

Analytical TEM

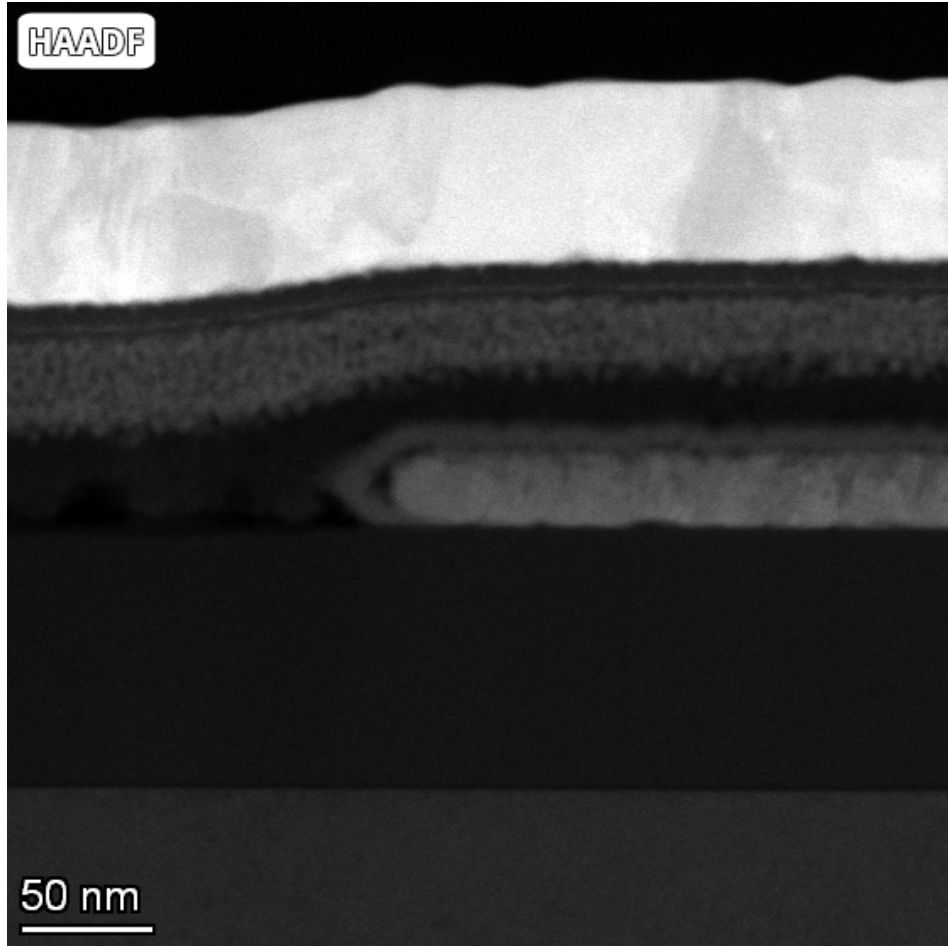
part I

Duncan Alexander

EPFL-IPHYS-LSME

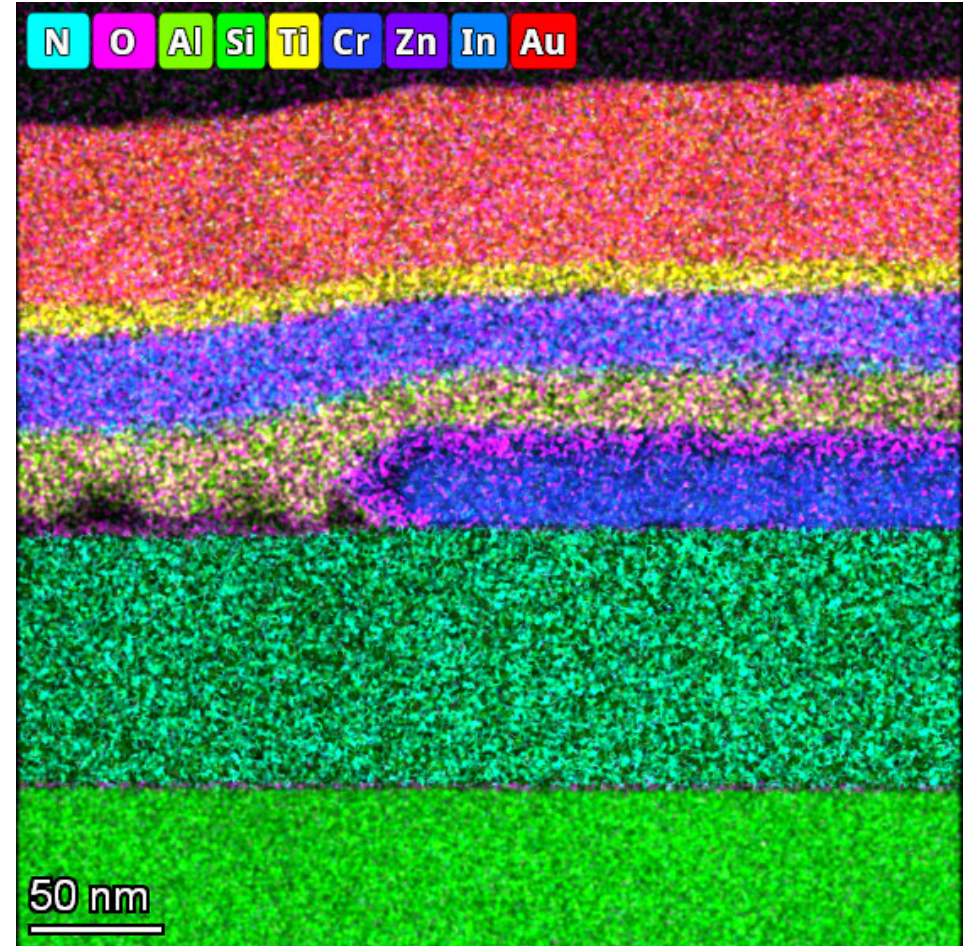
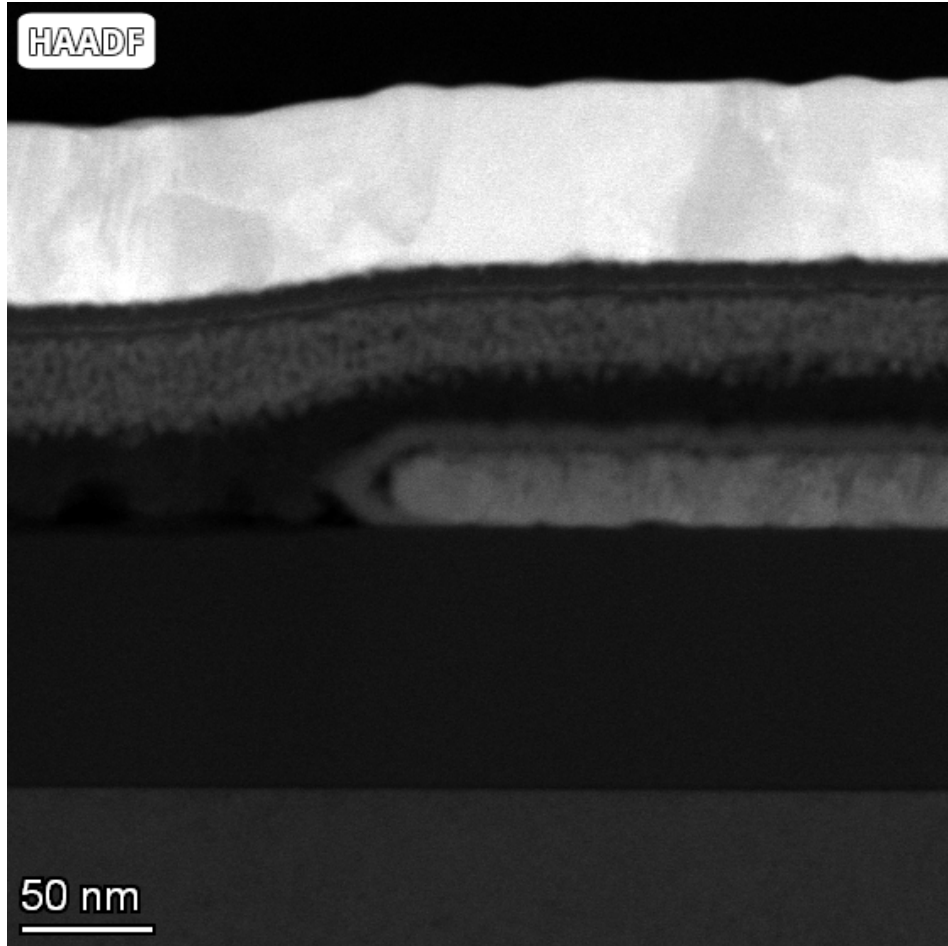
EPFL Adding colour to microscopy!

- Multilayer from first STEM lecture



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- Multilayer from first STEM lecture



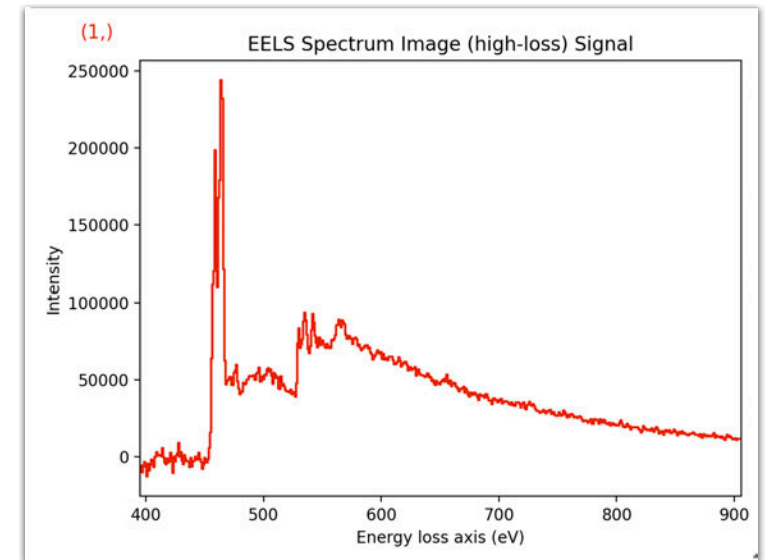
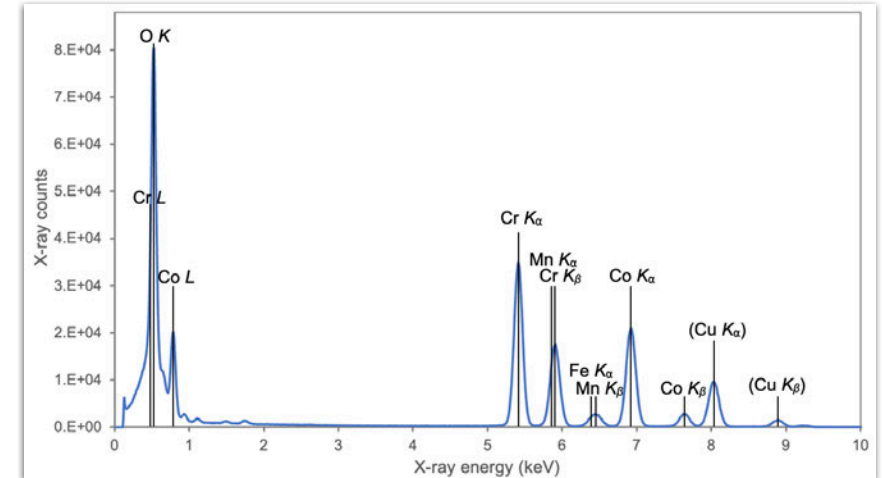
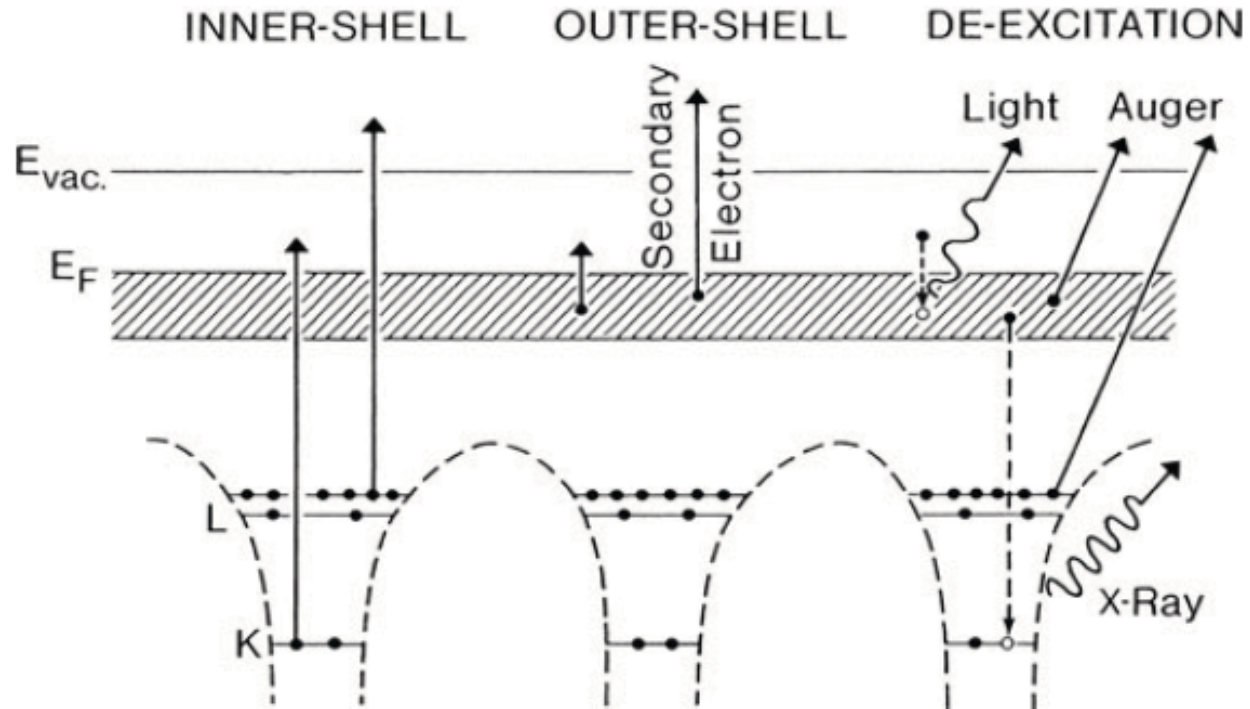
EPFL Contents

