Materials design & selection for Circular Economy

Module 3: Molecules and materials chemico-physical characterisation

Academic year 2026/2027

Lecturer: **Paolo Dolcet**

Electron microscopy: history

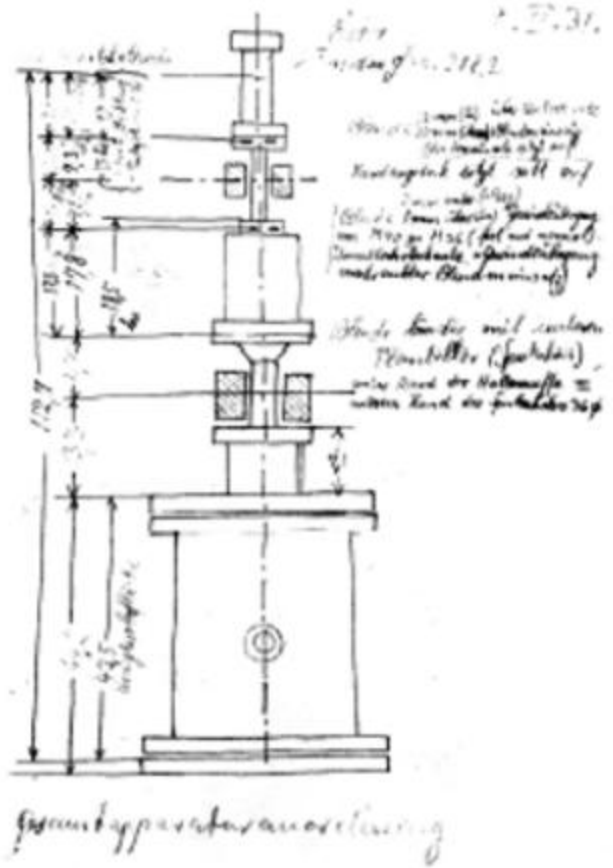
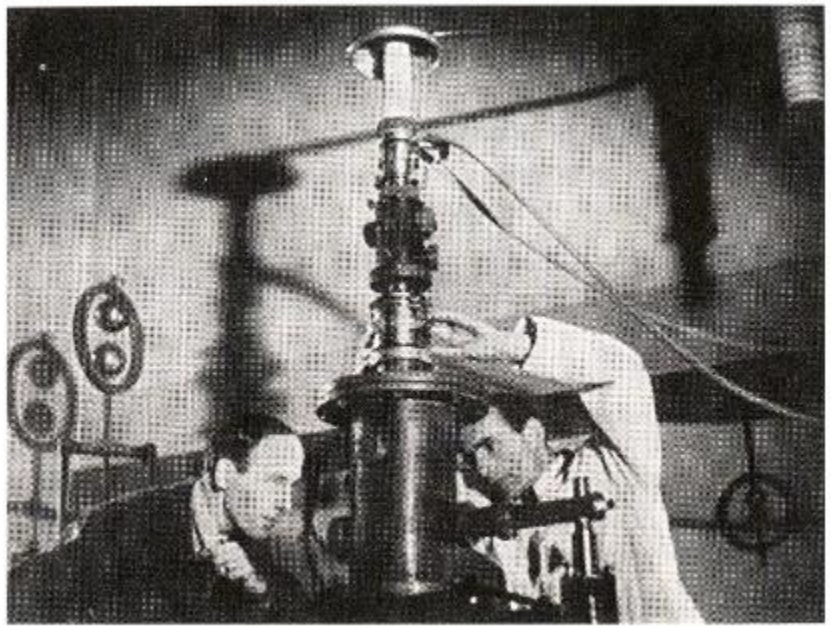


FIG. 2. Sketch by the author (9 March 1931) of the cathode-ray tube for testing one-stage and two-stage electron-optical imaging by means of two magnetic electron lenses (electron microscope). From Knoll and Ruska (1932a).



Ruska Knoll



The Nobel Prize in Physics in 1986 was divided:

- Ernst Ruska "*for fundamental work in e- optics and for the design of the first e- microscope*"
- Gerd Binning & Heinrich Rohrer "*for their design of the scanning tunnelling microscope"*

EM similarities

Transmission electron microscope

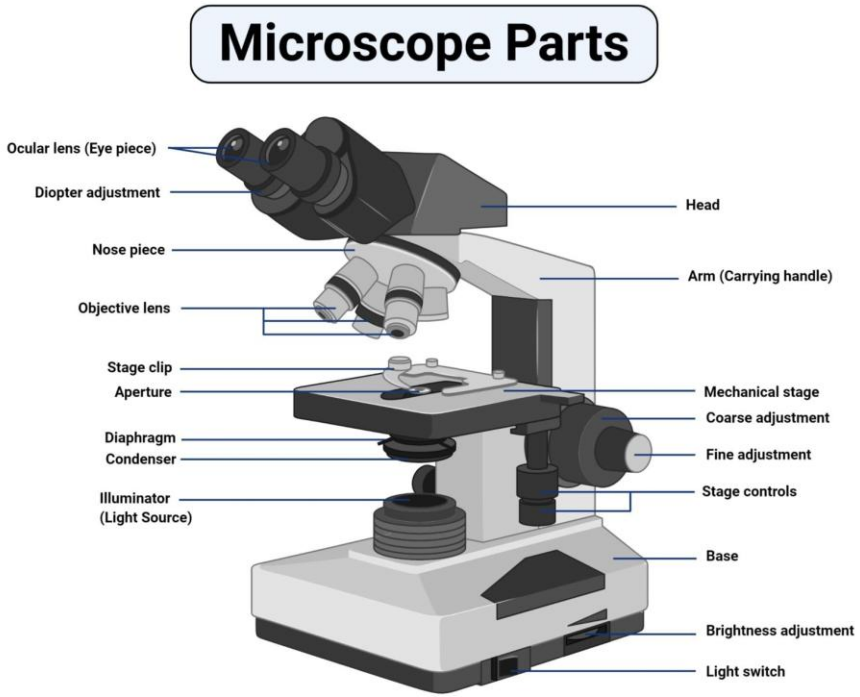
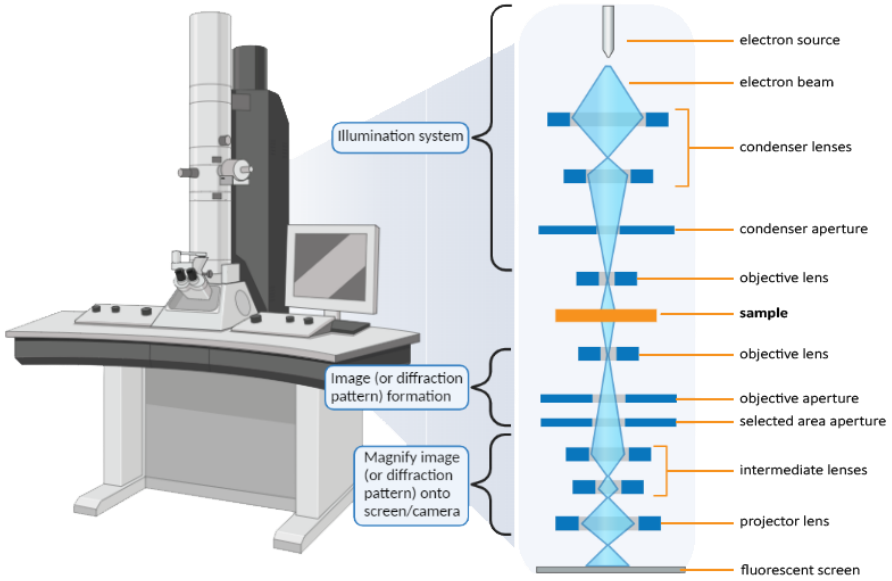


Figure: Parts of a microscope, Image Copyright © Sagar Aryal, www.microbenotes.com

