Dipartimento di Scienze Biologiche, Geologiche e Ambientali

FishMed-PhD Teaching week 2022

Electron Microscopy, theory, instrumentation and practical examples

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Microscopy facilities at BiGeA

CLSM

FEG-ESEM-STEM

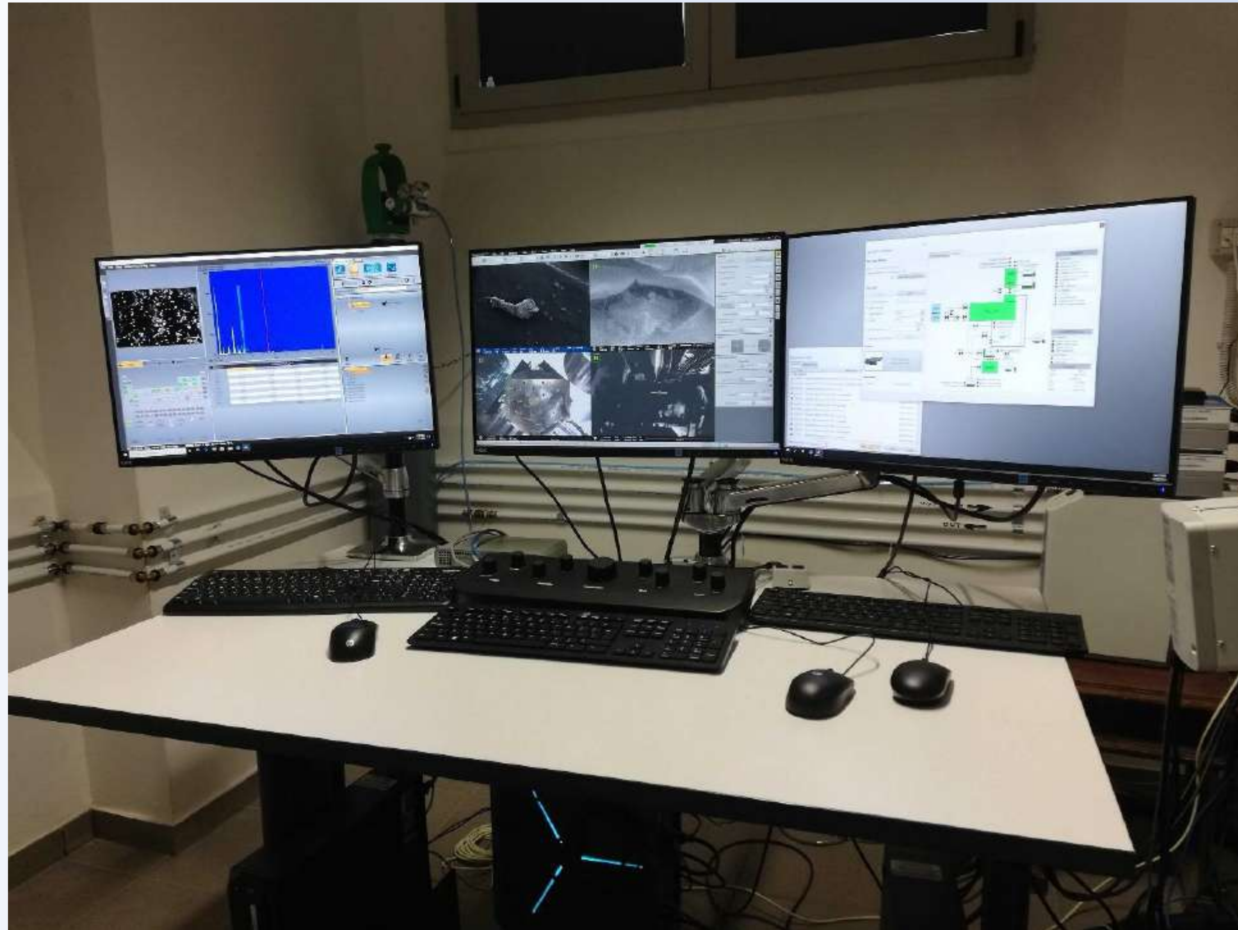
TEM

SEM

Available soon:

- Atomic Force Microscopy

Environmental (P, T, gas-type, mech, elect, etc) Scanning Electron Microscopy



Vacuum modes:

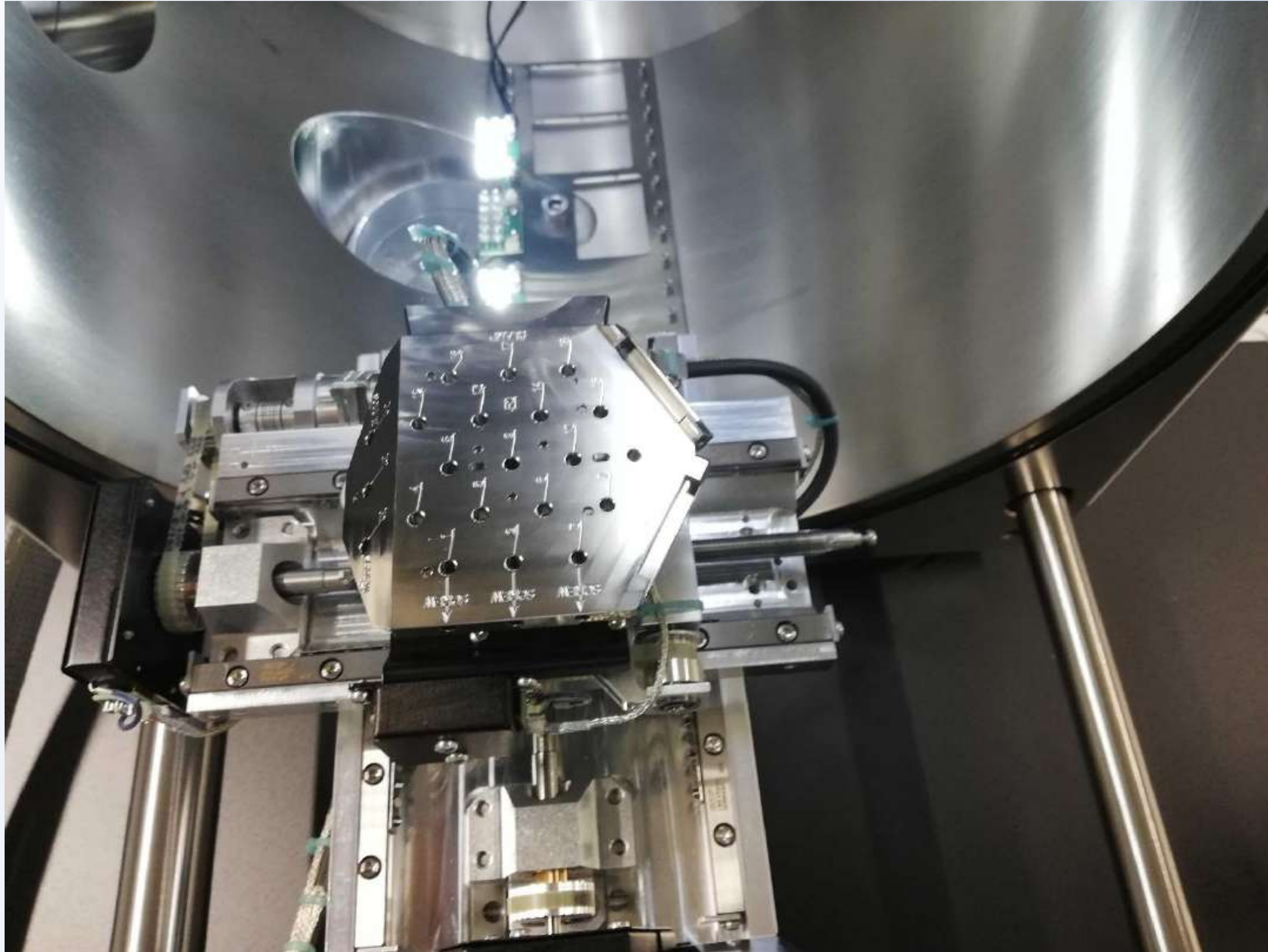
- High vacuum: < 6×10^{-4} Pa (~ 5×10^{-6} torr)
- Low vacuum: up to 200 Pa (~1.5 torr)
- Environmental-SEM: up to 4000 Pa (~30 torr) N_2; up to 2700 Pa (~20 torr) H_2O

Gas-type: most commonly air or water vapour, but also nitrogen.

***In situ* studies:**

- -25°C to 1400°C (Peltier and heating stages).

Environmental (P, T, gas-type, mech, elect, etc) Scanning Electron Microscopy



Simultaneous acquisition and display of images from multiple detectors and detector segments
=> reducing beam exposure.

- **Beam current: 1 pA – 200 nA**
- **Accelerating voltage: 200 V – 30 kV**
- **Landing energy: 20 eV – 30 keV**
- **Magnification: 6 – 2500000×**

✓ **Eucentric goniometer stage with a wide tilt range (105°)**
✓ **Multi-sample SEM holder (e.g., 18 stubs)**

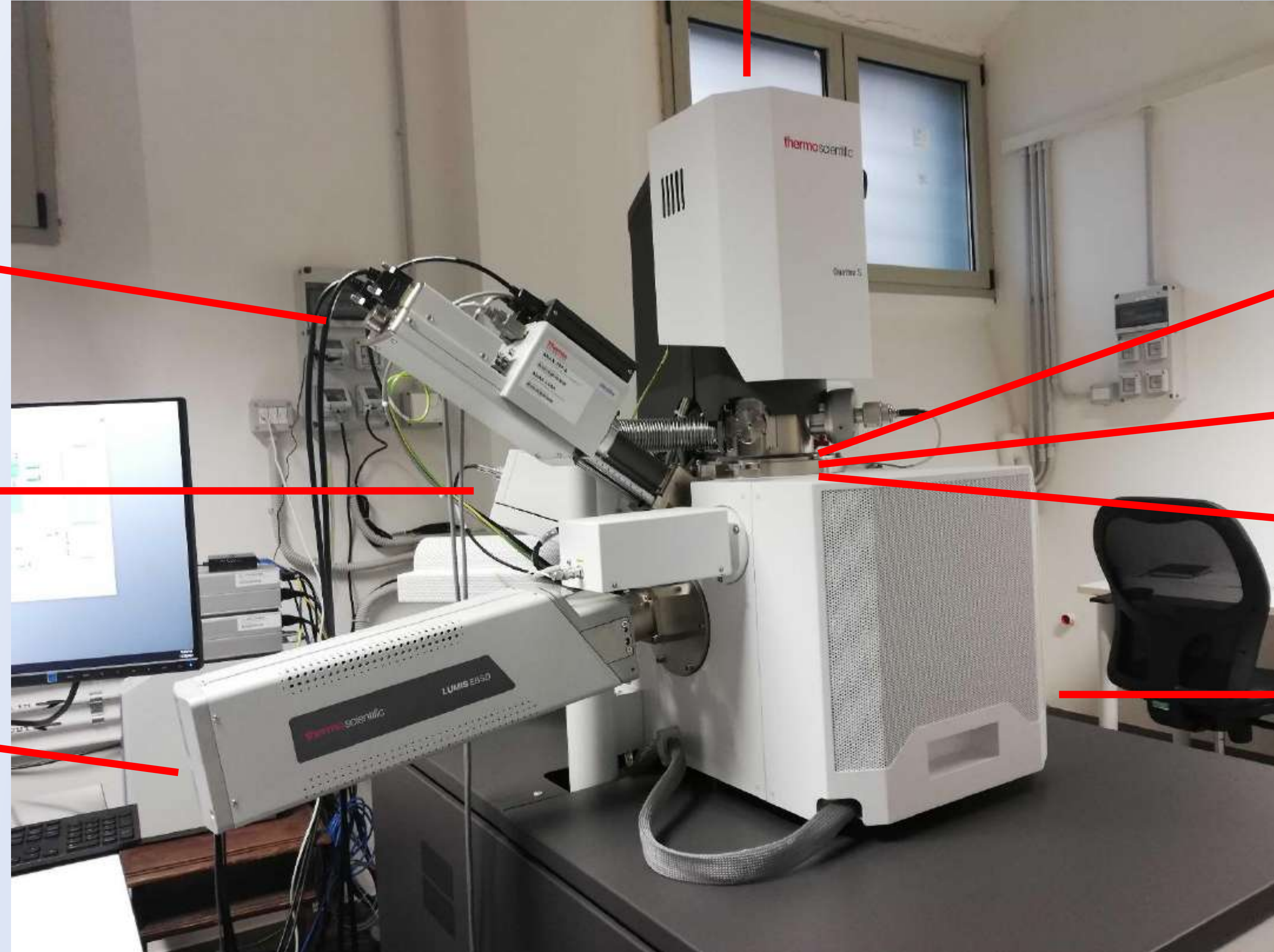
Environmental (P, T, gas-type, mech, elect, etc) Scanning Electron Microscopy

Field emission gun (FEG)

SDD X-ray microanalysis detector

Everhart-Thornley SE Detector (ETD)

Electron BackScatter Diffraction (EBSD)



Gaseous SED (GSED)

Lens-mounted **Gaseous Analytical Detector** (GAD)

Low Vacuum Detector (LVD

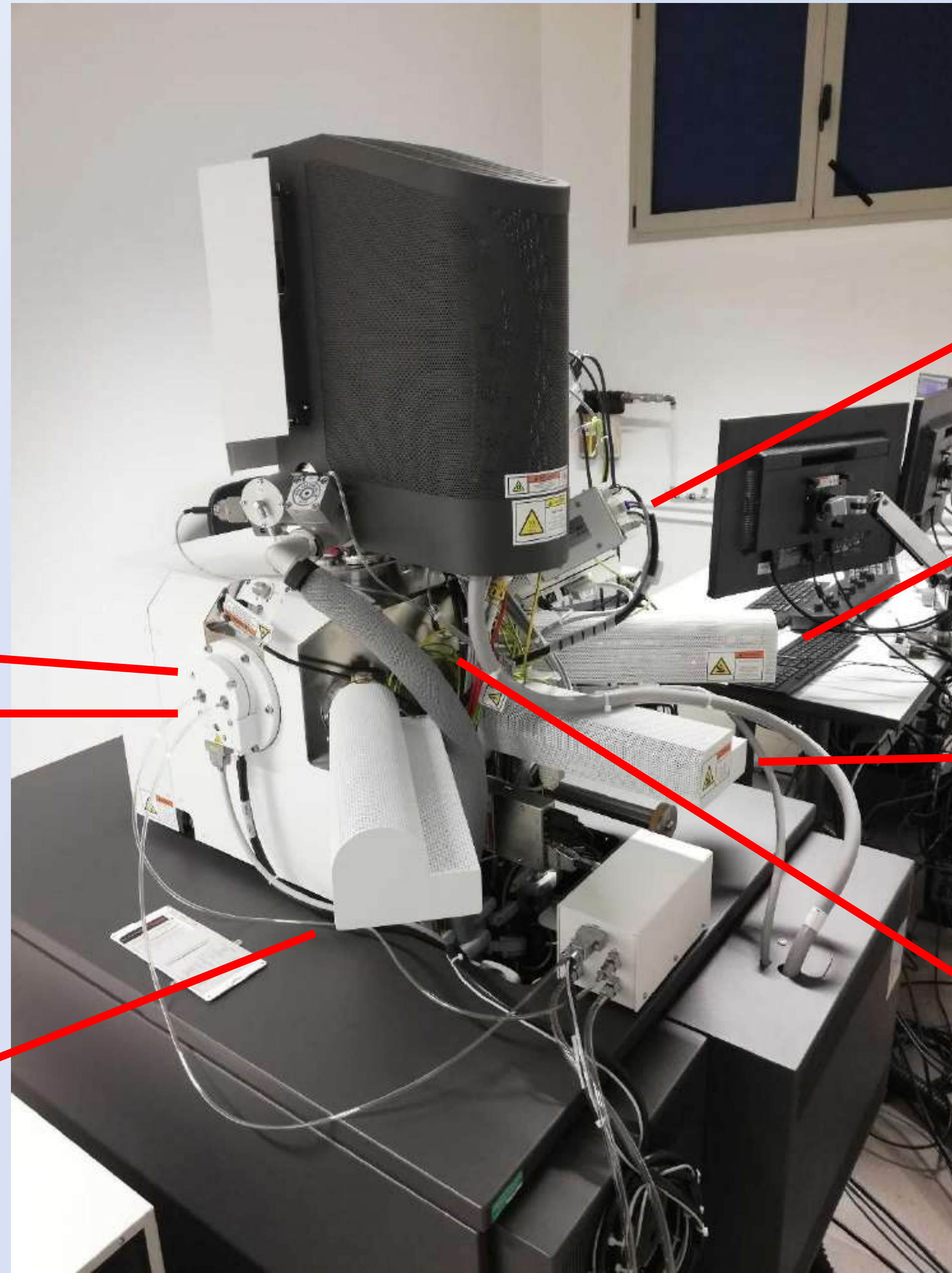
Sample chamber

Environmental (P, T, gas-type, mech, elect, etc) Scanning Electron Microscopy

Heating stage

Cooling Peltier stage

Cathodoluminescence



Plasma cleaner

STEM-in-SEM

Wet samples STEM-in-SEM

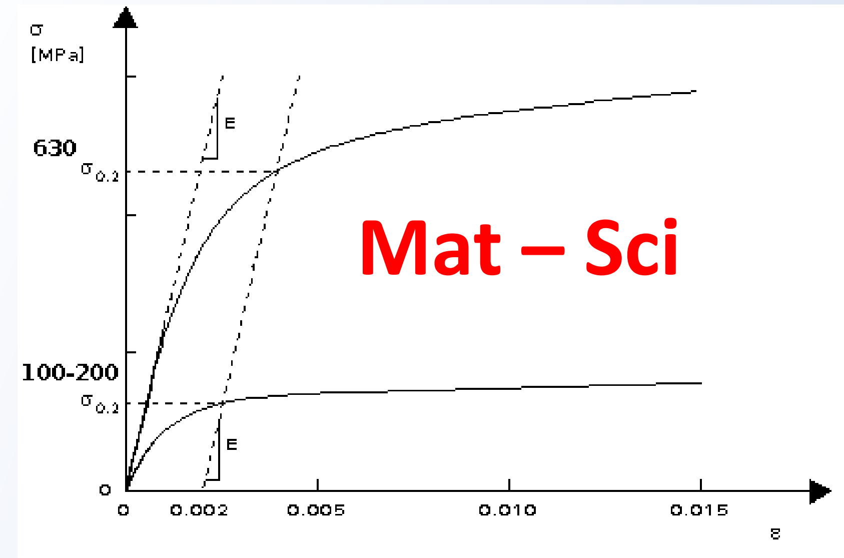
Retractable segmented under-the-lens **Directional BackScatter detector (DBS)**

Infrared CCD camera

ELECTRON – MATTER INTERACTION

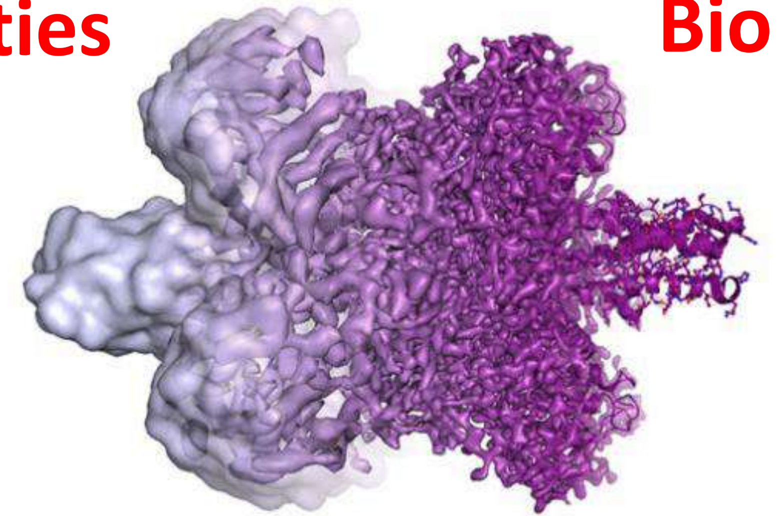
- **Important to understand electron microscopy and related instrumentation;**
- **Important to understand materials.**

Knowledge of materials properties



Sky Tree - Tokyo

Bio



The resolution progression of cryo-EM, illustrated by a representation of **glutamate dehydrogenase** with an increasing level of detail from left to right. For a protein of this size, 334 kDa, the **1.8 Å resolution** to the right could only be achieved after 2012/13.

