Analytical TEM
part I

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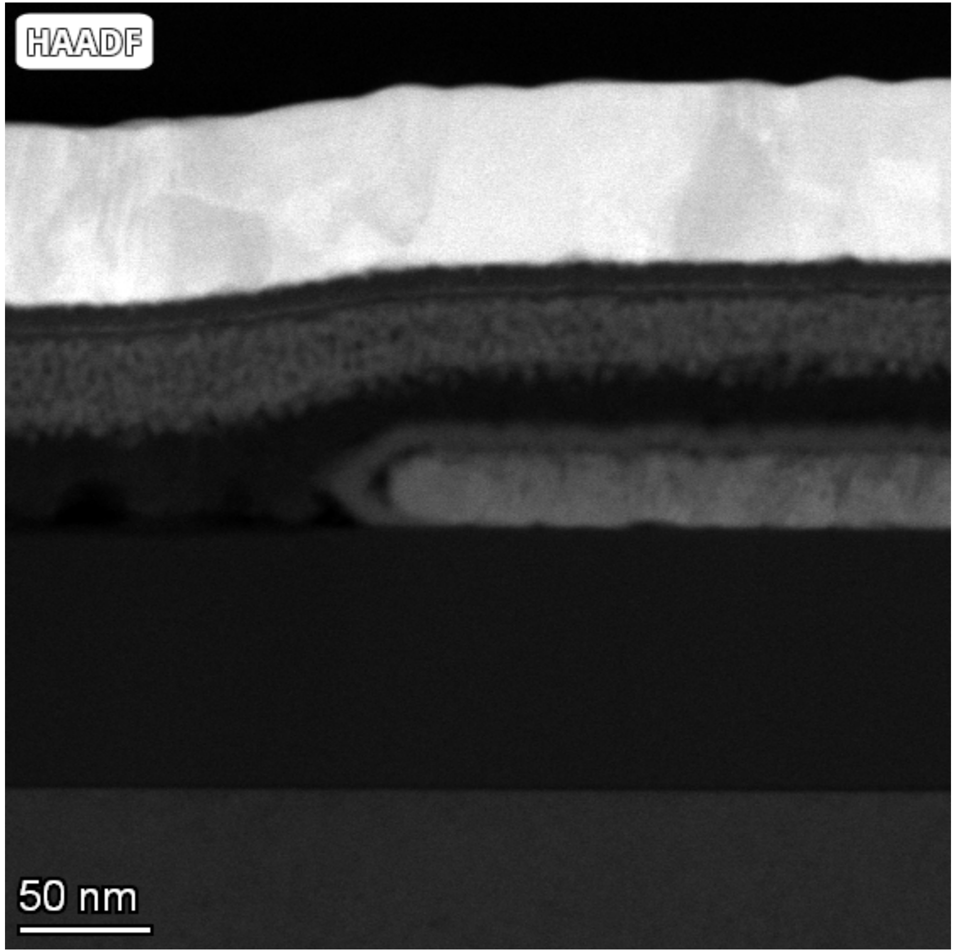
Adding colour to microscopy!

- Multilayer from first STEM lecture



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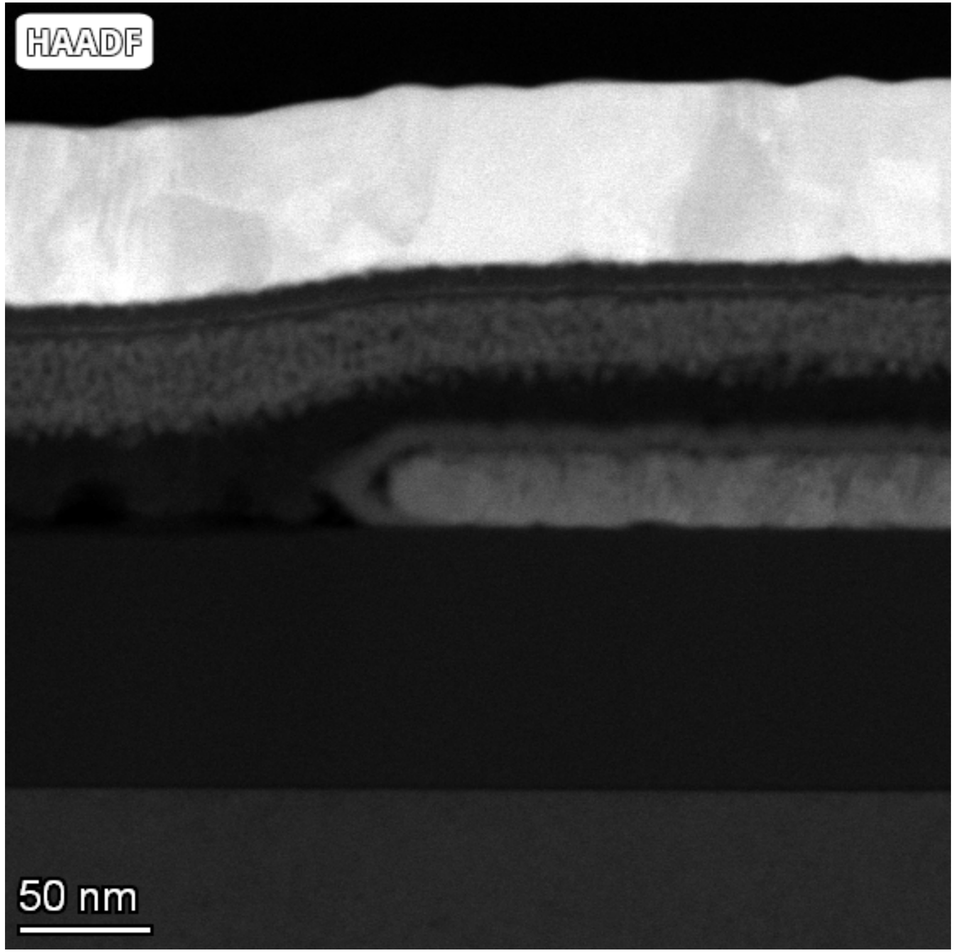