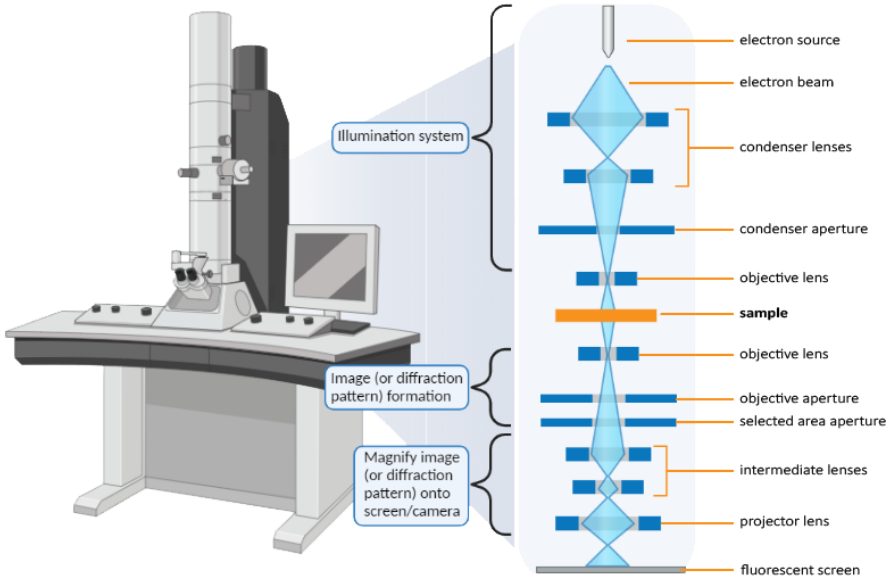
EM similarities

Transmission electron microscope

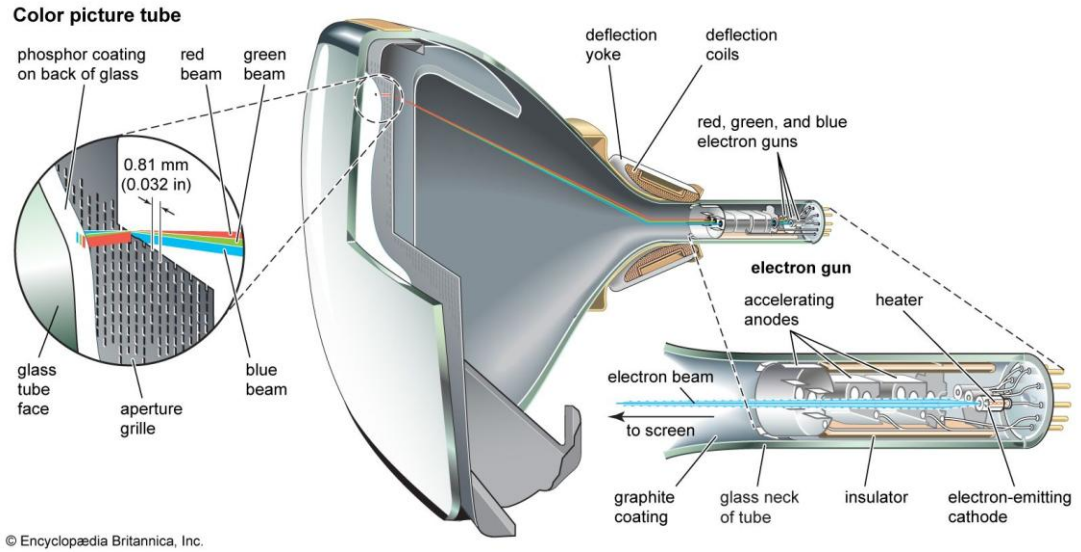


EM similarities

Transmission electron microscope

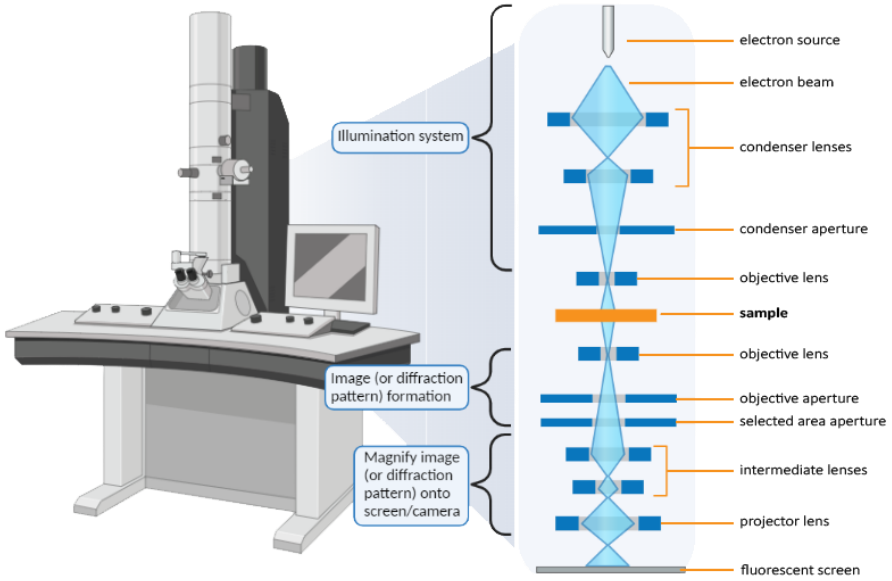


Scanning electron microscope

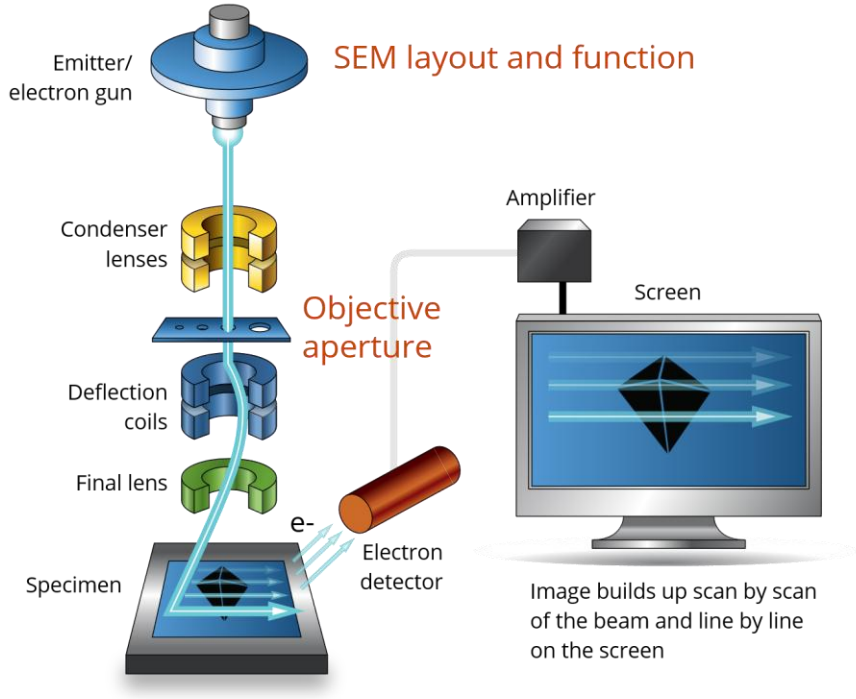


EM similarities

Transmission electron microscope



Scanning electron microscope



Why we need electron microscopy?

- **Resolution**: minimum distance that two point-source objects have to be in order to distinguish the two sources from each other

- Spatial resolution limit *d* (**Abbe diffraction limit**)

$$d = \frac{\lambda}{2NA}$$

NA = numerical aperture (ca. 1.5)

- For **green light**, λ=500 nm → *d*=167 nm

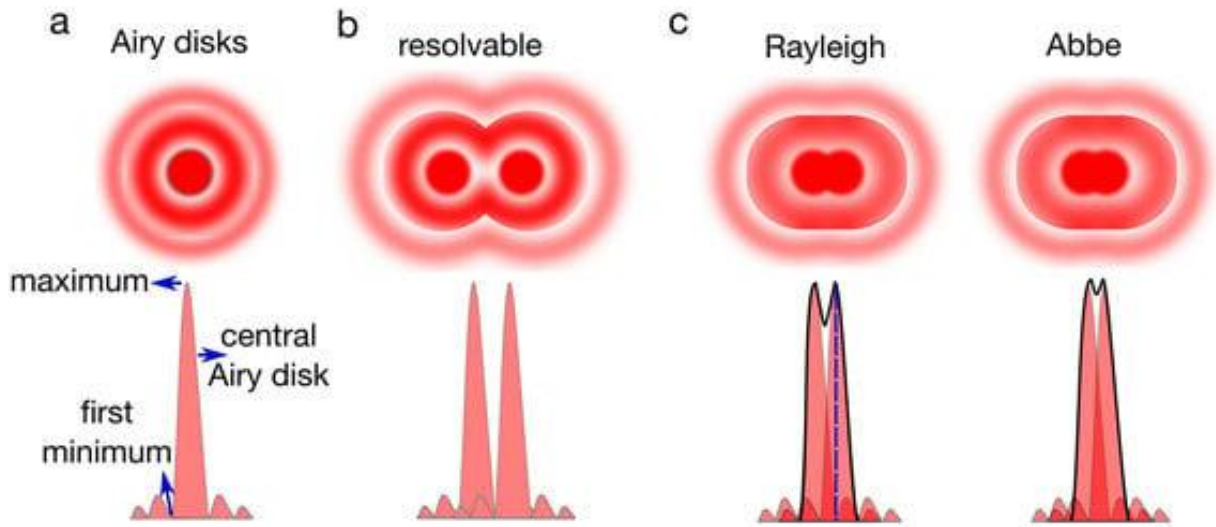
- This is a **theoretical value**! Polychromatic light source and lens design limit the resolution to 200 nm

The resolution problem

- Spatial resolution limit *d* (**Rayleigh criterion**)
  - $d = 0.61\frac{\lambda}{NA} = 0.61\frac{\lambda}{n \sin \alpha}$

n = refractive index of medium (air, vacuum)
α = semiangle of collection

- For **green light**, λ=500 nm → *d*=203 nm
- More useful from a practical point of view



J. Phys.: Condens. Matter **29** 273001**DOI** 10.1088/1361-648X/aa7185

How can we go beyond the visible light diffraction limit?

The solution to the resolution problem

- In case of an e^--beam

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2meV}}$$

- If expressed in pm (pm = 10^{-12} m):

$$\lambda = \frac{1.23\times10^3}{\sqrt{V}} \cong \frac{1.23\times10^3}{\sqrt{V(1+9.78\times10^{-7}V)}}$$

Typically V = 1-100 kV

Relativistic correction

- What is the wavelength of an e^--beam accelerated at 10 kV? At 100 kV?

The electron wavelength can be tuned by the potential applied. So, by **tuning the wavelength**, one can **tune the ultimate resolution** of the electron microscope.

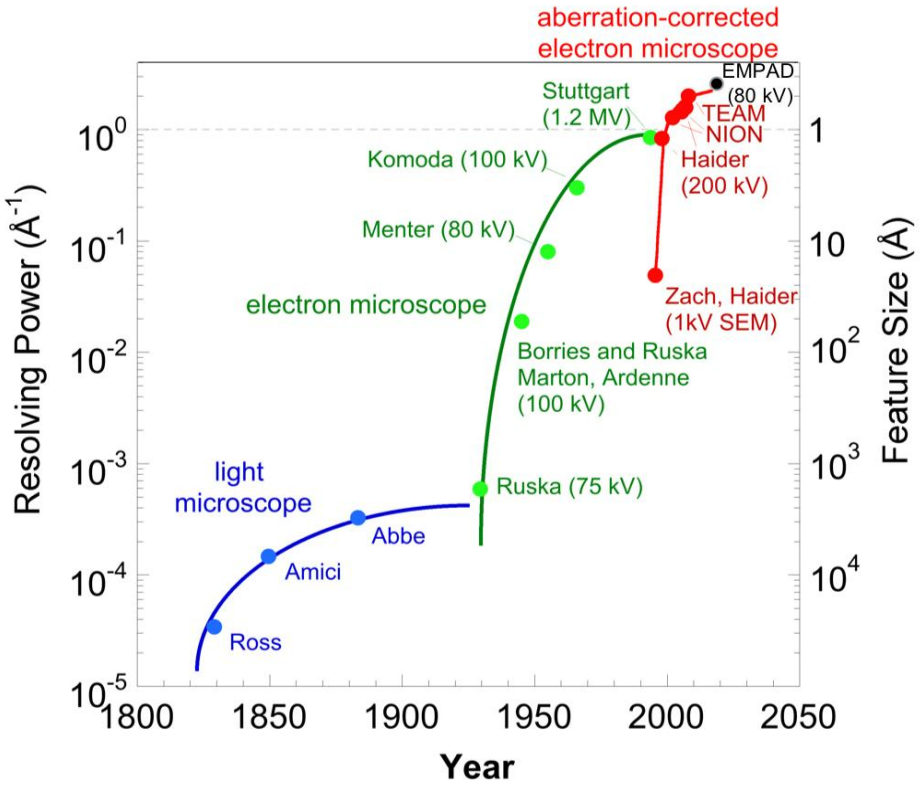
At 100 kV, in vac. → $d = 0.61\frac{3.7\ pm}{1*\sin(5*10^{-3}\ rad)}$ = **0.4 nm**

What is the limit of the resolution?

- If I increase the potential, I can improve without limit the resolution, correct?

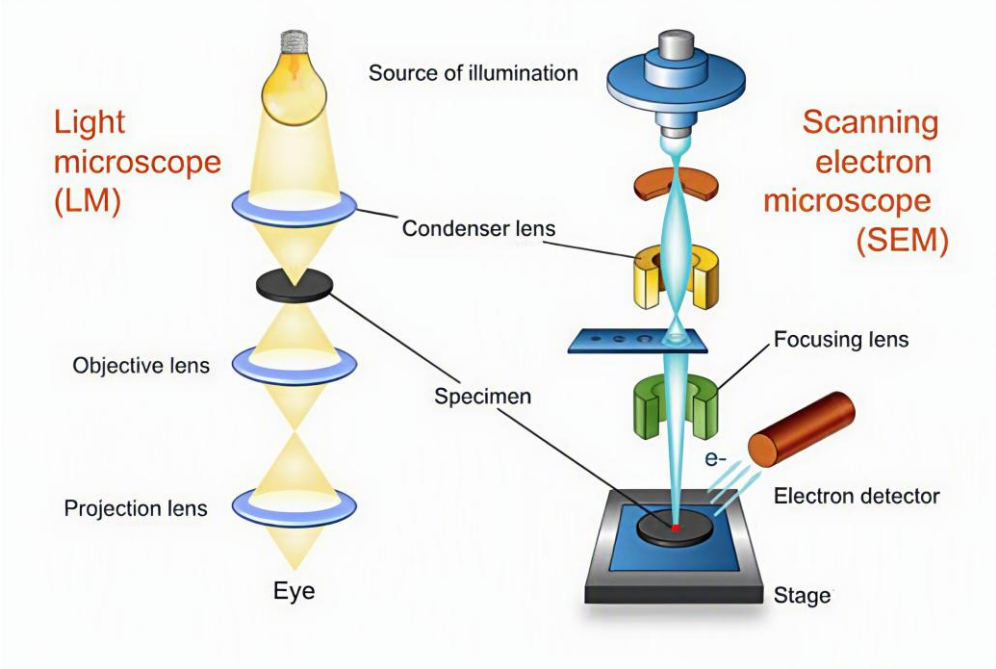
NO!