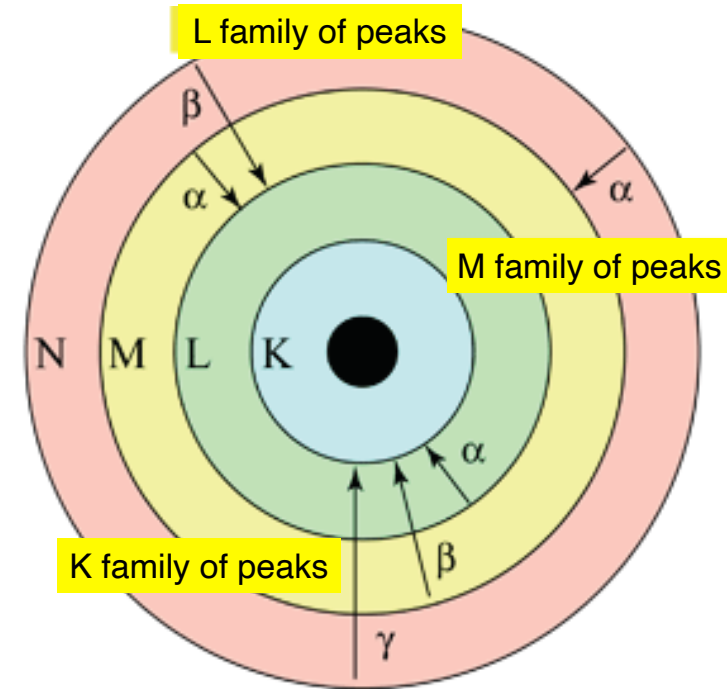
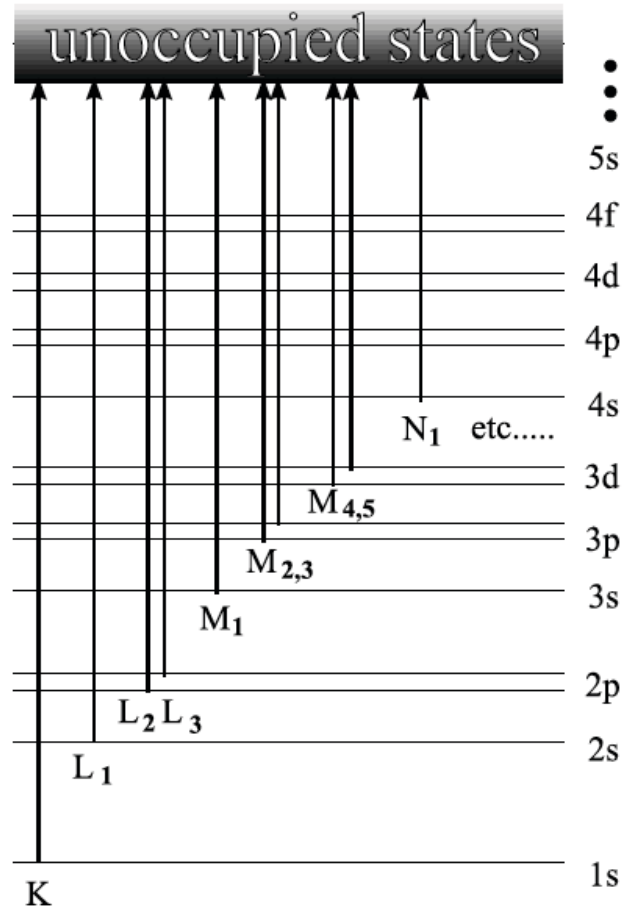
- Introduction to EDX spectroscopy and EELS
- Energy dispersive X-ray (EDX) spectroscopy
 - X-ray generation
 - EDX spectrum
 - Detector setup
 - Applications

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EPFL A way to probe chemistry





EPFL Quiz

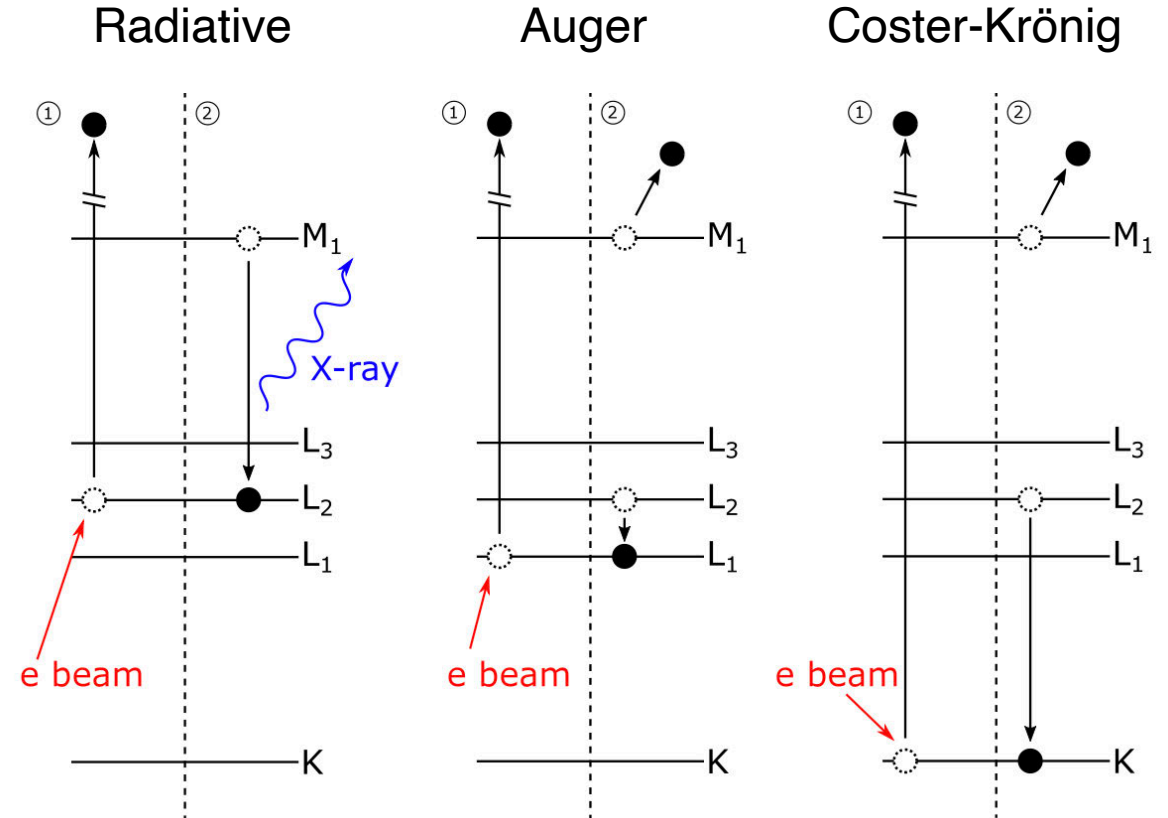
- EDXS: energy dispersive X-ray spectroscopy
⇒ intensity spectrum of X-ray peaks separated by energy
- EELS: electron energy-loss spectroscopy
⇒ intensity spectrum of energy lost by transmitting e^-
- We look at a sample containing Oxygen. We detect the Oxygen K-edge both in EELS and in EDXS. We find the transition at E_{EELS} in EELS and E_{EDXS} in EDXS
- Do we have:
 - 1) $E_{\text{EELS}} > E_{\text{EDXS}}$
 - 2) $E_{\text{EELS}} = E_{\text{EDXS}}$
 - 3) $E_{\text{EELS}} < E_{\text{EDXS}}$

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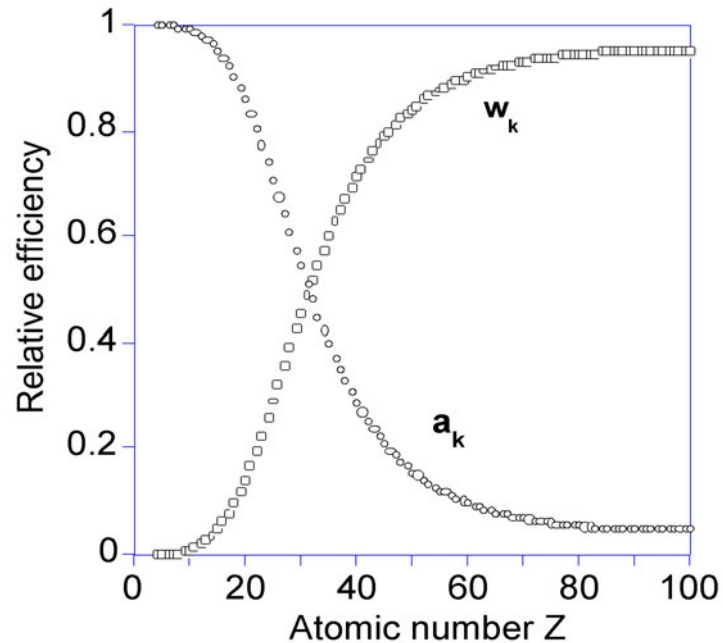
EPFL X-ray generation