Tour Eiffel
Paris

Year: 1889

Height: 324 m

Made of wrought iron

Yield stress: 100-200 MPa

Year: 2012

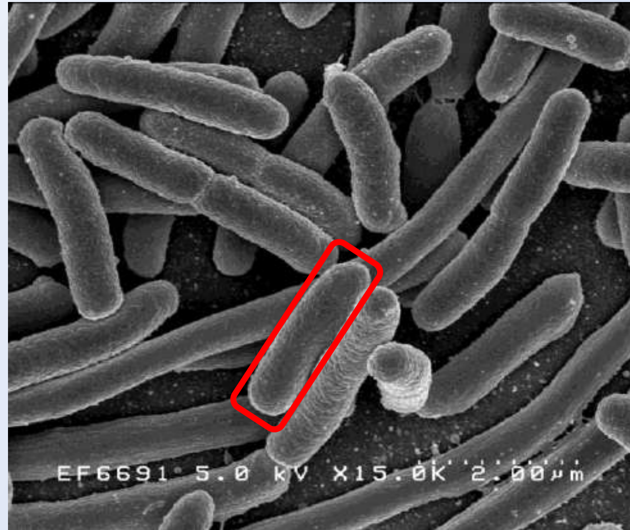
Height: 634 m

Made of weldable high-strength steel

Yield stress: 630 MPa

Kanamycin antibiotic on bacteria – Evanescent field

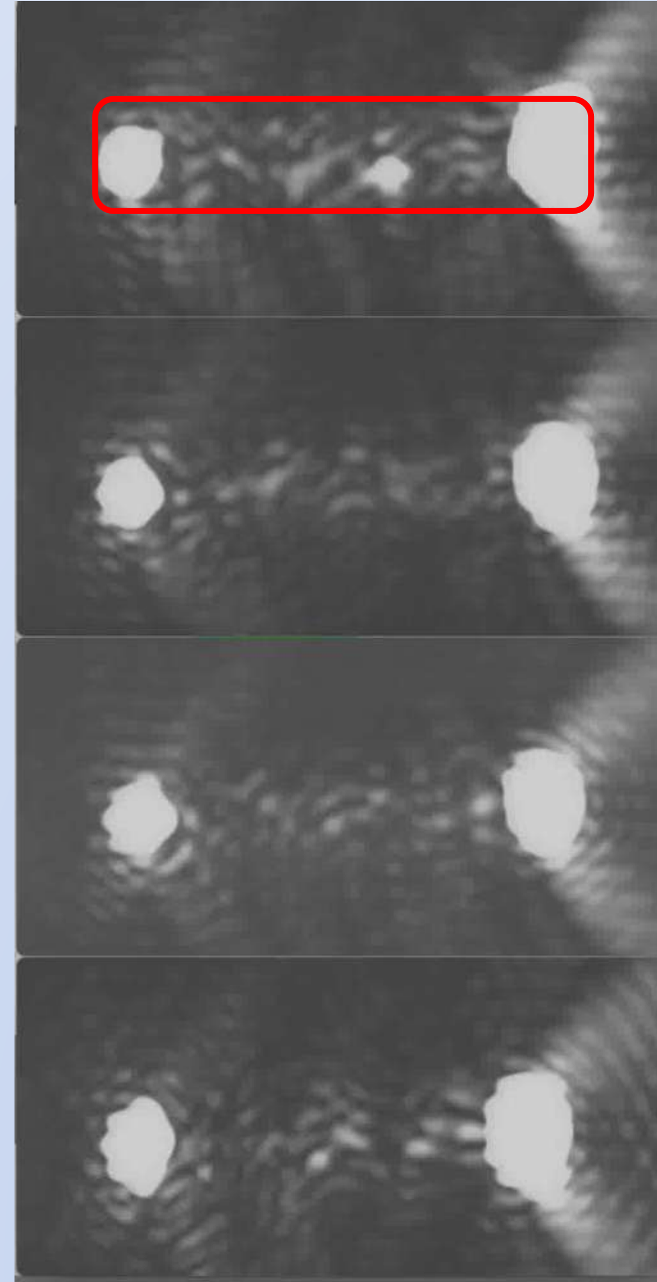
- SEM
- Scanning Probe
  (AFM-SPM)
- Optics



E. Coli bacterium

Antigen-antibody grafted onto a glass slide

Nanometric membrane vibrations



Worth to be noted !

- **Nobel Prize in Chemistry 2017**
  - to Jacques Dubochet, Joachim Frank and Richard Henderson
    - for developing **cryo-electron microscopy** for the high-resolution structure determination of biomolecules in solution (~ **1.8 Å**)
- **Nobel Prize in Chemistry 2014**
  - to Eric Betzig, Stefan W. Hell and William E. Moerner
    - for the development of **super-resolved fluorescence microscopy** **Photon Optics - Stimulated emission depletion, called STED** (~ **20 nm**)

- **Nobel Prize in Physics 1986**
  - to Ernst Ruska
    - for his fundamental work in electron optics, and for the design of the first **electron microscope**
  - to Gerd Binning and Heinrich Rohrer
    - for their design of the **scanning tunneling microscope**

Summary

Dipping into history

High Resolution and improved spectroscopy

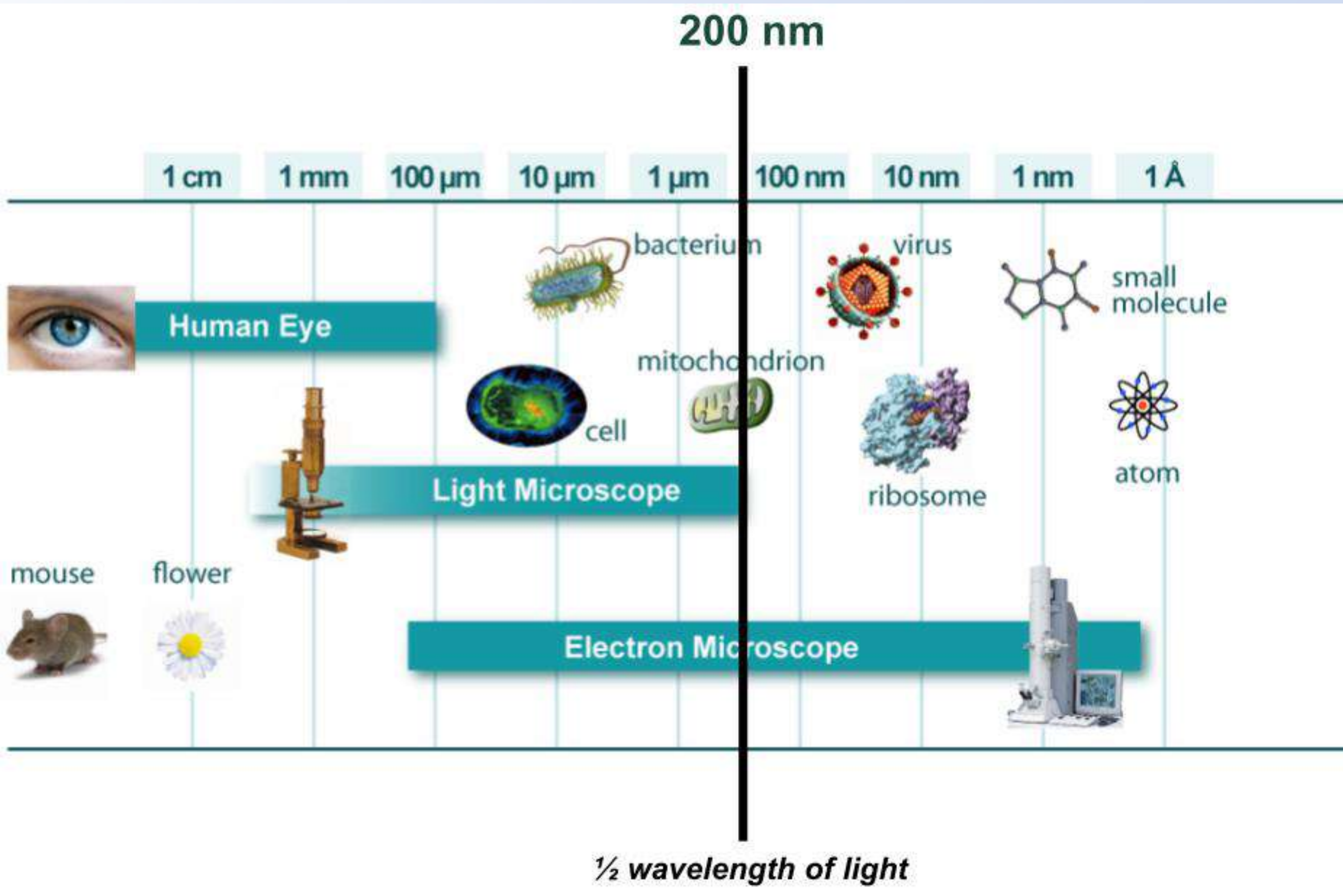
Applications

The diffraction limit ⇒ rush for ultrashort wavelength!

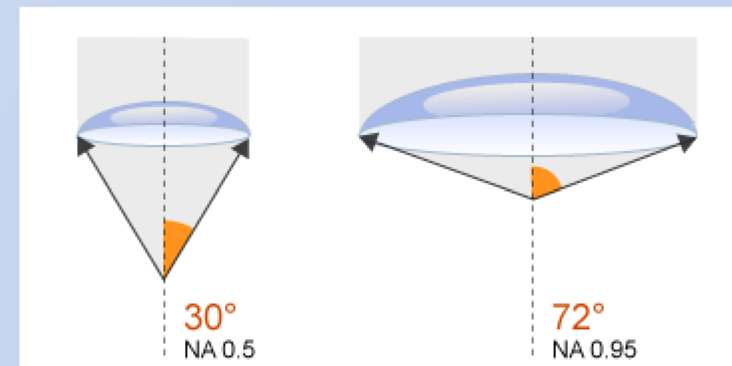
- Visibile light: 400 nm (violet) – 700 nm (red)

- Spatial resolution: diffraction limit $d = \lambda/(2\ n\cdot\sin\theta) \geq \lambda/2$

Ernst Abbe (1873)



- Objective – numerical aperture ($n\cdot\sin\theta$)



Everything has its Wavelength for Bragg Reflection!

$\lambda = hc/E$ (photons); $\lambda = h/\sqrt{(2mE)}$ for slow particles

Characteristic X-rays	Moseley (1914)	~ 1Å
Low energy electrons	Davisson (1927)	~ 1Å
High energy electrons	Thomson (1927)	~ 0.1Å
Thermal He atoms	Esterman, Stern (1930)	~ 1Å
Thermal neutrons	Wollan, Shull (1945-6)	~ 2Å

Technological frontiers in the developments of Electron Microscopy and other microscopy methods (only to cite a few …)

- Aberration-corrected TEM
- Aberration-corrected energy filtered TEM
- Dedicated STEM
- Environmental TEM
- Environmental SEM with STEM and EBSD and SDD-EDS
- Dual Beam FIB
- Scanning Probe Microscopy (SPM)
- Stimulated Emission Depletion (STED) Microscopy

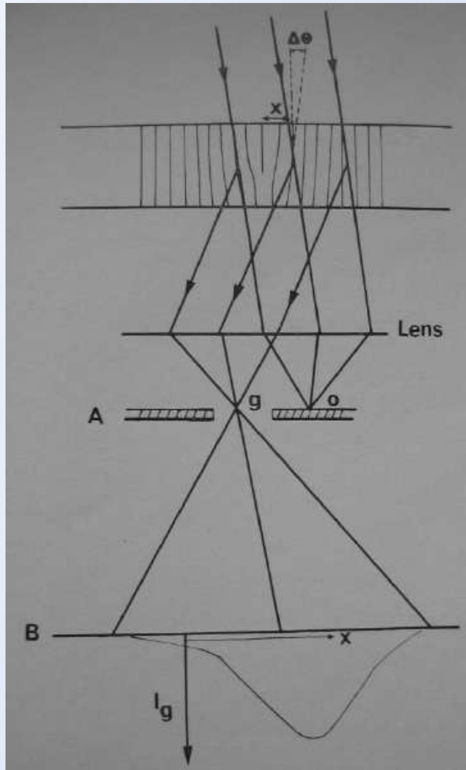
Summary

Dipping into history

High Resolution and improved spectroscopy

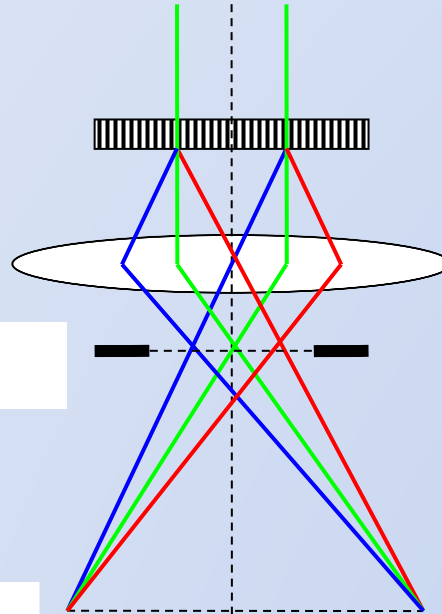
Applications

Progressive Development of TEM Imaging

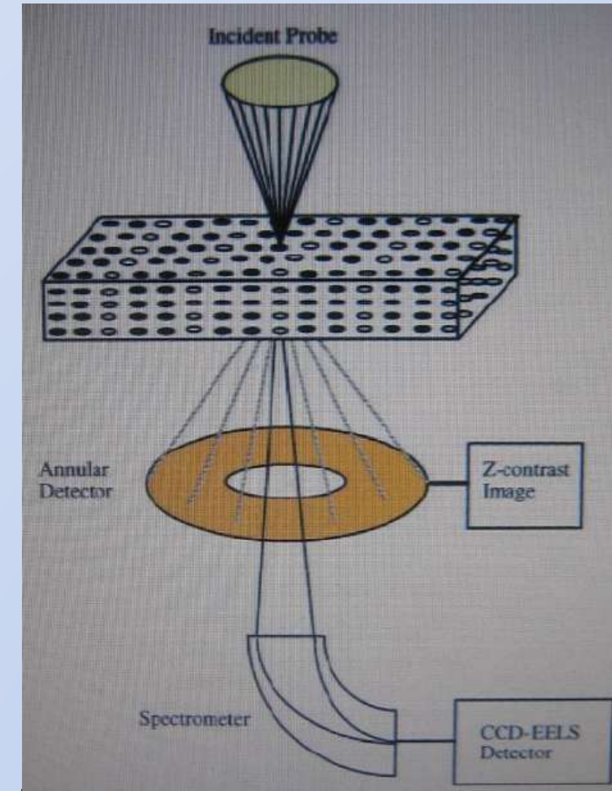


diffraction

image



Axial illumination



Coherent CTEM

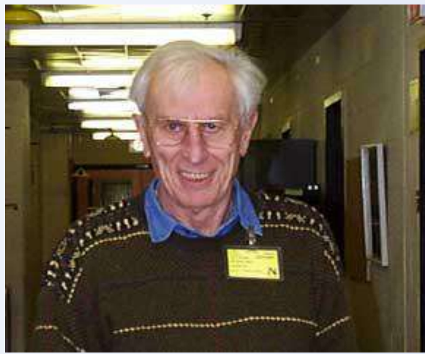
Incoherent STEM HAADF

DIFFRACTION CONTRAST IMAGING OF DEFECTS
(Crystal not resolved)

STRUCTURE IMAGING OF ATOMIC COLUMNS
(resolution ~ 0.2nm = 80λ -> 16nm depth of field)

Aberration Correction

A long saga and continuing revolution!



Harald Rose

Max Haider

Ondrej Krivanek

Not "just" the expected improved spatial resolution!

Visibility of light atoms in negative C_s HREM

Much greater probe current in STEM

Reduced depth of field

Production of improved ancillary equipment – ETEM

More efficient use of other signals – EELS, X-ray, SE?

Over 500 aberration-corrected instruments sold!

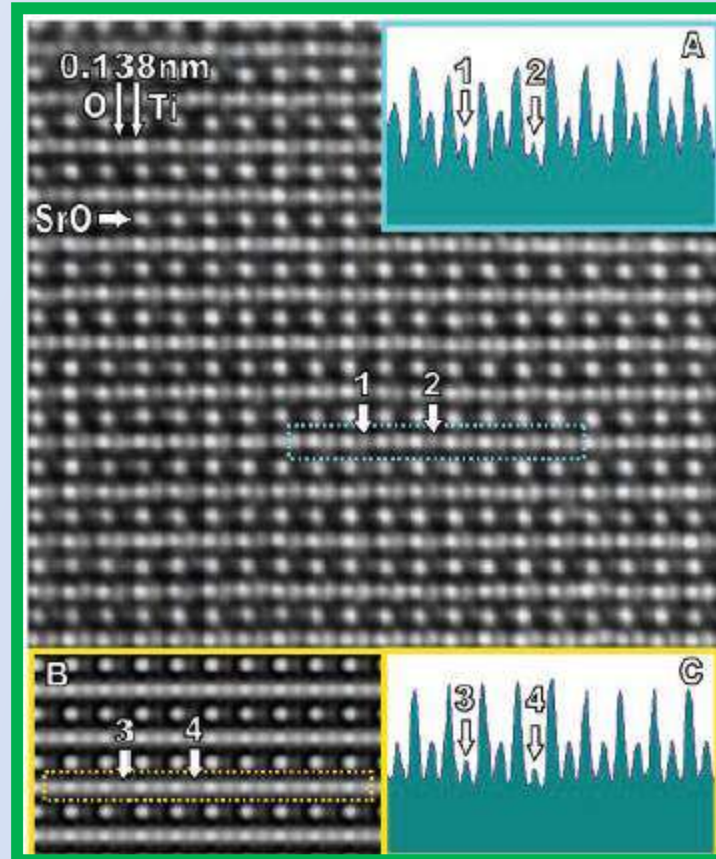
Move towards more centralised facilities?