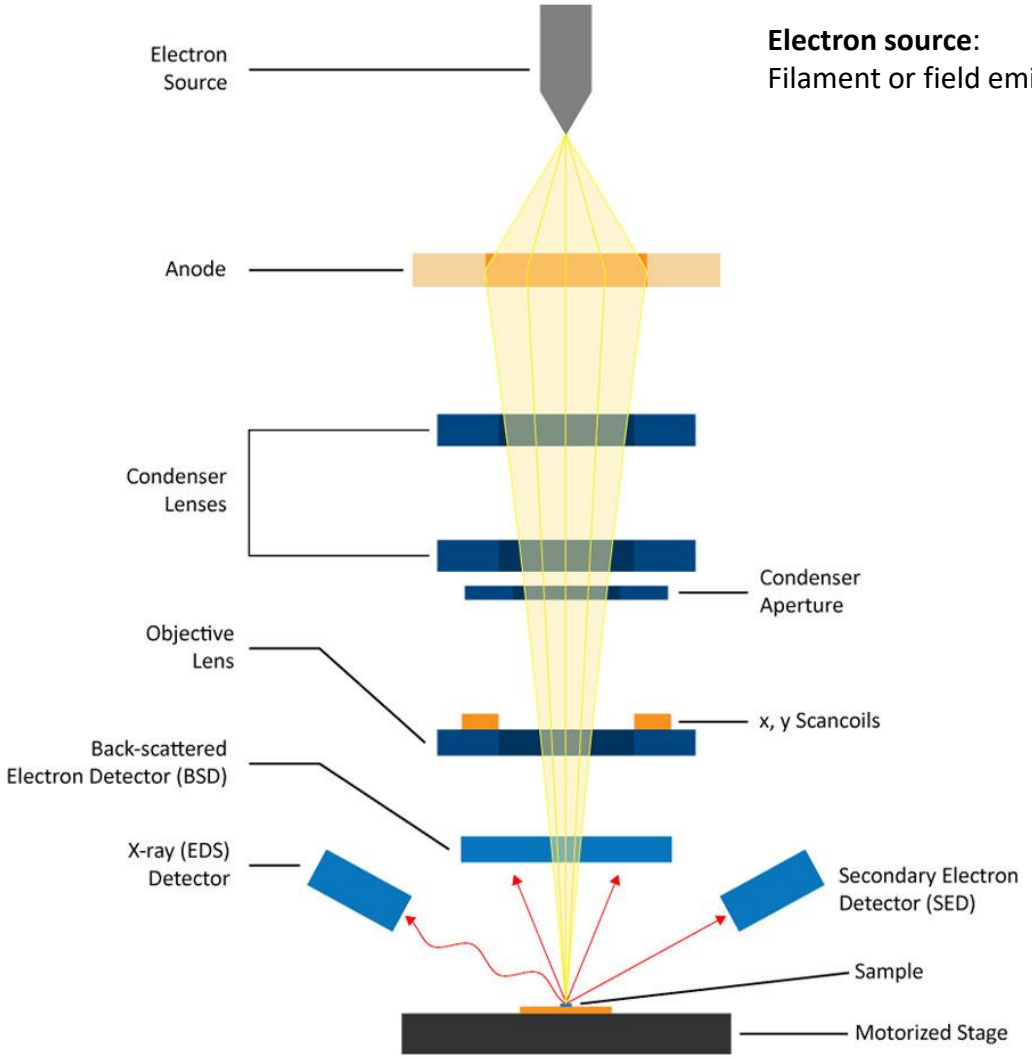
- The resolution is limited by the electromagnetic lenses
  - High V require stronger lenses
  - Stronger lenses requiring bigger instruments
  - High V causes more instability
  - High V causes more beam damage



https://communities.springernature.com/posts/smaller-than-the-space-between-atoms-the-technology-behind-the-highest-resolution-microscope-image

SEM working principle





Electron source:
Filament or field emission gun

https://myscope.training/SEM_Structure_of_an_SEM
https://www.nanoscience.com/techniques/scanning-electron-microscopy/

Electron sources

Thermoionic emitters

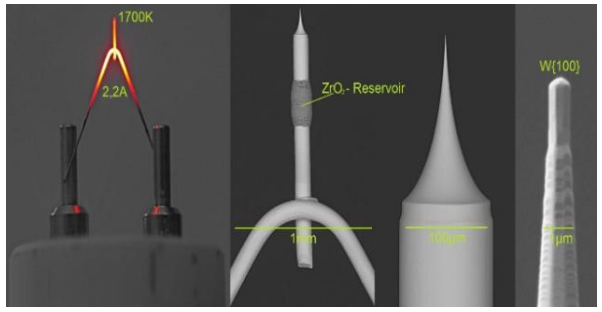
- Electrons are released by **resistive heating**
- If provided **E > work function** of emitter → e^- emission (10^9/s)
- Most common type of source
- **W filament**: cheap, work also at lower vacuum levels, limited lifetime and resolution
- **LaB_6 or CeB_6 crystal**: highly polished crystals, lower w.f., higher e^- emission than W, better resolution





Field emission guns

- Emitter is shaped into an extremely fine tip
- Application of a potential on the tip → e^- emission by electron tunneling
- **Schottky FEG** (ZrO_2-coated W): TE + FE, high brightness, high resolution, very stable
- **Cold FEG** (W single crystal): FE only, highest brightness and resolution (especially at low kV), require high vacuum and tip can be contaminated



Electron sources

TABLE 5.1 Characteristics of the Principal Electron Sources

	Units	Tungsten	LaB_6	Schottky FEG	Cold FEG
Work function, Φ	eV	4.5	2.4	3.0	4.5
Richardson's constant	A/m^2K^2	6×10^9	4×10^9		
Operating temperature	K	2700	1700	1700	300
Current density (at 100 kV)	A/m^2	5	10^2	10^5	10^6
Crossover size	nm	$> 10^5$	10^4	15	3
Brightness (at 100 kV)	A/m^2sr	10^{10}	5×10^{11}	5×10^{12}	10^{13}
Energy spread (at 100 kV)	eV	3	1.5	0.7	0.3
Emission current stability	%/hr	<1	<1	<1	5
Vacuum	Pa	10^{-2}	10^{-4}	10^{-6}	10^{-9}
Lifetime	hr	100	1000	>5000	>5000

Richardson's law (describing thermoionic emission)

$$J = AT^2 e^{-\frac{\Phi}{kT}}$$

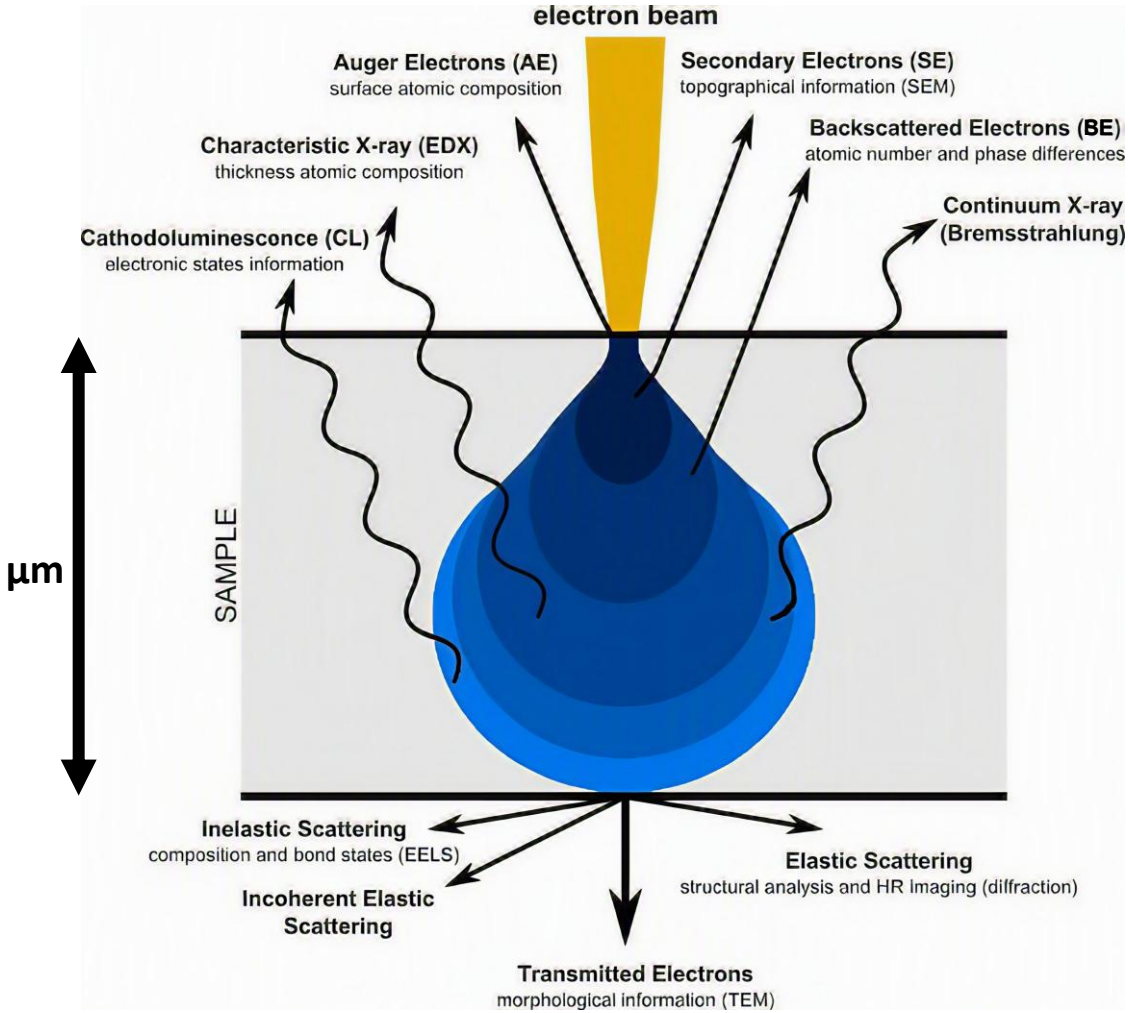
J = current density
A = Richardson's constant
Φ = work function

SEM need small, bright probes at low kV
TEM need stable, low E spread sources at high kV

SEM working principle

SEM operates in vacuum:

- Typically 10^{-4}-10^{-6} Pa
- For delicate, non-conductive samples: 10-3000 Pa



Secondary e$^-$: inelastic scattering or other interaction with E transfer. $E_{sec} < 50$ eV