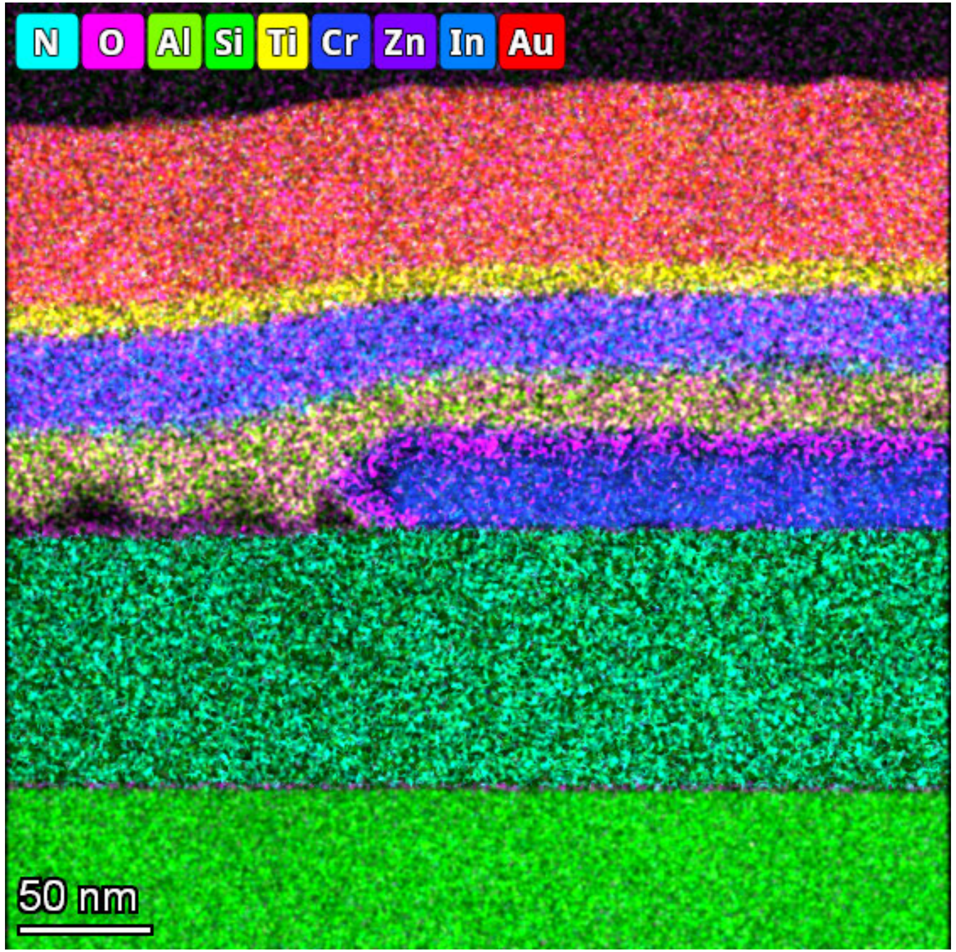

Contents

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

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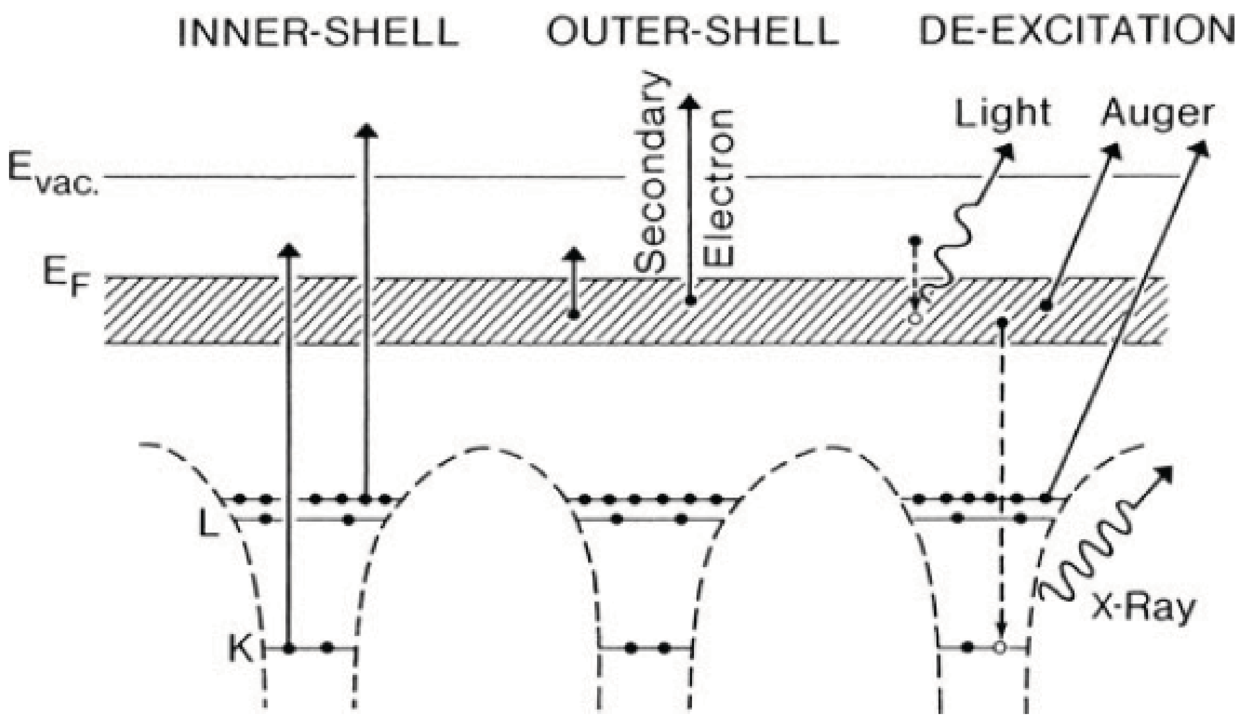
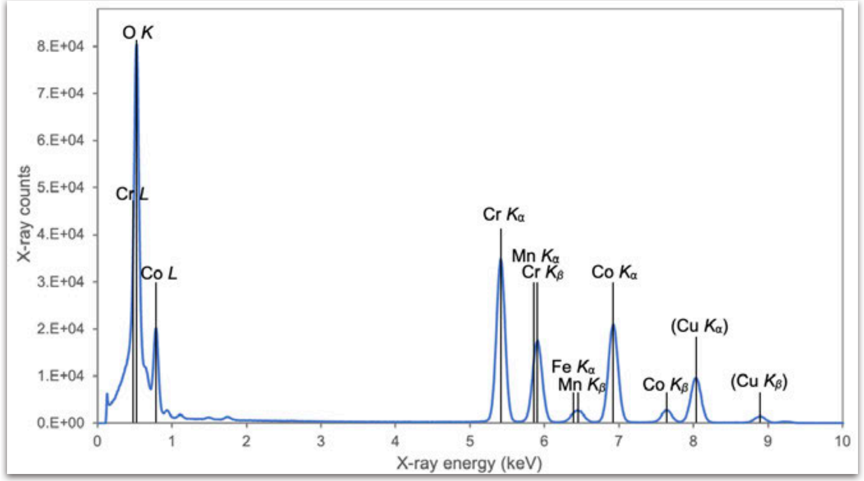
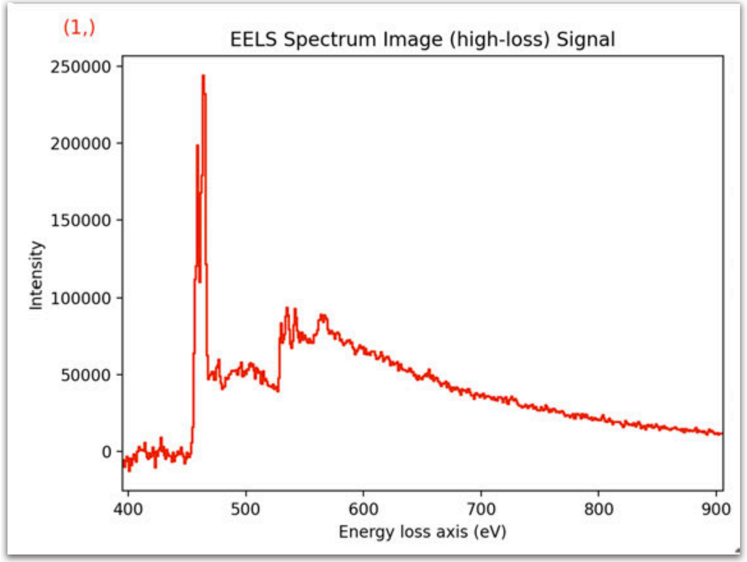
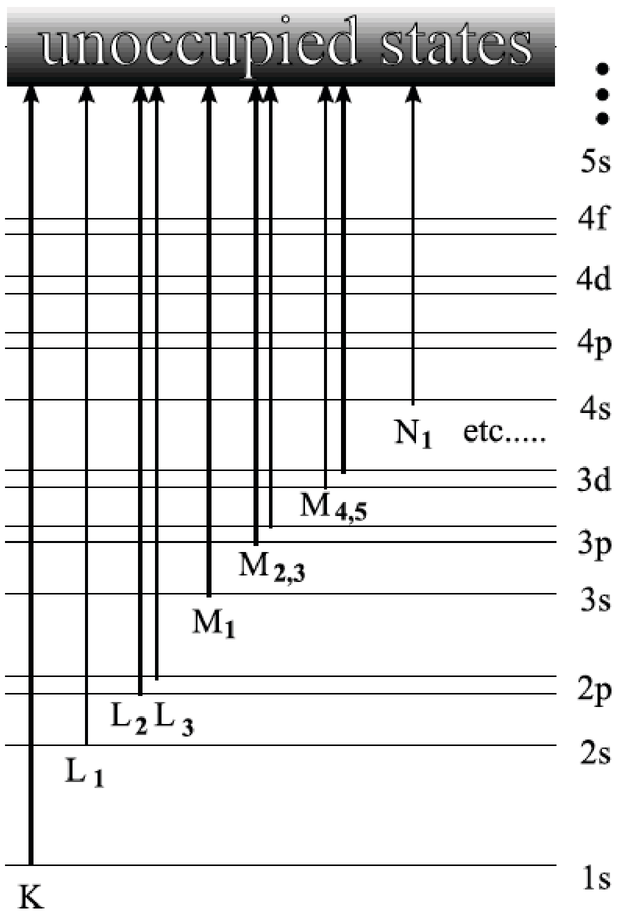
A way to probe chemistry

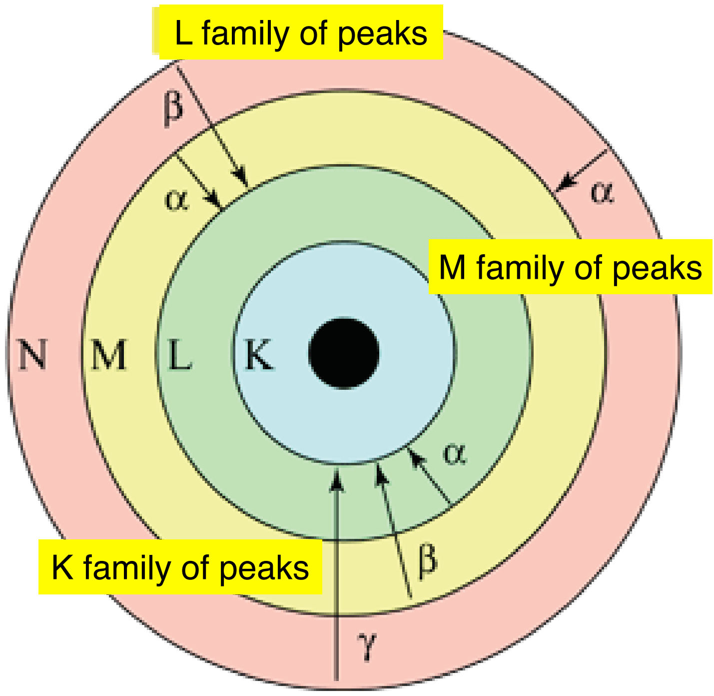






Edges and peaks nomenclature





Quiz

- EDXS: energy dispersive X-ray spectroscopy
  $\Longrightarrow$ intensity spectrum of X-ray peaks separated by energy

- EELS: electron energy-loss spectroscopy
  $\Longrightarrow$ 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) $E_{EELS} > E_{EDXS}$
  - 2) $E_{EELS} = E_{EDXS}$
  - 3) $E_{EELS} < E_{EDXS}$

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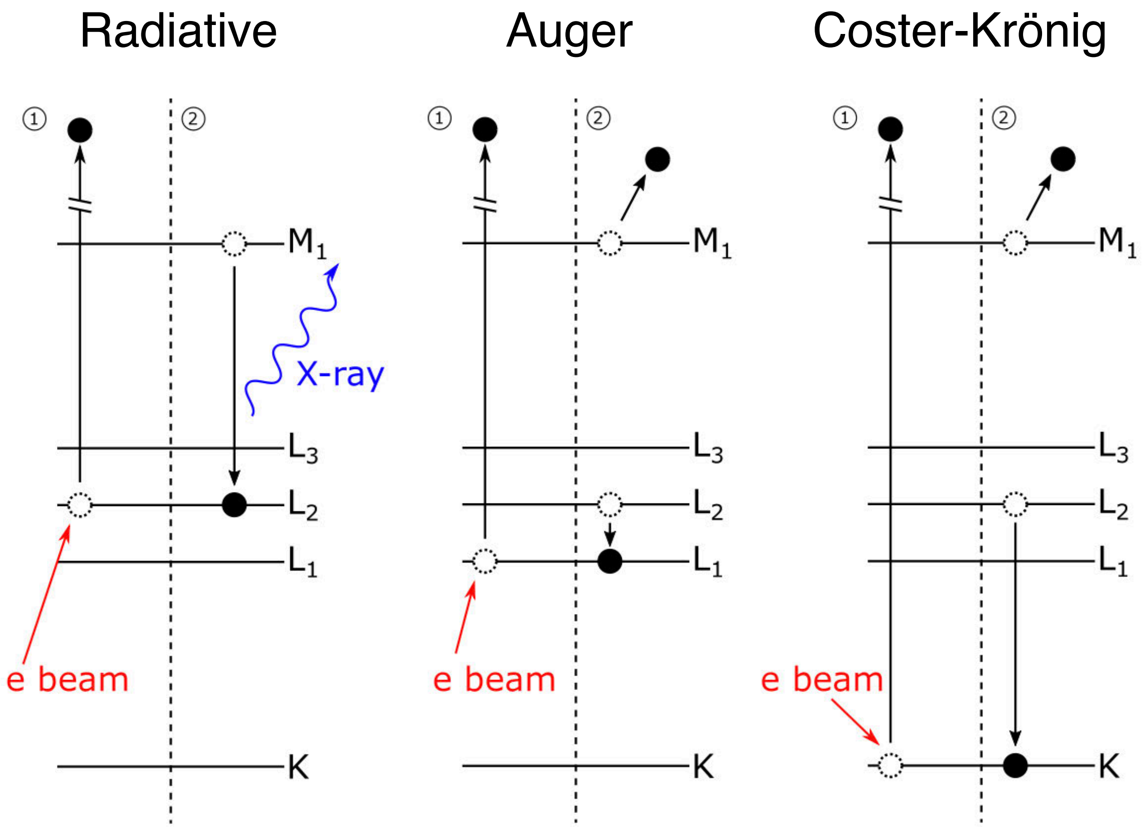
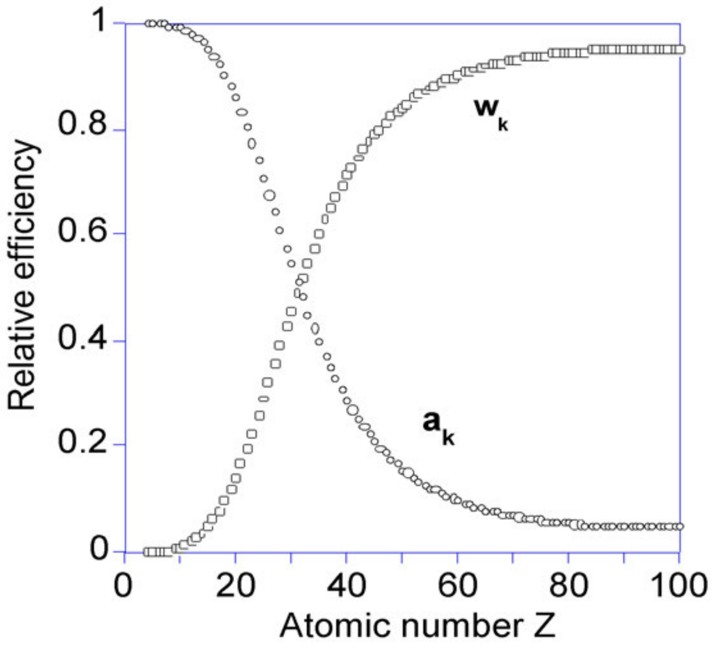
X-ray generation

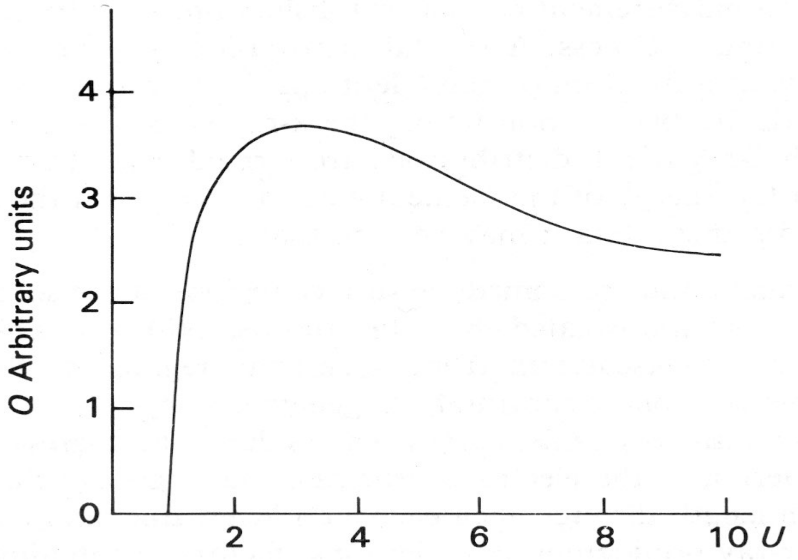
- 3 basic de-excitation process:
  - Radiative X-ray emission
  - Auger transitions/emission
  - Coster-Krönig transitions
- Complex “cascade” effects possible