- 3 basic de-excitation process:
 - Radiative X-ray emission
 - Auger transitions/emission
 - Coster-Krönig transitions
- Complex “cascade” effects possible

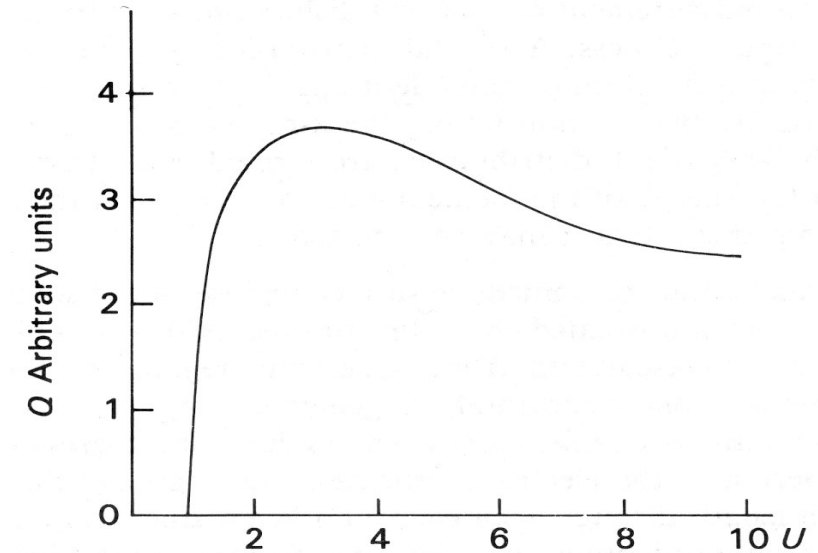


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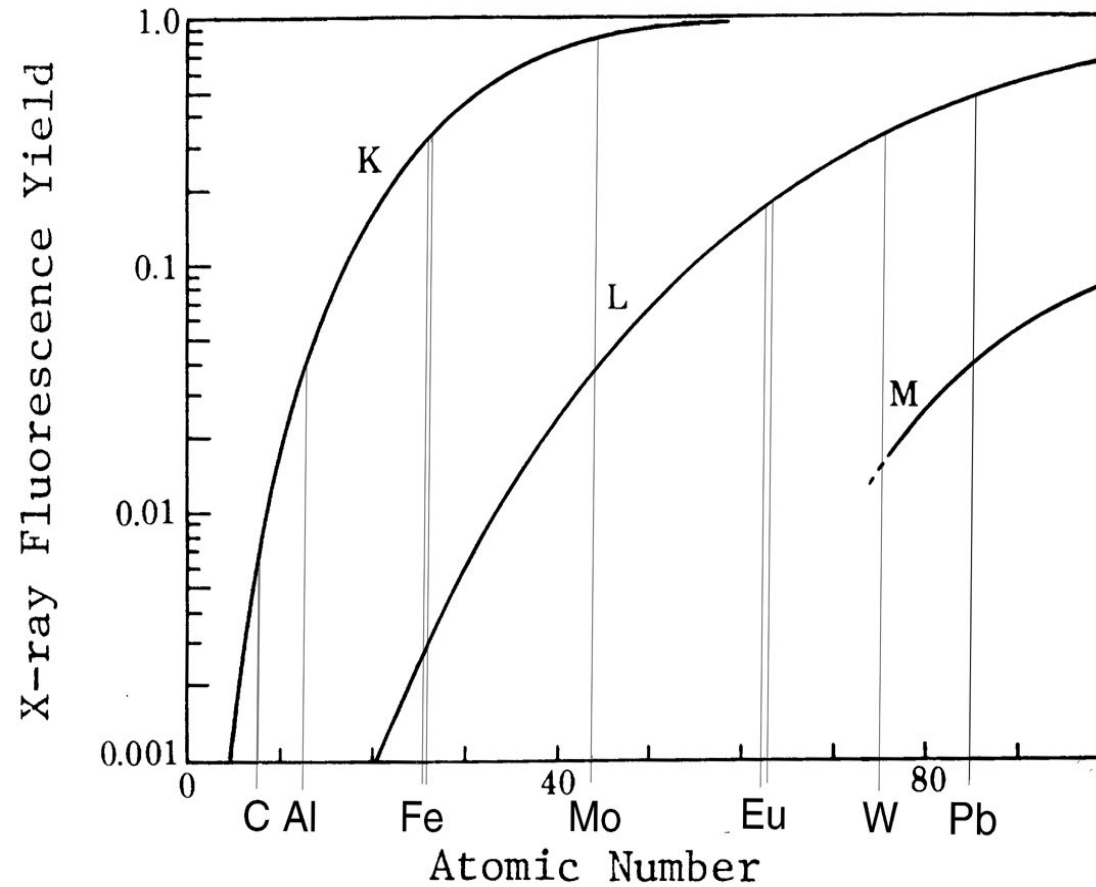
Relative efficiency of X-ray and Auger emission vs. atomic number for K lines



Light element atoms return to fundamental state mainly by Auger emission. For that reason, their K-lines are weak. In addition their low energy makes them easily absorbed.

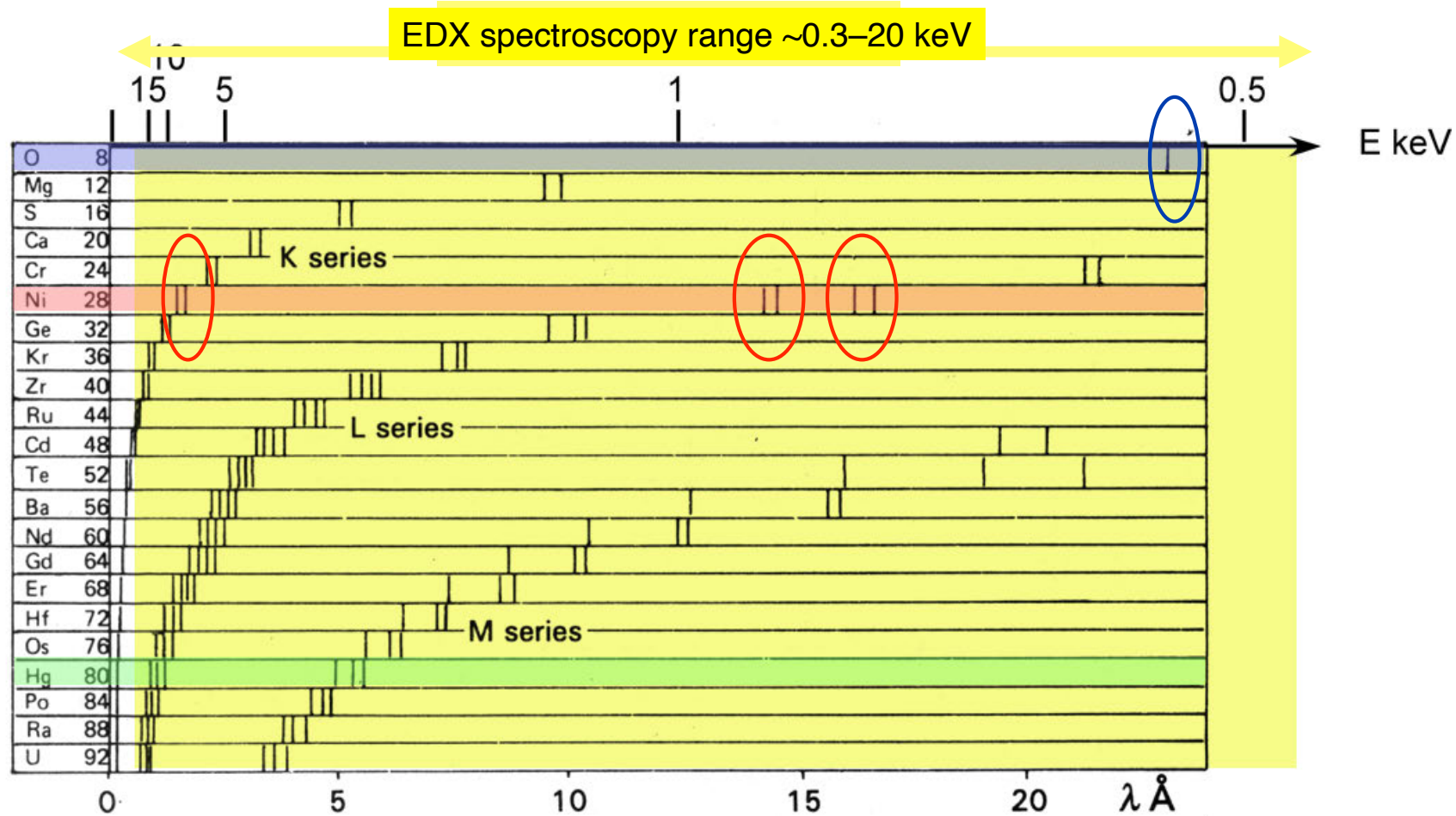


To ionise an atom, the incident electron MUST have an energy larger than the core shell level $U > 1$. To be efficient, it should have about twice the edge energy $U > 2$.



X-ray fluorescence yield for *K*-, *L*-, and *M*-shells, as a function of atomic number.

Separation of EDX peaks



Periodic table of X-ray peaks

IA

11.008

H

Hydrogen

36.941

Li

Lithium

22.990

Na

Sodium

39.098

K

Potassium

85.468

Rb

Rubidium

132.905

Cs

Cesium

(223)

Fr

Francium

IIA

49.012

Be

Beryllium

24.305

Mg

Magnesium

40.08

Ca

Calcium

87.62

Sr

Strontium

137.33

Ba

Barium

226.025

Ra

Radium

IIIB

44.956

Sc

Scandium

47.88

Ti

Titanium

50.942

V

Vanadium

51.996

Cr

Chromium

54.938

Mn

Manganese

55.847

Fe

Iron

58.933

Co

Cobalt

58.70

Ni

Nickel

63.546

Cu

Copper

65.39

Zn

Zinc

69.72

Ga

Gallium

72.61

Ge

Germanium

74.922

As

Arsenic

78.96

Se

Selenium

79.904

Br

Bromine

83.80

Kr

Krypton

85.468

Rb

Rubidium

87.62

Sr

Strontium

88.906

Y

Yttrium

91.22

Zr

Zirconium

92.906

Nb

Niobium

95.94

Mo

Molybdenum

(98)

Tc

Technetium

101.07

Ru

Ruthenium

102.906

Rh

Rhodium

106.42

Pd

Palladium

107.868

Ag

Silver

112.41

Cd

Cadmium

114.82

In

Indium

118.71

Sn

Tin

121.76

Sb

Antimony

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Te

Tellurium

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Actinium

Atomic Number

Atomic Weight

Alkali Metals

Alkaline Earth

Rare Earth

Other Metals

Non-Metals

Halogens

Transition Metals

Metalloids

Noble Gases

Actinides

Symbol

K: Energy (-)

L: Energy (-)

M: Energy (-)