Backscattered e$^-$: elastic scattering, angles > 90°

Characteristic X-rays: ionized atom relaxes, emitting X-rays

https://atriainnovation.com/en/blog/scanning-electron-microscopy-uses/

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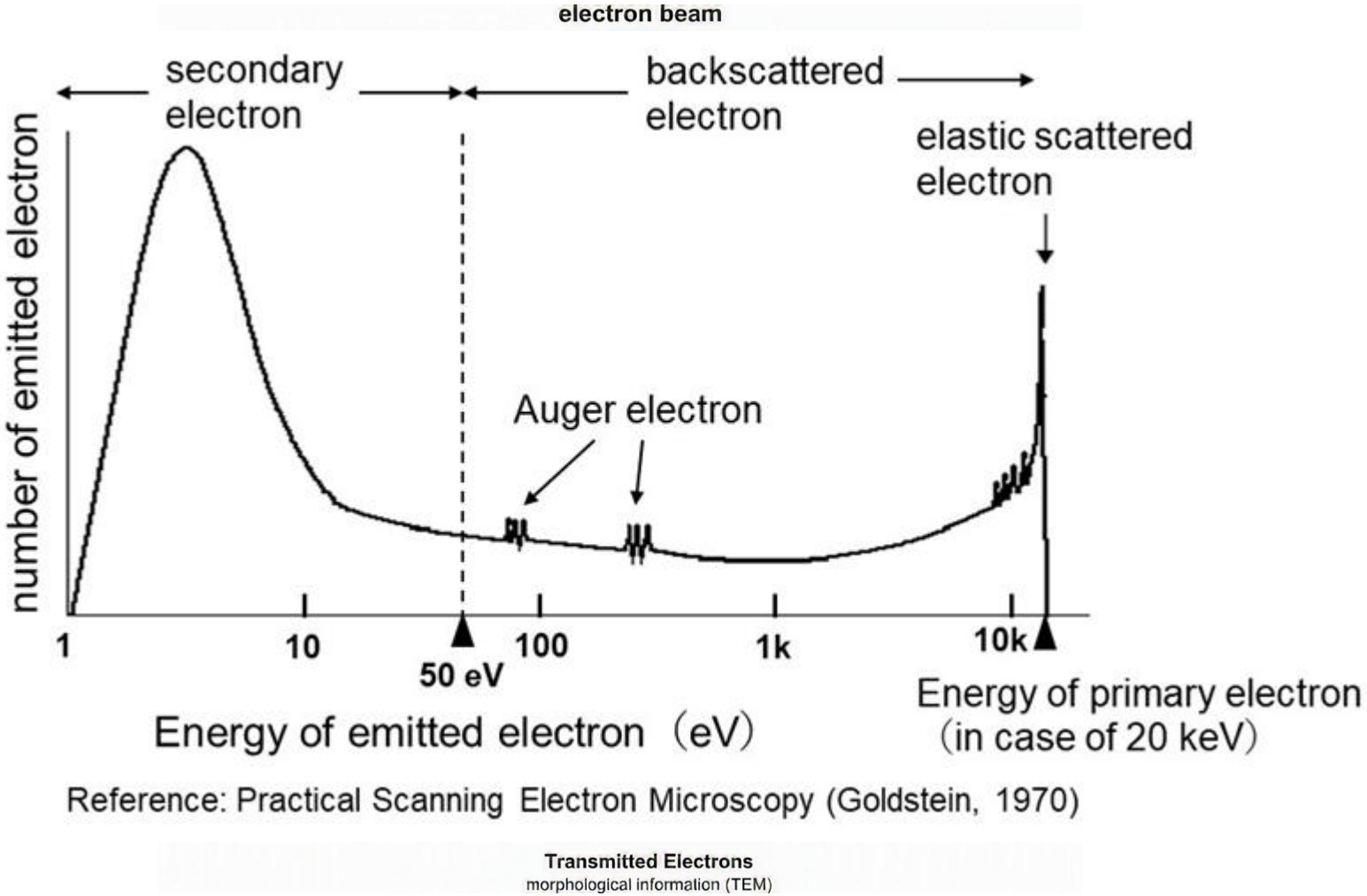

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: elastic scattering,

rays: ionized atom
X-rays

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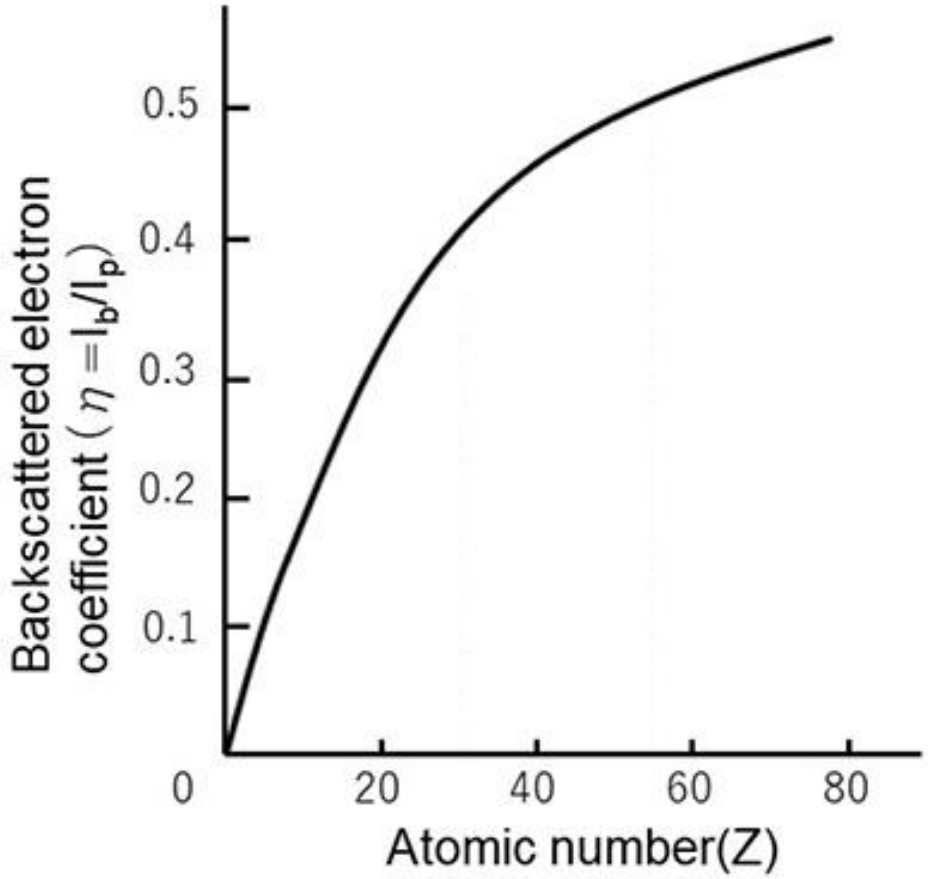

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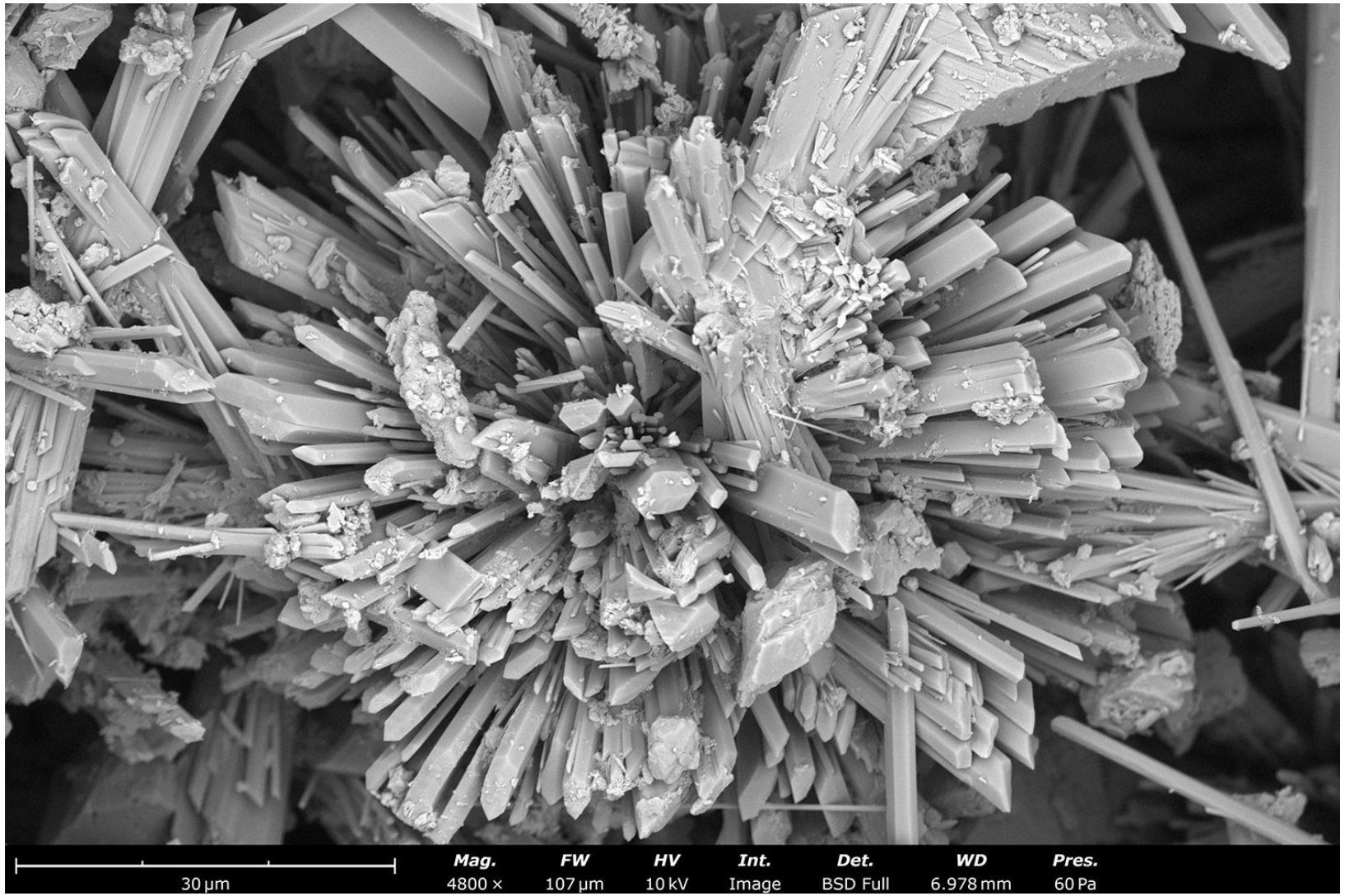
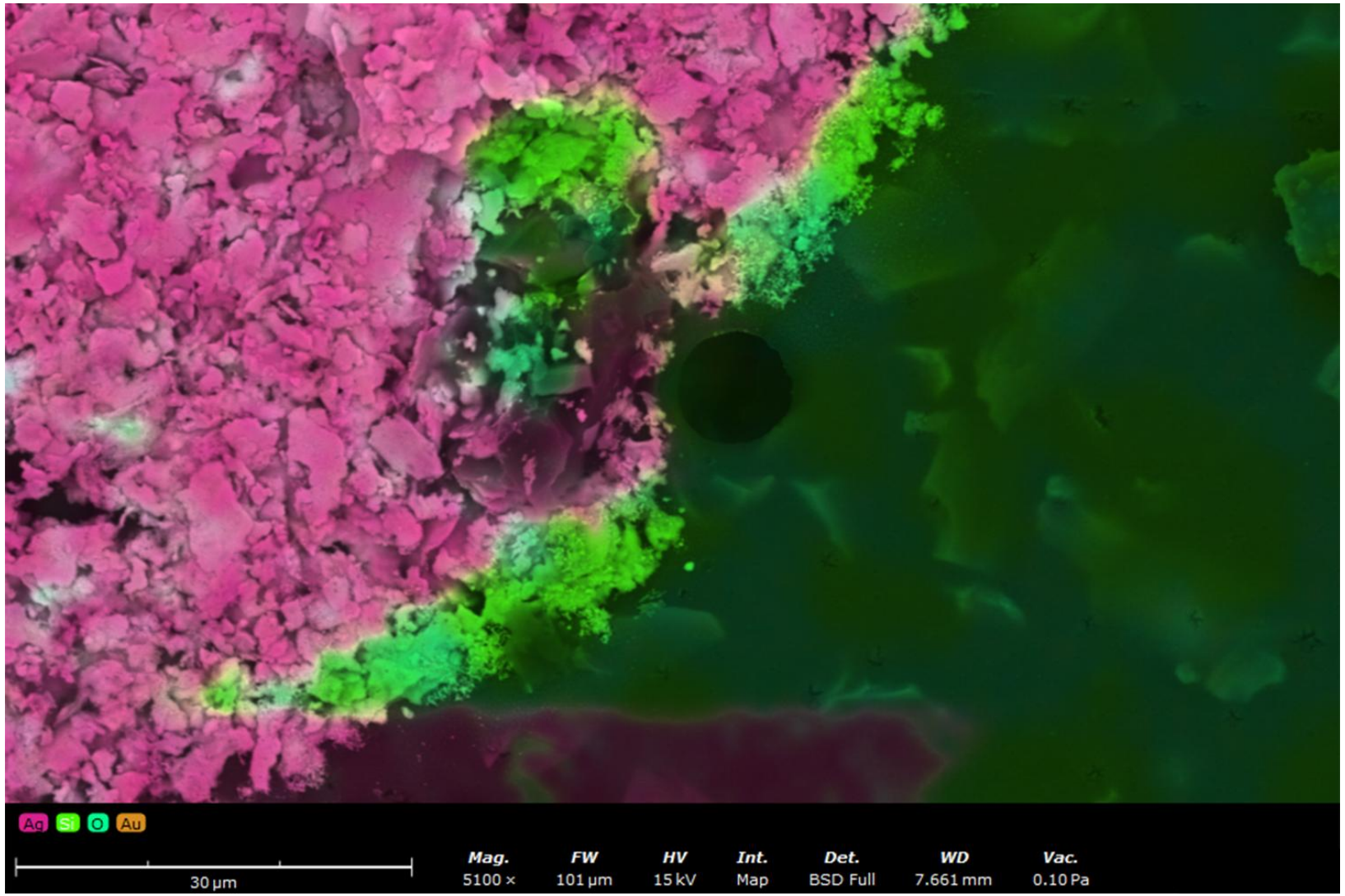
SEM examples