X-ray generation

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

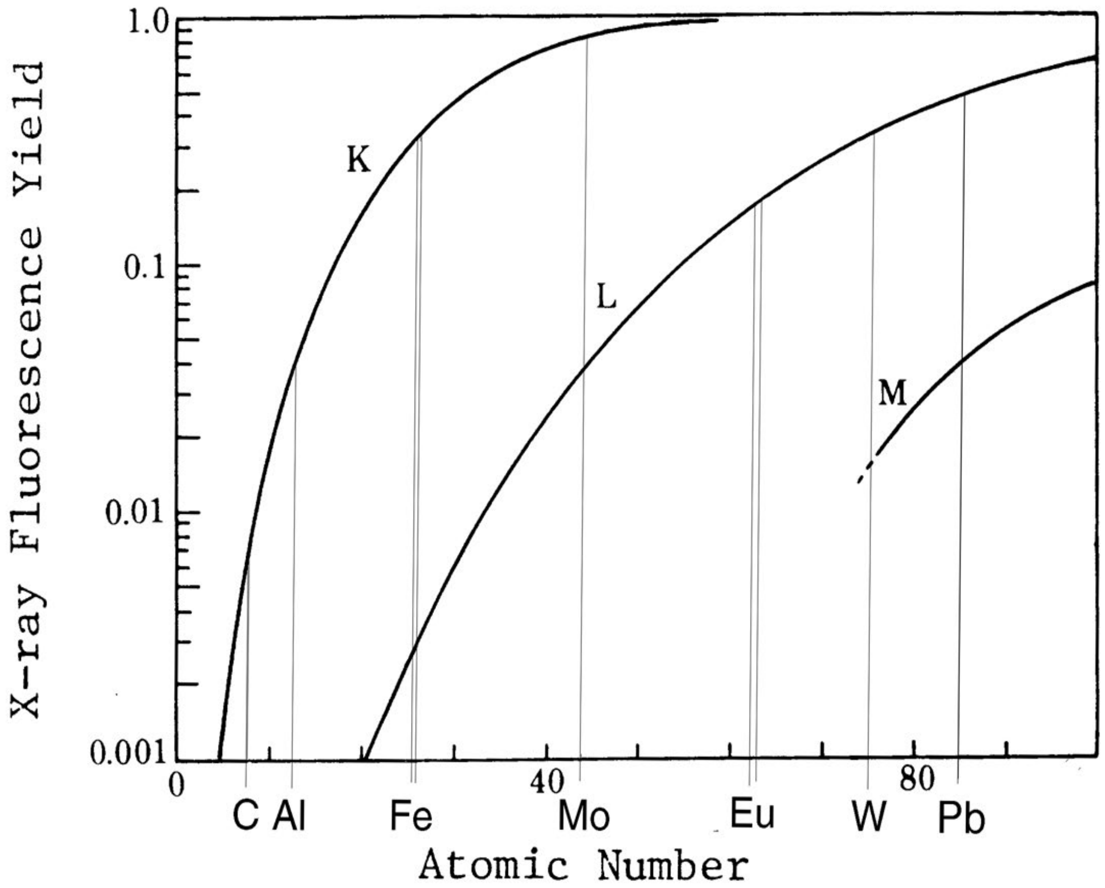




Light element atoms return to fundamental state mainly by Auger emission. For that reason, their K-lines are weak. In addition their low energy makes them easily absorbed.

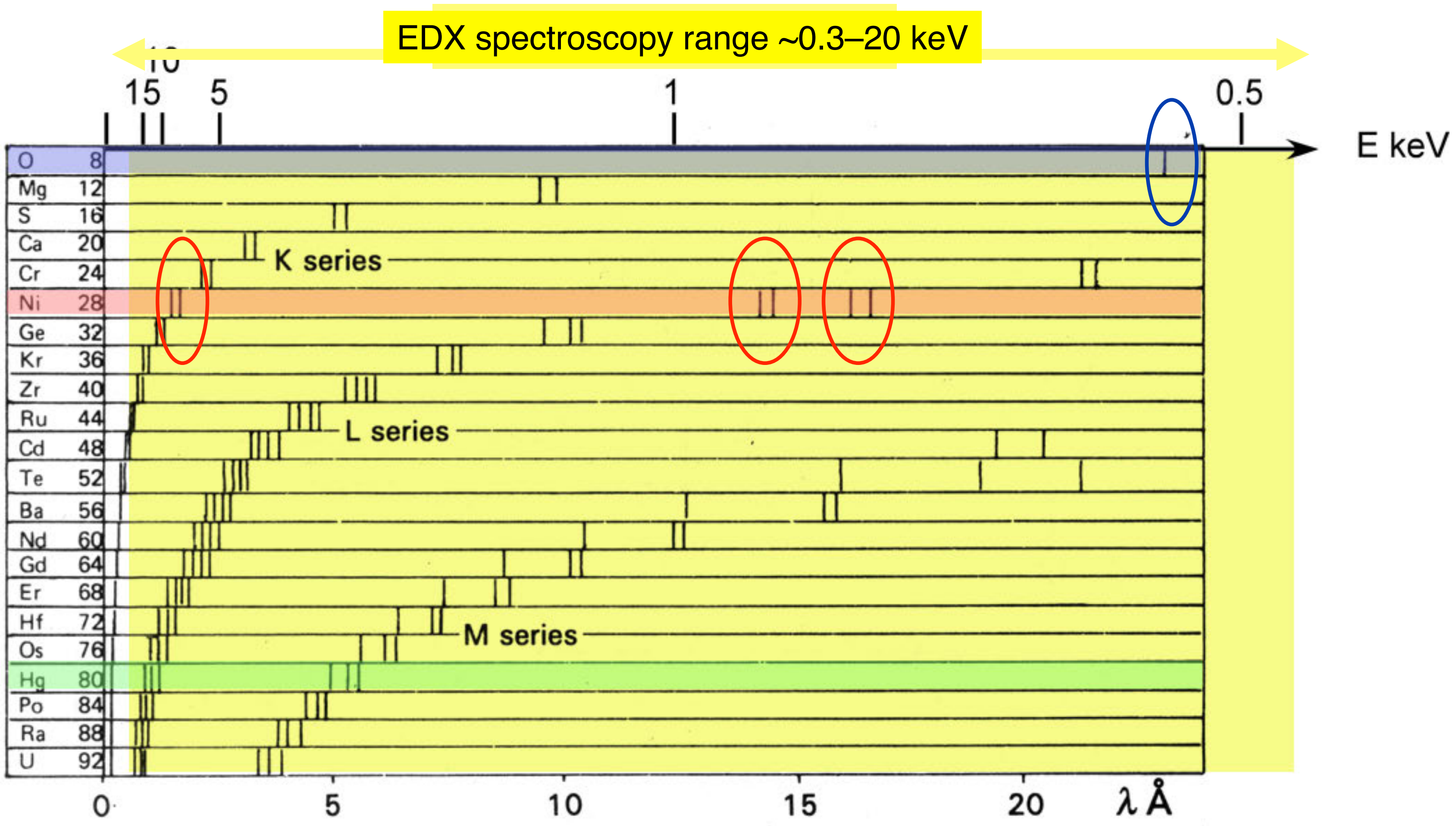
To ionise an atom, the incident electron MUST have an energy larger than the core shell level U>1. To be efficient, it should have about twice the edge energy U>2.

Fluorescence yield

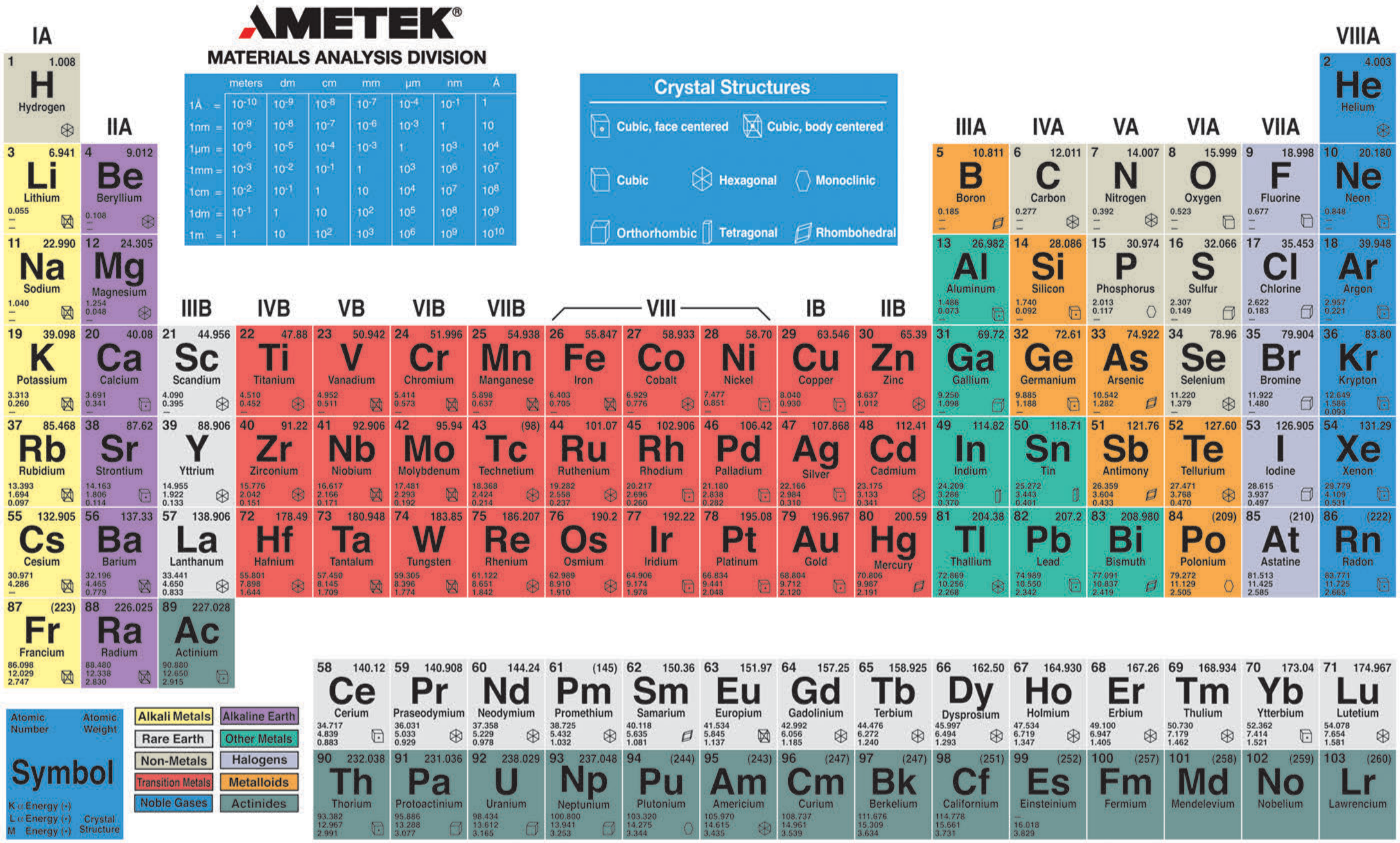


X-ray fluorescence yield for *K*-, *L*-, and *M*-shells, as a function of atomic number.