Crystal Structure

Crystal Structures

Cubic, face centered

Cubic, body centered

Cubic

Hexagonal

Monoclinic

Orthorhombic

Tetragonal

Rhombohedral

1A = 10⁻¹⁰

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1cm = 10⁻²

1dm = 10⁻¹

1m = 1

dm = 10⁻¹

cm = 10⁻²

mm = 10⁻³

μm = 10⁻⁶

nm = 10⁻⁹

Å = 10⁻¹⁰

Crystal Structures

Cubic, face centered

Cubic, body centered

Cubic

Hexagonal

Monoclinic

Orthorhombic

Tetragonal

Rhombohedral

1A = 10⁻¹⁰

1nm = 10⁻⁹

1μm = 10⁻⁶

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Crystal Structures

Cubic, face centered

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Monoclinic

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



















Tetragonal

Rhombohedral

1A = 10⁻¹⁰

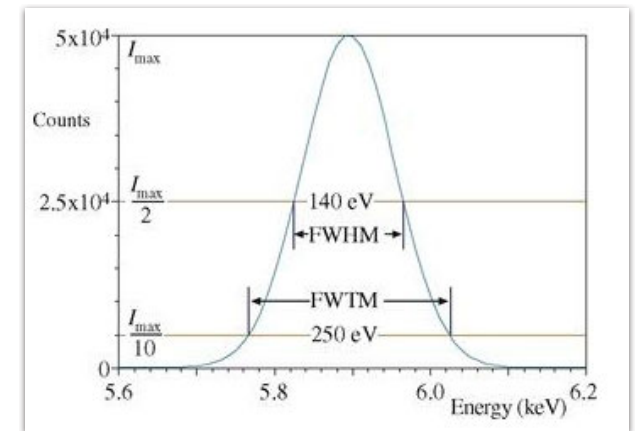
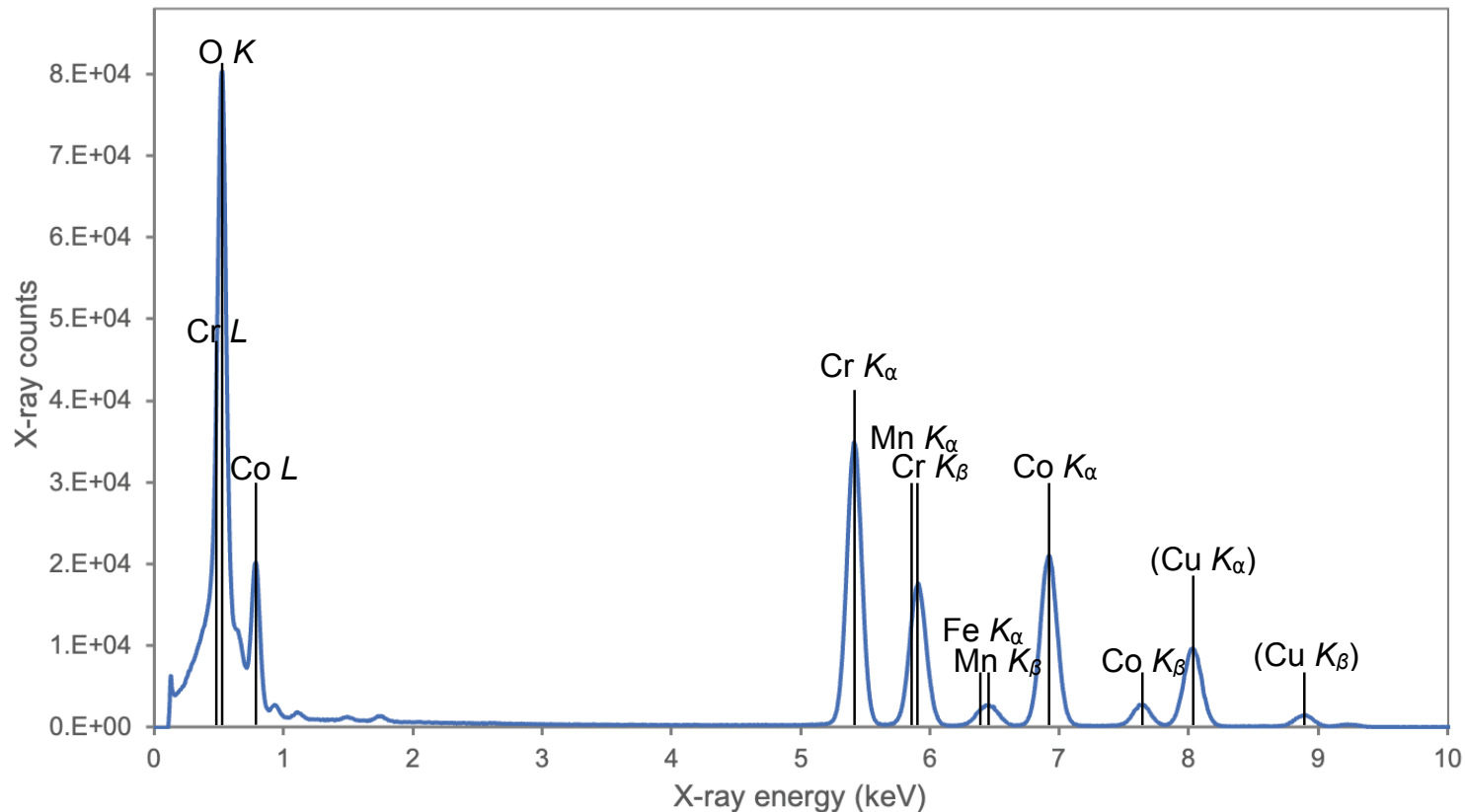
1nm =

Periodic table of X-ray peaks

					2 4.003 He Helium 
IIIA	IVA	VA	VIA	VIIA	
5 10.811 B Boron 0.185 — 	6 12.011 C Carbon 0.277 — 	7 14.007 N Nitrogen 0.392 — 	8 15.999 O Oxygen 0.523 — 	9 18.998 F Fluorine 0.677 — 	10 20.180 Ne Neon 0.848 — 
13 26.982 Al Aluminum 1.486 0.073 — 	14 28.086 Si Silicon 1.740 0.092 — 	15 30.974 P Phosphorus 2.013 0.117 — 	16 32.066 S Sulfur 2.307 0.149 — 	17 35.453 Cl Chlorine 2.622 0.183 — 	18 39.948 Ar Argon 2.957 0.221 — 
31 69.72 Ga Gallium 9.250 1.098 — 	32 72.61 Ge Germanium 9.885 1.188 — 	33 74.922 As Arsenic 10.542 1.282 — 	34 78.96 Se Selenium 11.220 1.379 — 	35 79.904 Br Bromine 11.922 1.480 — 	36 83.80 Kr Krypton 12.649 1.586 0.093 — 
49 114.82 In Indium 24.209 3.286 0.370 — 	50 118.71 Sn Tin 25.272 3.443 0.401 — 	51 121.76 Sb Antimony 26.359 3.604 0.433 — 	52 127.60 Te Tellurium 27.471 3.768 0.470 — 	53 126.905 I Iodine 28.615 3.937 0.497 — 	54 131.29 Xe Xenon 29.779 4.109 0.531 — 

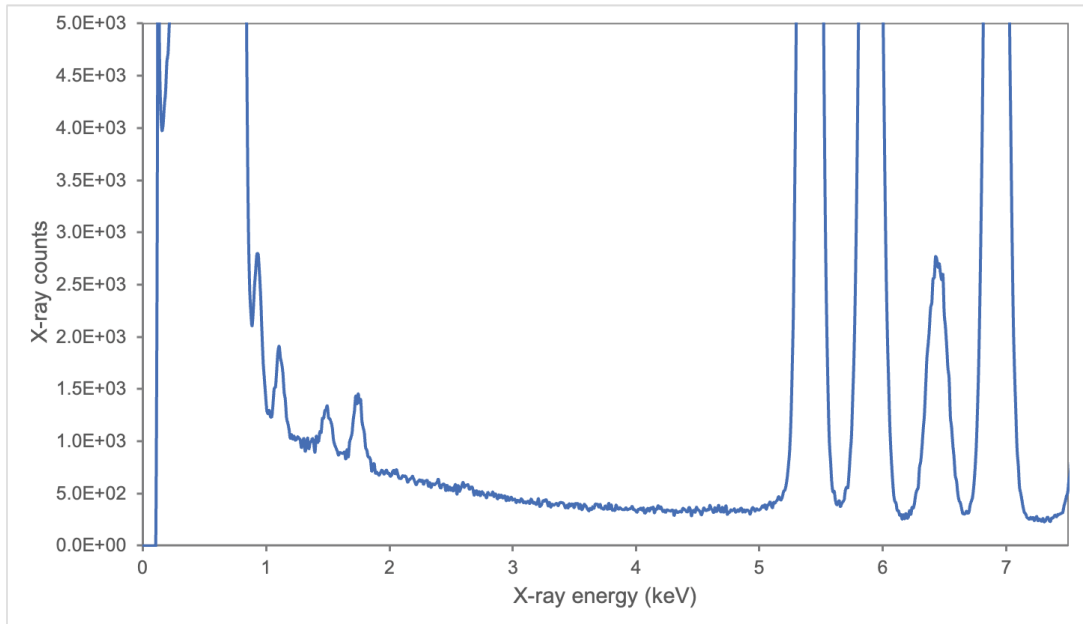
EPFL The EDX spectrum

- Example spectrum from fuel cell sample containing O, Cr, Mn, Fe, Co
- Spectrum of mostly well-defined peaks that e.g. can be fitted with Gaussians



EPFL Bremsstrahlung background

- Continuum background of radiation emitted when e⁻ velocity changed by atomic field
- Stronger at low keV; depends on atomic number Z



“State-of-the-art” model by Chapman (down to 1 keV): $I_{\text{brem}} = \frac{\beta_0}{E_{\text{X-ray}}} + \beta_1 + \beta_2 E_{\text{X-ray}}$

EPFL EDXS quantification

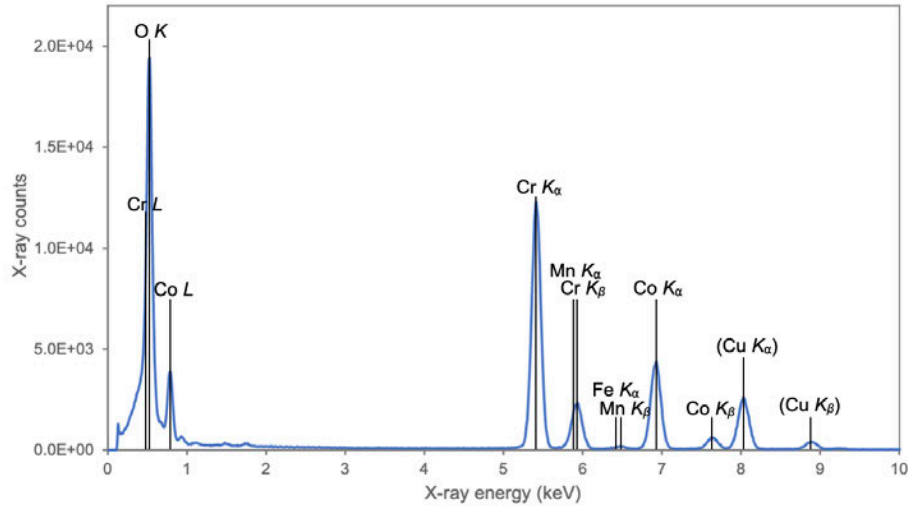
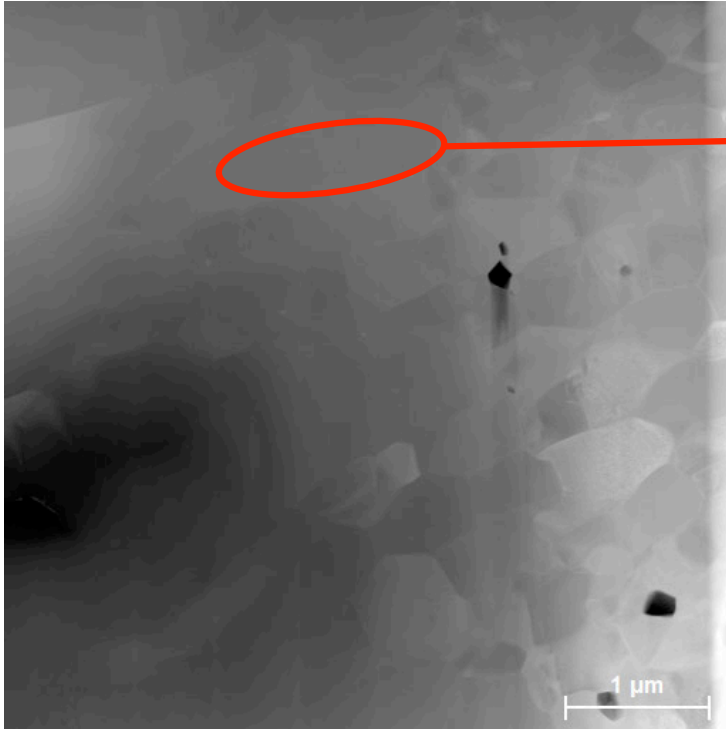
- To go from qualitative to quantitative: measure the intensities I_j of the X-ray peaks (area under the peak)
- Typically apply “Cliff-Lorimer” approach where calculate ratios of constituent elements:

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}$$

- k_{AB} : k -factor
 - determined empirically by: standards / theoretical calculations / empirical models
- k -factors relate to probability of X-ray emission, probability of X-ray absorption and probability of unabsorbed X-ray being detected
- Rule of thumb: quantification accuracy 10–20%. However, much better (e.g. 1%) can be achieved in certain cases
- Detection limit: ~0.1 – a few at. %

EPFL EDXS quantification

- Example: Cr-rich grain in fuel cell spinel layer



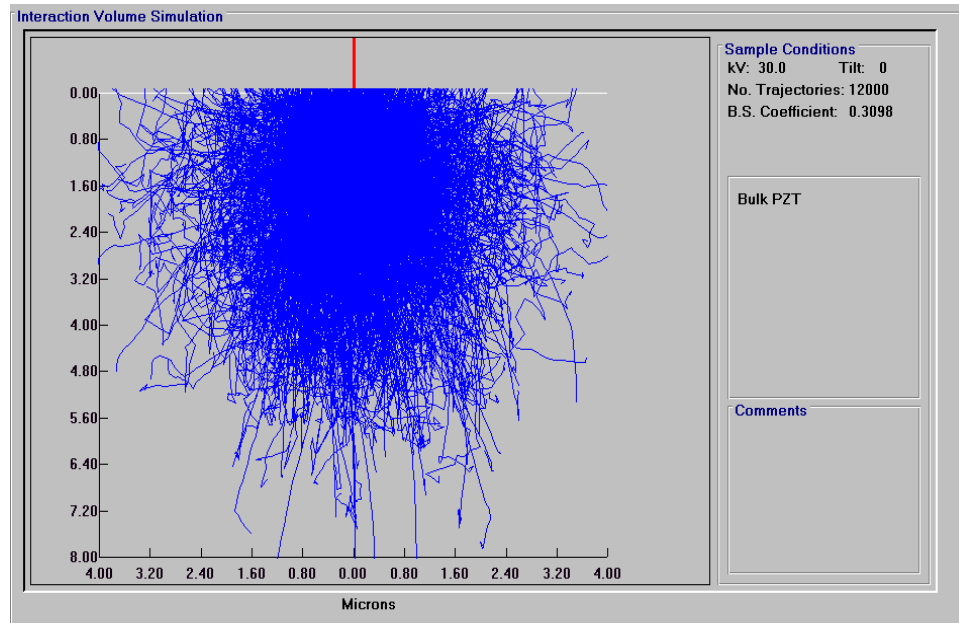
Element	Peak series	At. %
Cr	K	33.7
Co	K	13.8
Mn	K	2.5
Fe	K	0.1
O	K	49.9

EPFL Compared to SEM-EDXS

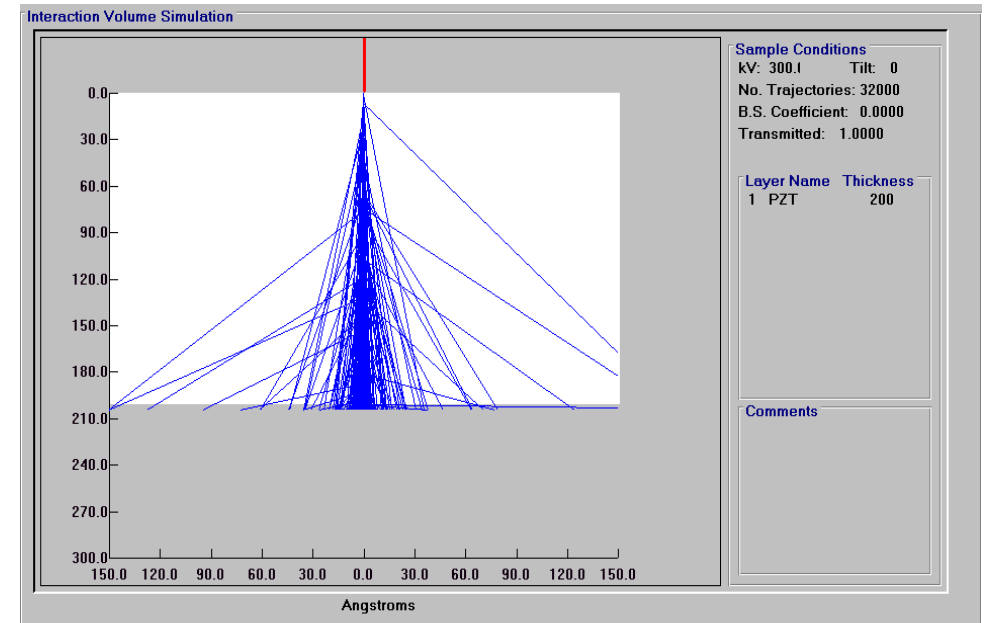
- (Can) Neglect correction factors for absorption and fluorescence in quantification
- High energy e-beam and thin sample \Rightarrow X-rays emitted from narrow/confined volume of sample in beam path direction

Pb(Zr,Ti)O₃ scattering models

SEM: 30 keV beam, bulk sample

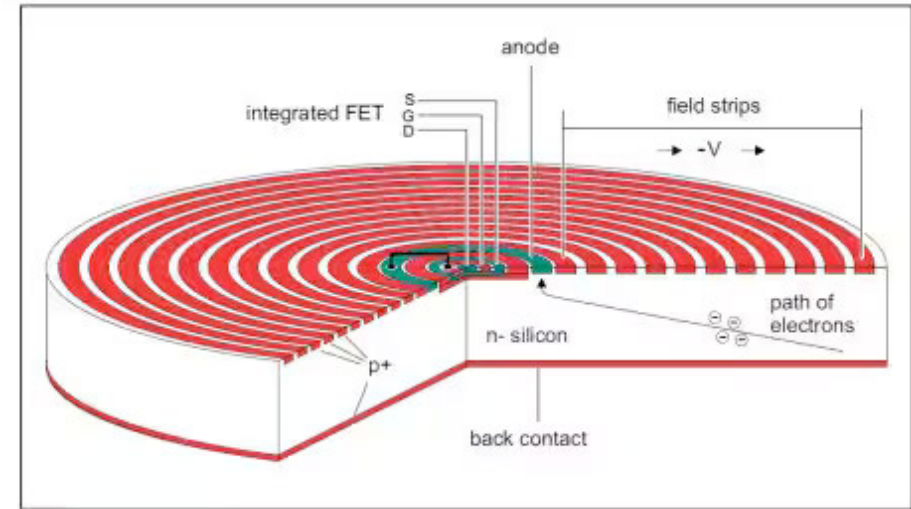


STEM: 300 keV beam, thin sample



EPFL EDX detection

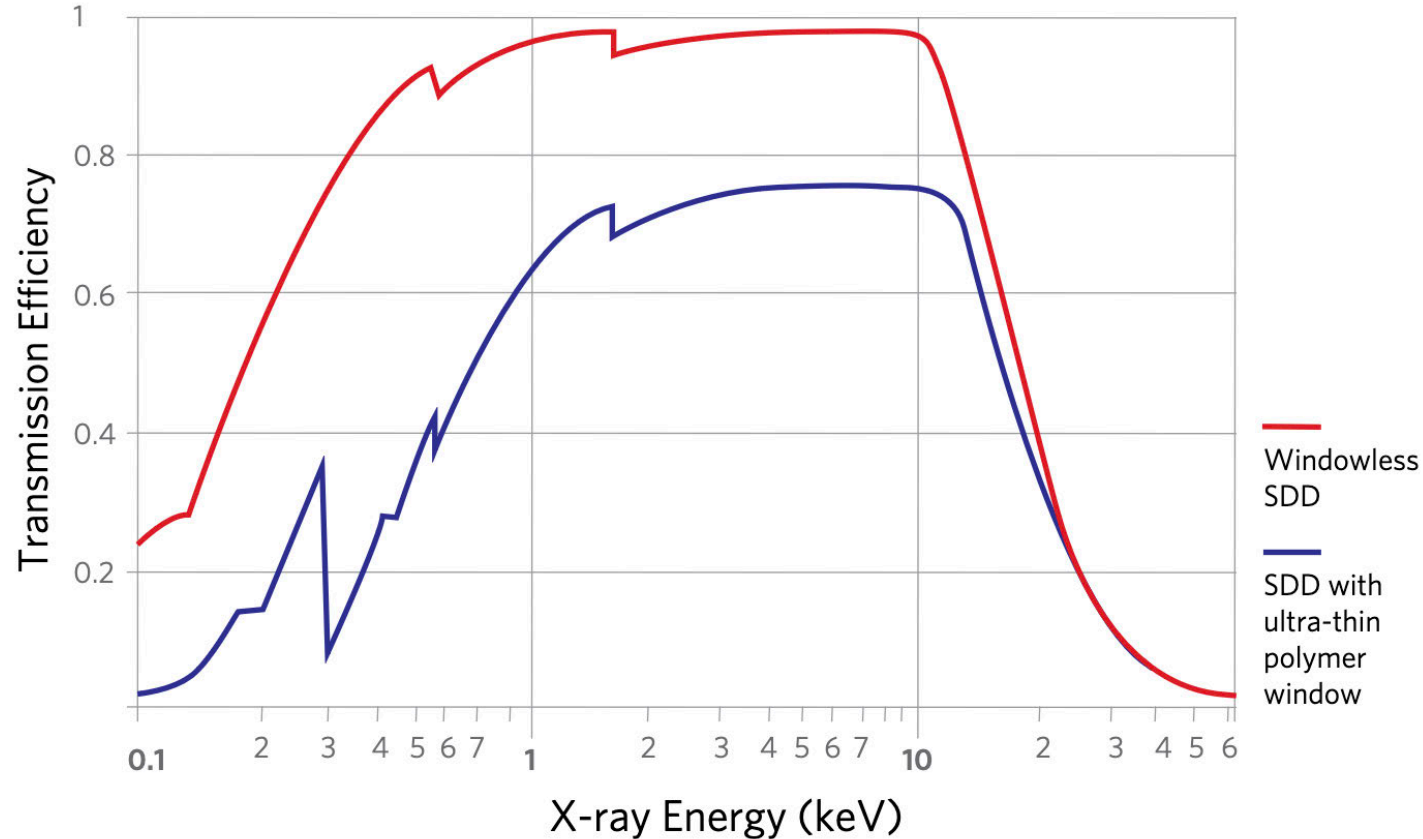
- Modern standard is the *Silicon Drift Detector (SDD)*
- Incident X-ray absorbed in Si creates e^-h^+ pairs
- Internal electric field drifts e^- charge towards anode
- Accumulated charge converted to voltage by a pre-amplifier
- Quantity of charge carriers depends on X-ray energy
⇒ measured voltage corresponds to energy of detected X-ray