https://www.nanoscience.com/blogs/sem-characterization-of-recycled-materials-for-the-circular-economy

Secondary electrons-micrographs of plaster in recycled concretes

SEM examples



https://www.nanoscience.com/blogs/sem-characterization-of-recycled-materials-for-the-circular-economy

EDS map superimposed to a SEM image of a solder joint in e-waste

Automated mineralogy

- **Trace metal production** might become increasingly profitable
- Good understanding of their mineralogical and textural characterization is necessary
- Identification and quantification of trace minerals is difficult and requires the use of advanced micro-analytical techniques

  → **fast** and **reliable quantification** of the mineralogy and textures in a sample

Automated Scanning Electron Microscopy (ASEM)

Quantitative Evaluation of Mineralogy by a SCANning electron microscope (QEMSCAN®)

Mineral Liberation Analyzer (MLA)

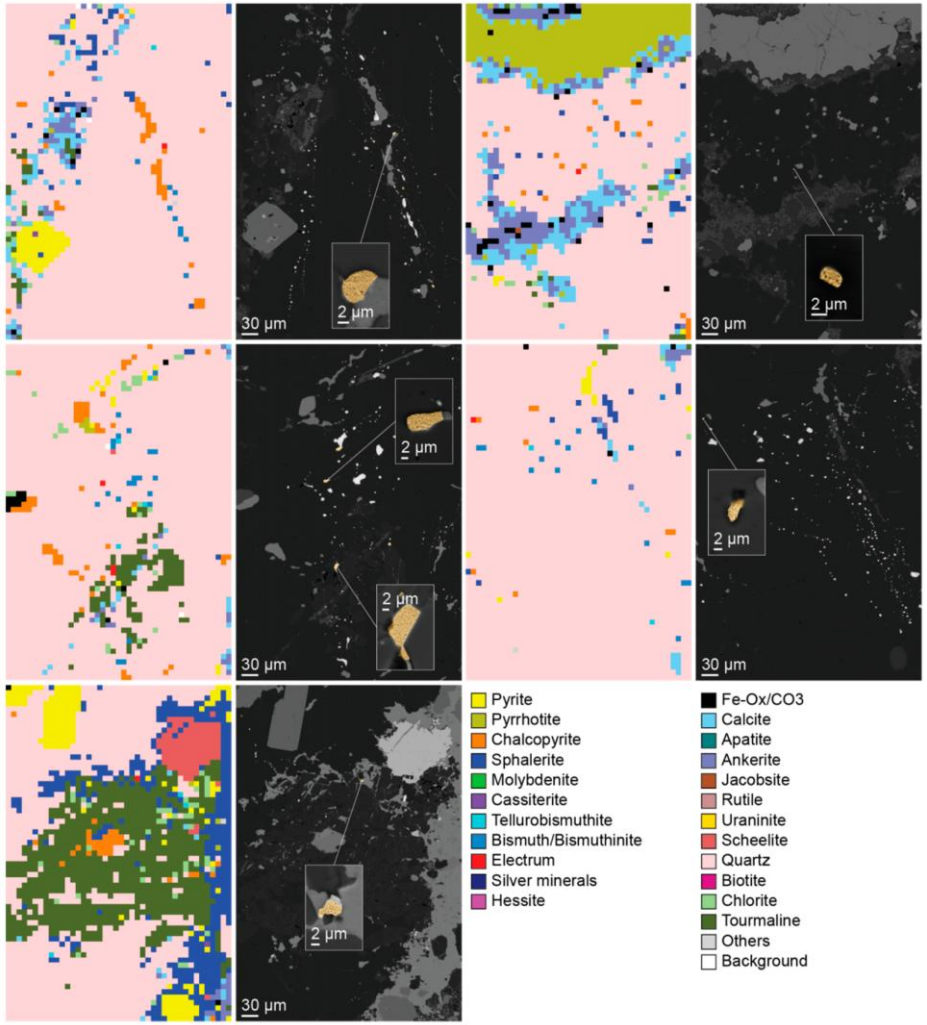
Automated mineralogy

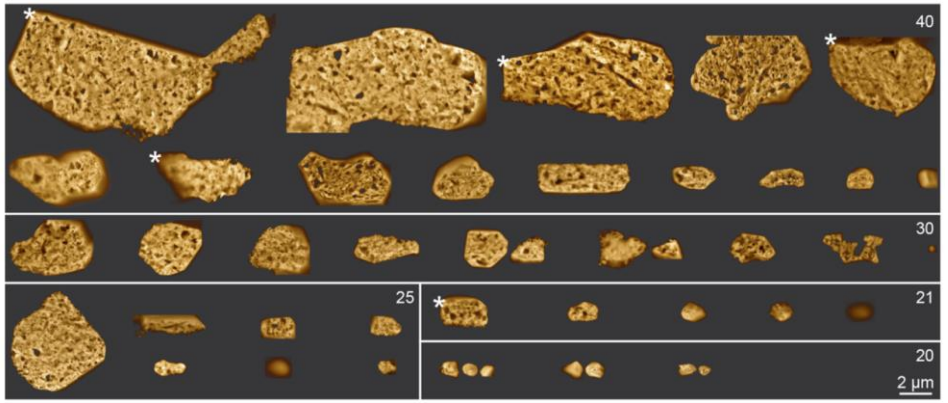
- Both QEMSCAN and MLA utilize backscattered electrons (BSE) and energy dispersive X-ray spectra (EDS)

- **QEMSCAN**
  - X-ray spectra used for mineral classification, against internal databases
  - BSE brightness is used to distinguish particles from the mounting media

- **MLA**
  - Particles first defined by BSE brightness
  - Subsequent confirmation by X-ray spectra

Automated mineralogy – the ore case

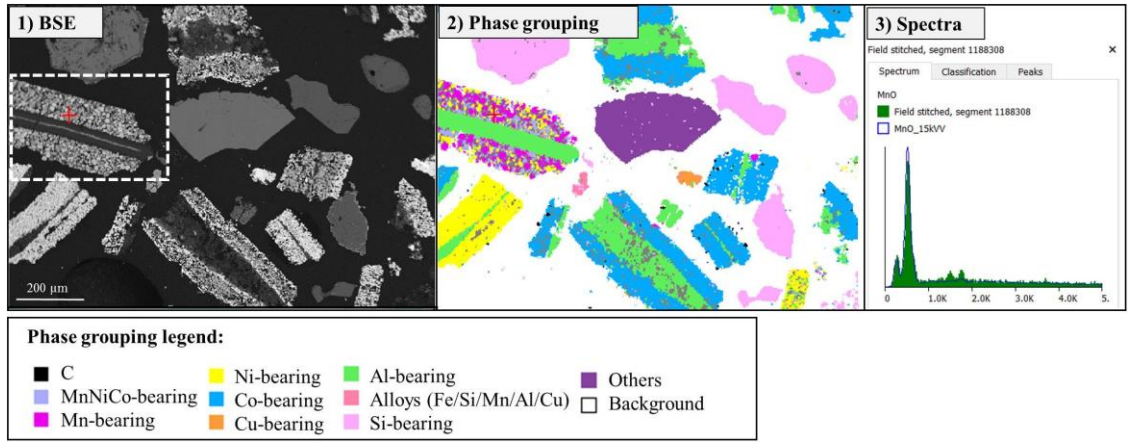




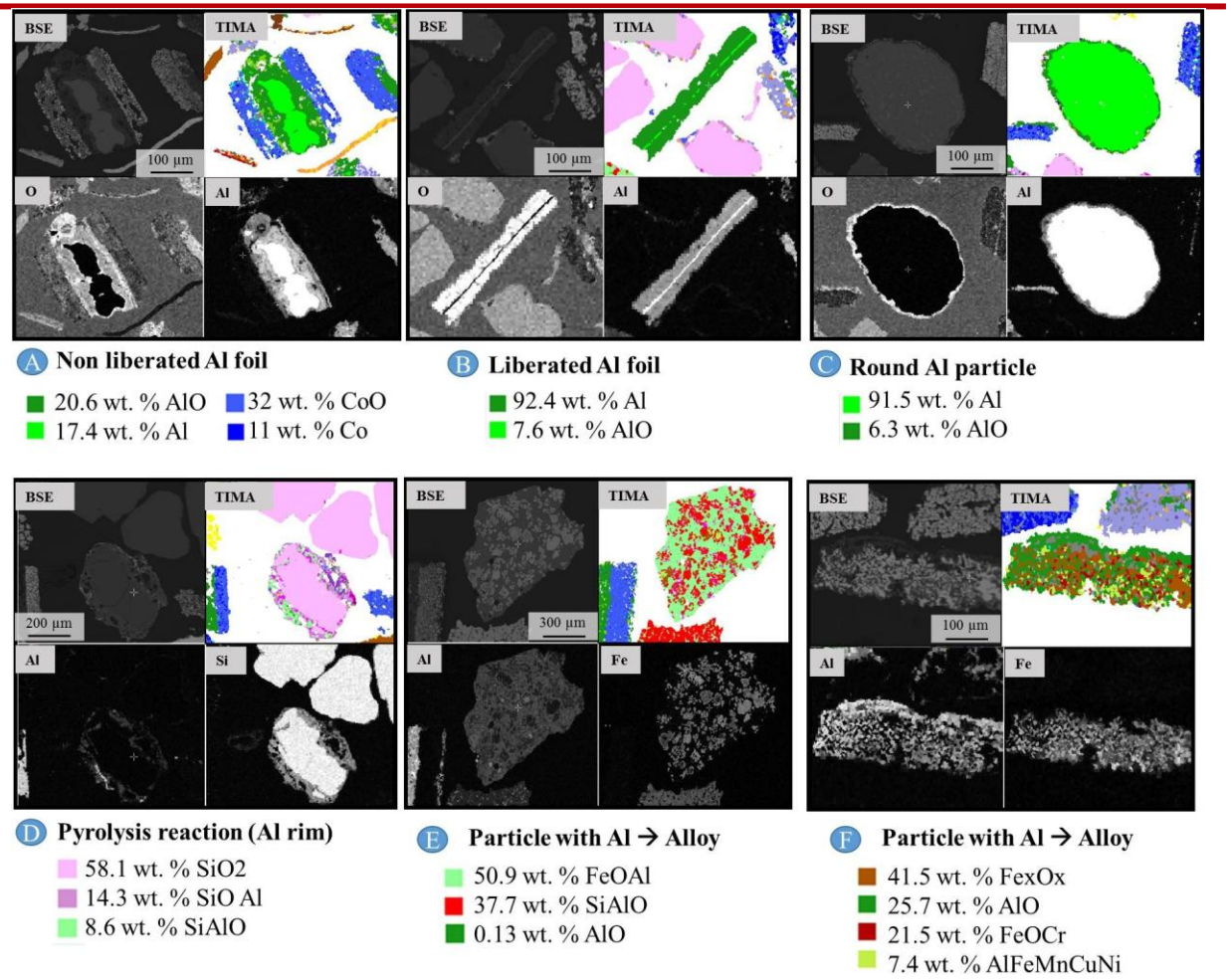
- Critical assessment of QEMSCAN protocols → difficult sample
- For very low content, automated metrology has to be considered as add-on
- Au and Ag grains less than 2 µm could be correctly identified