Aberration-corrected Projection Images

Negative C_s imaging of O in $SrTiO_3$
Jia et al Science 2003, 299, 870

Expt.

Calc.



No signs of surface reconstruction !

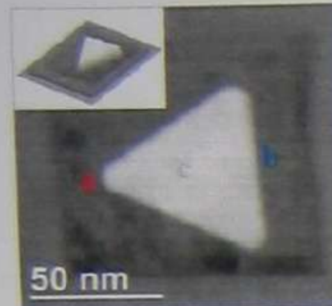
NOTES

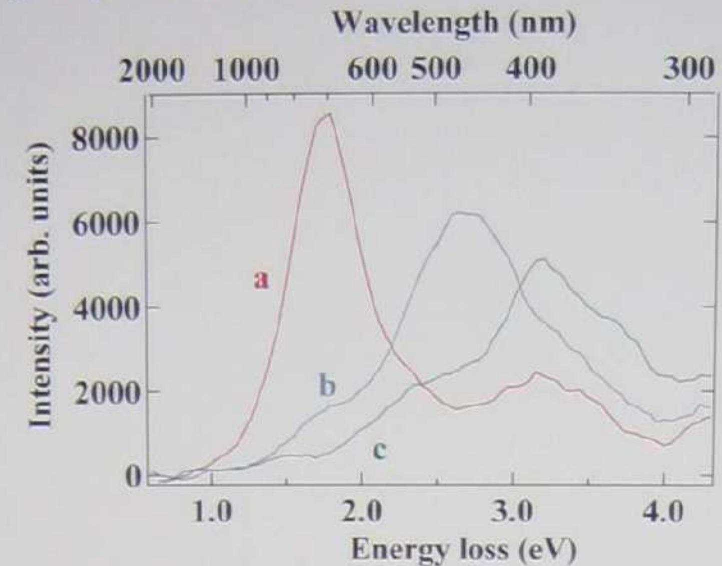
Plasmon imaging was already an old subject but really took off in the region < 3eV for Au and Ag.

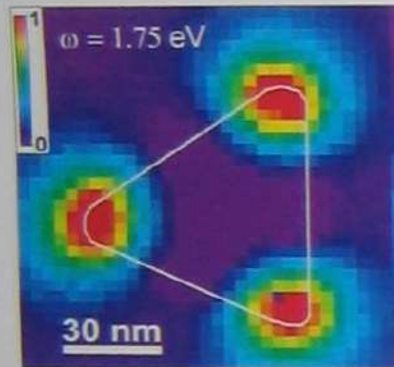
At these and even lower energies would better space and energy resolution be useful ?

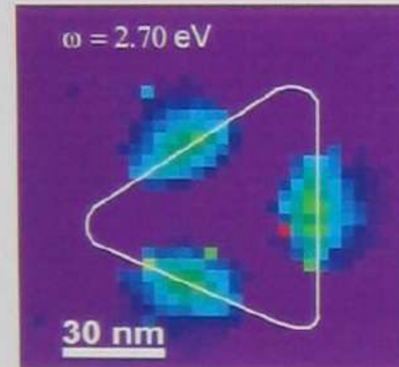
Plasmonic Euphoria!

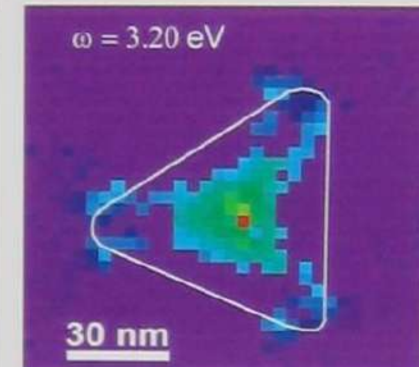
Nelayah et al. Nature Physics 3 (2007) 348









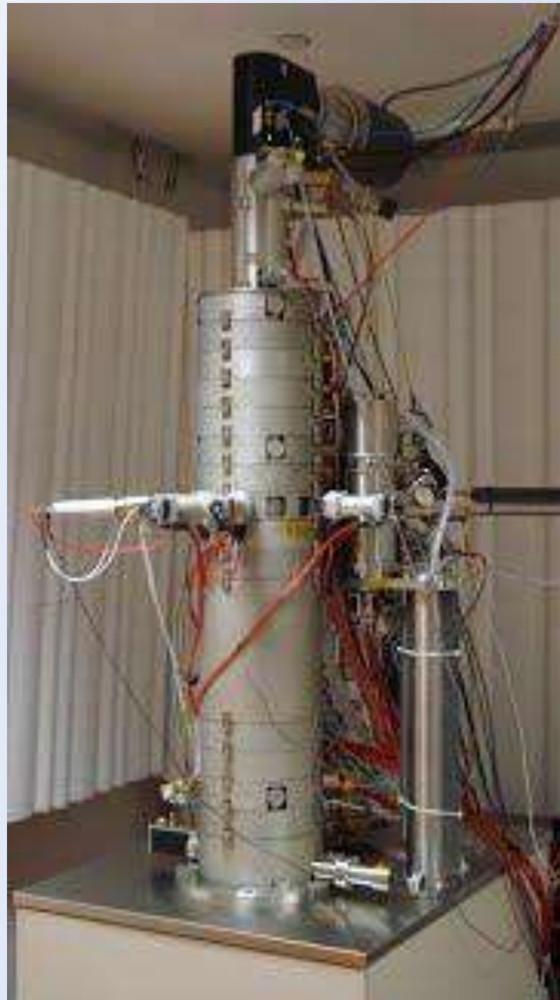


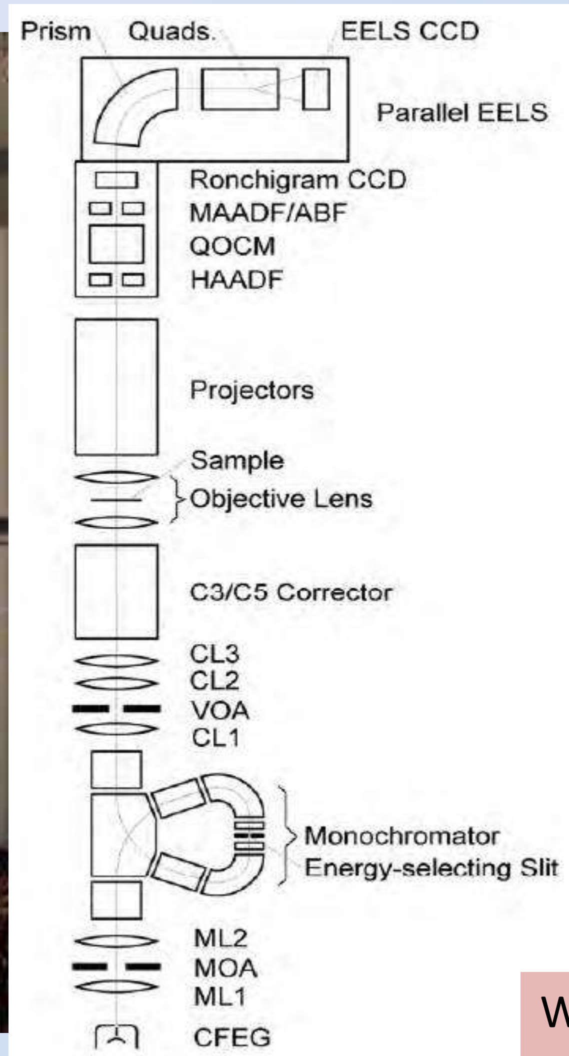
EELS amplitude maps

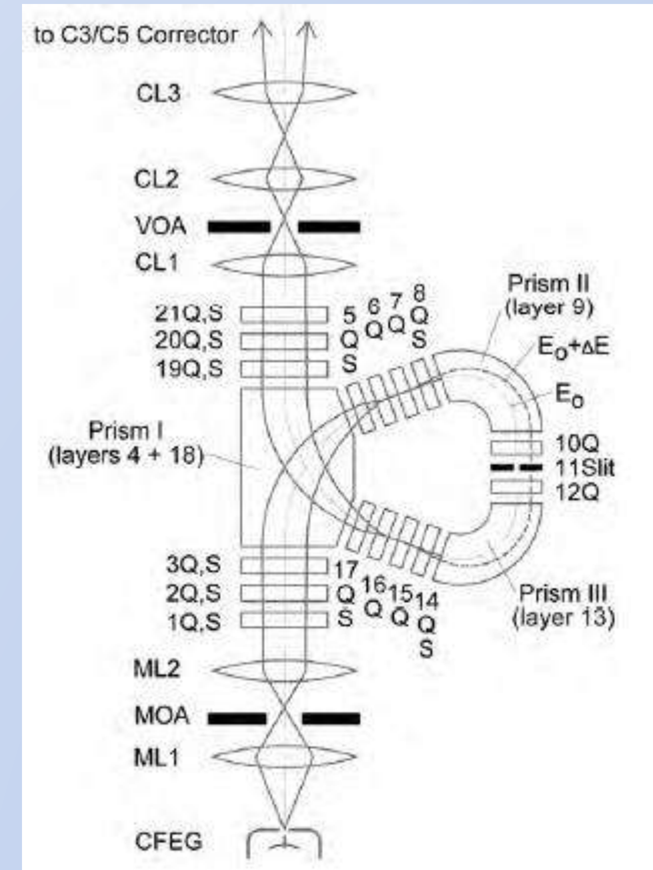
- three main SPR's are resolved in the UV- NIR domain
- their spatial distributions exhibit a 3-fold symmetry

Nion Super STEM -

new prospects for ultra low energy EELS



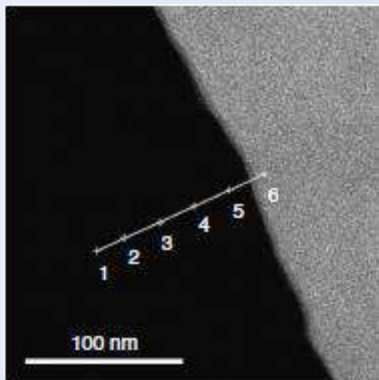


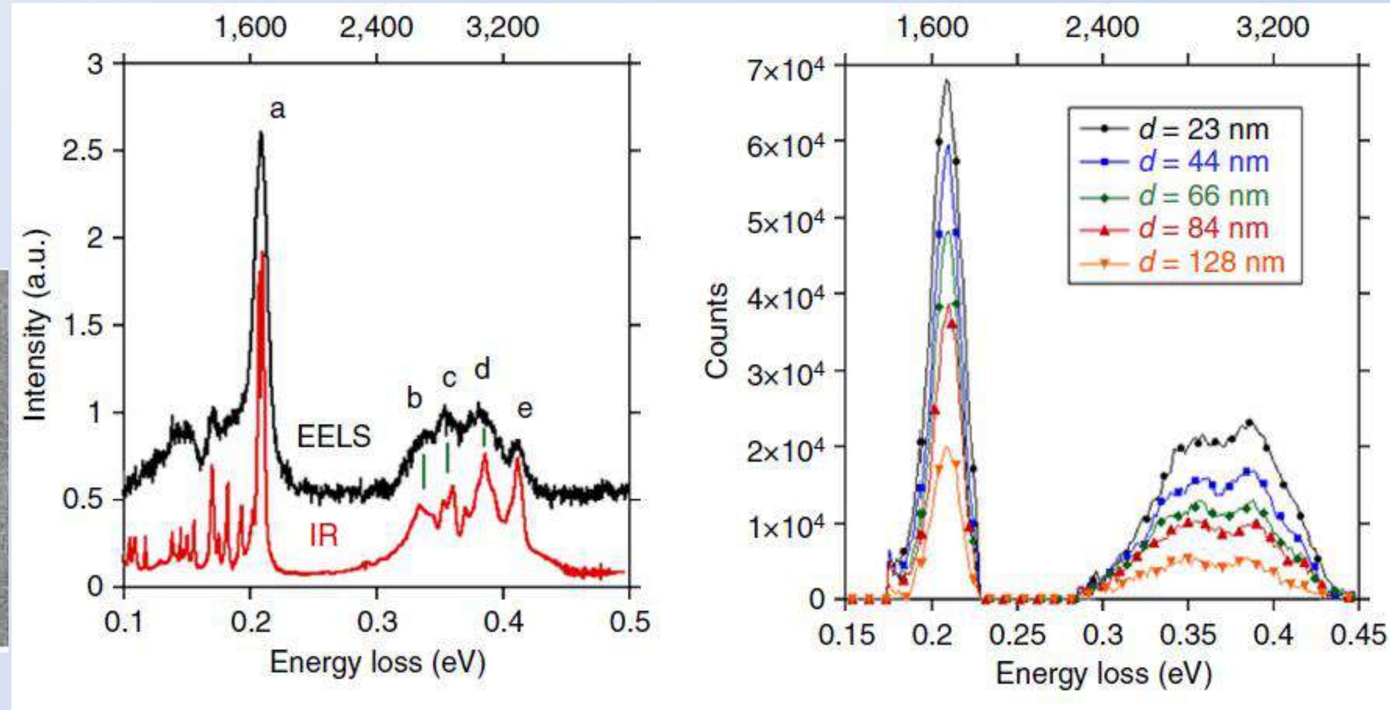


With the monochromator EELS resolution approaches 10 meV

Vibrational EELS for Guanine

Rez et al (2016) Nature Comms. (10 March issue)





Guanine crystal vacuum region for spectroscopy

EELS spectrum at point 4 compared with published IR data for guanine

Decrease of different loss peaks with increasing impact parameter

Ionisation damage is greatly suppressed at these large impact parameters

FEG – ESEM – STEM

Field Emission Gun

Environmental Scanning Electron Microscopy

Scanning Transmission Electron Microscopy

SEM – an outline of history

1895/97 J. J. Thomson discovers the electron.

1924 H. L. De Broglie describes the dual nature of matter: $p = h/\lambda$

~1926 Axial electromagnetic fields are shown to behave as "lenses" for charged particles
- The first cathode-ray tubes (CRT) are built.

1934 E. Ruska: first TEM prototype.

1937 M. Von Ardenne builds the first scanning microscope (STEM).

~1950 The first SEM prototype is built by Dennis Mc Mullan, under the supervision of Prof. Charles Oatley at the Cavendish Laboratory in Cambridge.

(Prof. Castaing develops the first microanalytical system in France using electronic excitation and characteristic X-ray detection)

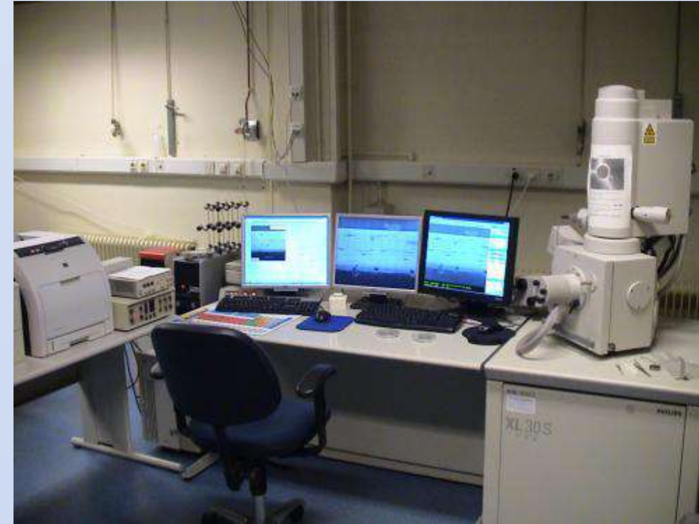
~1955 The first commercial SEM is sold to study “FIBRES” at the Paper Industry of Canada.

~1985 Dr. Danilatos at the New South Wales University, Sydney, develops the first gaseous detector for ESEM.

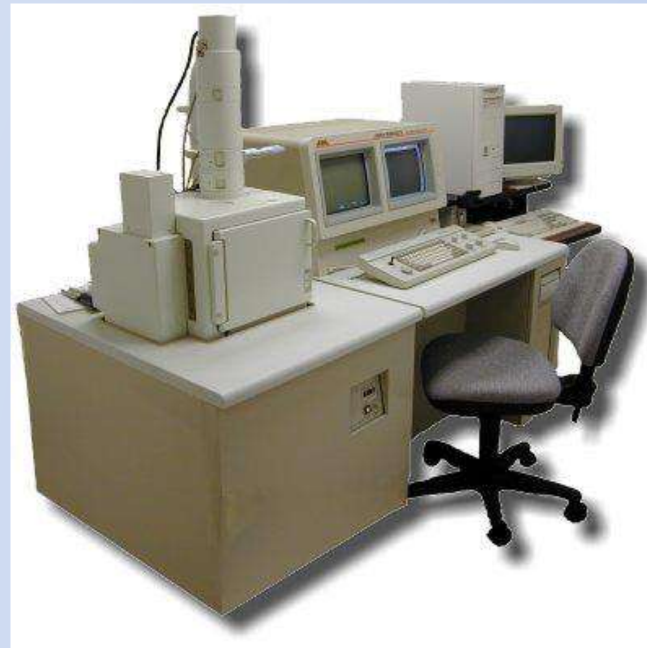
~2000 Prof. Athene Donald, Cavendish Laboratory, Cambridge (UK): investigations on basic physics of ESEM.