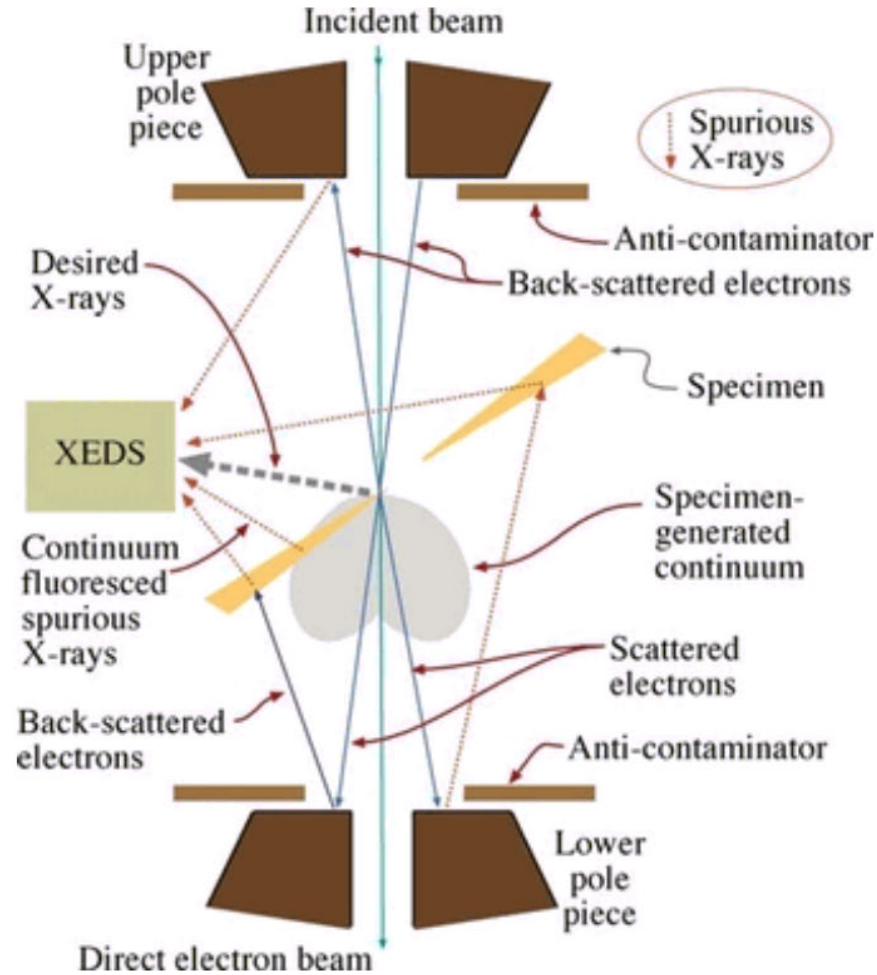
Example SDD detector design



- SDD detectors are compact and fast, but poor DQE for X-rays ≥ 20 keV



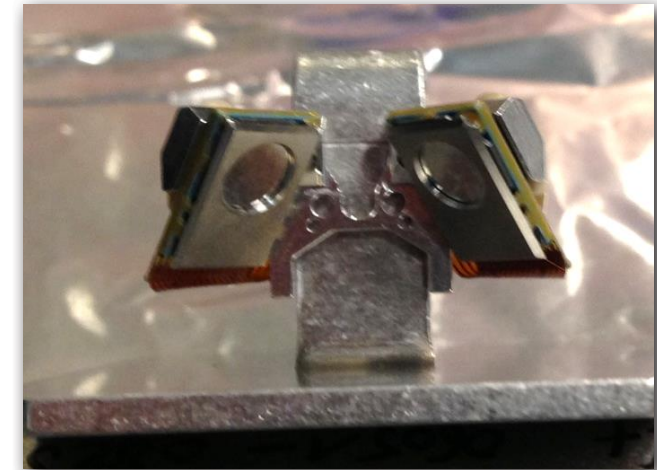
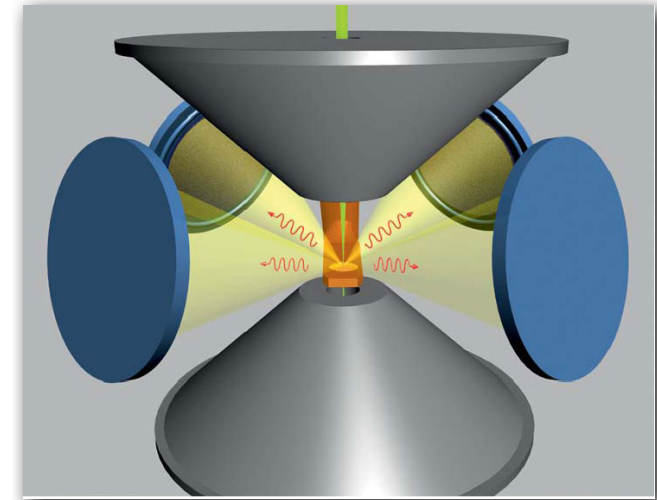
EPFL Detection geometry



- Take care of spurious artefact X-ray peaks

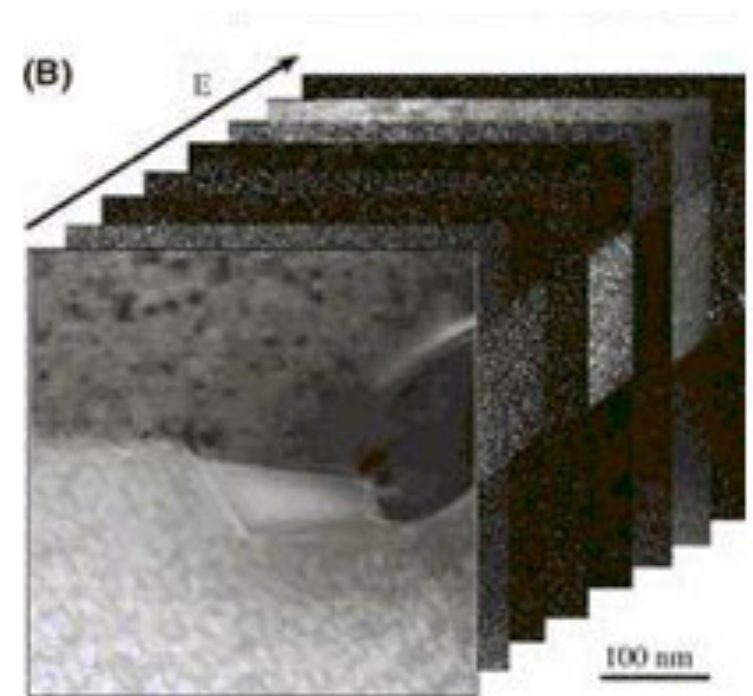
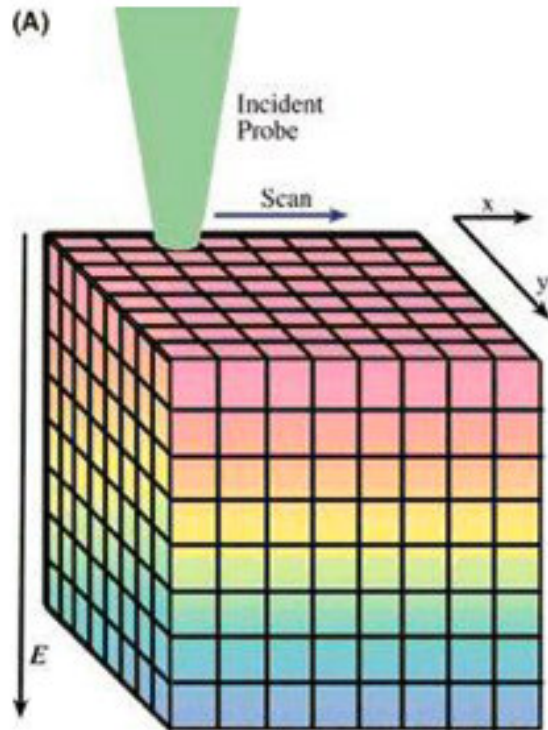
EPFL Detection geometry

- New standard is to use multiple SDDs to increase solid angle of collection and hence detection efficiency
- For example: “Super-X” on Osiris, Titan with 4 quadrants giving ~ 1 Sr solid angle of collection
- State-of-the-art: Thermo Fisher Scientific Ultra with ~ 4 Sr



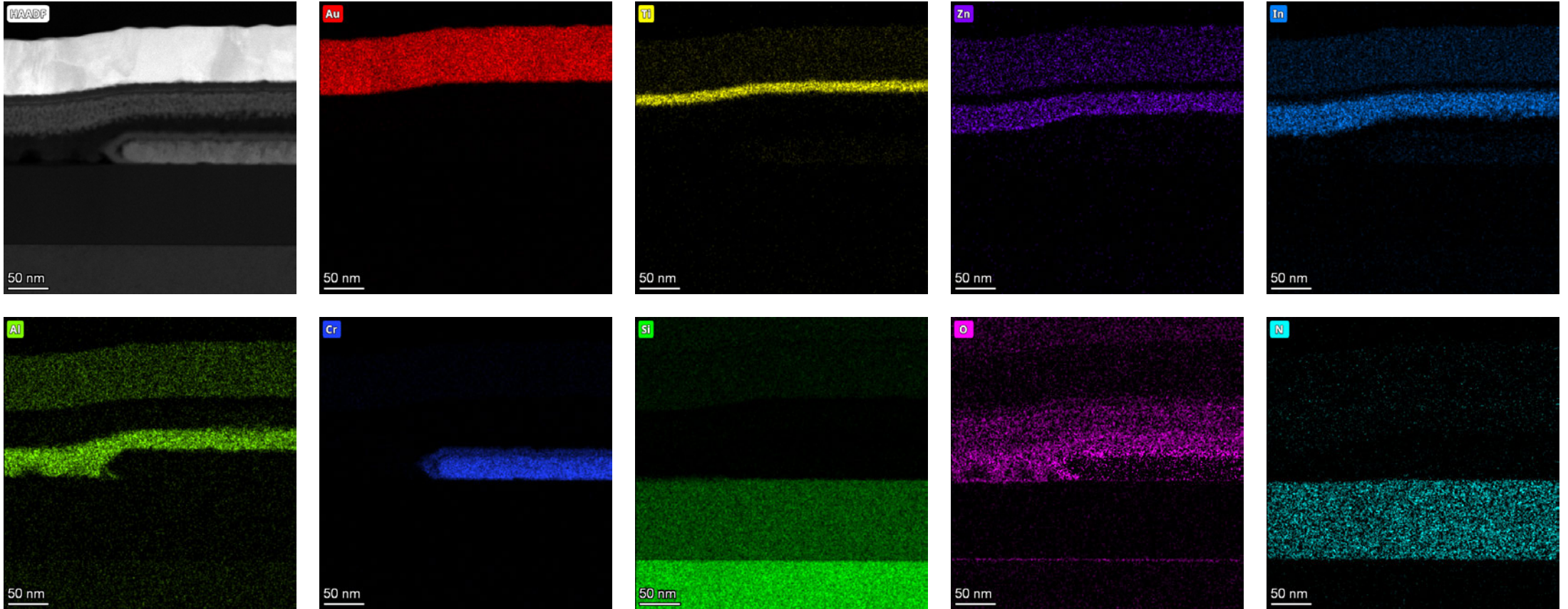
EPFL STEM-EDXS data-cube

- EDXS map: acquire one spectrum per pixel position (x, y)
- Gives 3D data-cube of information with axes (x, y, E)
- Data can be post-processed – integrate area under peak to generate qualitative elemental map