https://www.mdpi.com/2075-163X/9/7/440

Automated mineralogy – the spent Li ion batteries

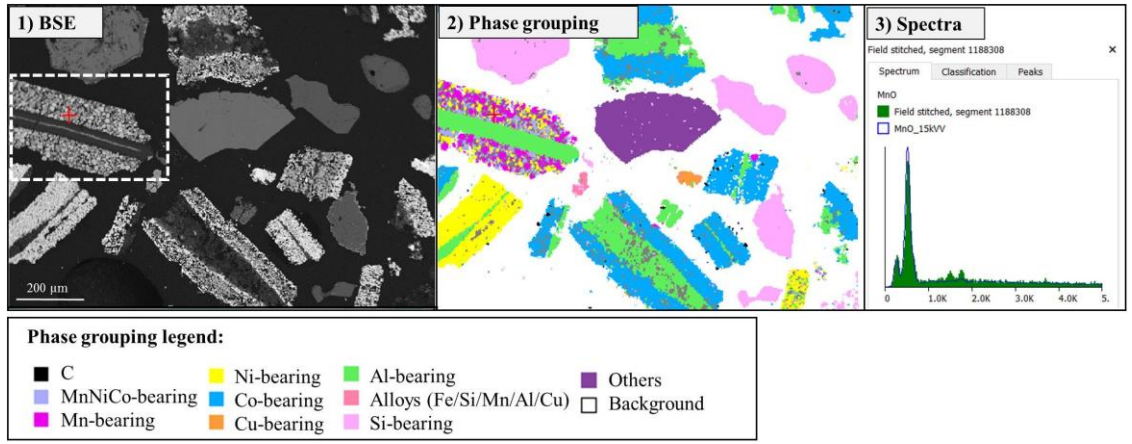


- Challenge: for secondary materials, reliable databases still lacking
- Identification of metal alloy particle with different sizes
- Selective liberation of Cu foils was achieved
- Graphite particles were individually liberated



Minerals Engineering,**169** (2021),106924,
https://doi.org/10.1016/j.mineng.2021.106924.

Automated mineralogy – the spent Li ion batteries



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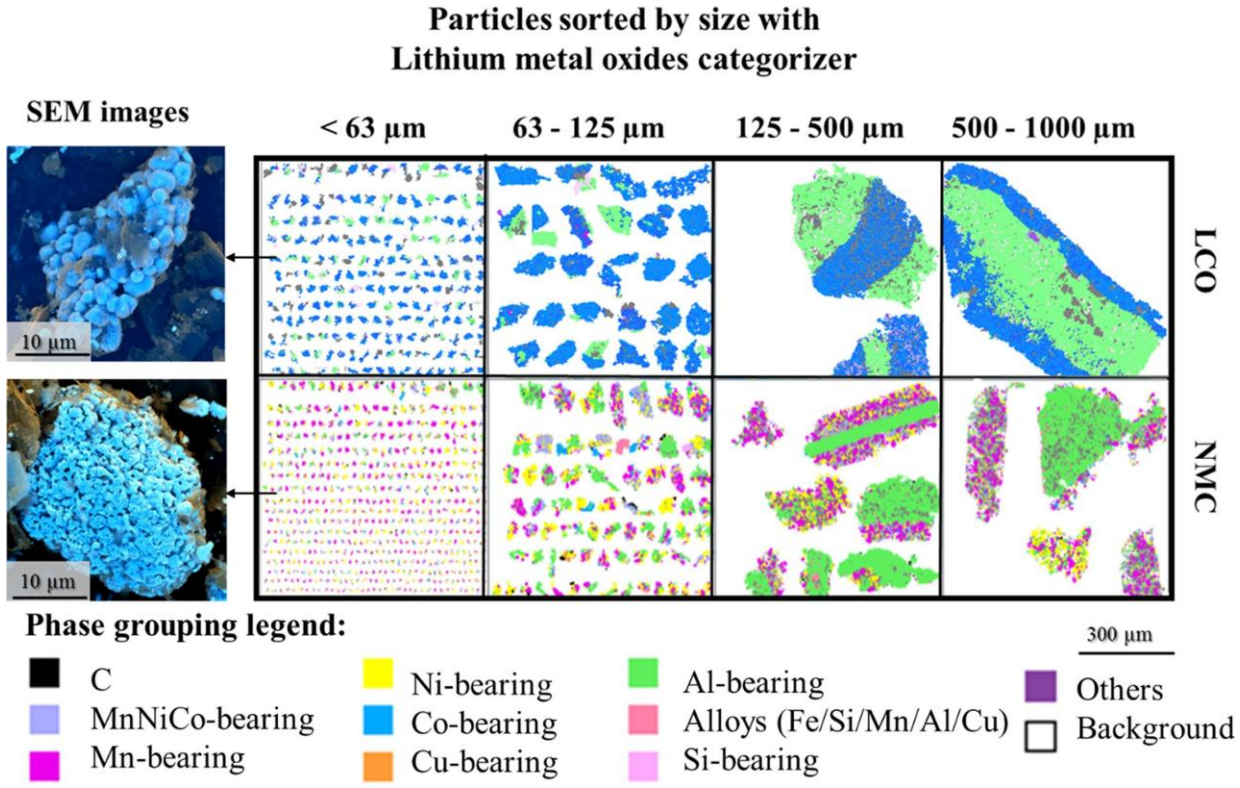

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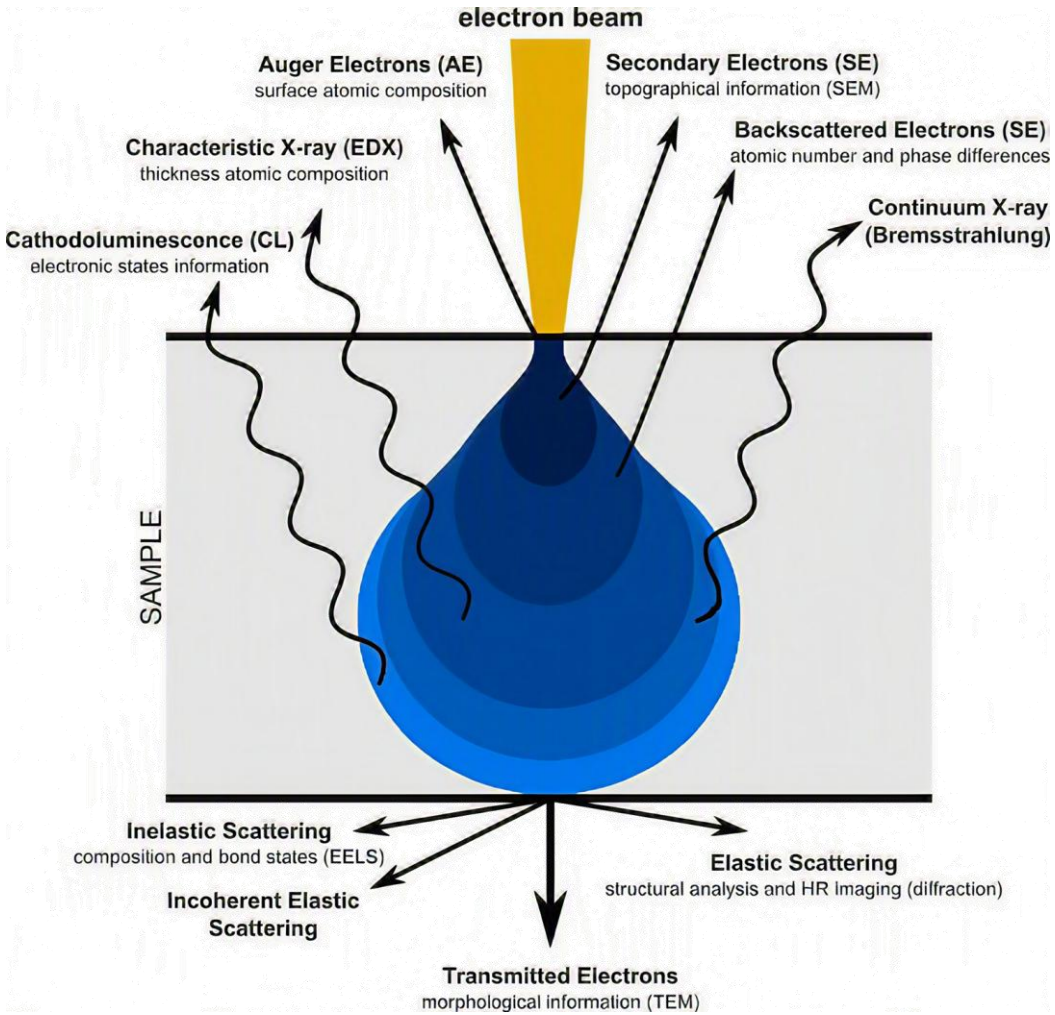
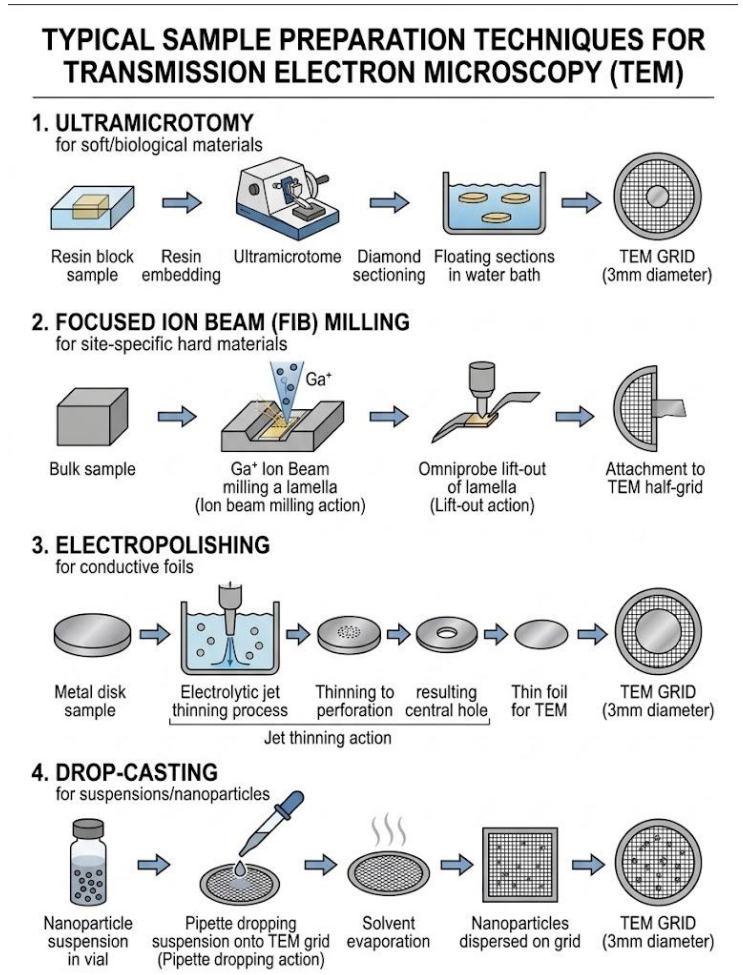
Transmission electron microscopy