SCANNING ELECTRON MICROSCOPE (SEM)

SEM - Hitachi S-3000N



SEM – FEI XL30s

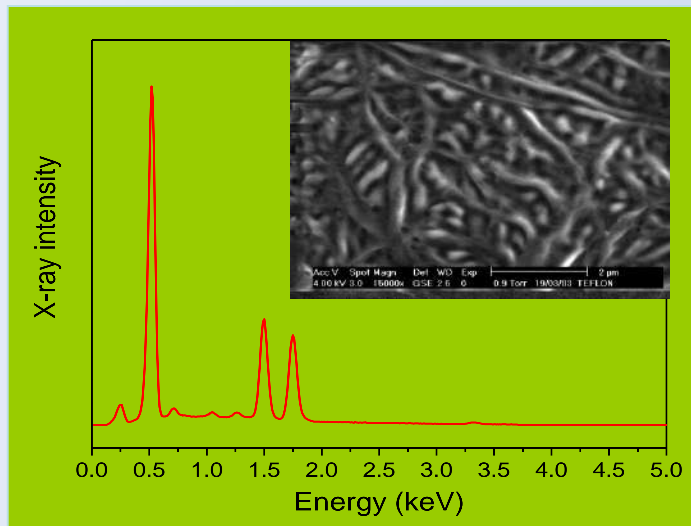


SEM - JEOL 5800LV

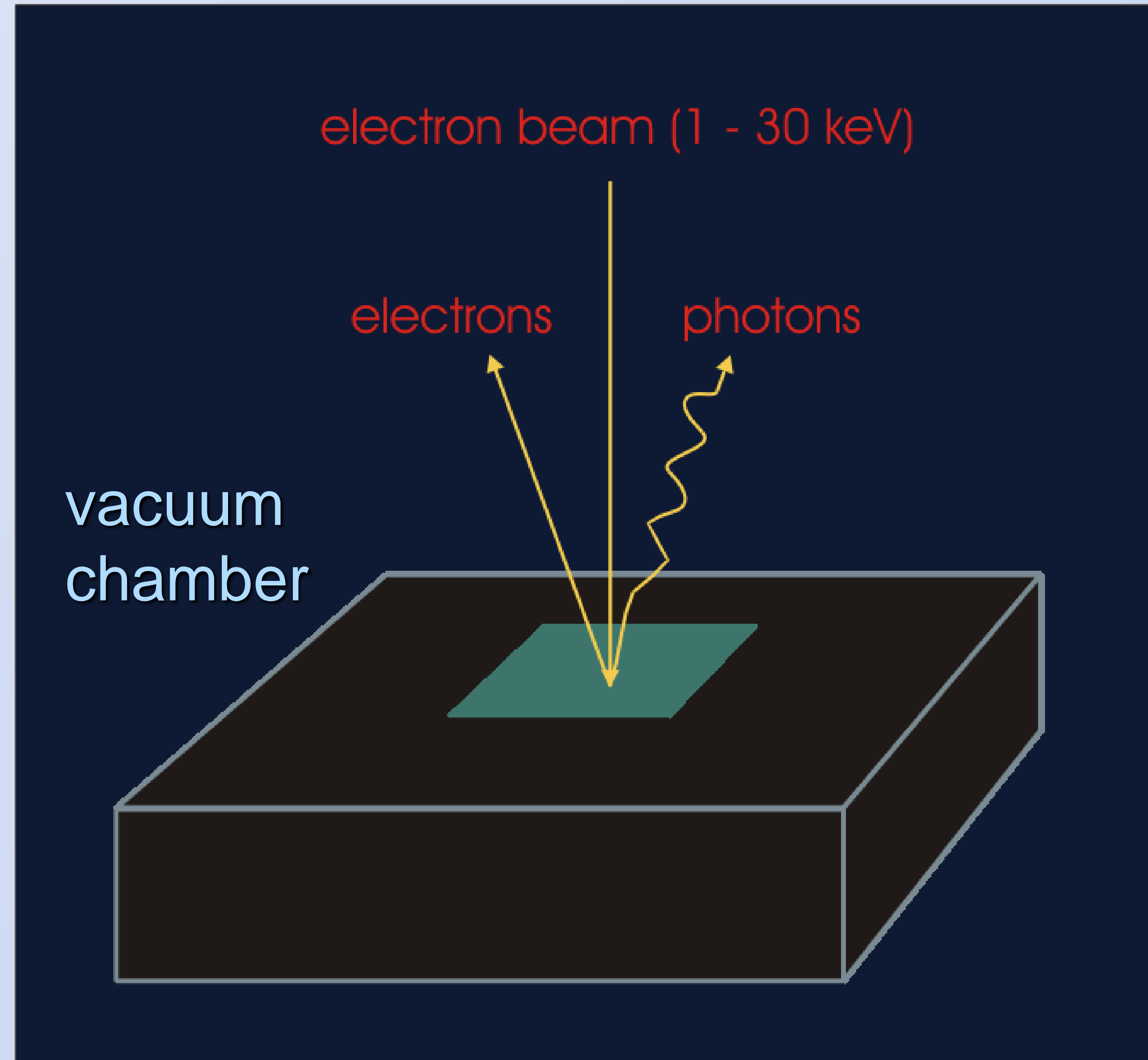
ELECTRON – MATTER INTERACTION
SEM-ESEM

SEM: imaging and spectroscopy

Imaging
lateral variations of intensity
Spectroscopy
X-ray energy distributions

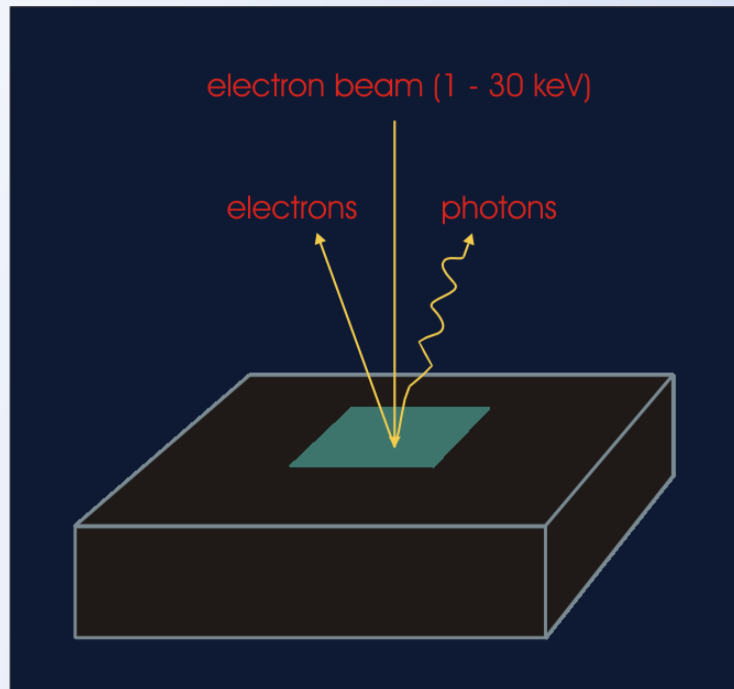


[mica, 4 kV, 0.2 torr, 10 mm, V_e = 550 V, 2000 l. sec]



SEM: electron imaging

- SE imaging
- BSE imaging

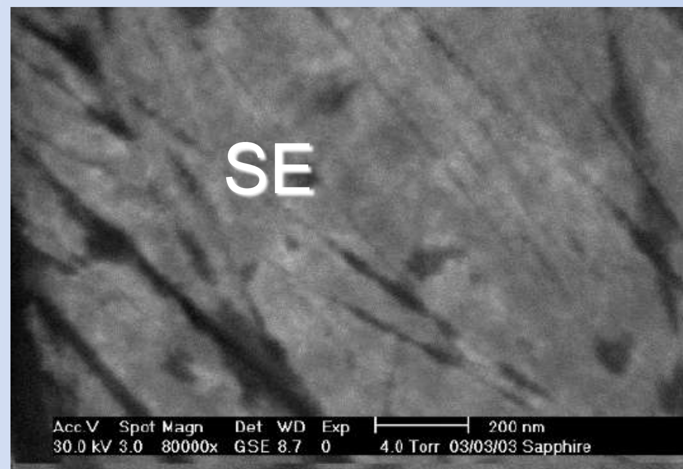


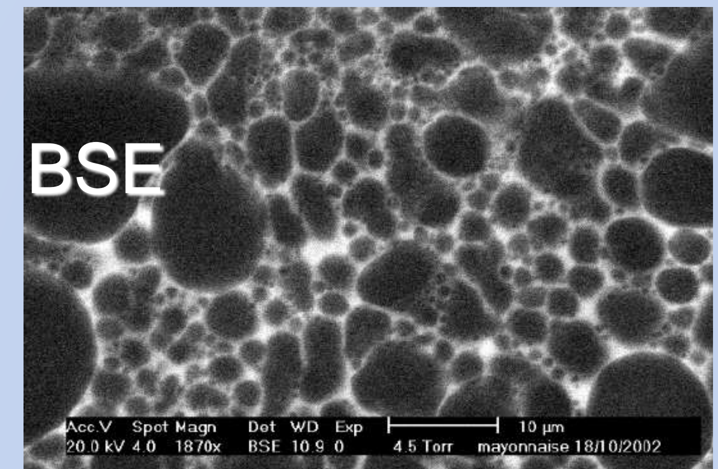
Secondary electrons (SE)

Low energy (< 50 eV).
High spatial resolution (~ 1 nm).
Toporgaphic contrast.

Backscattered electrons (BSE)

High energy (50 eV $\rightarrow$ E_{beam}).
Resolution depends on the beam energy.
Contrast by atomic number.

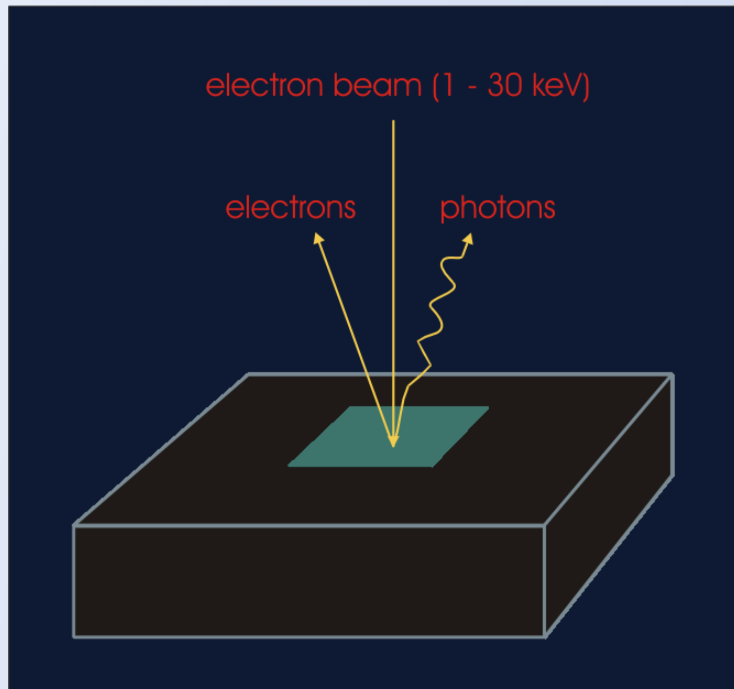




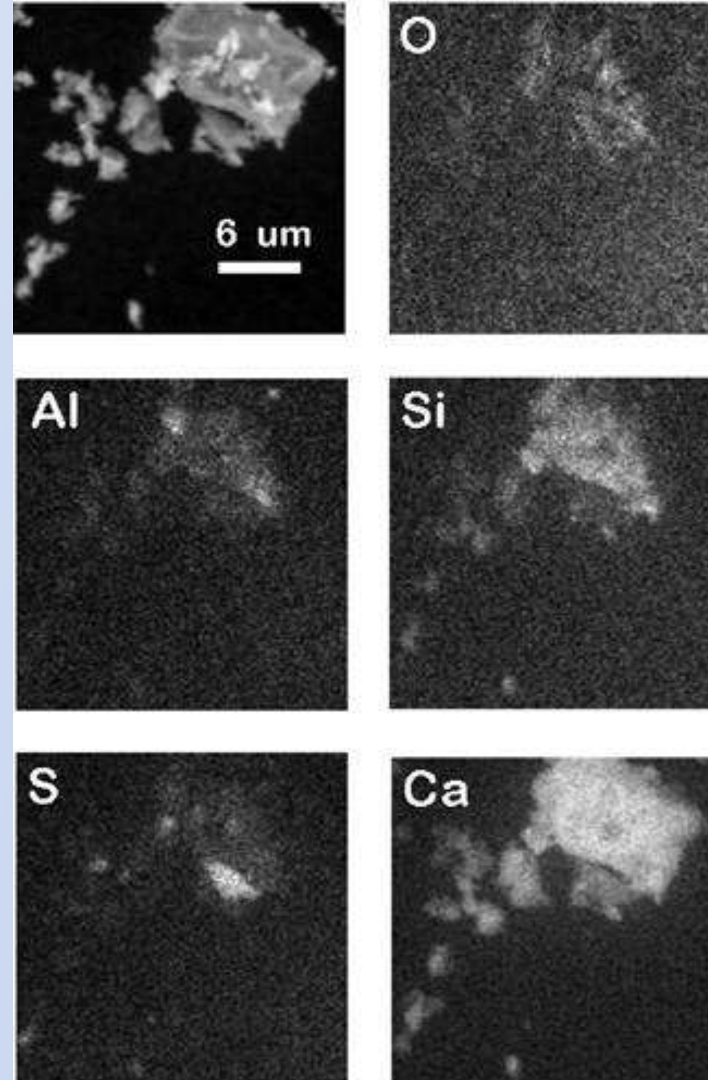
X-ray Mapping:

Information:

Lateral distribution of elements.



Cement



The merits of SEM

High spatial resolution (limit: ~ 1nm)

High magnification

High depth of field

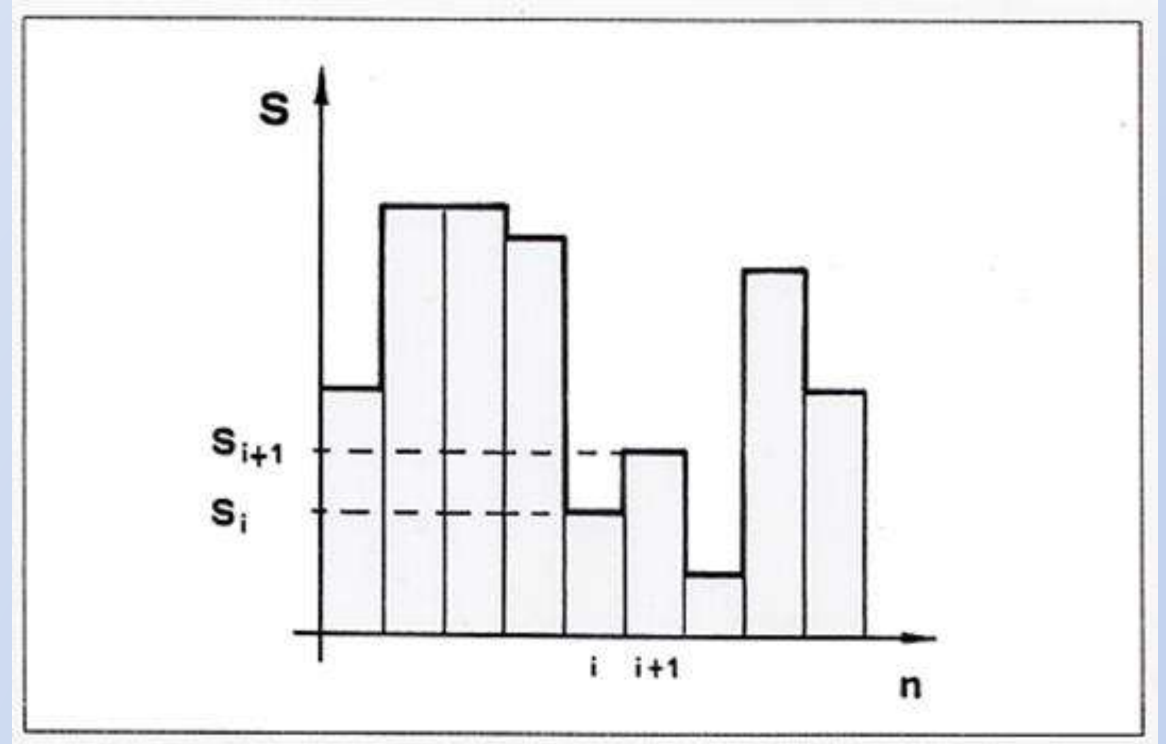
Easy sample preparation, **but must be high vacuum tolerant and conductive!**

Digital image (per pixels)

VI century Ravenna mosaic fragment to illustrate the concept of pixel or image element.

An ordered sequence of pixels (e.g. according to parallel lines) provides a quantized image.