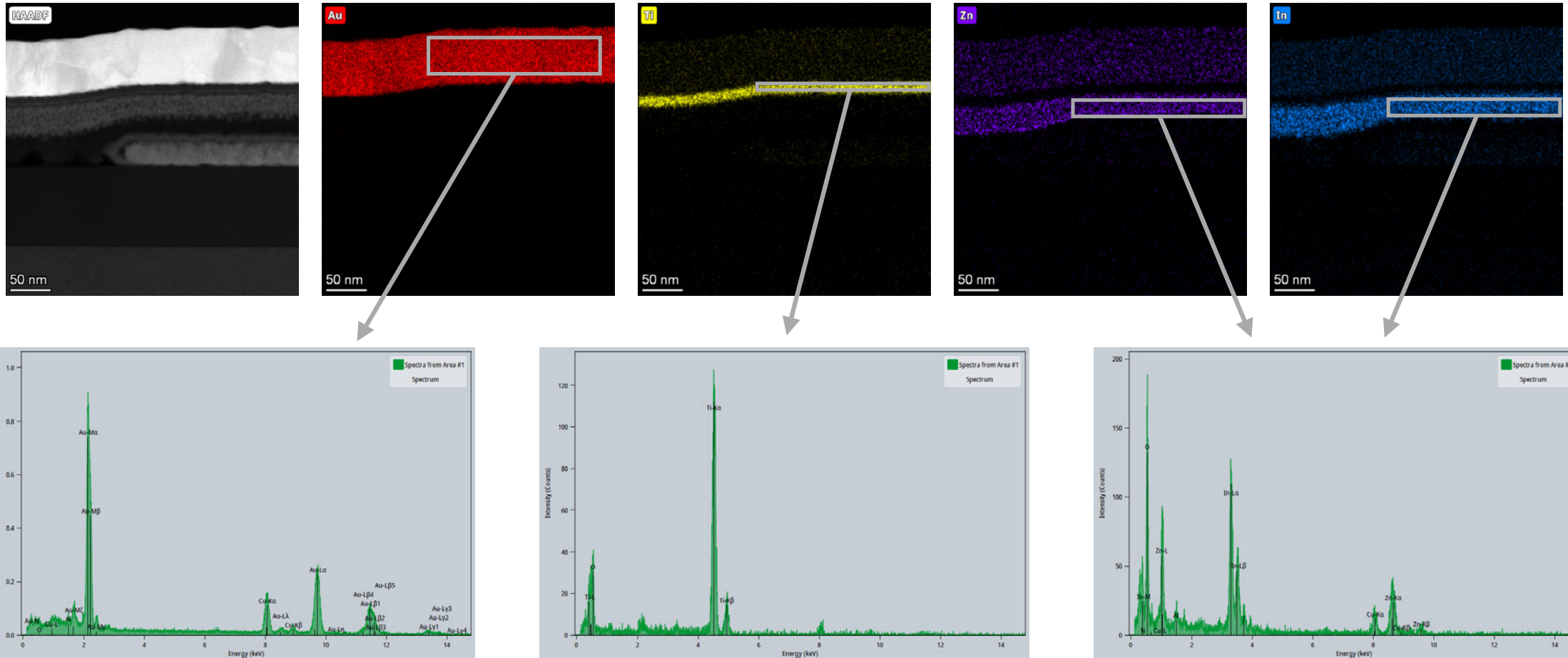
EPFL EDXS mapping: applications

- Multilayer sample – *net counts* maps



EPFL EDXS mapping: applications

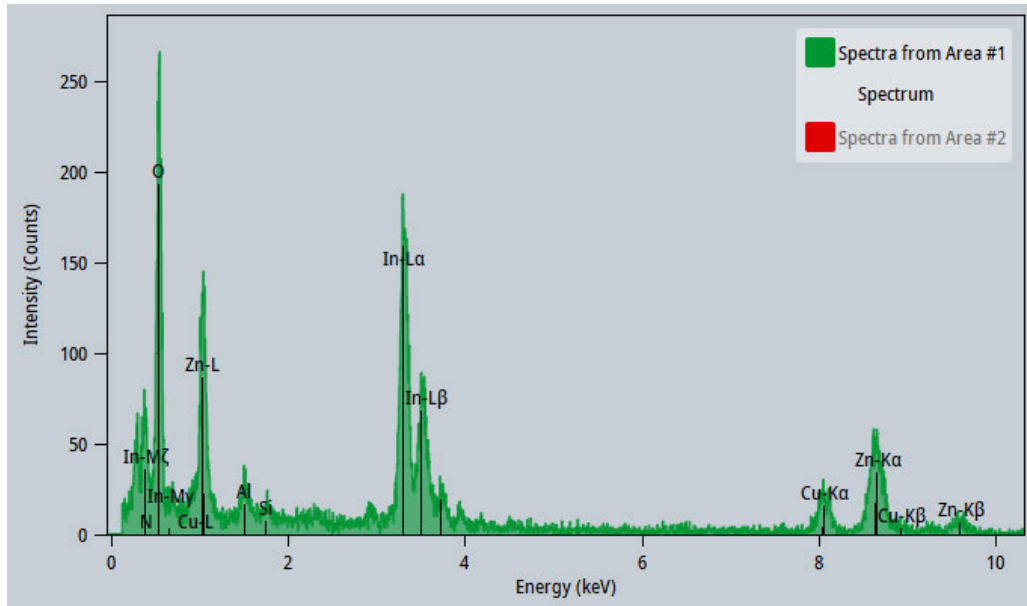
- Multilayer sample – *integrated counts* EDX spectra



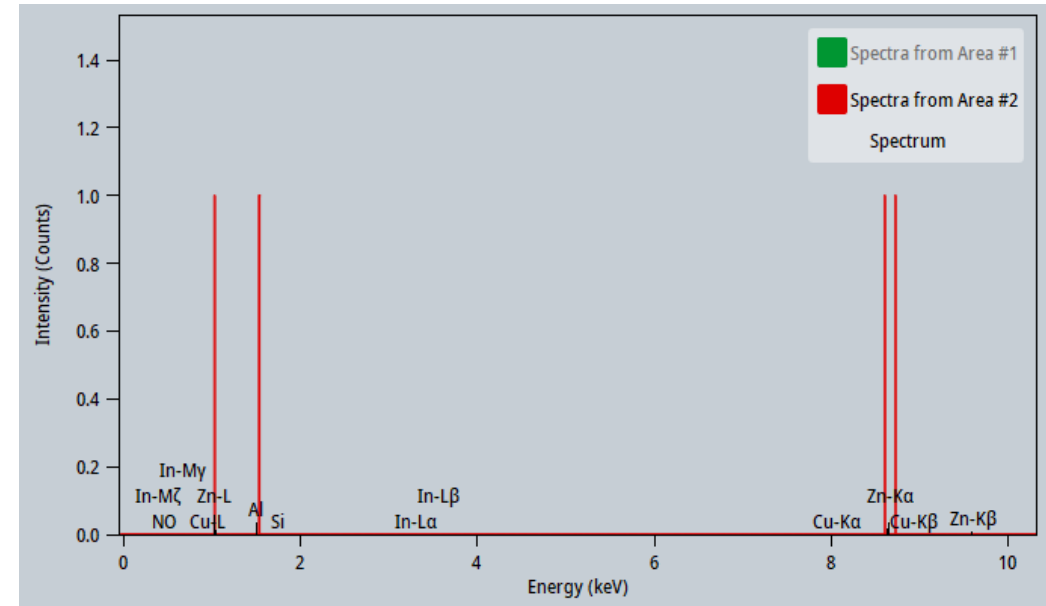
Why integrate counts across spatial ROI?

- In-Zn-O layer:

Integrated from $270 \times 25 = 6'750 \text{ px}^2$

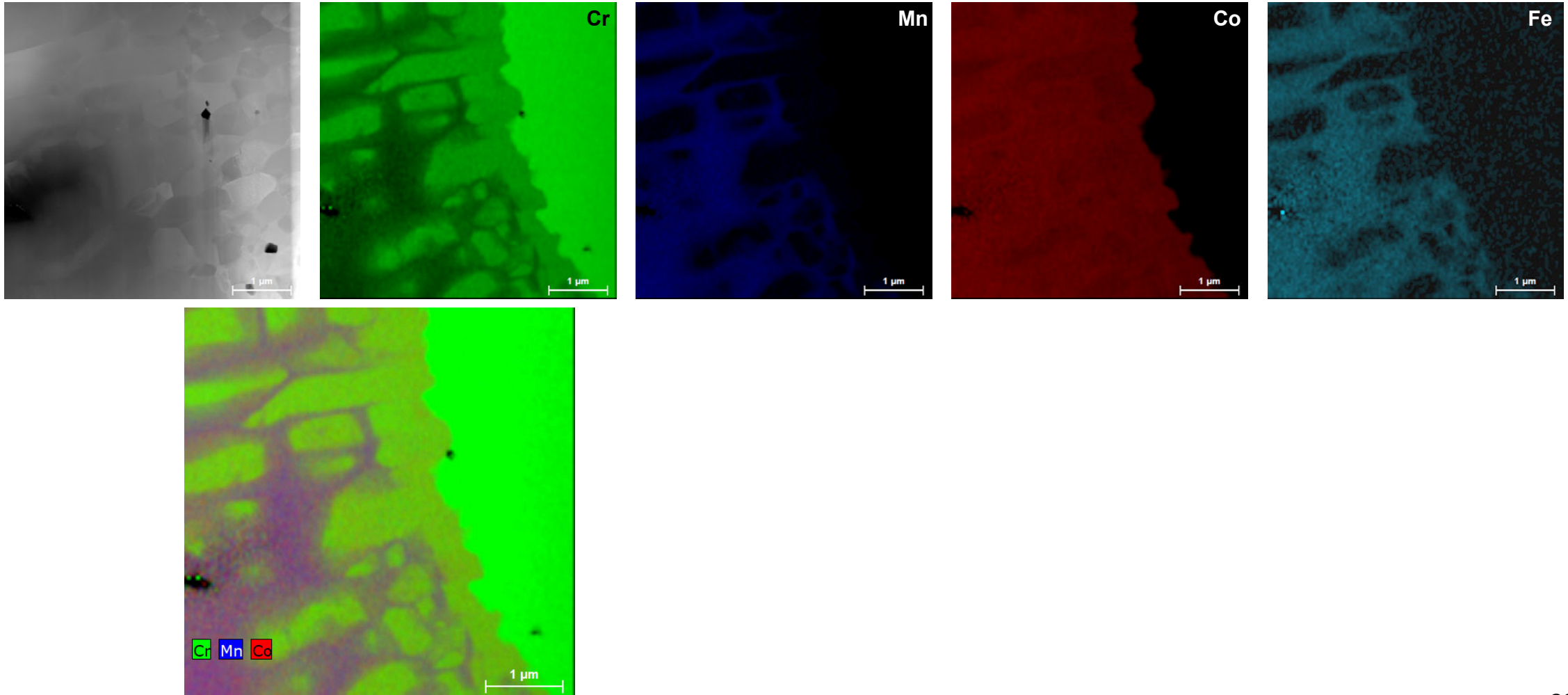


Single pixel spectrum



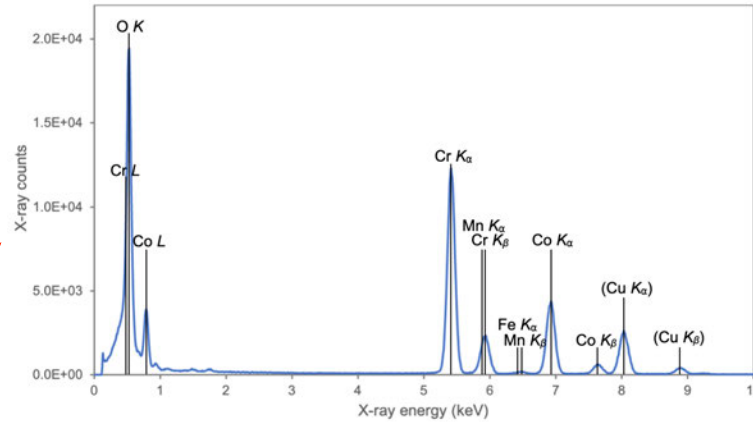
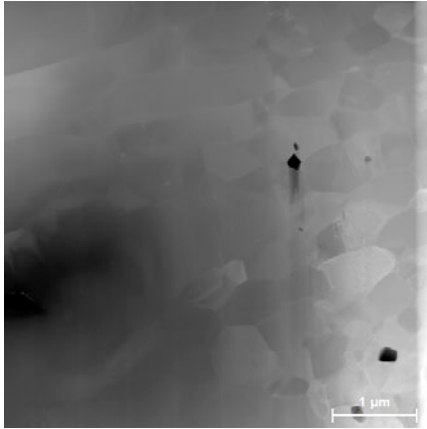
EPFL EDXS mapping: applications