Separation of EDX peaks



Periodic table of X-ray peaks



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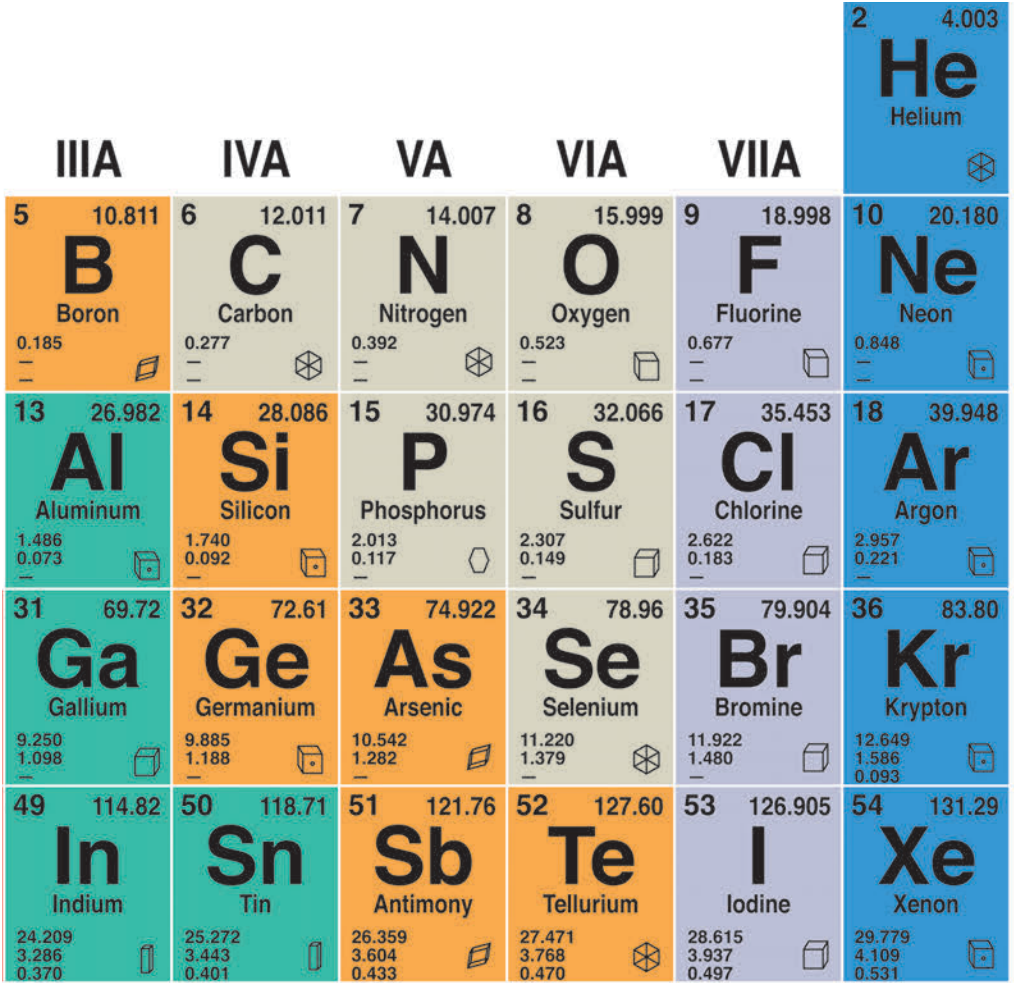
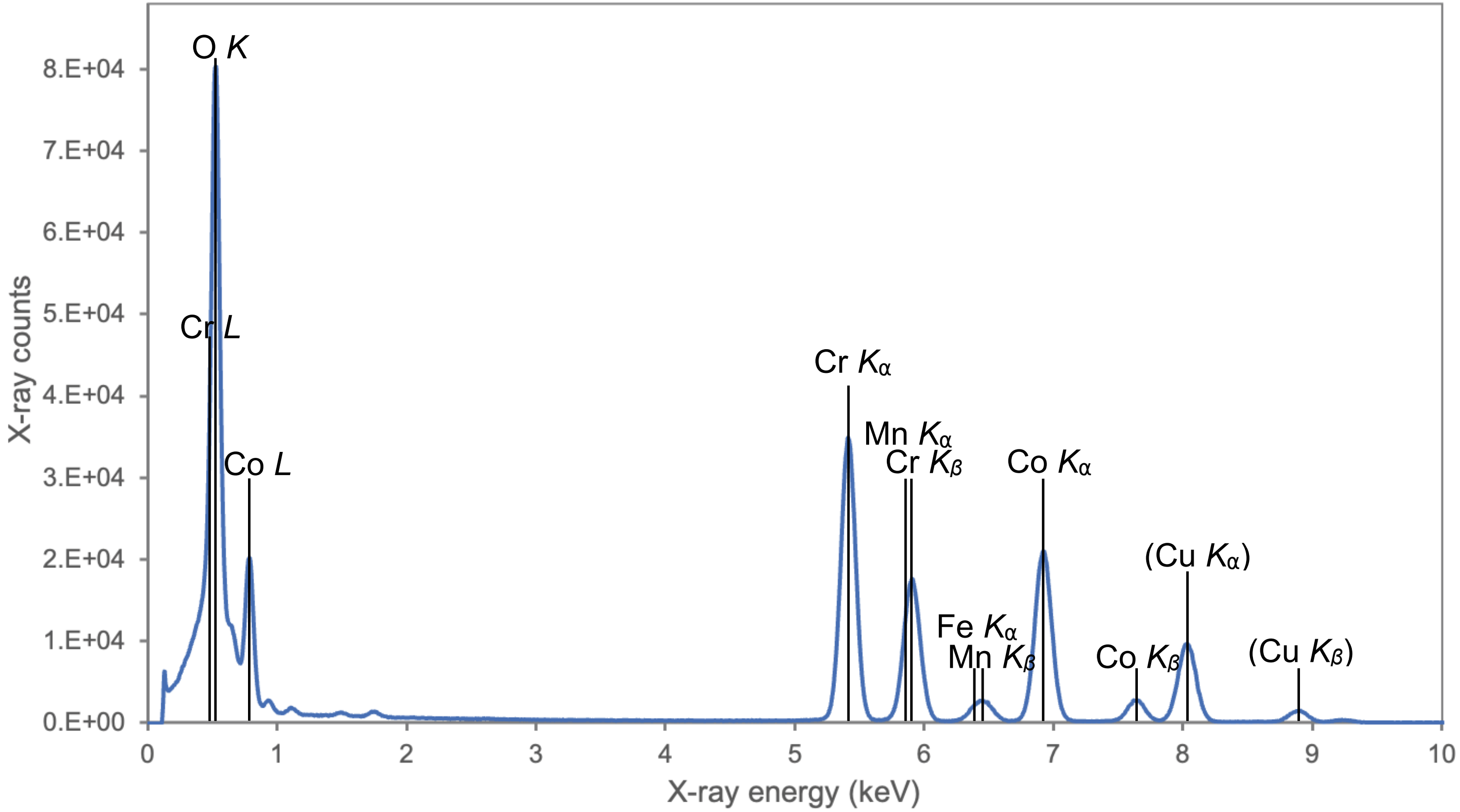
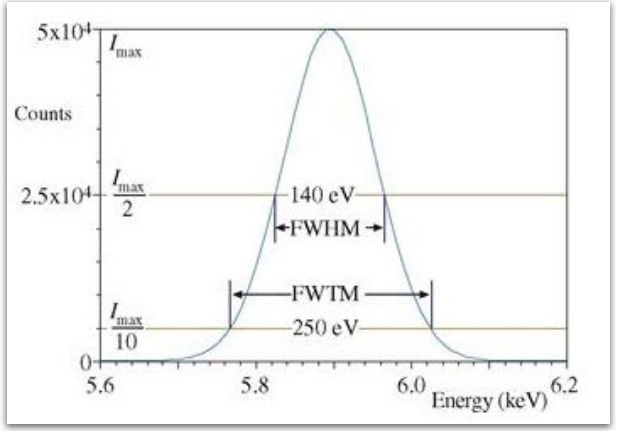


The EDX spectrum

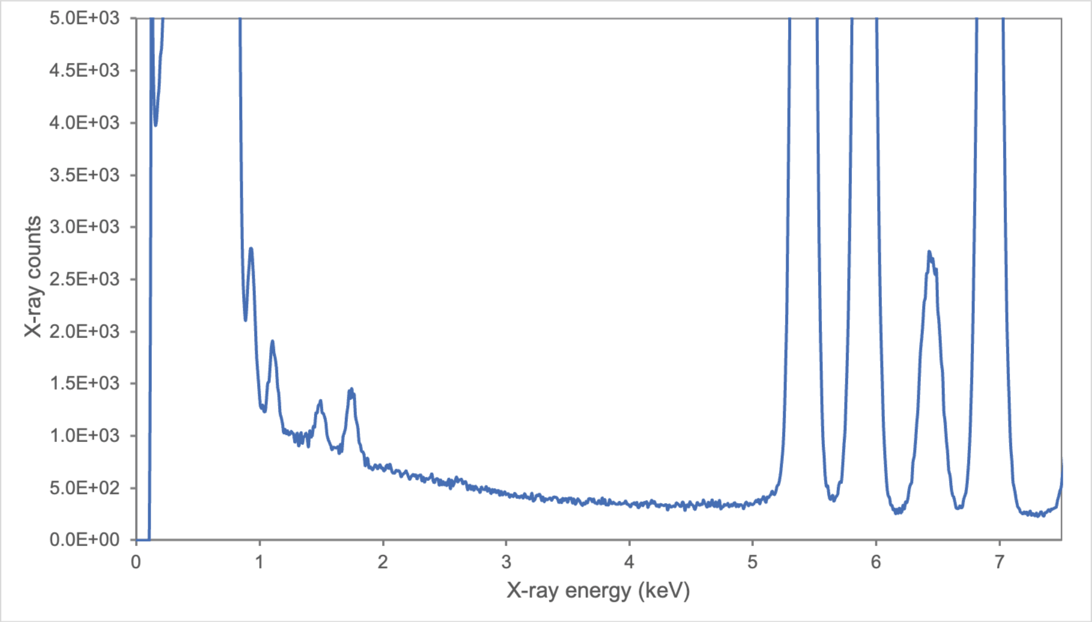
- Example spectrum from fuel cell sample containing O, Cr, Mn, Fe, Co
- Spectrum of mostly well-defined peaks that e.g. can be fitted with Gaussians





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): $I_{\text{brem}} = \frac{\beta_0}{E_{\text{X-ray}}} + \beta_1 + \beta_2 E_{\text{X-ray}}$

EDXS quantification

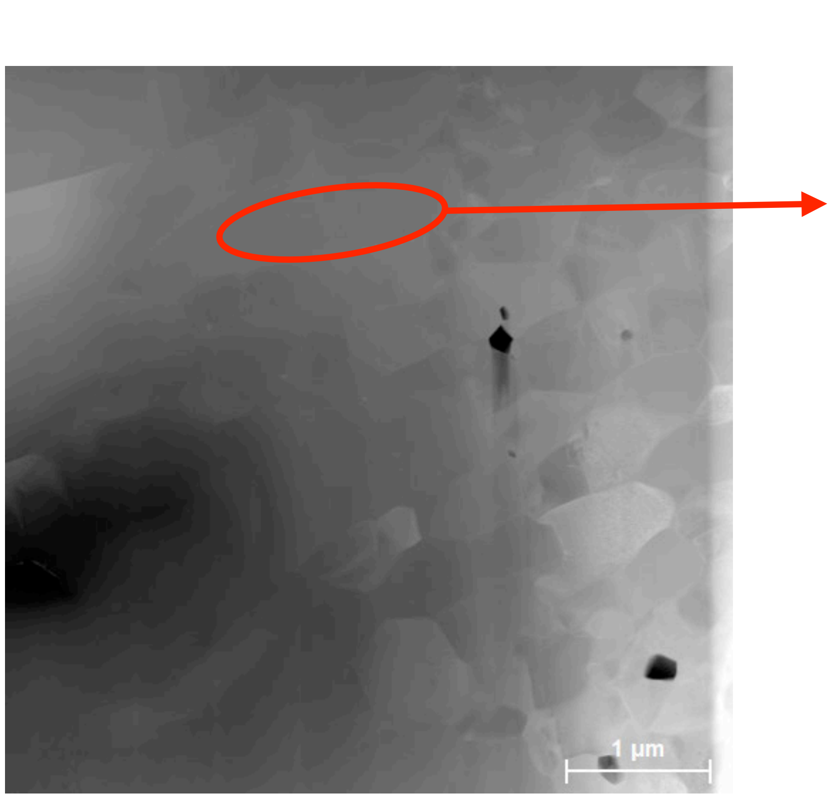
- To go from qualitative to quantitative: measure the intensities I_j of the X-ray peaks (area under the peak)
- Typically apply “Cliff-Lorimer” approach where calculate ratios of constituent elements:

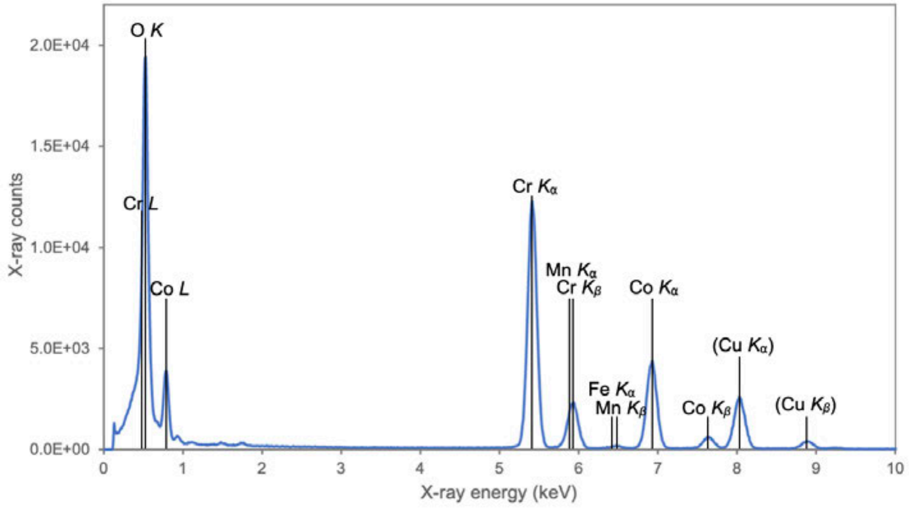
$$\frac{C_A}{C_B} = k_{AB}\frac{I_A}{I_B}$$

- 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. %

EDXS quantification

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





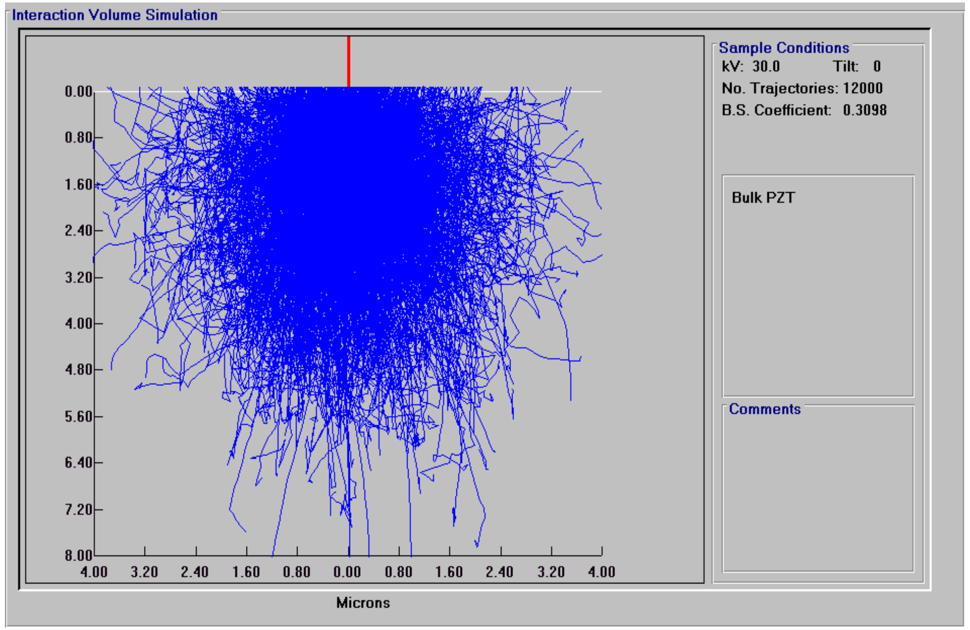
Element	Peak series	At. %
Cr	K	33.7
Co	K	13.8
Mn	K	2.5
Fe	K	0.1
O	K	49.9

Compared to SEM-EDXS

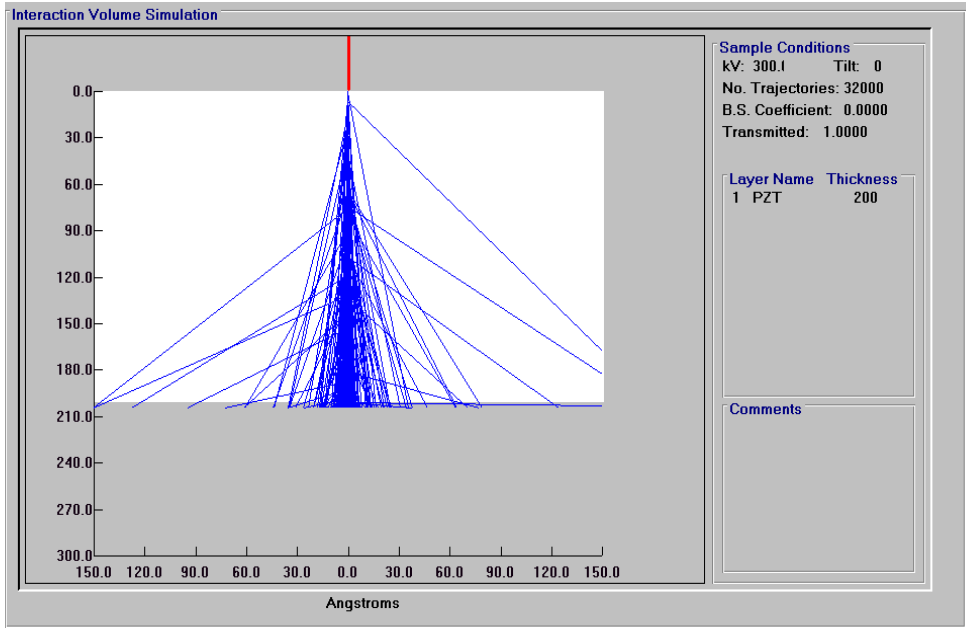
- (Can) Neglect correction factors for absorption and fluorescence in quantification
- High energy e⁻-beam and thin sample ⟹ X-rays emitted from narrow/confined volume of sample in beam path direction

Pb(Zr,Ti)O_3 scattering models

SEM: 30 keV beam, bulk sample

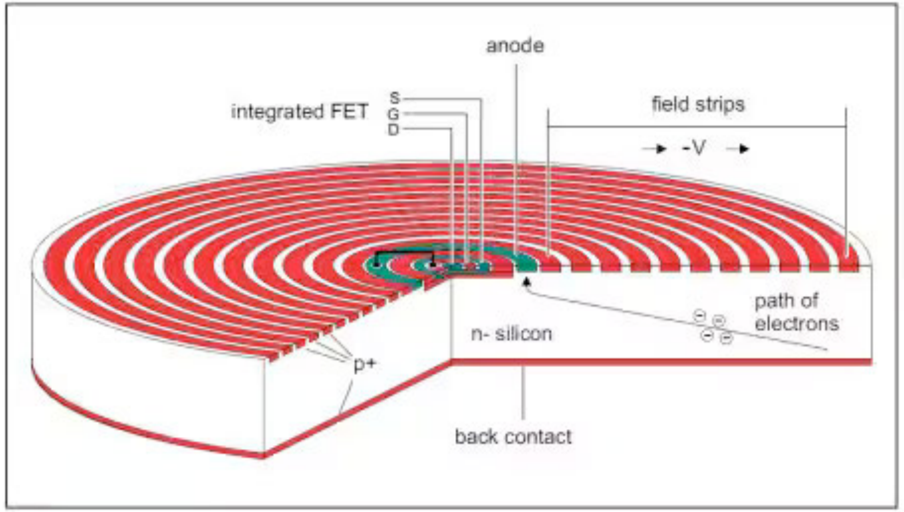


STEM: 300 keV beam, thin sample

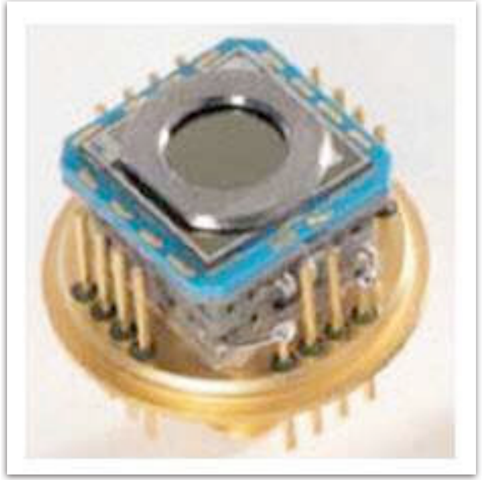


EDX detection

- 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
  $\Longrightarrow$ measured voltage corresponds to energy of detected X-ray