Contrast

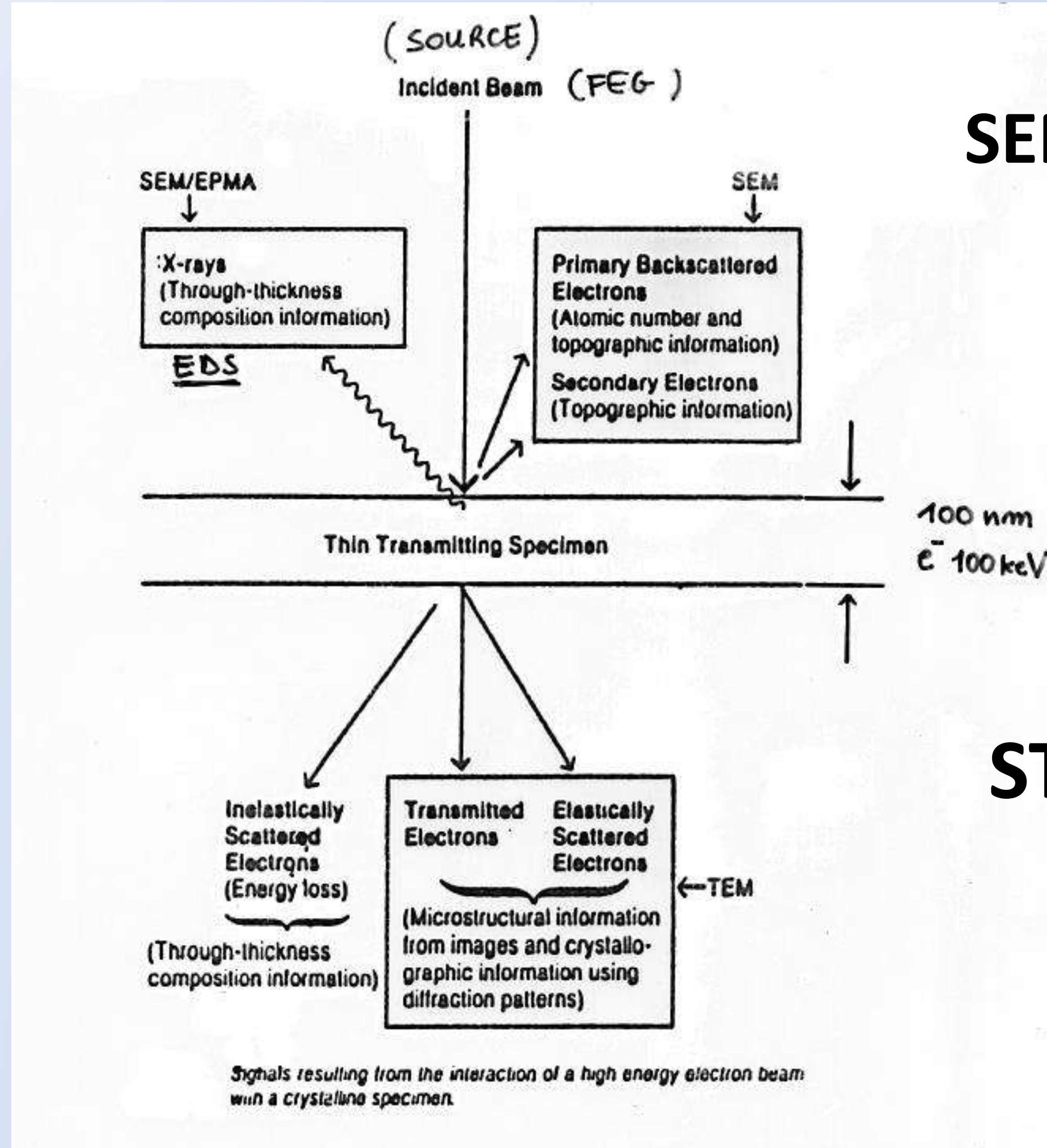


Contrast $C = (S_i - S_{i+1})/S_i = \Delta S_i/S_i$

Empirical criterion of Rose $\Delta S_i/S_i > 5\%$

Electrons-matter interaction

EDS microanalysis in SEM-ESEM - STEM

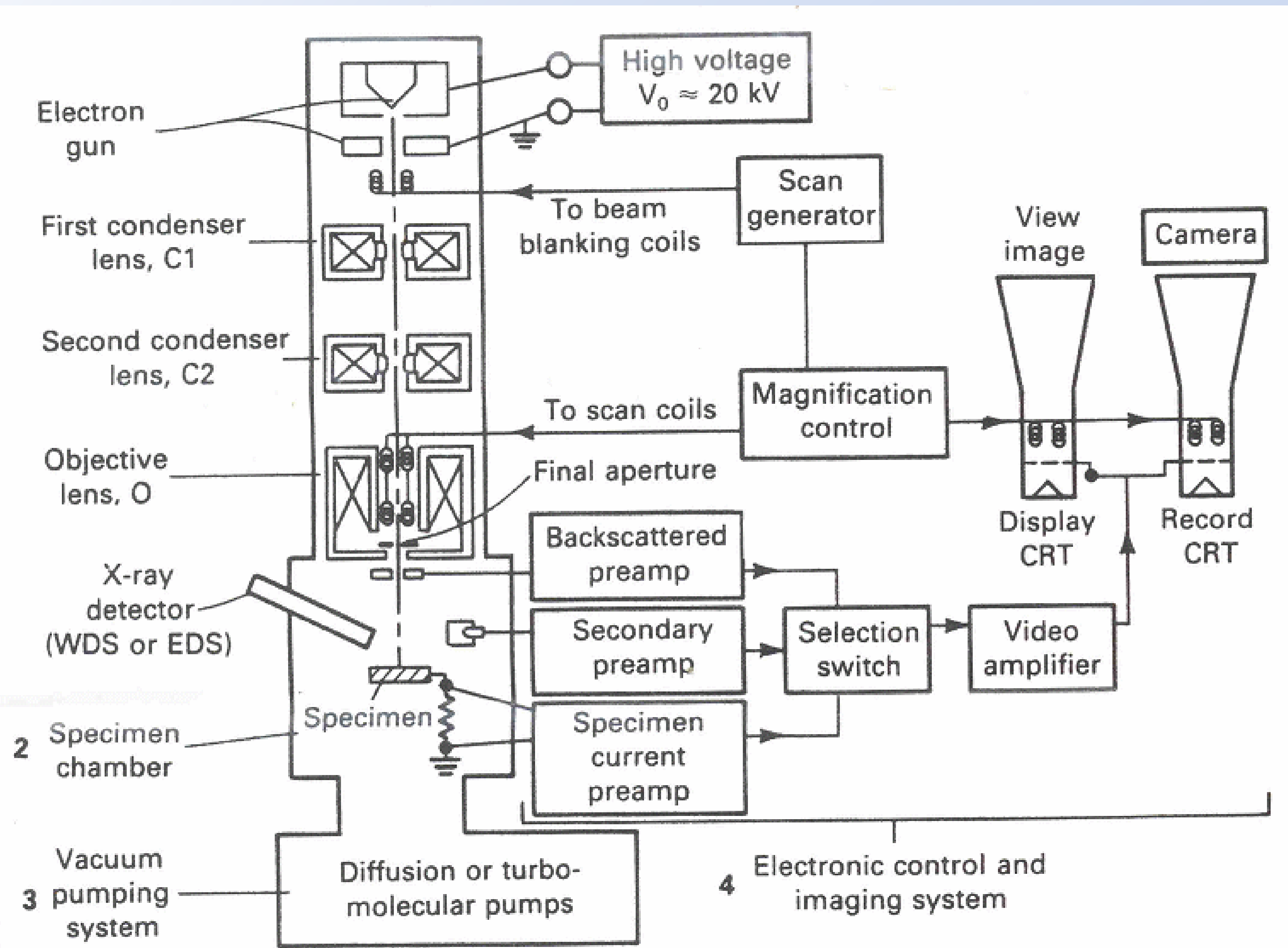


Signals resulting from the interaction of a high energy electron beam with a crystalline specimen.

SEM-ESEM

STEM

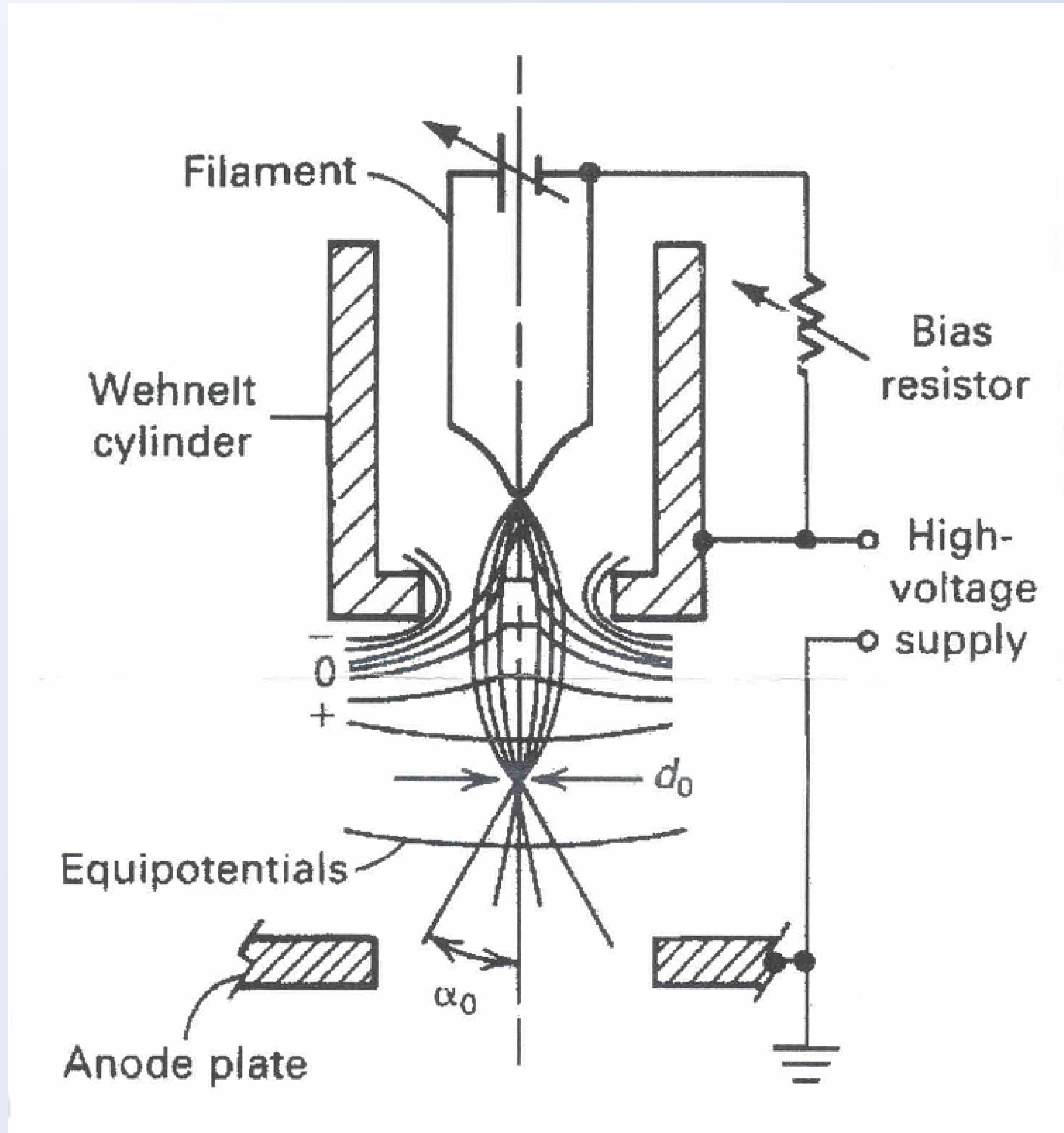
Scheme of a conventional SEM



Types of sources

- THERMO-ELECTRONIC EMISSION
- FIELD EMISSION – FIELD EFFECT

Sources: thermo-electronic emission



Current Density

Thermionic cathodes

$$j_c = AT_c^2 \exp(-\varphi / kT_c)$$

(Richardson)

where,

K Boltzmann constant

T_C cathode temperature

A ~ 120 A K^{-2} cm^{-2} cathode material constant

φ work function

Emission by field effect

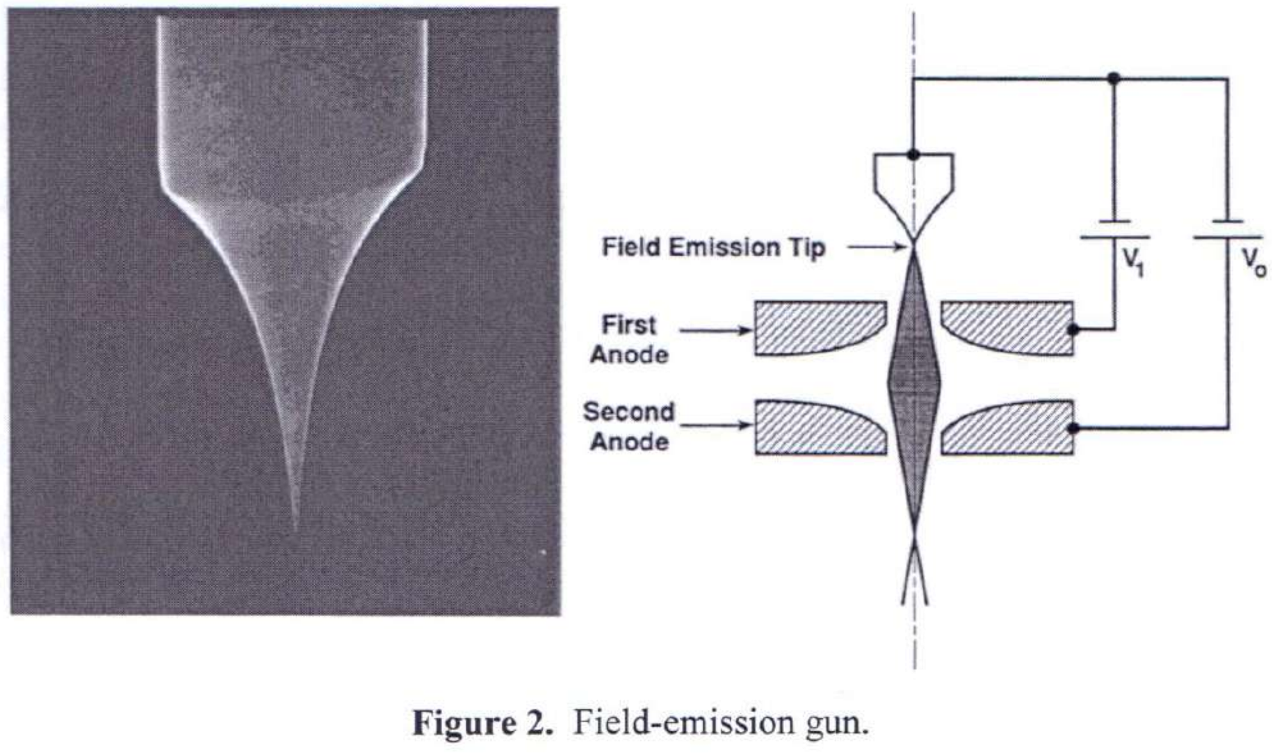
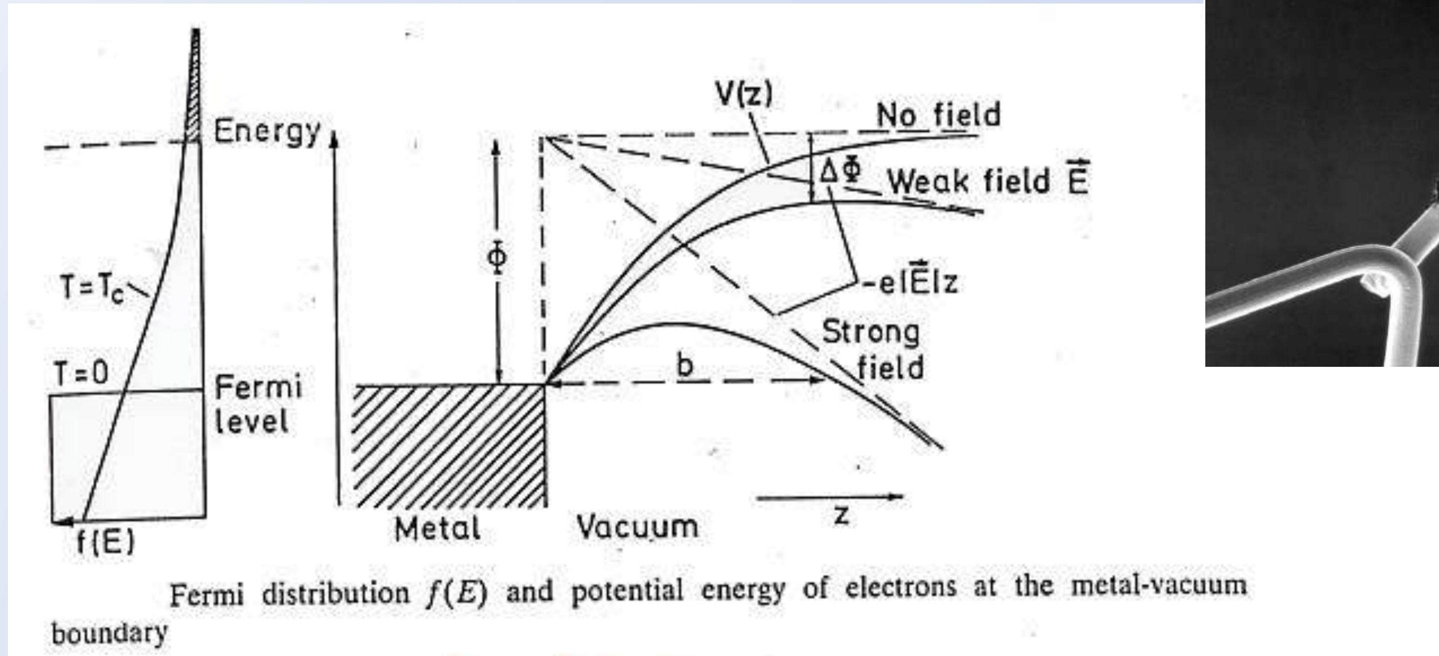


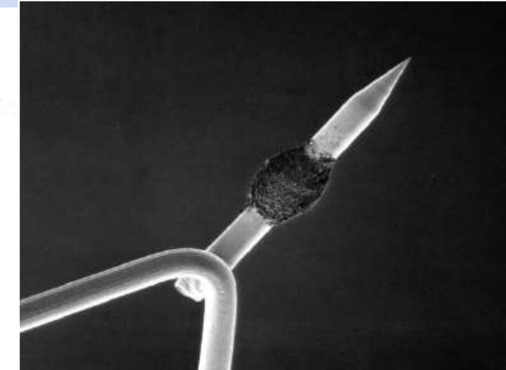
Figure 2. Field-emission gun.

- Emission due to the ability to extract electrons from a sharp Tungsten monoblock by strong electric fields.
- Radius of curvature of the crystal: 20-200 nm.
- Vacuum required: 10^{-7} Pa.

Field emission



Fermi distribution $f(E)$ and potential energy of electrons at the metal-vacuum boundary



Current Density

Field emission

$$j = \frac{K_1 |E|^2}{\varphi} \exp\left(- \frac{K_2 \varphi^{32}}{|E|} \right)$$

(Fowler - Nordheim)

Quantitative differences between FEG e thermo-el.