- Many considerations about SEM are valid also for TEM
- TEM is more focused on nanoscale/atomic-scale information
  - Structure of nanoparticles
  - Defects in the crystal structure
  - Interfaces
- The information can arise from three different processes:
  - **Mass-thickness contrast**: scattering increases with atomic number and thickness
  - **Diffraction contrast**: e^- are deflected by crystalline structures
  - **Phase contrast**: interference between transmitted (unscattered) beam and scattered beams
- These three processes coexist, but depending on sample/imaging condition one is dominating

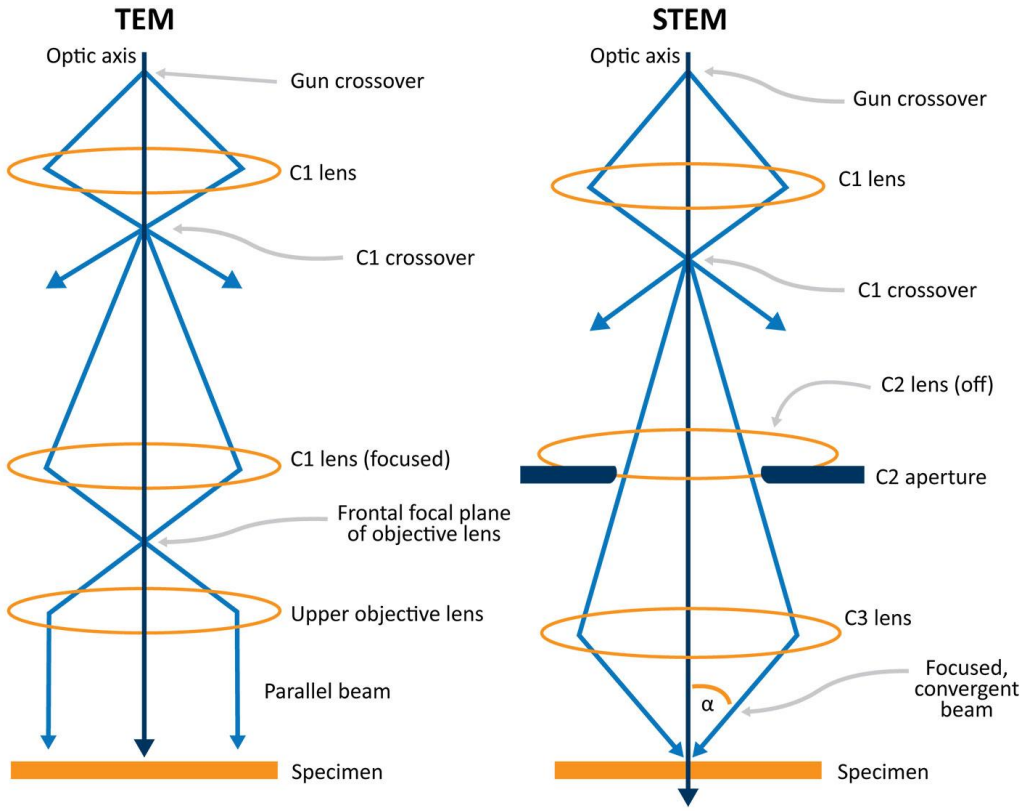
Sample preparation for TEM

- Sample must be transparent to e^-, typically **< 100 nm thick**
- Sample should be compatible with vacuum → no outgassing, no volatile components
- Sample should be stable under the beam → always check for beam damage
- Some preparation methods (e.g. FIB) can introduce contamination and induce thermal damage/oxidation



Scanning transmission electron microscopy

- STEM is a combination of SEM and TEM:
  - In TEM, the beam is ⊥ to sample
  - In STEM, the beam comes with a large cone
  - Similar to SEM, the beam is rastered across the sample
- Sample requirements are same as for SEM
- Multiple detectors available
  - **Bright-field**: collects unscattered e^- + e^- scattered at very low angles (< 10 mrad)
  - **Annular dark field**: collects e^- scattered at intermediate angles (10-50 mrad); contains diffraction contrast
  - **High-angle annular dark field**: collects e^- scattered at high angles (> 50 mrad), Z-dependence



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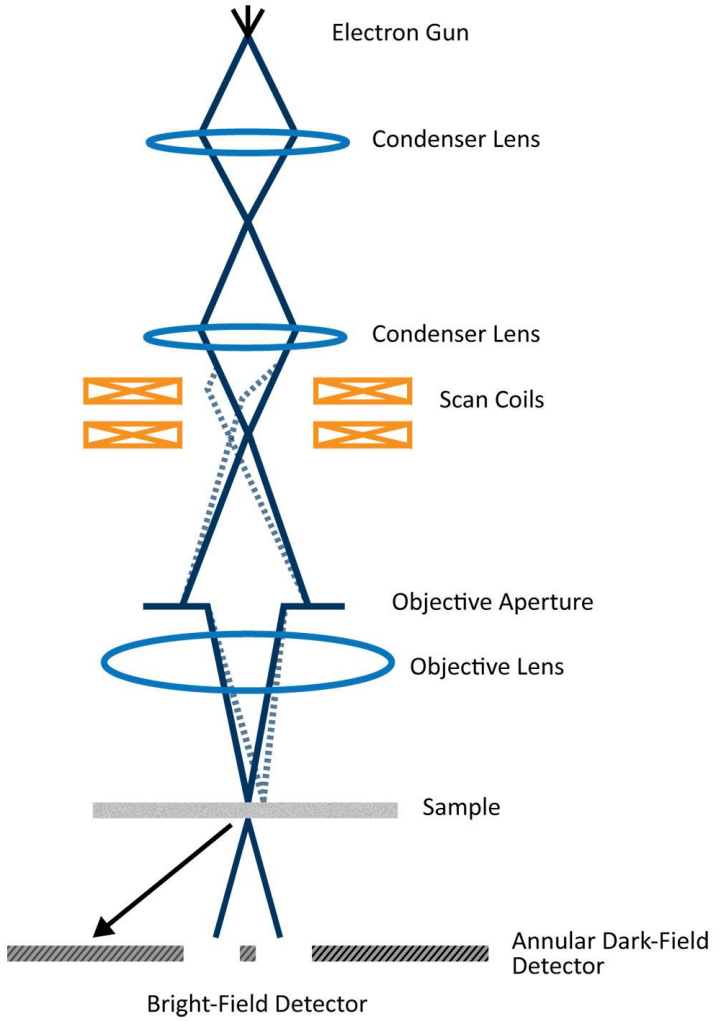
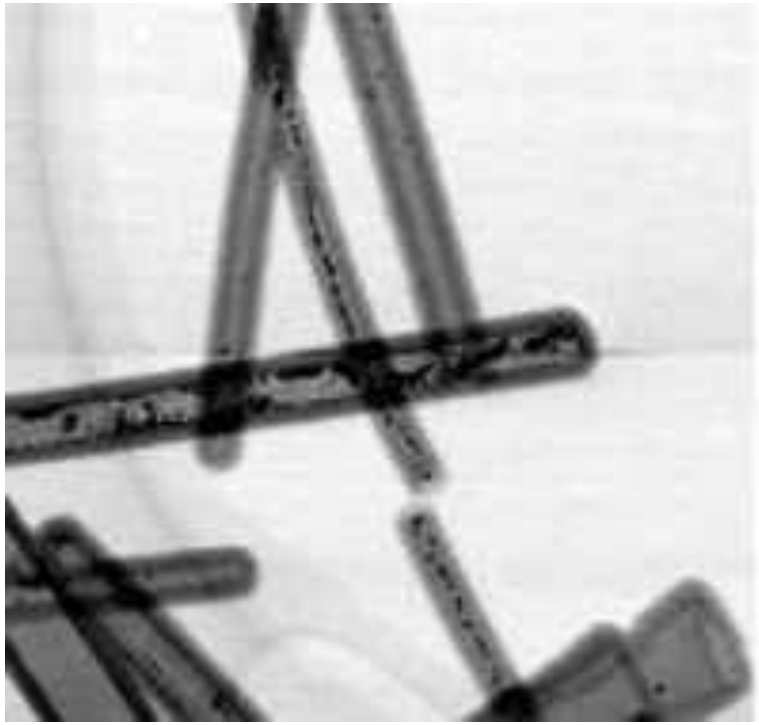
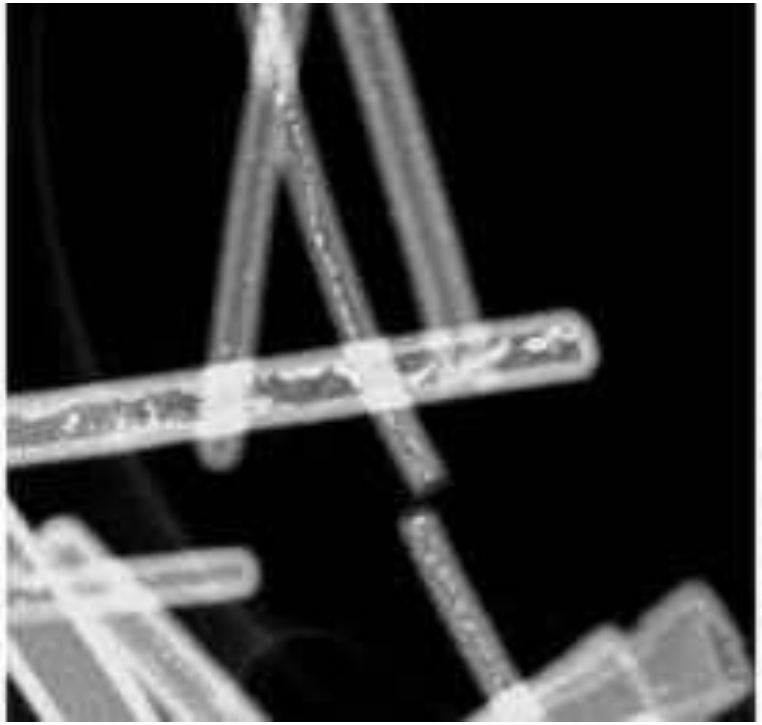