- Fuel cell sample: Fe-doped MnCo_2O_4 spinel layer

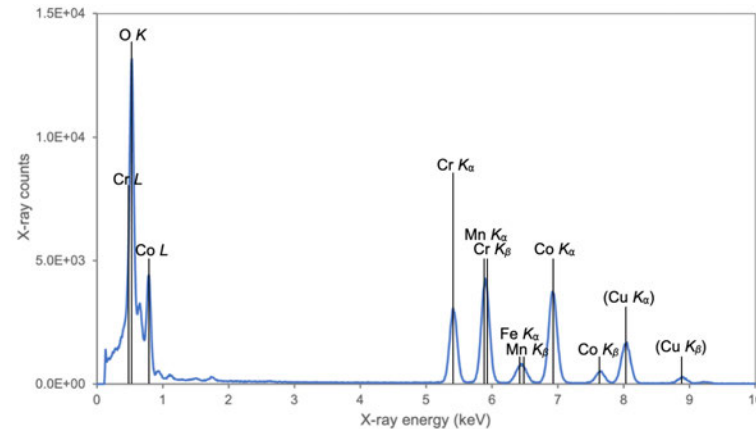
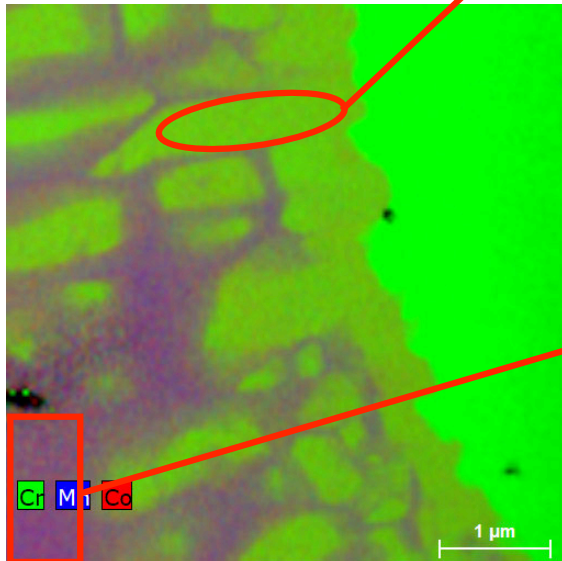


EPFL EDXS mapping: applications

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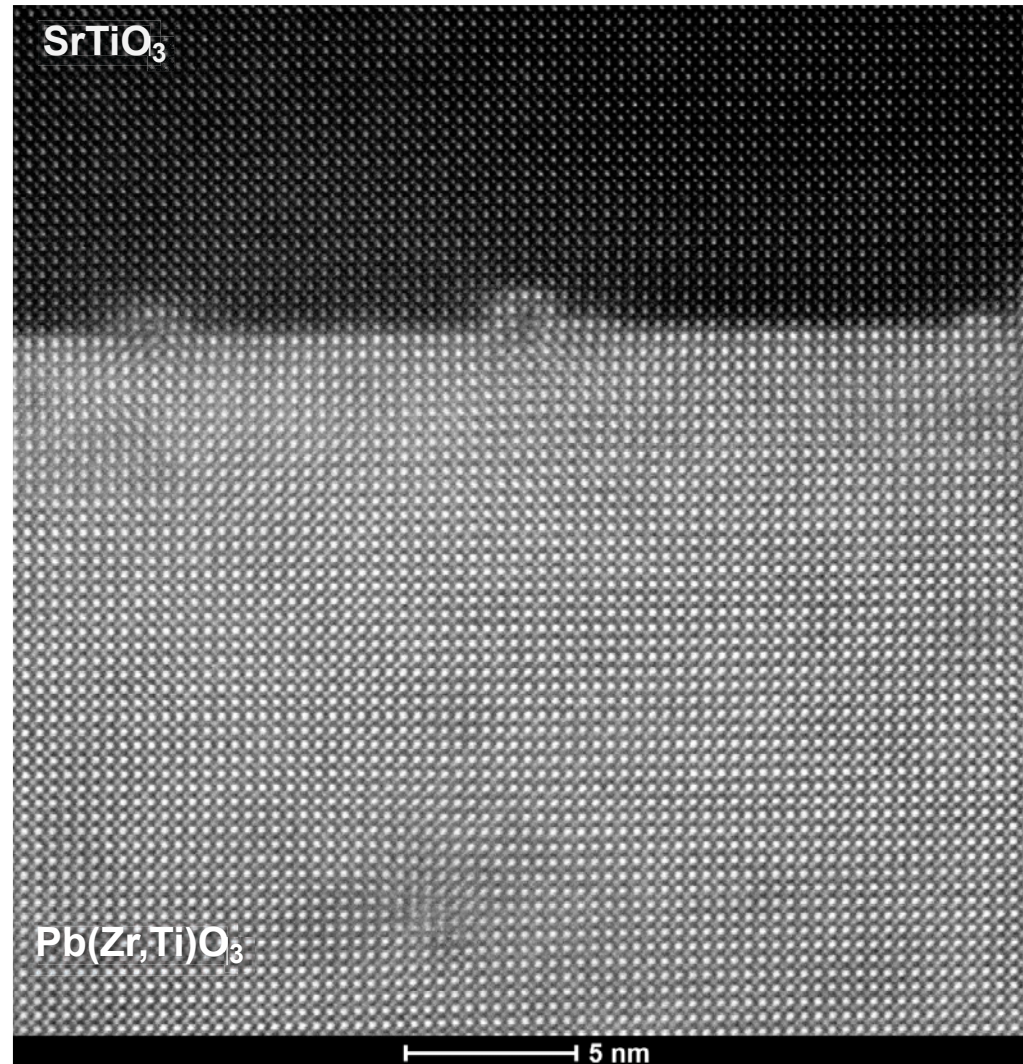
Element	Peak series	At. %
Cr	K	33.7
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O	K	49.8

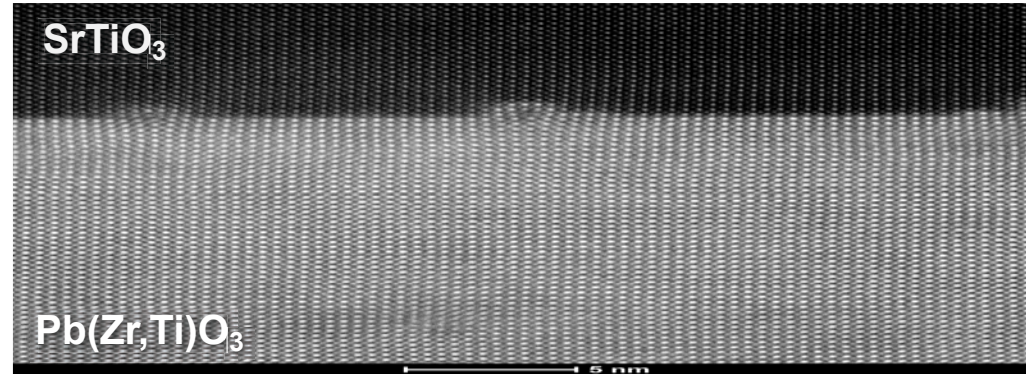
EPFL Atomic resolution EDXS with Cs-STEM

- Sample of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ on SrTiO_3

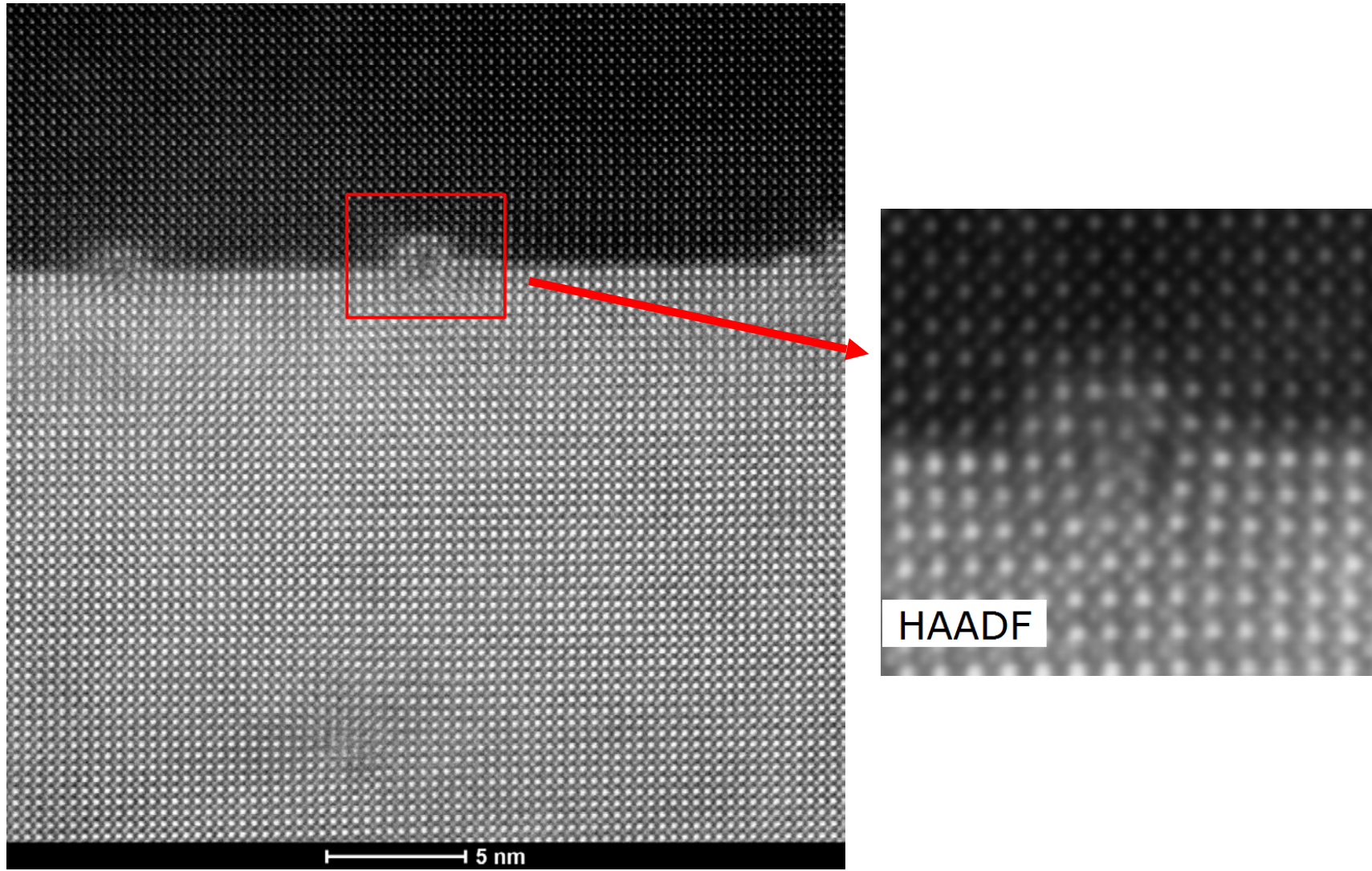


EPFL Atomic resolution EDXS with Cs-STEM

- Sample of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ on SrTiO_3



- Sample of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ on SrTiO_3



EPFL Atomic resolution EDXS with Cs-STEM

- Sample of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ on SrTiO_3 – atomic resolution elemental mapping