	Thermionic emission		Field emission
	W	LaB_6	W
Work function ϕ	4.5 eV	2.7 eV	4.5 eV
Richardson constant A	75–120	30 A cm^{-2} K^{-2}	–
Emission current density j_c	1–3 A cm^{-2}	25 A cm^{-2}	10^4–10^6 A cm^{-2}
Total current emitted I	10–100 µA		1–10 µA
Working temperature T_C	2800 K	1400–2000 K	(1000–1800 K)
Gun brightness β [A cm^{-2} sr^{-1}]	5×10^4 (E = 10 keV) 1–5×10^5 (100 keV)	3×10^5 (15 keV)	5×10^7–5×10^8 (20 keV) 2×10^8–2×10^9 (100 keV)
$J = dI/d\Omega$ [A sr^{-1}]	$\simeq 10^{-2}$		$\simeq 10^{-4}$
Crossover diameter d_c	20–50 µm (hairpin) 10–30 µm (pointed cathode)	10–20 µm	5–10 nm
Energy width ΔE	1–2 eV	0.5–2 eV	0.2–0.5 eV
Lifetime	25 h	150–200 h	–
Vacuum	10^{-2}–10^{-3} Pa	10^{-3}–10^{-5} Pa	10^{-7}–10^{-8} Pa

(1 Pa = 1 N m^{-2} = 10^{-2} mbar)

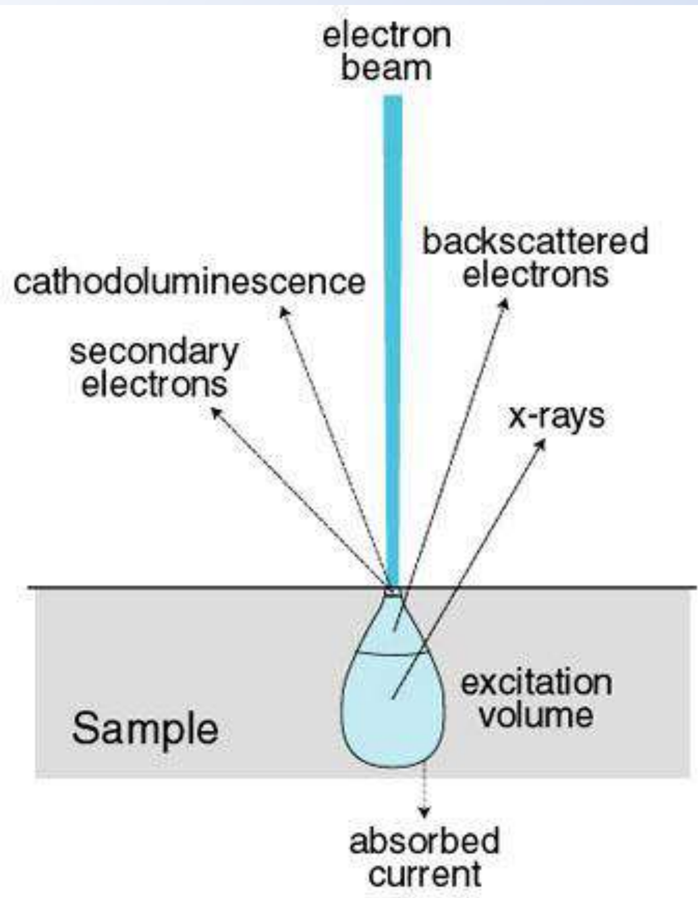
SEM-ESEM

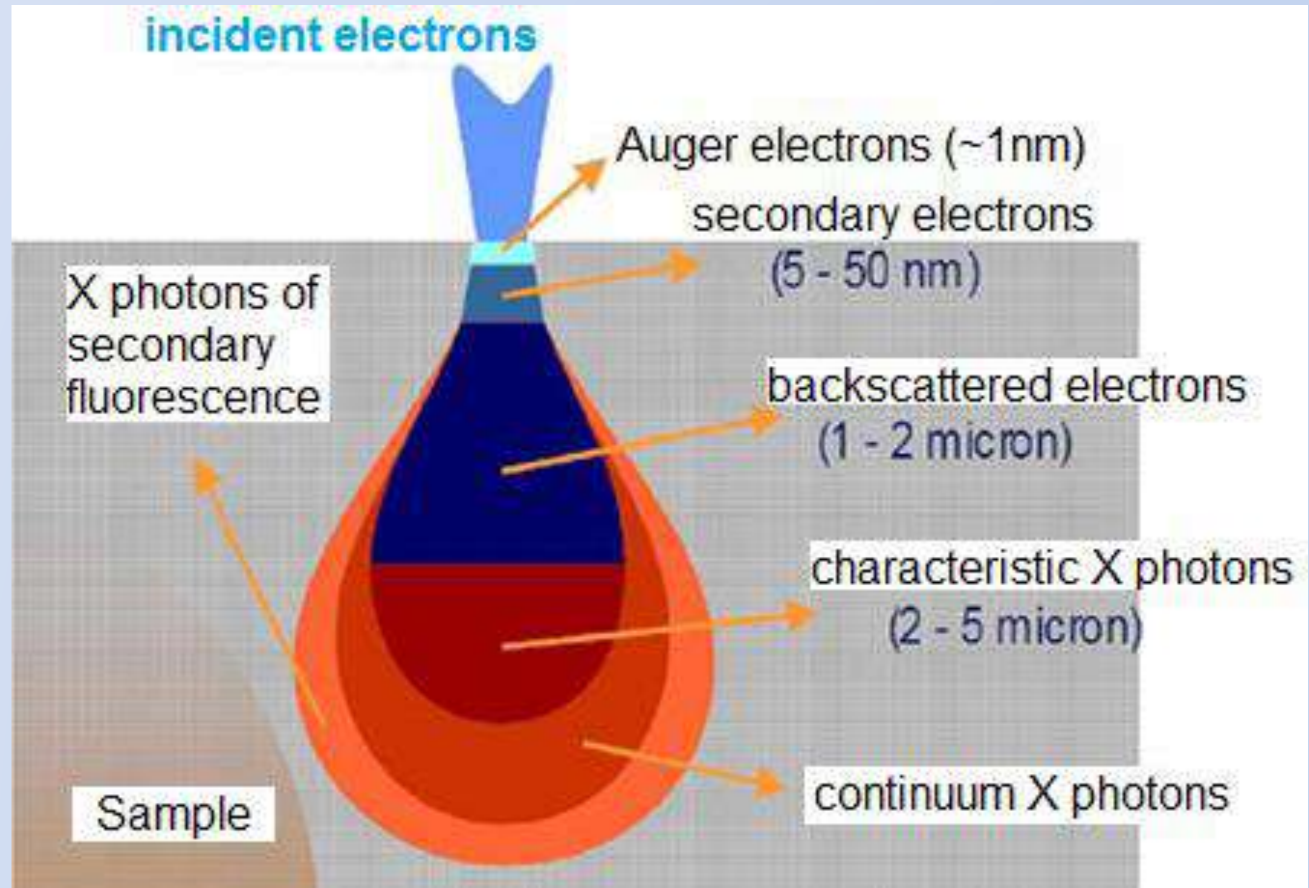
A atomic weight (g/mol)
E_0 beam energy (keV)
ρ density (g/cm^3)
Z atomic number

Penetration depth

$$x(\mu m) = \frac{0.1 E_0^{1.5}}{\rho}$$ empirical

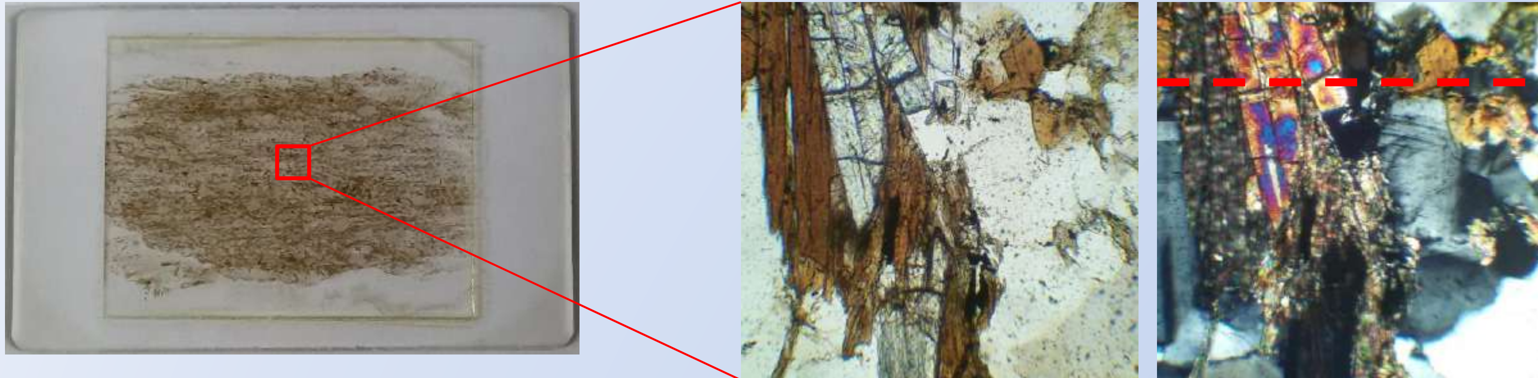
$$r(\mu m) = \frac{2.76 \times 10^{-2} A E_0^{1.67}}{\rho Z^{0.89}}$$ theoretical



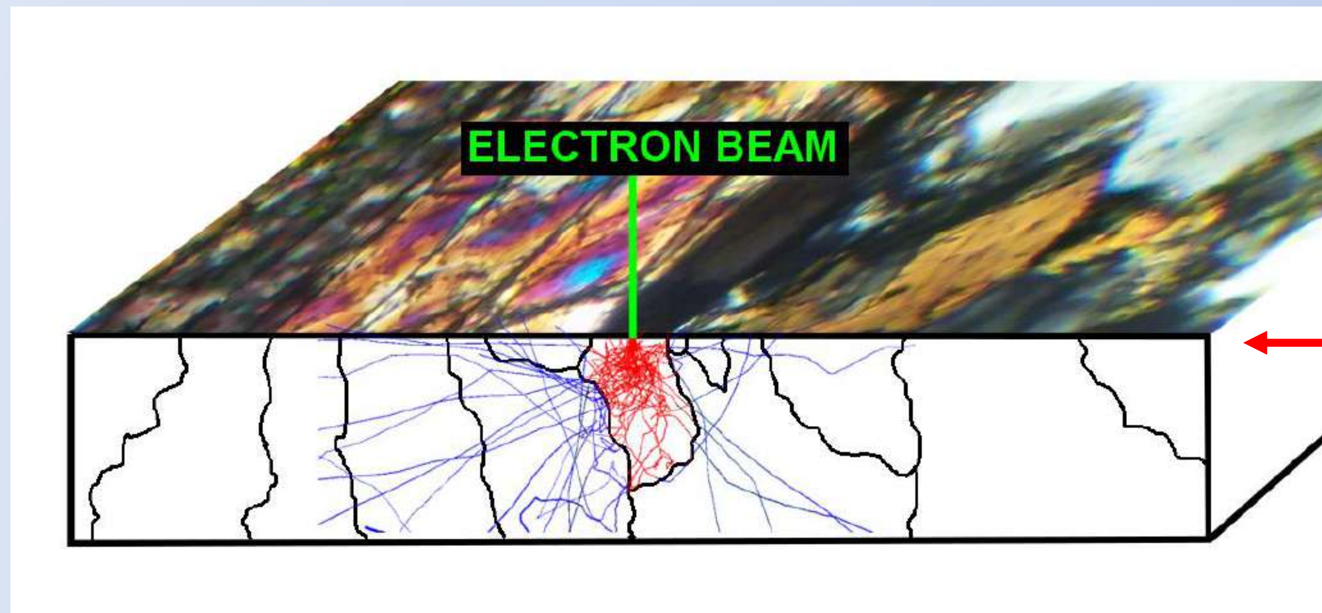


Composite material/polycrystalline/metals, alloys, minerals, bio-minerals, corals

Mineralogical thin section, micro-nano crystalline materials



WARNING
Electron – matter interaction



Attention

Caveat: SEM-EDS-EDS measurement strategy by Monte Carlo micro- and nanoanalysis simulations

SEM-EDS quantitative micro-nanoanalysis of ultrathin layers and sub-micrometric particles

Quantitative micro-analysis by SEM-EDS may suffer from **systematic errors** because of small object thickness (< 1 μm).

Several phenomena had to be considered:

- **Elastic scattering** of electrons in the finite size (mass) of the object, strongly affected by the average atomic number;
- Reduced **X-ray absorption**, mainly related to the object geometry, which influences both the length of the X-ray absorption path within the specimen, fluorescence contribution and the take-off angle;
- **EDS detector – sample surface configuration**.

Monte Carlo SEM-EDS quantitative micro-nanoanalysis of ultrathin layers and sub-micrometric particles

This method is useful when **the dimensions of the object in analysis approaches** the ones of **the electron penetration volume** (ultra-thin layers, substrates, composites, micro-nano-objects, powder materials), for instance:

- **SEM analysis of bulk and thin sections of minerals, biominerals, textures, concretions, layer superpositions and rocks;**
- **Study of pigments and layers in paintings;**
- **Study of surface protective treatments;**
- **Contamination and alteration layers;**
- **Micro- and sub-microscopic compounds and surface disomogeneity;**
- **Oxidized metal surfaces, etc.**

X-ray generation in 1 µm thick gold leaves (Au-Ag-Cu alloy) in a glass matrix

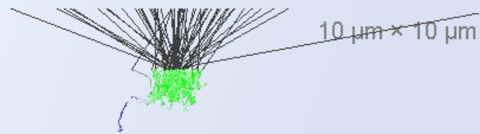
Generation of **detected x-rays** as a function of position for a centred beam.

Beam energy: 25 keV

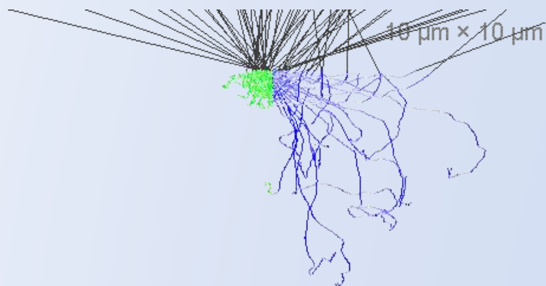
Gold alloy

Glass main elements

Centred beam



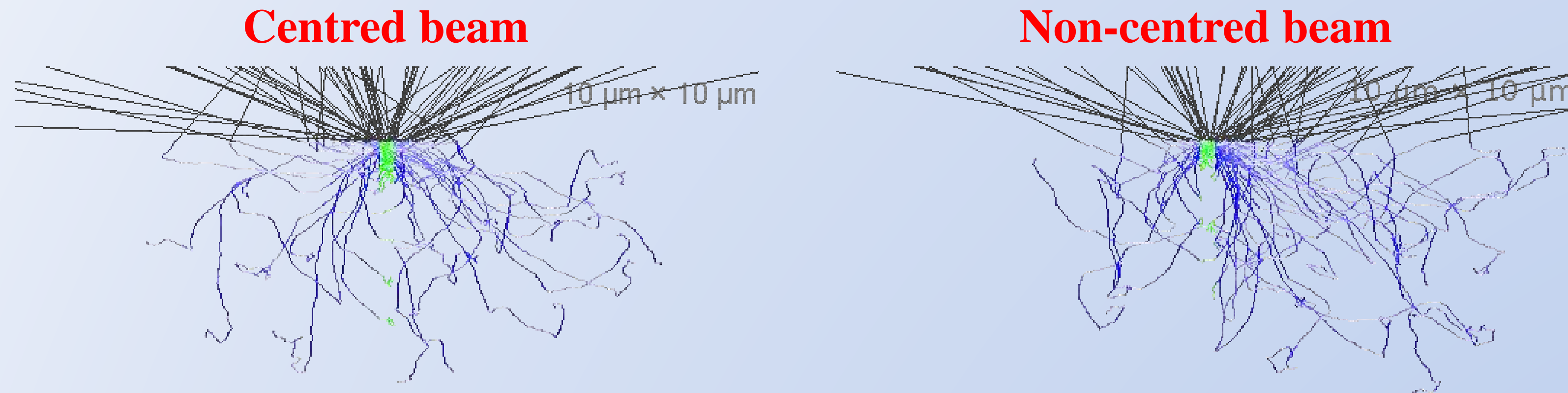
Non-centred beam



Trajectories of electron scattering in the cases of a centered and non-centred beam.

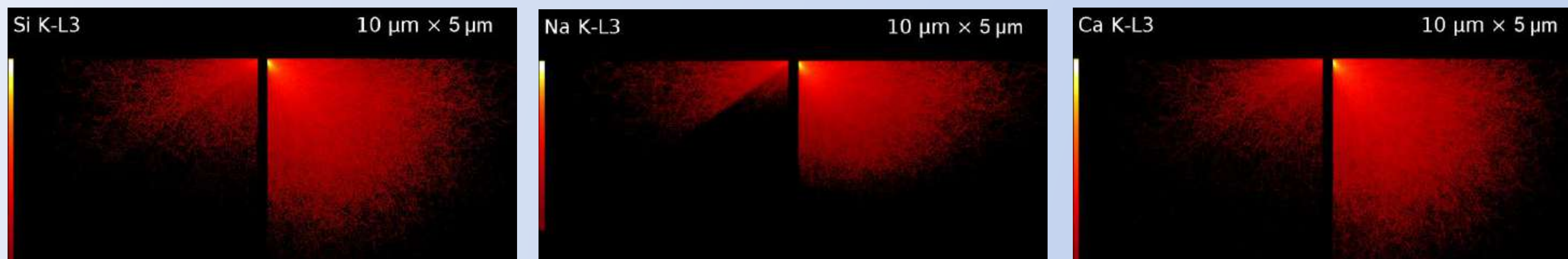
X-ray generation in 0.2 μm thick gold leaves

Beam energy: 25 keV



Trajectories of electron scattering in the cases of a centered and non-centred beam.

Glass main elements

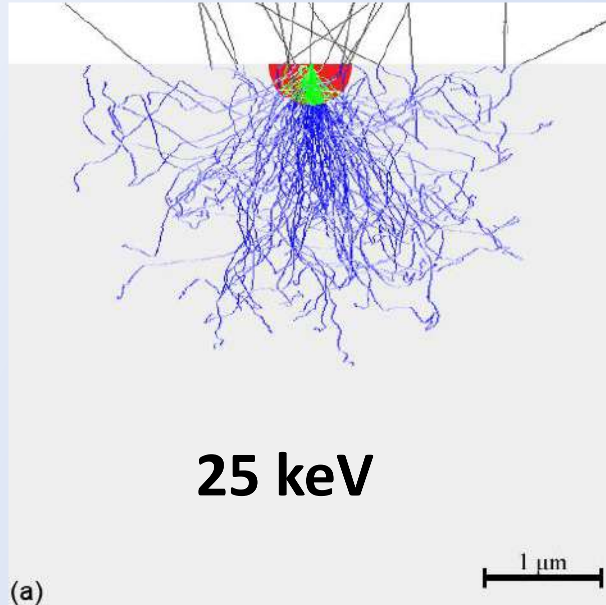


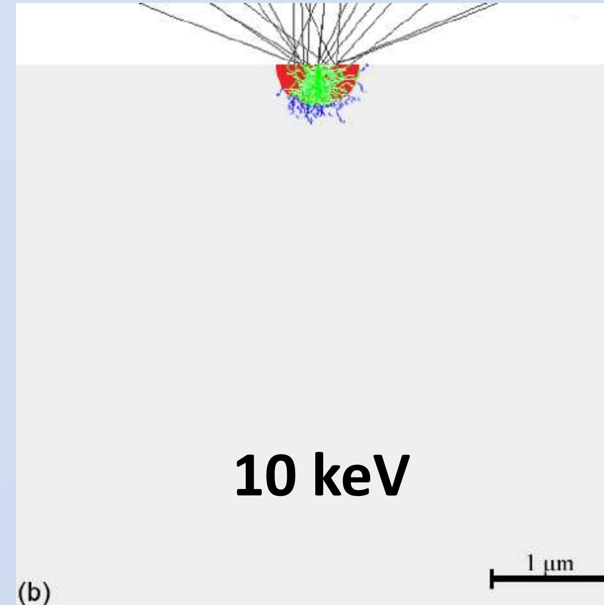
Generation of detected x-rays as a function of position for a non-centred beam.