BF vs ADF vs HAADF

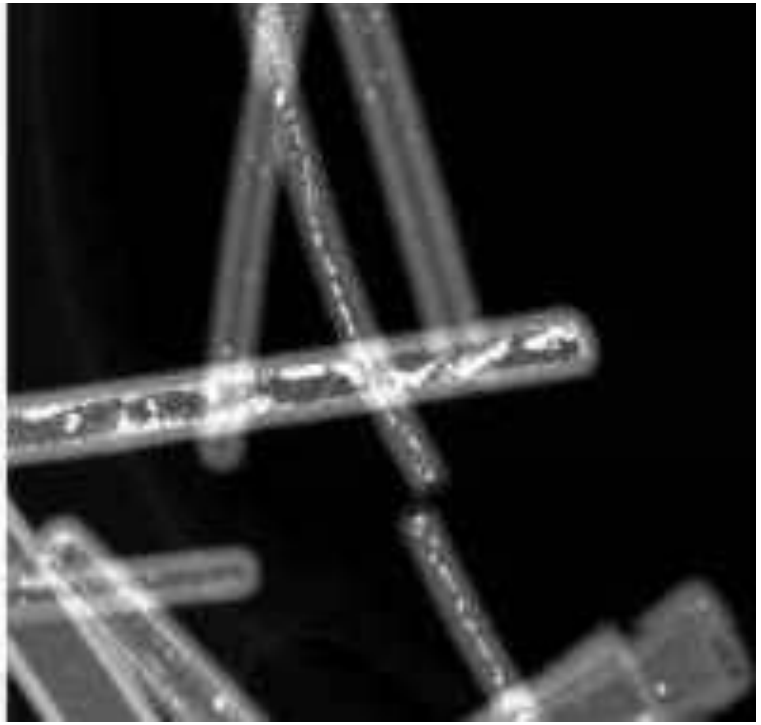
Bright field



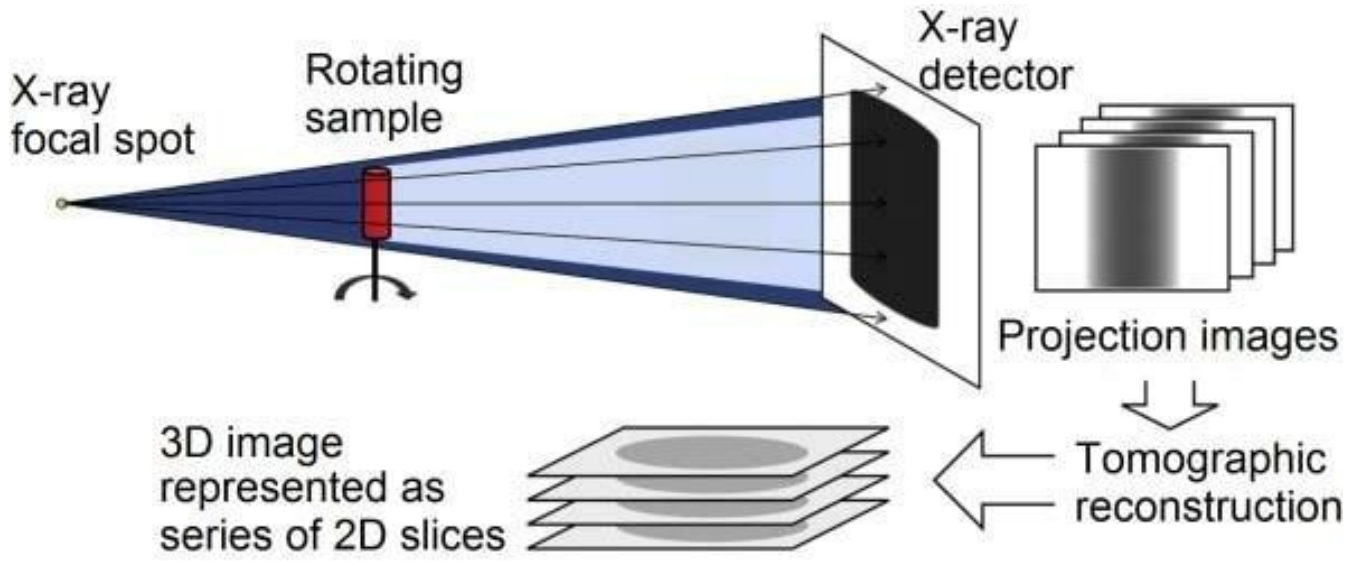
Annular dark field



High angle annular dark field

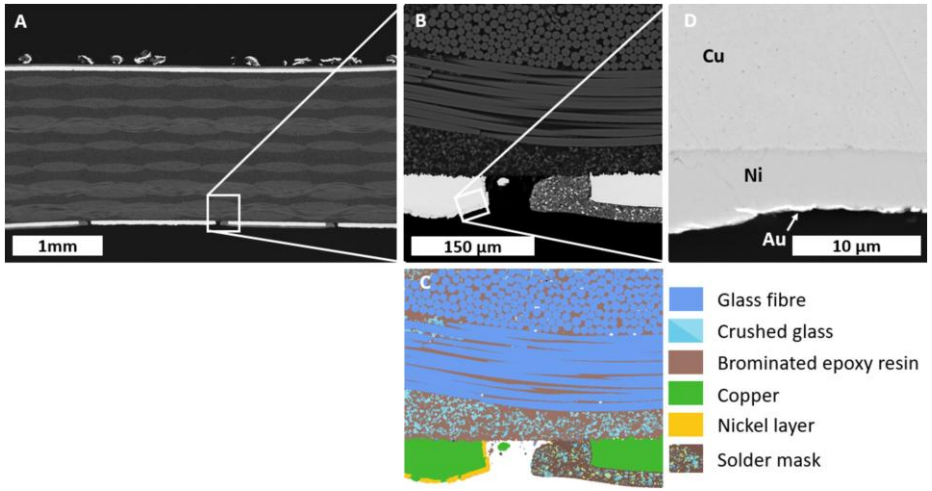


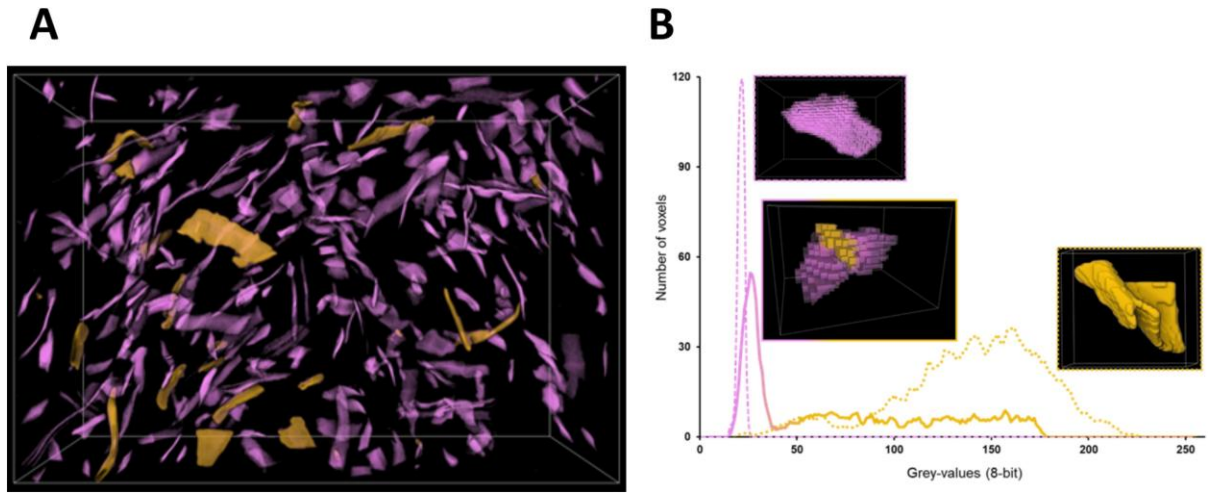
X-ray computed tomography



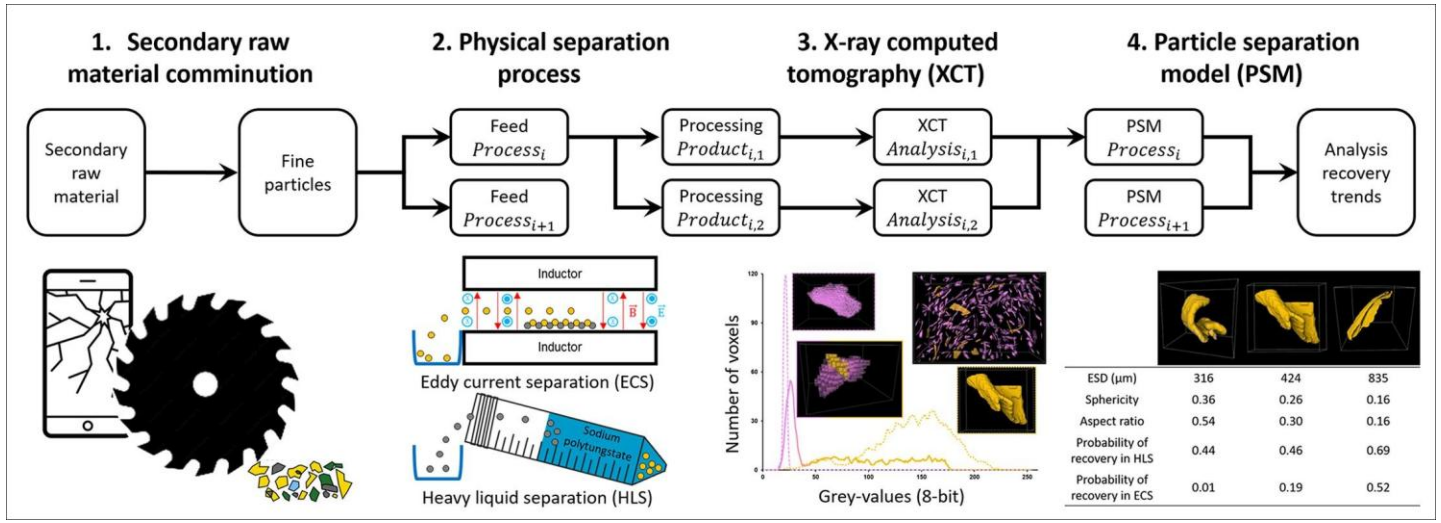
- Not strictly a microscopy, rather a tomography
- Excitation source: X-rays (but e-beam possible)
- Sample is rotated in the beam → projections (containing scattering or absorption information) are recorded
- Reconstruction yields a 3D representation

X-ray computed tomography – the PCB study





- PCB are complex wastes to handle → many constituents are lost during pyrometallurgy
- Particle-based separation methods can improve separability (> 90 % liberated particles)
- XCT critical in correlating particle shape with separability



Waste Management, **193** (2025), 561-570, https://doi.org/10.1016/j.wasman.2024.12.040.

Summary

Property	SEM	TEM	STEM
Principle	A focused beam scans the surface; signals from the sample surface are collected	A broad, parallel beam passes through a thin sample; the transmitted electrons form an image	A focused beam scans a thin sample; transmitted electrons are collected on detectors
Accelerating voltage	~0.5-30 kV	~80-300 kV	~80-300 kV (also available in some SEMs at 30 kV, "STEM-in-SEM")
Sample requirement	Bulk solids, any thickness, must be conductive (or coated)	Electron-transparent: ≲100 nm (ideally <50 nm)	Same as TEM; thinner samples give better results
Sample preparation	Simple (mounting, coating)	Demanding (ultramicrotomy, FIB, ion milling, grids)	Same as TEM
Signals used	SE, BSE, EDX, (EBSD, CL)	Transmitted and diffracted electrons	BF, ADF, HAADF, EDX, EELS
Image formation	Serial (scan)	Parallel (whole field at once)	Serial (scan)
Main contrast	Topography (SE), composition (BSE)	Mass-thickness, diffraction, phase	Z-contrast (HAADF), diffraction (BF/ADF), mass-thickness
Resolution	~1-10 nm	Down to <0.1 nm (atomic)	Down to <0.1 nm (atomic, aberration-corrected)
Information gained	Morphology, surface texture, composition, grain orientation (EBSD)	Internal structure, crystal structure, defects, lattice imaging, diffraction patterns	Atomic-scale imaging, elemental and chemical mapping (EDX/EELS), Z-contrast
Diffraction	Only EBSD (surface)	Selected-area and nano-beam diffraction	Convergent-beam and 4D-STEM
Complexity and cost	Low-moderate, routine	High	Highest (often a TEM with a scanning mode)
Typical use	Surface and fracture analysis, particles, coatings, morphology	Crystallography, defects, nanostructures, biological sections	Chemical mapping, heavy elements in a light matrix, interfaces, catalysts