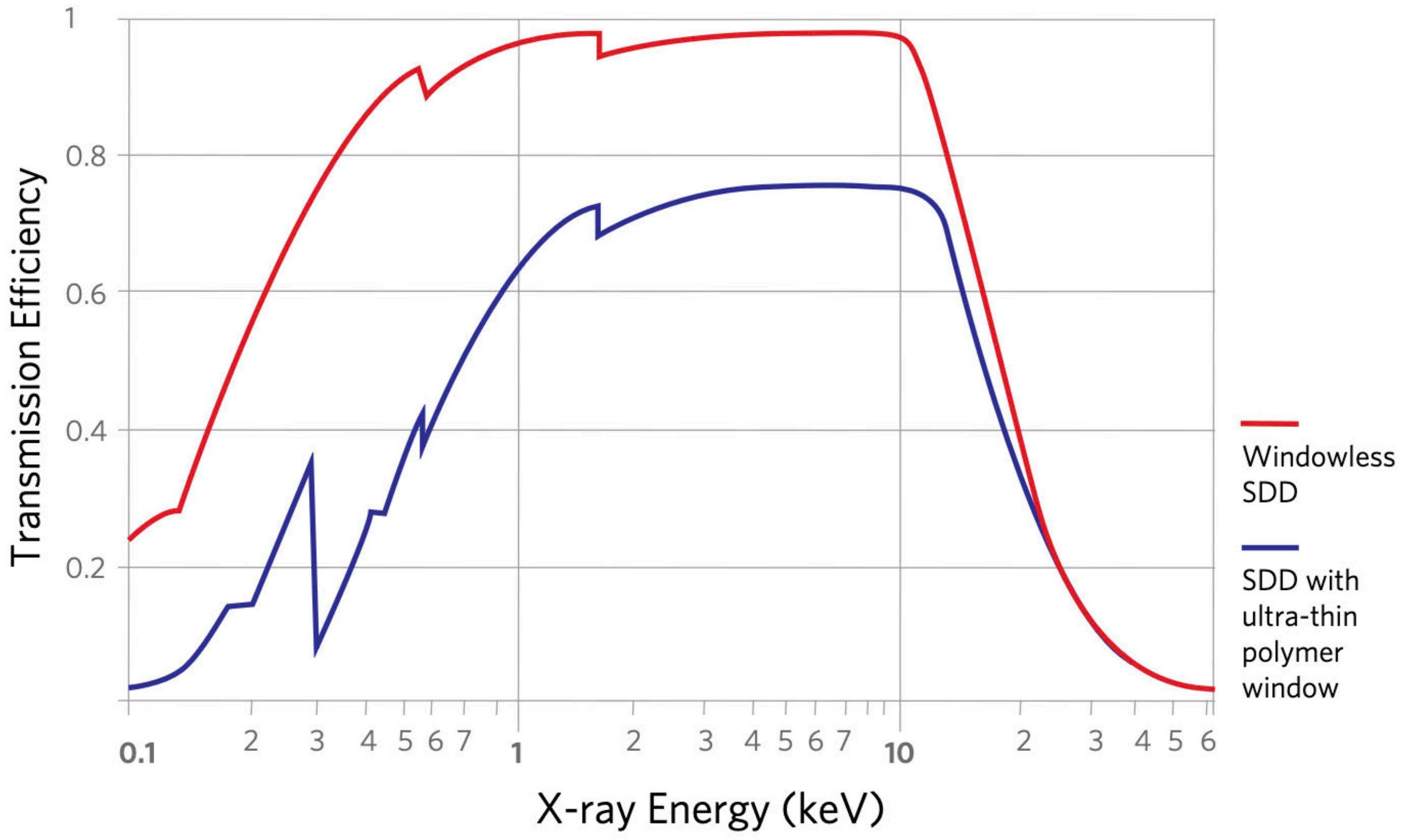


Example SDD detector design

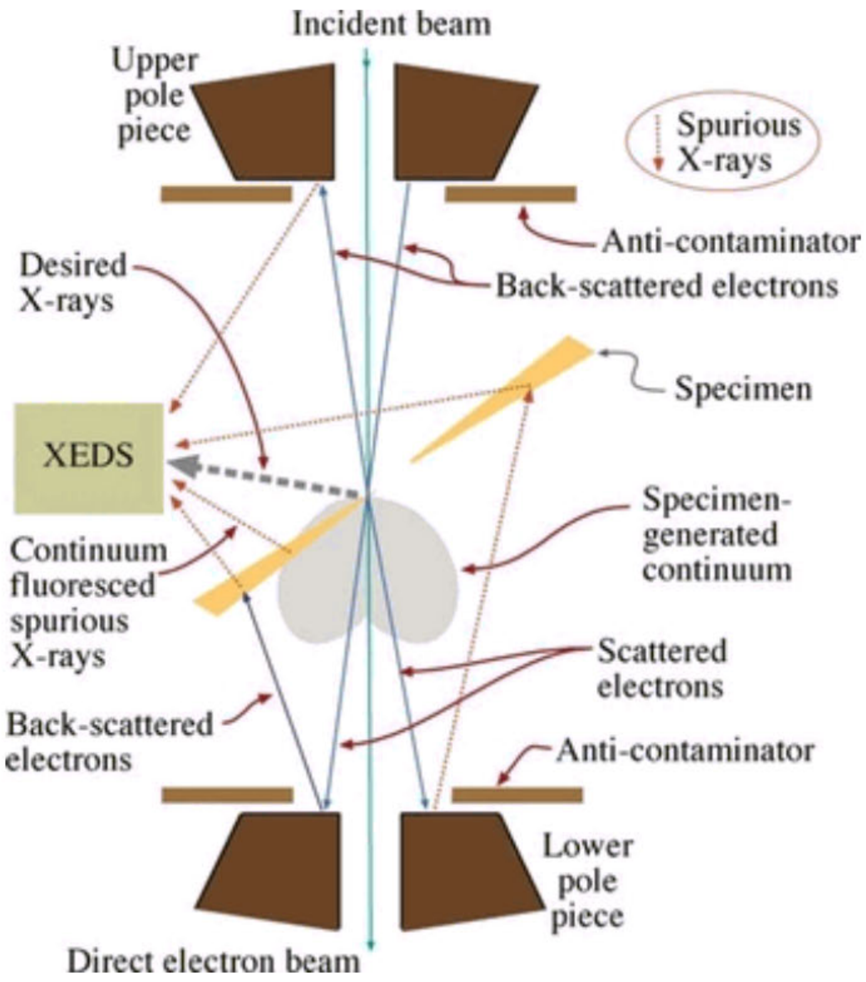


Detective quantum efficiency (DQE)

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



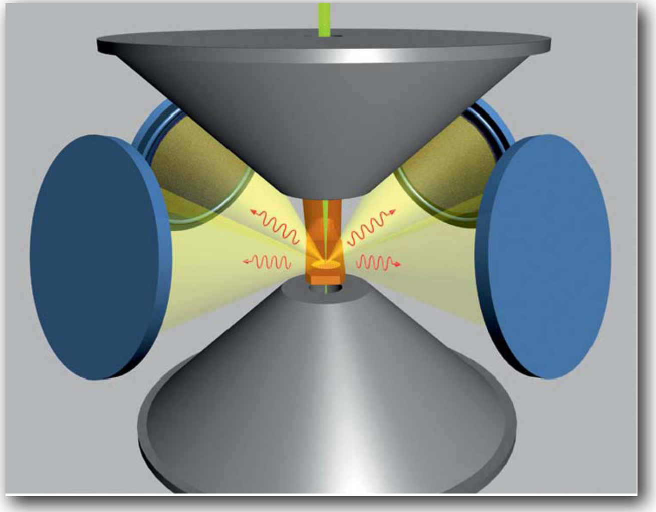
Detection geometry

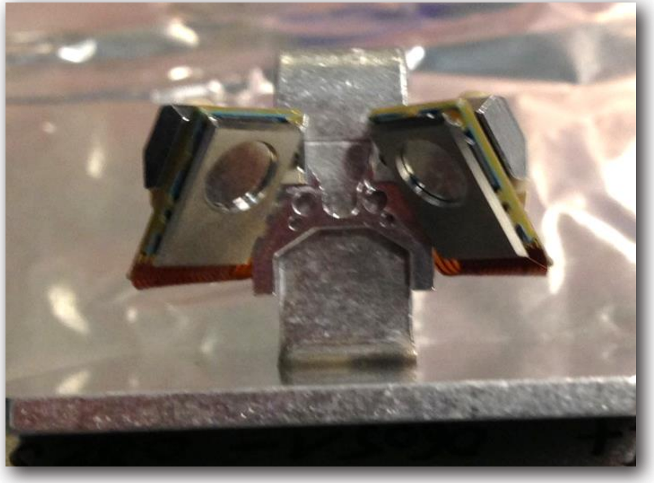


- Take care of spurious artefact X-ray peaks

Detection geometry

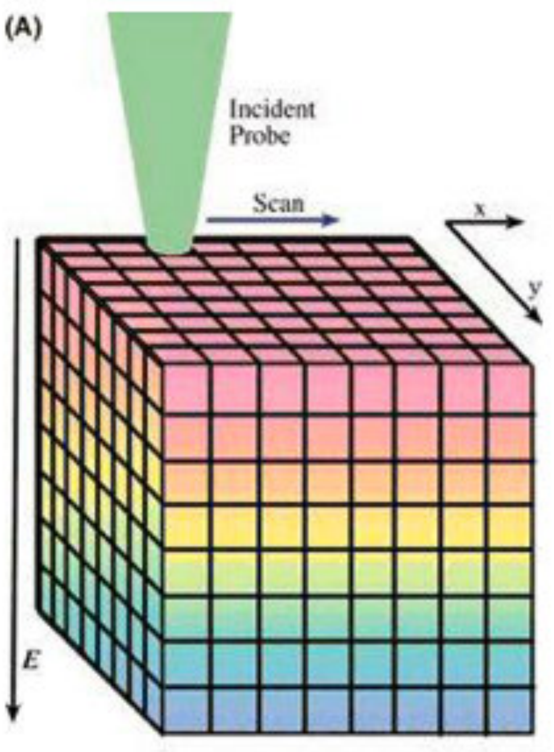
- New standard is to use multiple SDDs to increase solid angle of collection and hence detection efficiency
- For example: “Super-X” on Osiris, Titan with 4 quadrants giving ~1 Sr solid angle of collection
- State-of-the-art: Thermo Fisher Scientific Ultra with ~4 Sr