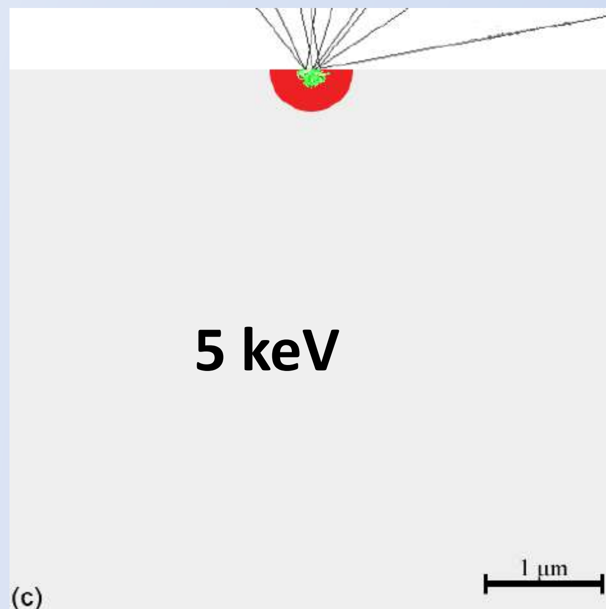
Glass fibre-reinforced cementitious composite

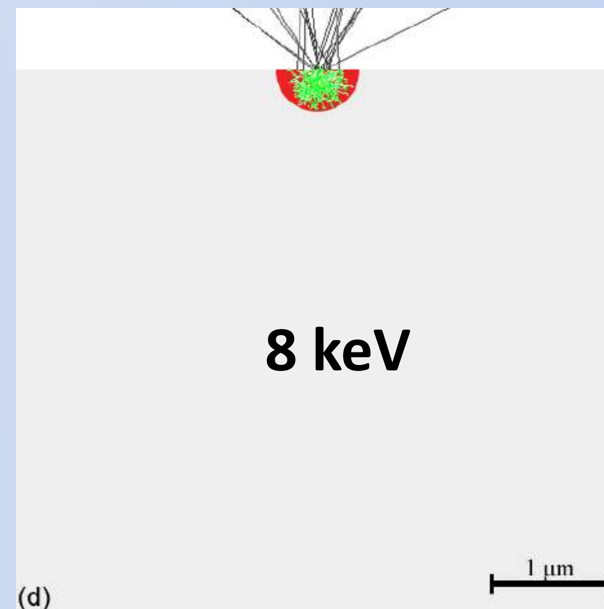
Glass fibre analysis: fibre radius of 700 nm

Grey: silica based cement
Red: emicircle silica-based glass fibre

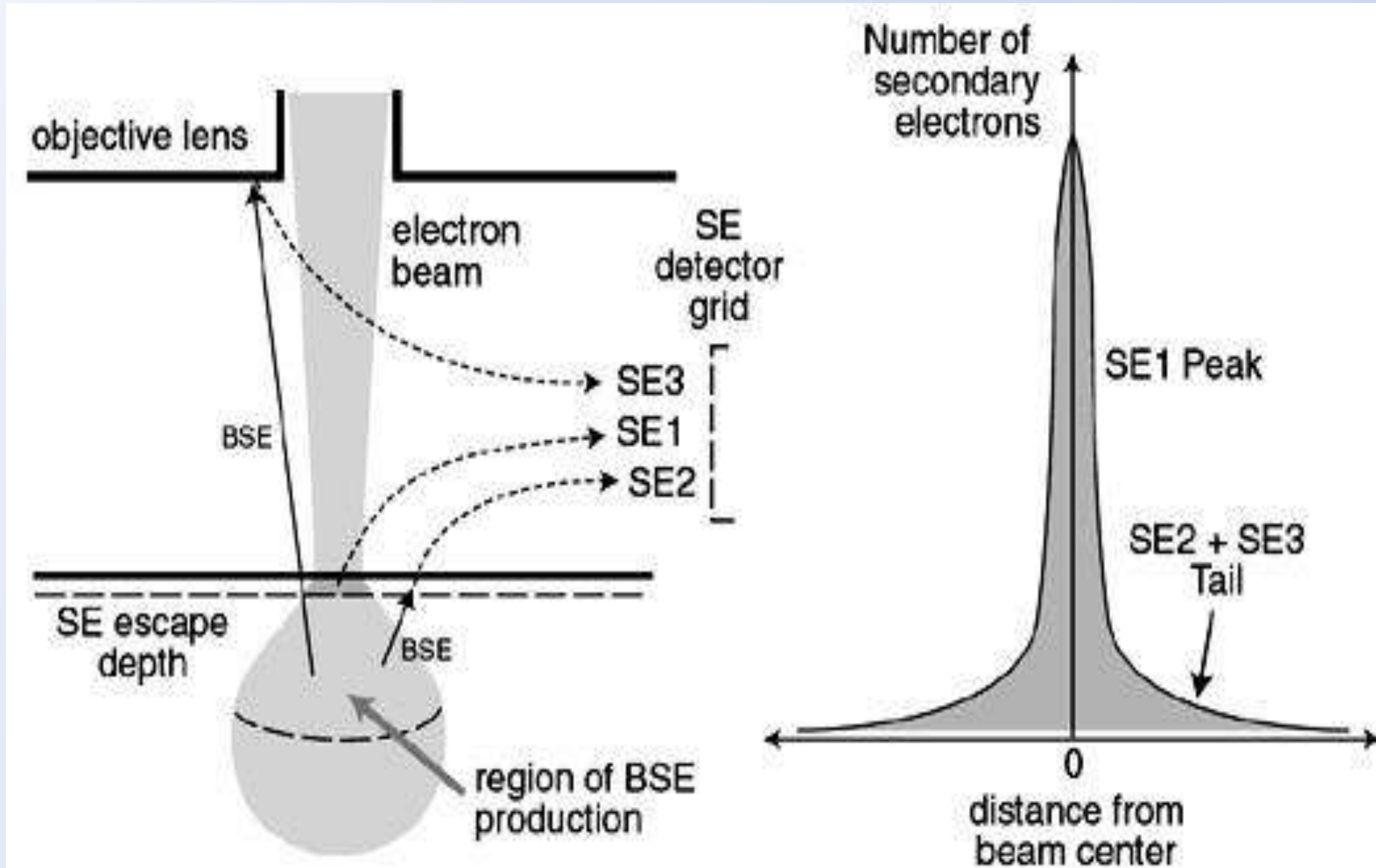








Secondary electrons (SE)



Scanning electron microscopy – imaging

Basic information. Size, shape, fine structure at the micrometer to nanometre scale.

Specimen types:

- General: thick, bulk (millimetre to centimetre dimensions), solid, low vapor pressure (no water); conductors (at least semiconducting)
- Special: microscopic particles; film(s)-on-substrate; fixed biological specimens; wet specimens (variable-pressure or environmental SEM); nonconductors with conductive coating (conventional high beam energy and high vacuum) or uncoated (low beam energy, high vacuum; or high beam energy, variable-pressure or environmental SEM)

Signals detected:

- Backscattered electrons (BSE)
- Secondary electrons (SE)
- Specimen, absorbed, induced currents (SC)

Scanning electron microscopy – imaging

Resolution (lateral):

- Conventional electron source: 10-50 nm
- Field emission electron source: 1-5 nm

Resolution (depth):

- 10-1000 nm (BSE)
- 1-10 nm (SE)

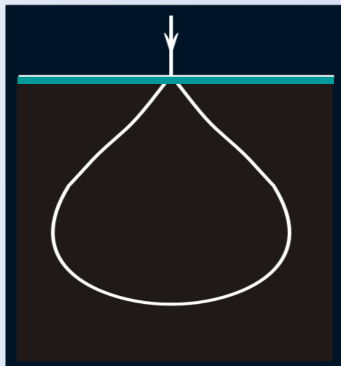
Depth of field. Selectable with final aperture: 0.1-1 unit of the image field width; high value enables stereomicroscopy for three-dimensional recognition.

Types of image information:

- Topography (SE, BSE)
- Composition (BSE)
- Crystal orientation (BSE)
- Electrical field (SE)
- Magnetic field (SE, BSE)
- Beam-induced current (SC), Cathodoluminescence (CL)

Limits of conventional SEM

- Samples must tolerate vacuum.
- The sample surface must have an electrical ground connection.

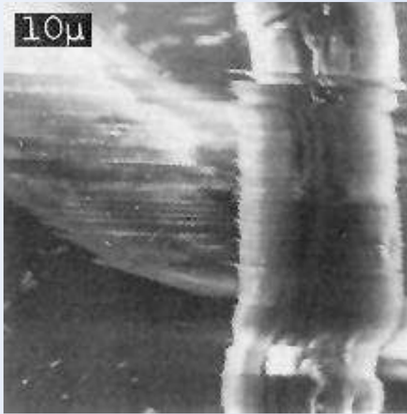


Hydrated materials must be dehydrated before analysis.

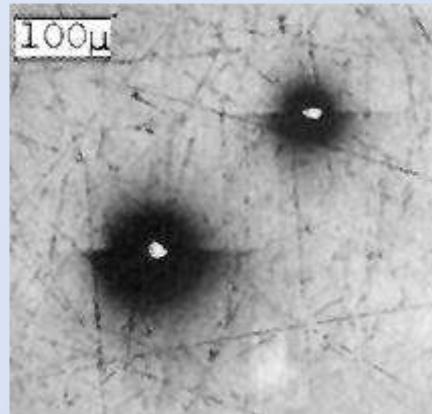
Insulating materials must be covered with conductive films - dynamic *in-situ* experiments that break the film cannot be performed.

Artifacts from accumulation of charge in imaging with SE in high vacuum

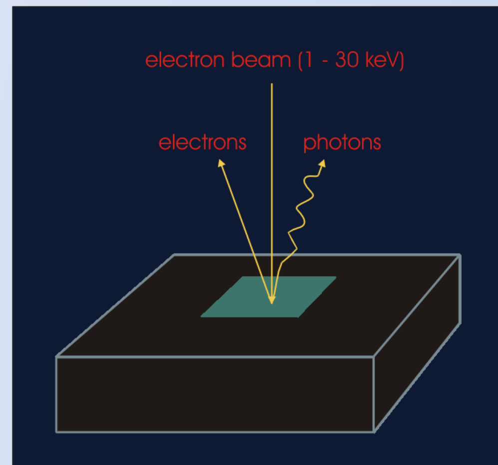
Nylon fibers



Dust particles

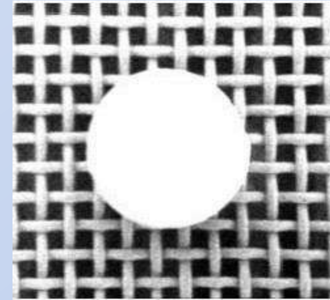


T.J. Shaffner & J.W.S. Hearle, Scanning Electron Microscopy (O.M. Johari, ed.) 62 (1976). [20 kV]

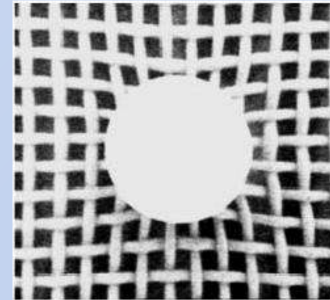


Al_2O_3 sphere

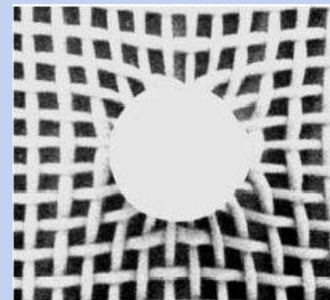
t = 0



t = 17 s



t = 70 s



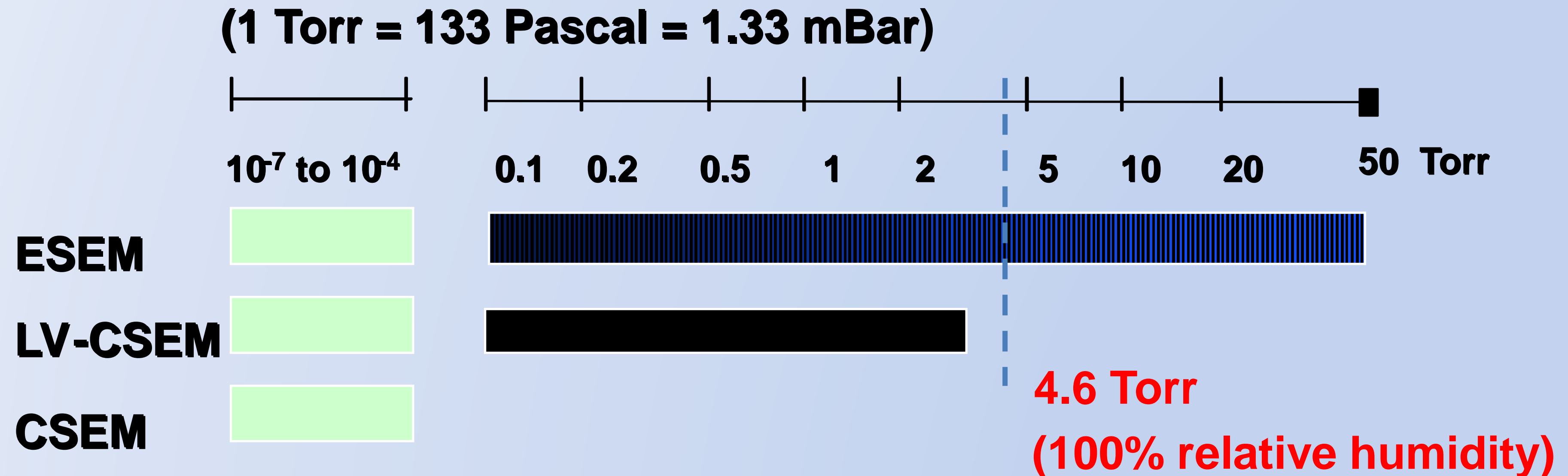
M. Belhaj *et al.*, J. Appl. Phys. 88, 2289 (2000).
[13 kV, 3 nA, sphere diameter = 1.5 mm]

ESEM

Environmental Scanning Electron Microscope

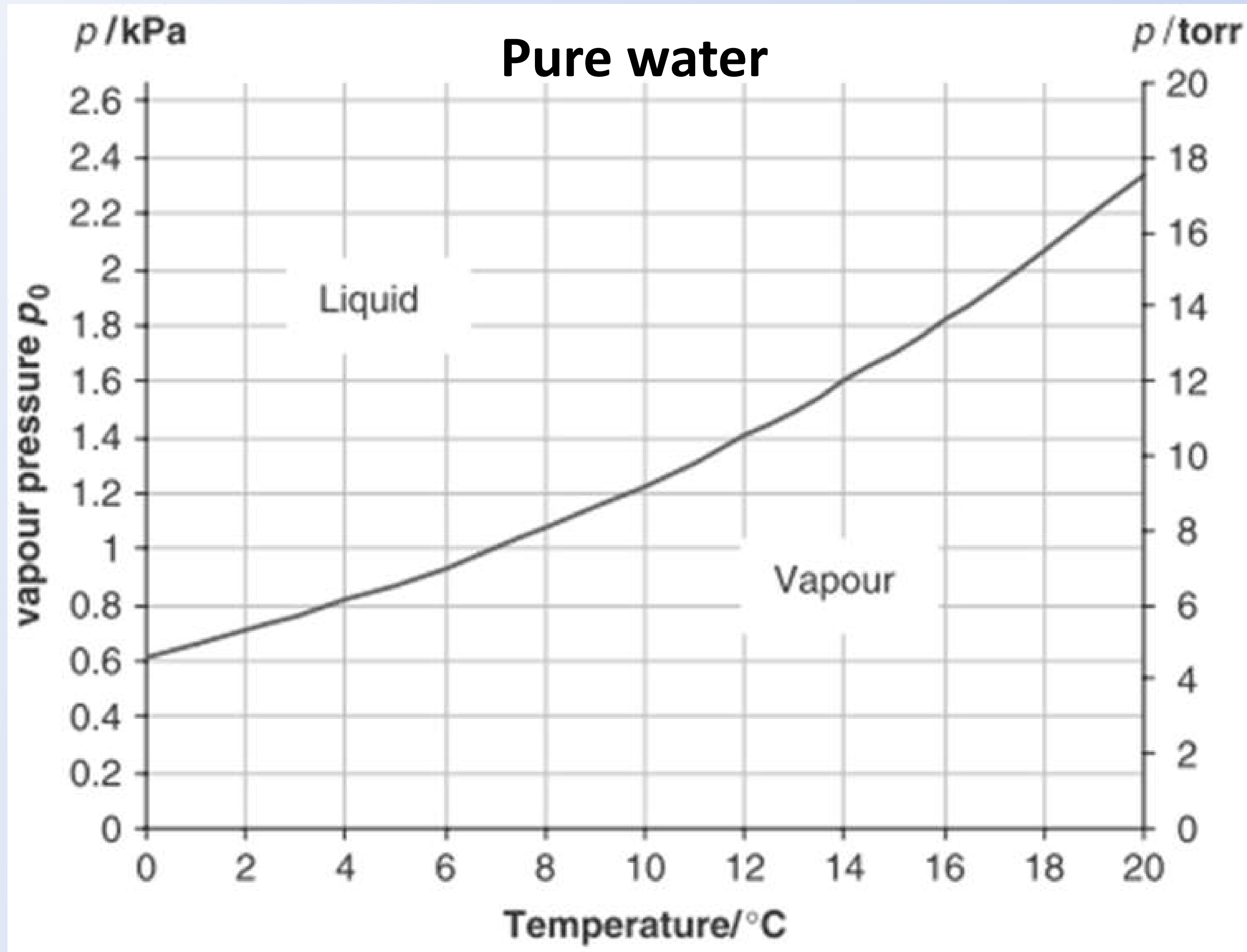
Field of pressure

- Low Vacuum: until ca 1 Torr
- ESEM until ca 30 Torr



Imaging with water vapour

Thermodynamic equilibria



Advantages of environmental SEM

- Samples do not necessarily have to be vacuum tolerant.
- The sample surface does not require an electrical ground connection.

