth

Low Z-elements: C-Fe (0.3-8 keV)

abundant on Earth

Biology: occur in human body (C,P,S)

Energy research: Use in Batteries (Li), new: Na, S, P

Carbon storage technologies e.g. CaMgCO<sub>3</sub>

Cement formation (Al, Si, Mg, Ca)

Catalysis: Zeolites (Al, Si)

Silicon

Riving

Ron

Calcium

Sodium

Potassium

Magnesium

Oxygen

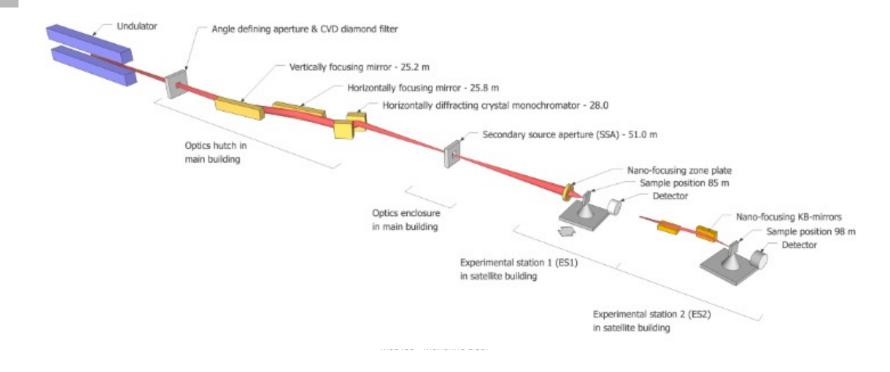
Relative abundance of Rare Earth Elements

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## Examples of other beamlines

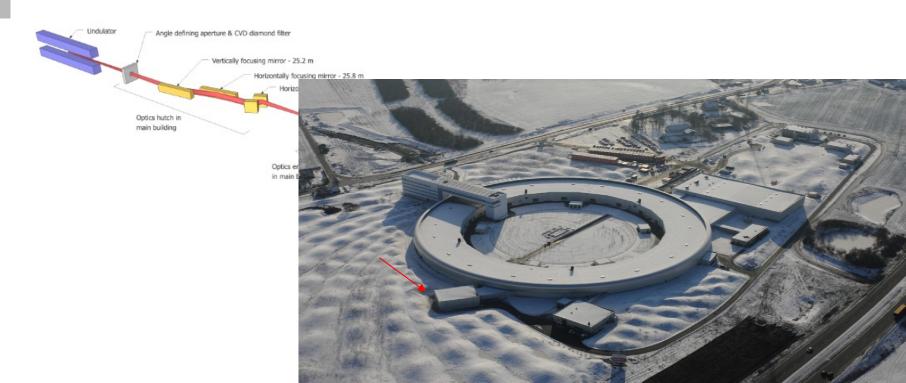
### NanoMAX at MAXIV: 98m long for a small focus





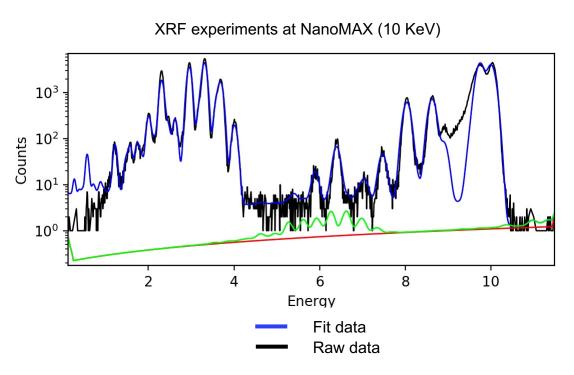
## Examples of other beamlines

### NanoMAX at MAXIV: 98m long for a small focus





## XRF: X-ray fluorescence spectroscopy

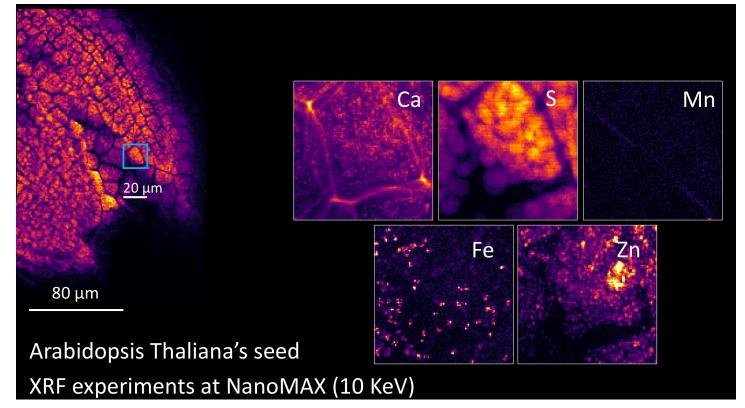


Sandra Cuellar-Baena, MAXIV

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## XRF: X-ray fluorescence spectroscopy



NanoMAX@MAXIV: 60 nm beamsize at 14keV energy

Sandra Cuellar-Baena, MAXIV

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