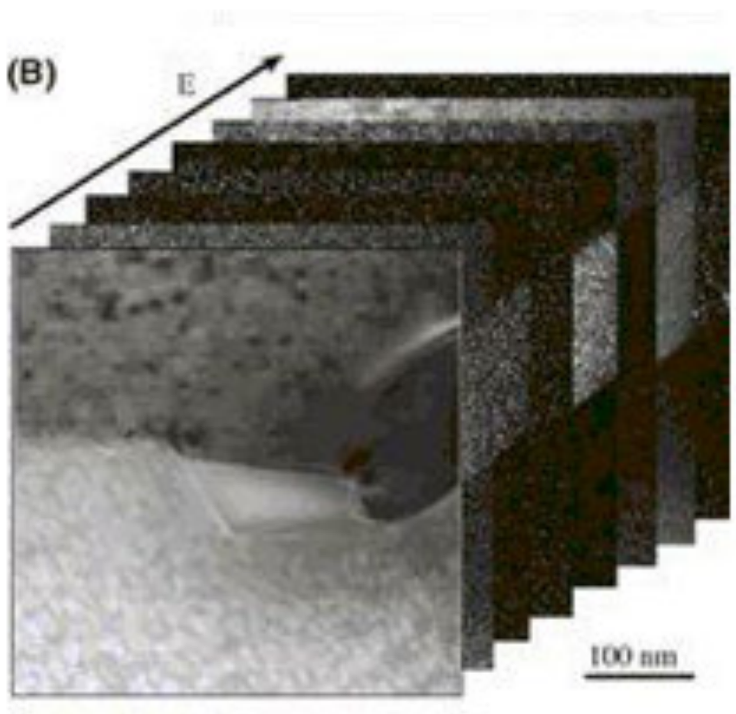




STEM-EDXS data-cube

- 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

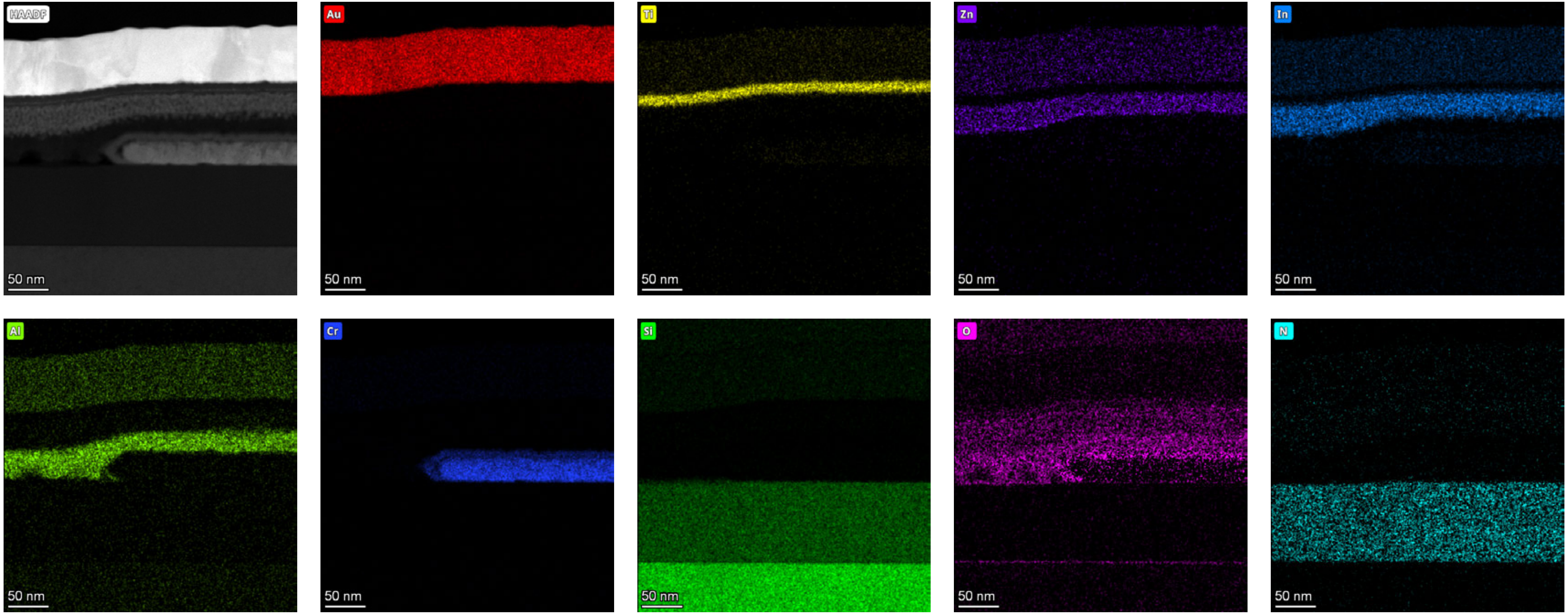




EPFL

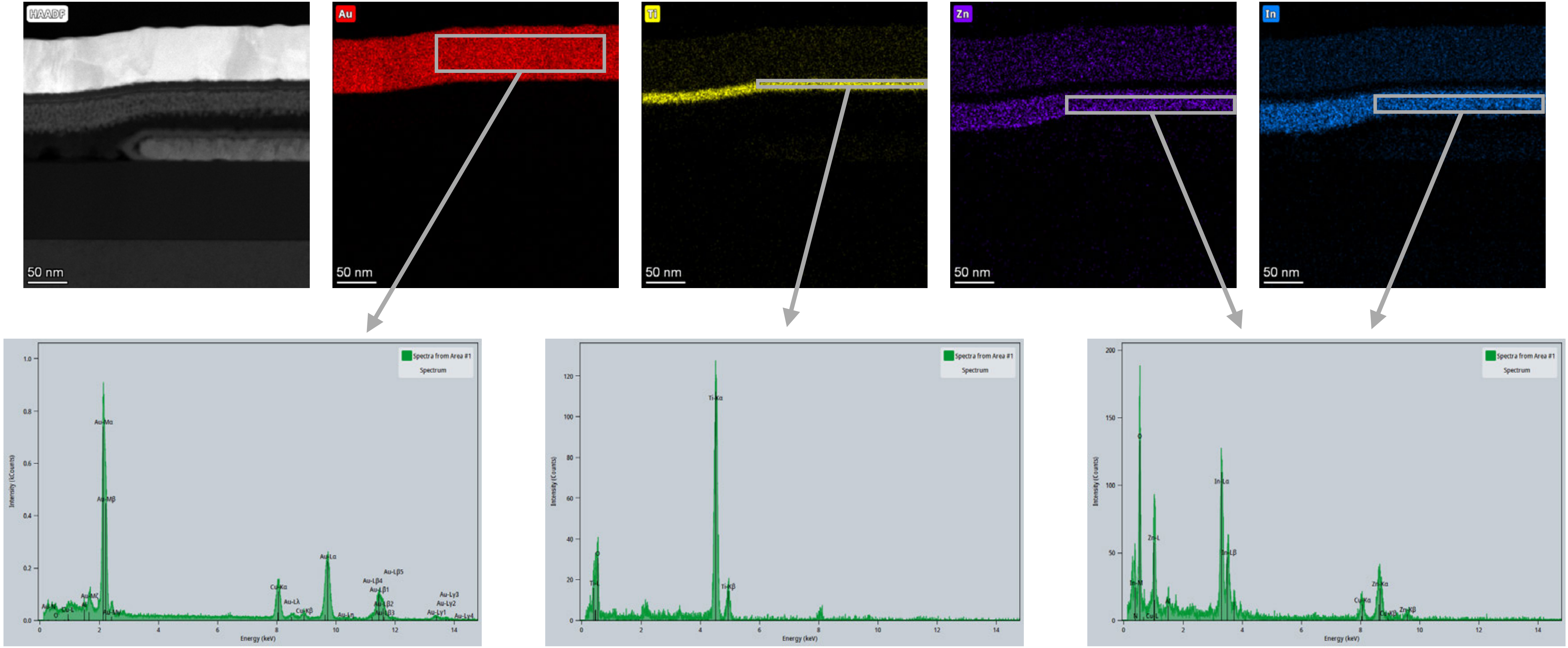
EDXS mapping: applications

- Multilayer sample – *net counts* maps



EDXS mapping: applications

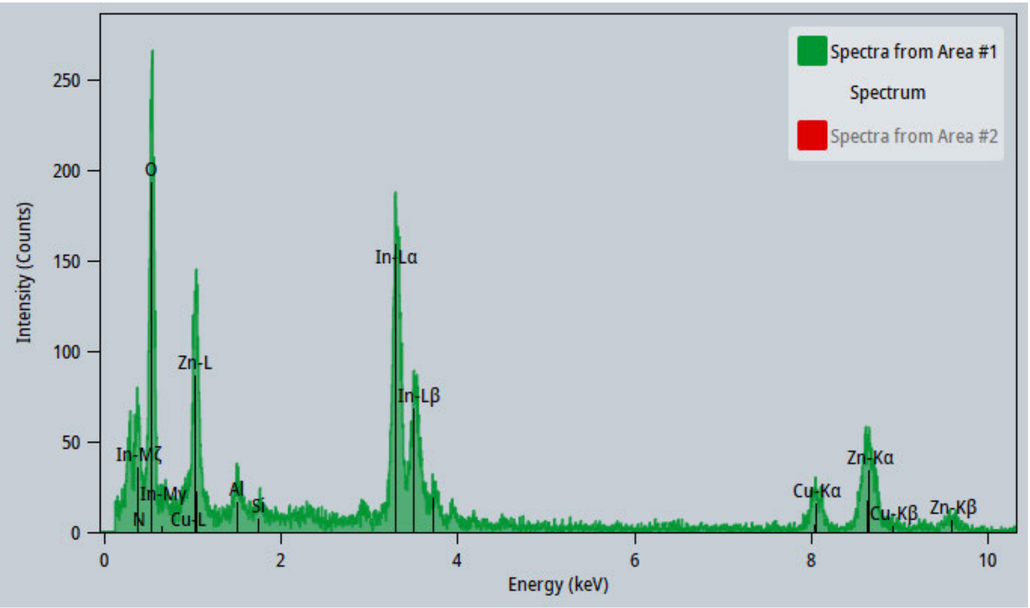
- Multilayer sample – *integrated counts* EDX spectra



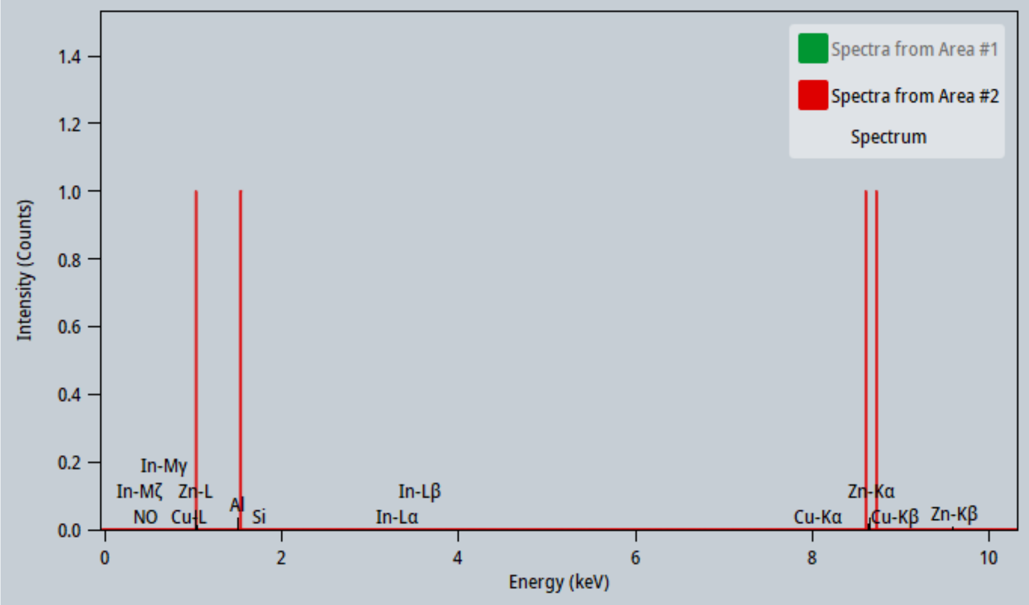
Why integrate counts across spatial ROI?

- In-Zn-O layer:

Integrated from 270 x 25 = 6’750 px²

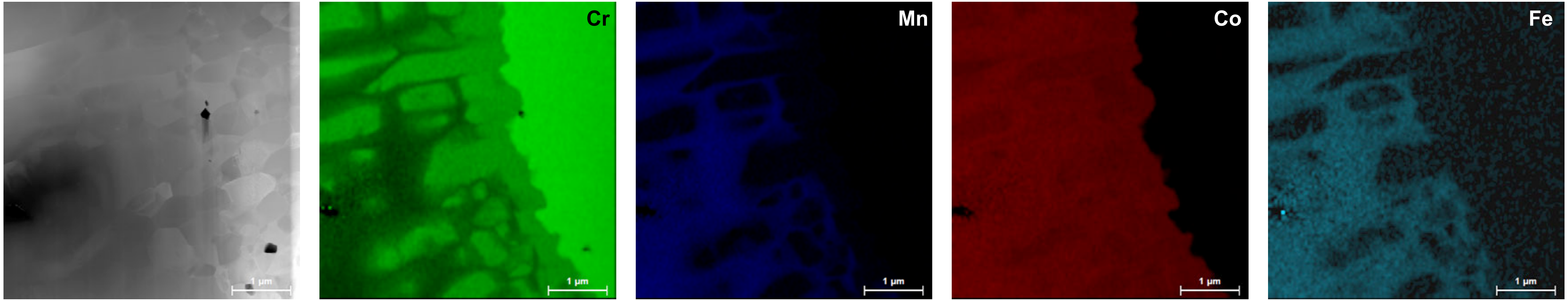


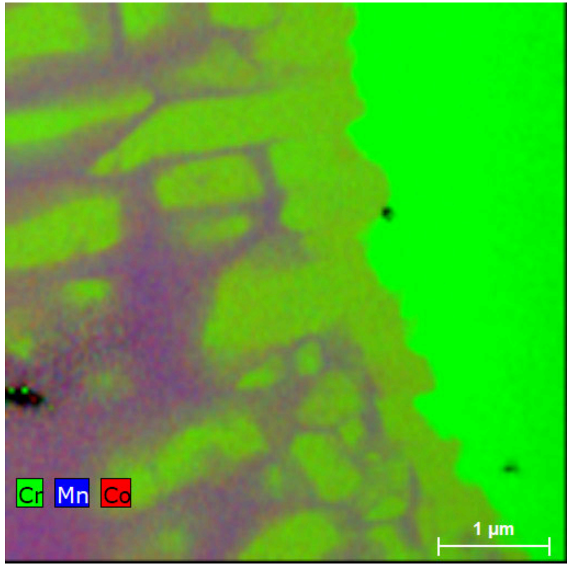
Single pixel spectrum



EDXS mapping: applications

- Fuel cell sample: Fe-doped $MnCo_2O_4$ spinel layer





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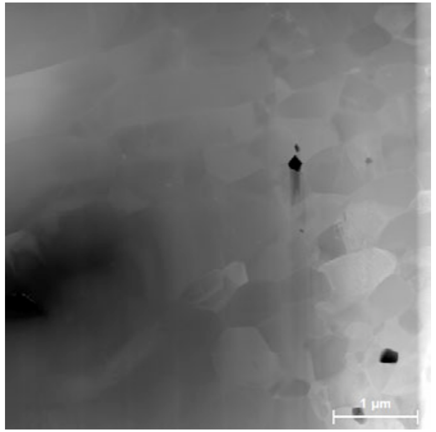

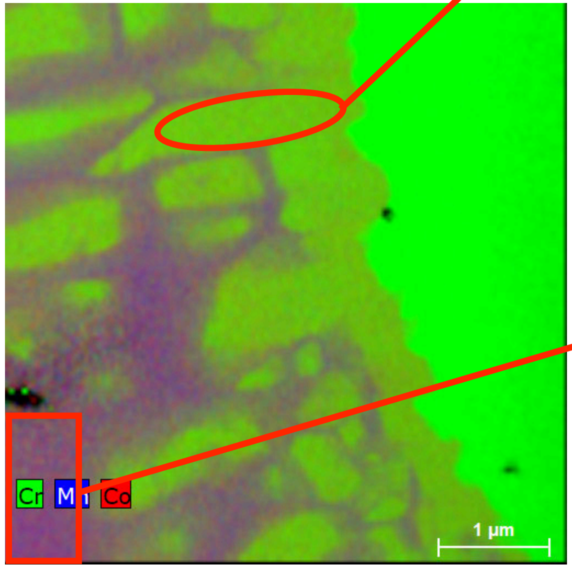

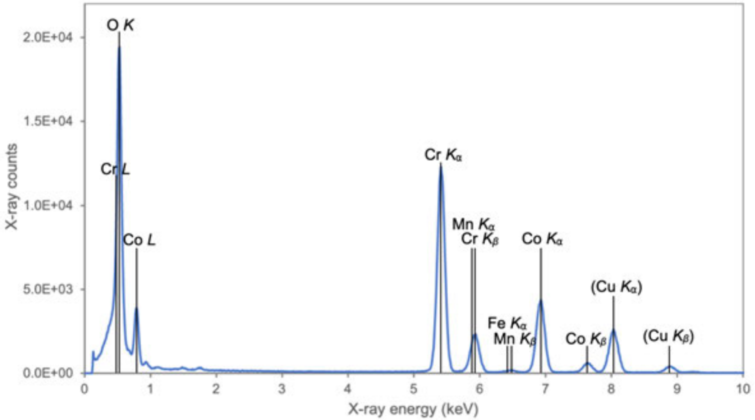

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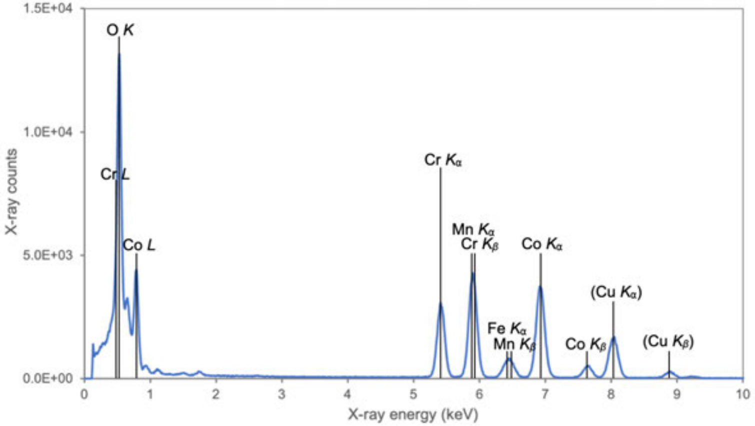
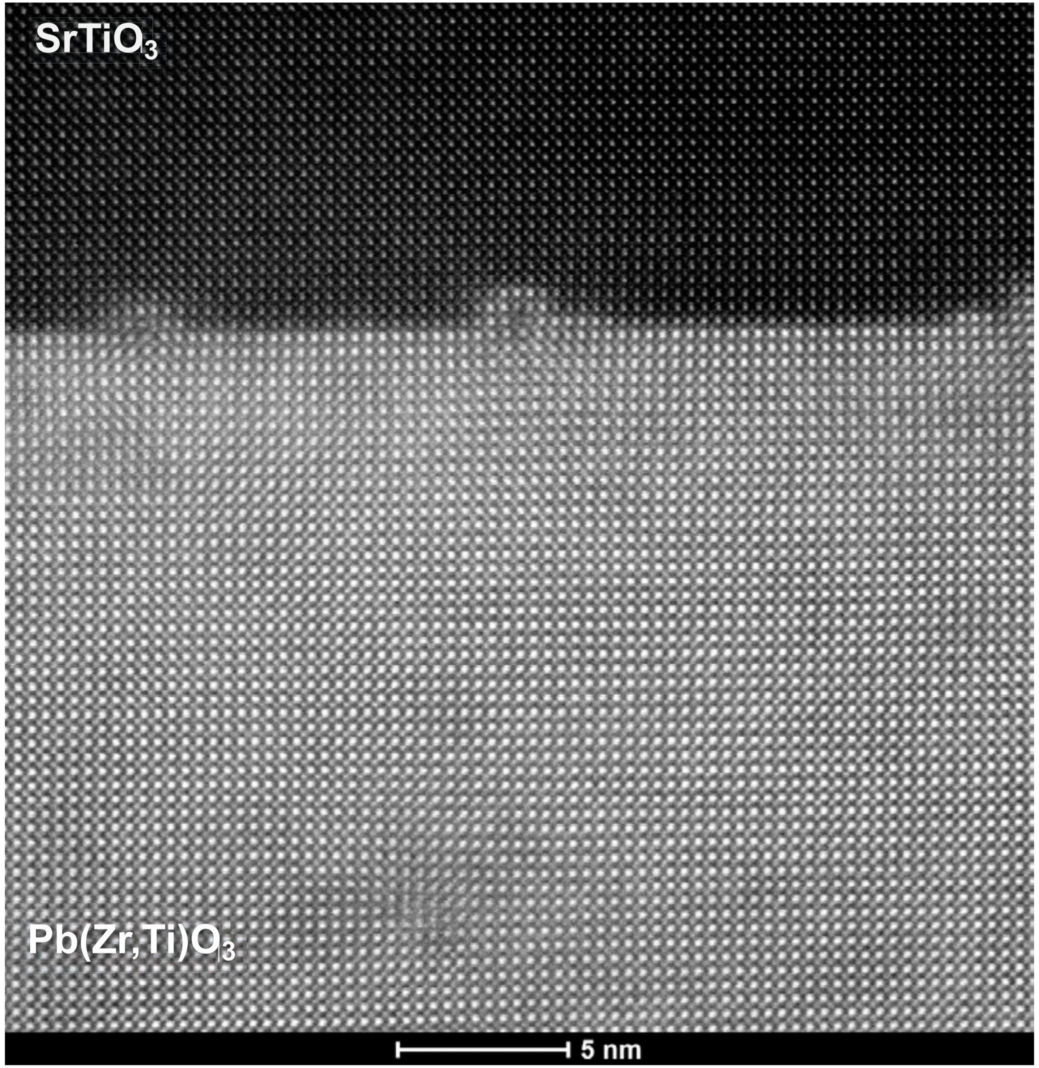


Element	Peak series	At. %
Cr	K	12.5
Co	K	18.3
Mn	K	17.2
Fe	K	2.2
O	K	49.8

Atomic resolution EDXS with Cs-STEM

- Sample of $Pb(Zr,Ti)O_3$ on $SrTiO_3$



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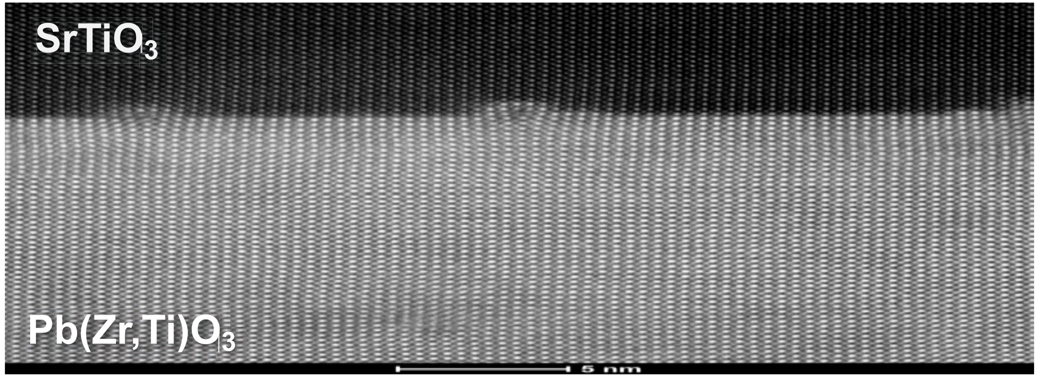

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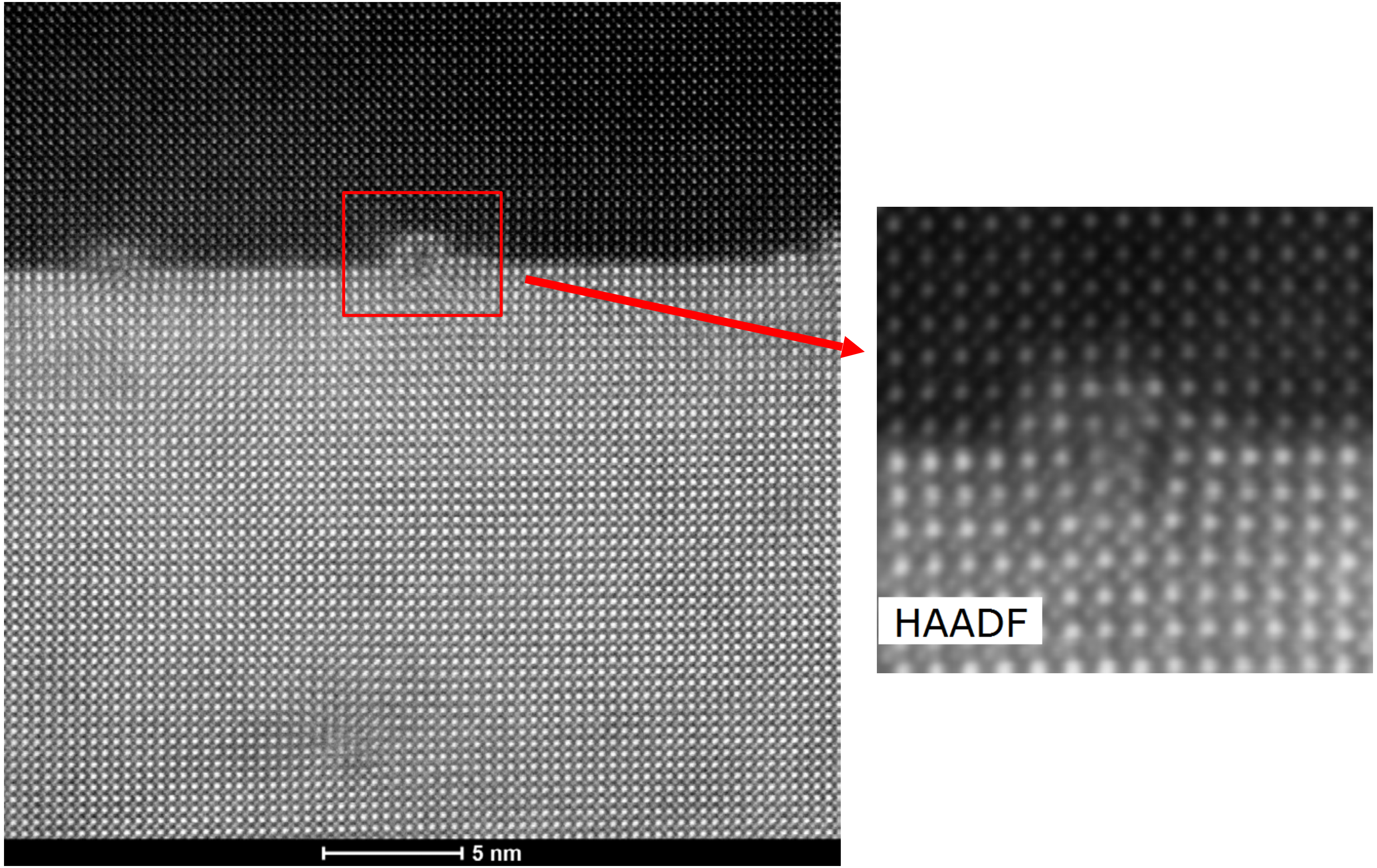

Atomic resolution EDXS with Cs-STEM

- Sample of $Pb(Zr,Ti)O_3$ on $SrTiO_3$ – atomic resolution elemental mapping