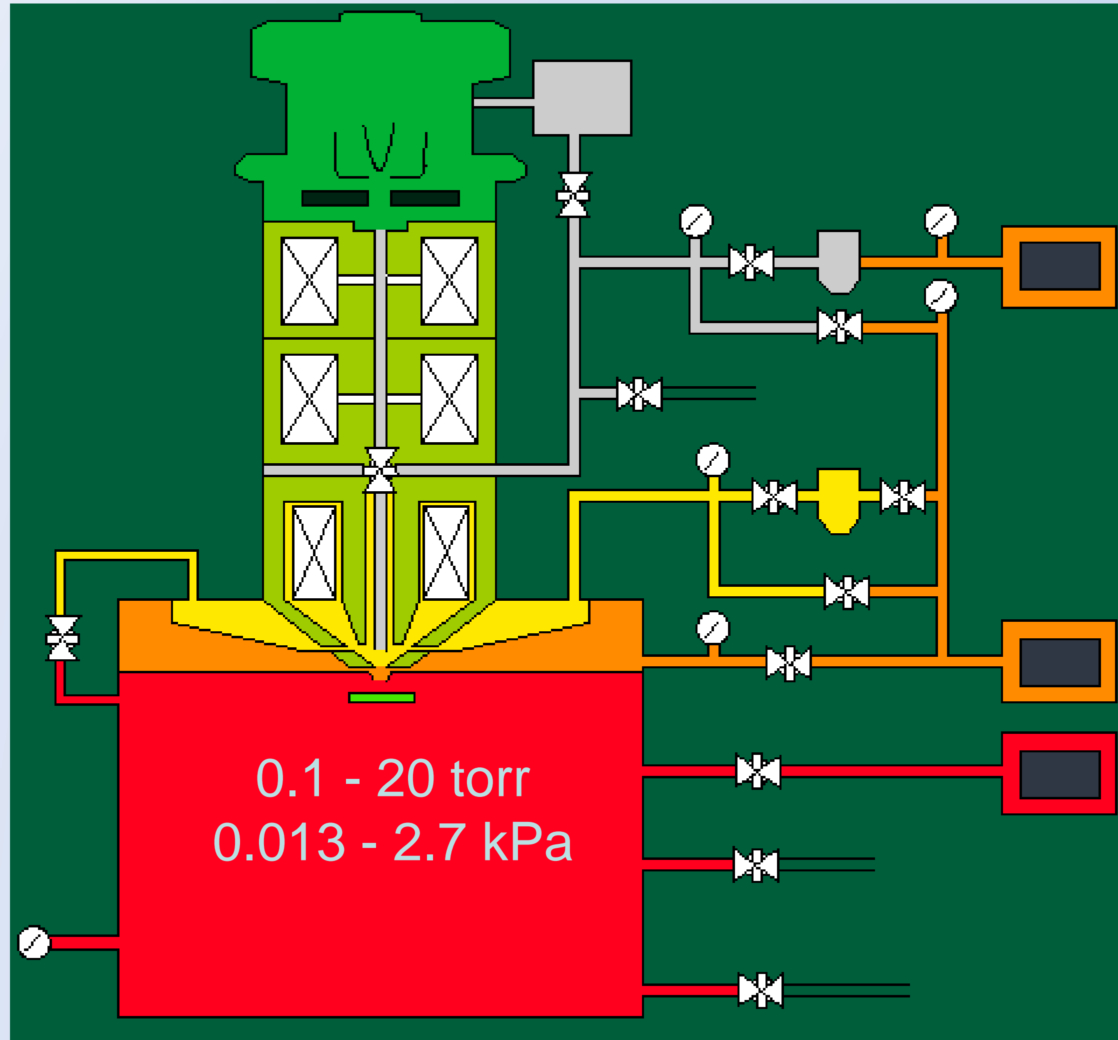
Samples can be solid, hydrated, or liquid.

Samples can be conductors, semiconductors or insulators.

Dynamic *in-situ* experiments (e.g., hydration-dehydration, traction, gas-surface reaction) can be performed.

Environmental SEM

- Pressure Limiting Apertures **PLA**.
- Differential pumping.

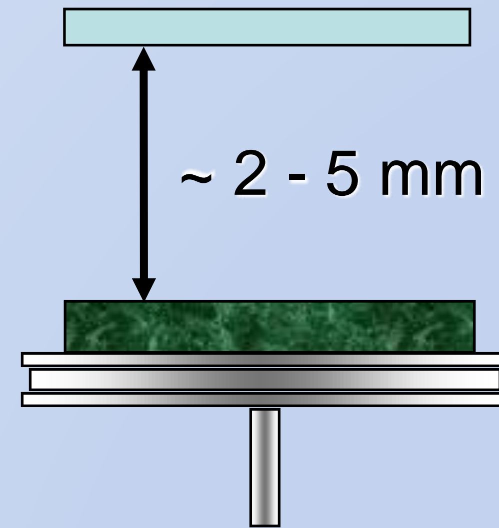


Mean free path of primary electrons in the gas

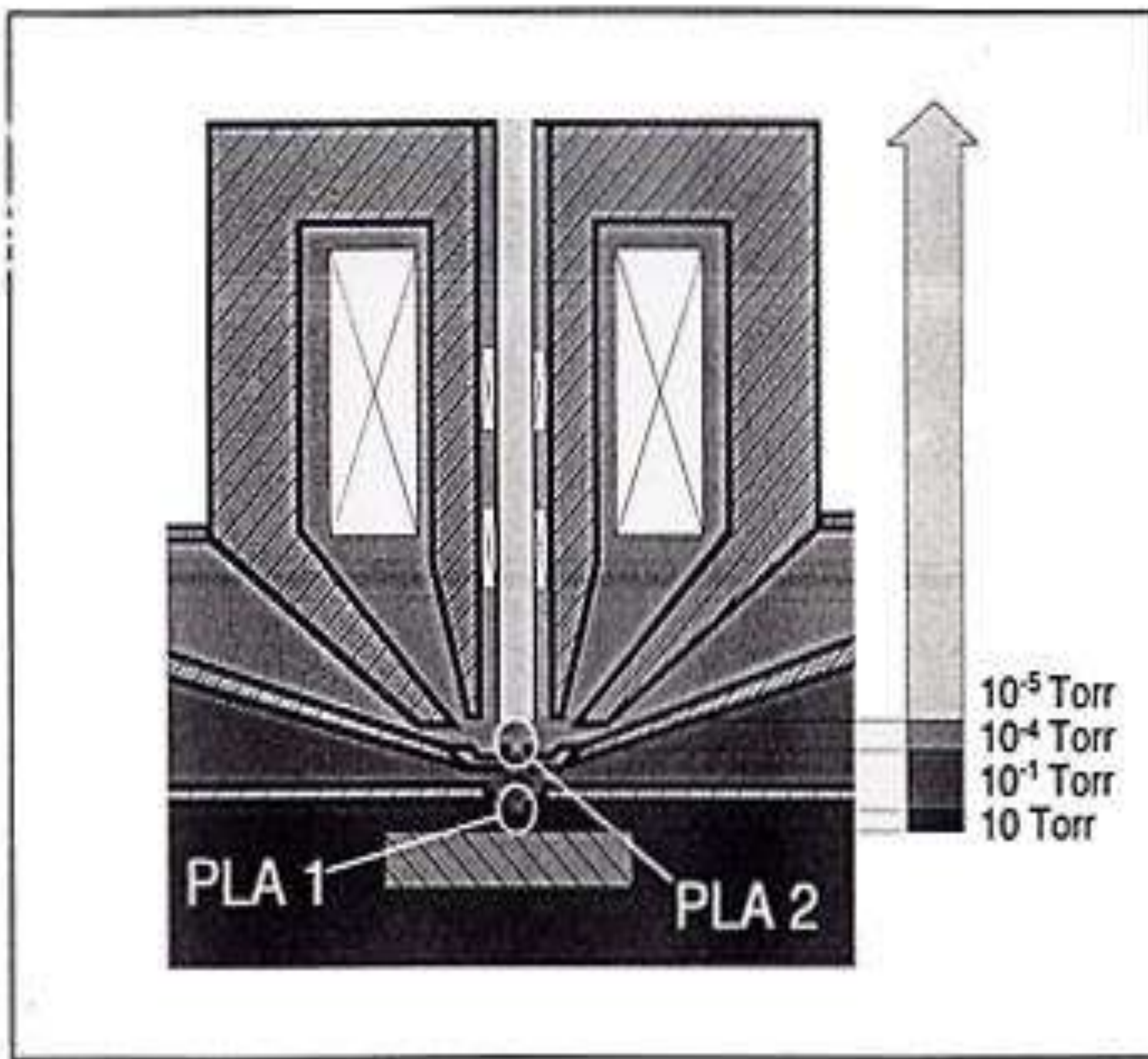
10
8
6
4
2
0

0 5 10 15 20 25 30

1 torr
5 torr
10 torr

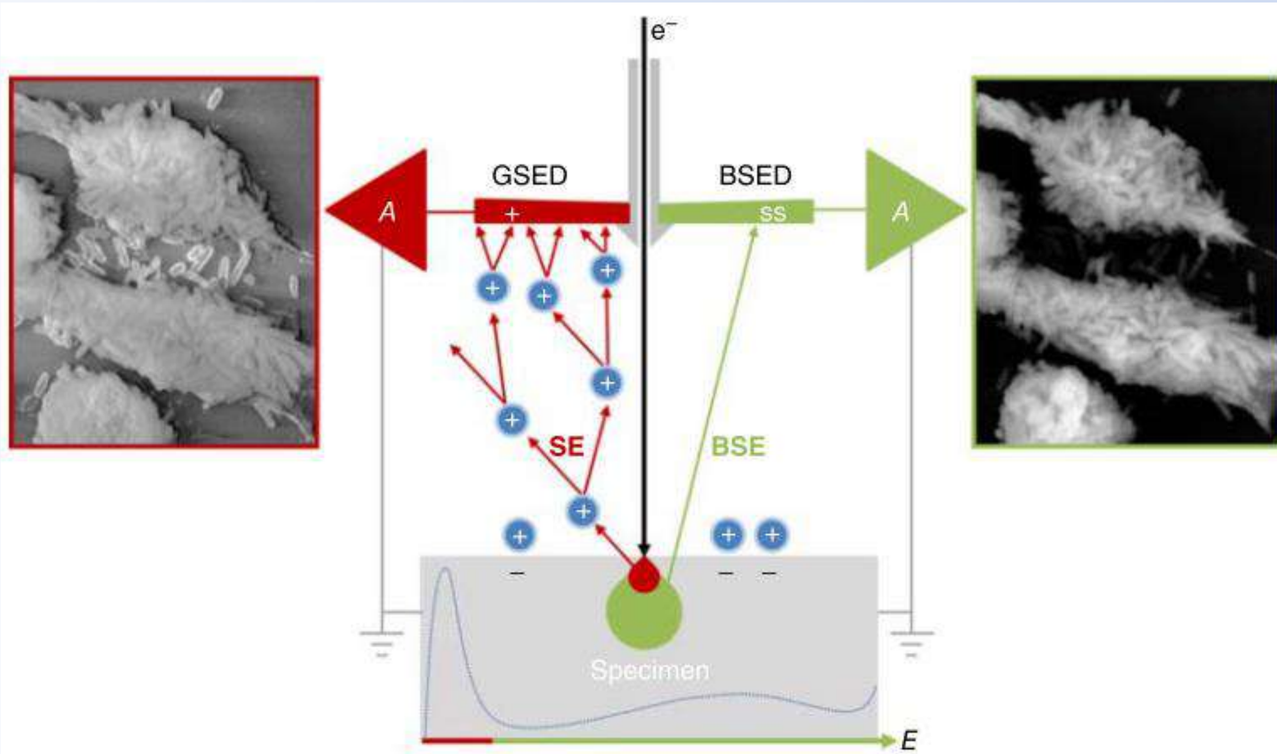


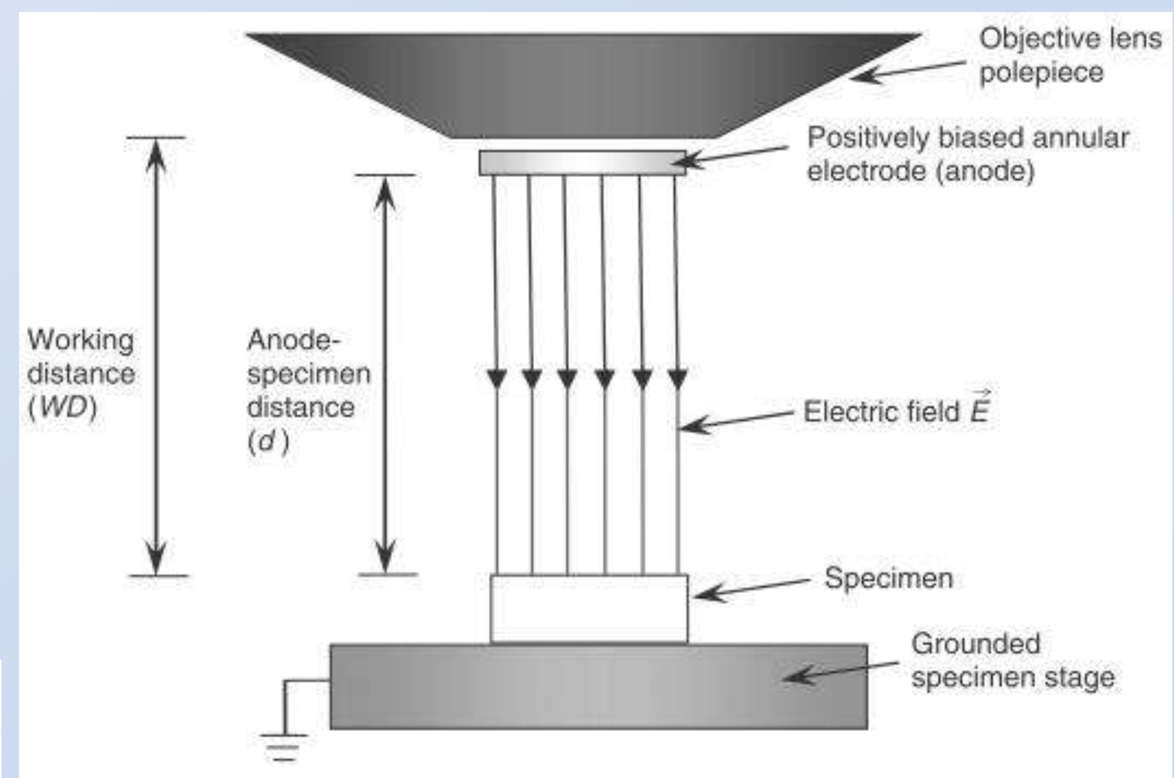
Two Pressure Limiting Apertures (PLA's) integrated into the final lens assembly permit vacuums as low as 50 Torr in the sample chamber while maintaining high vacuum conditions in the gun. Keeping the apertures close together at the bottom of the column minimizes the effects of electron scattering.



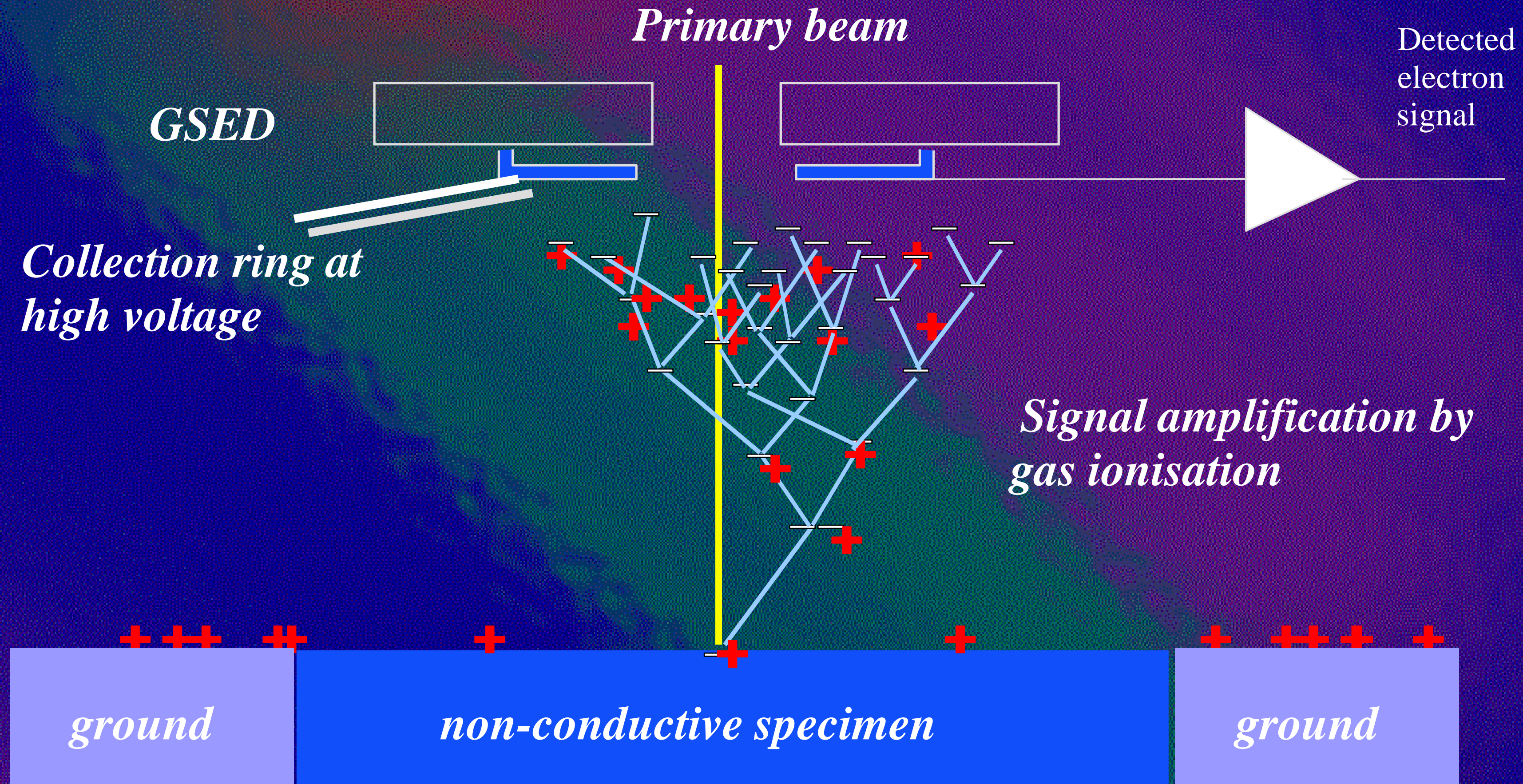
Signal generation in a gas

Ionised Gas Cascade Signal Amplification





Principle of operation of the detector GSED (Gaseous Secondary Electron Detector)

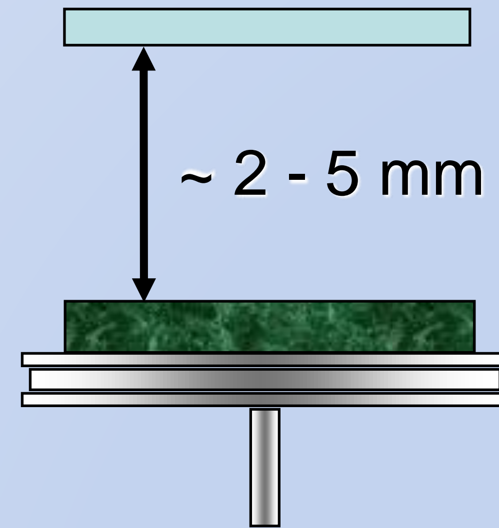


Mean free path of primary electrons in the gas

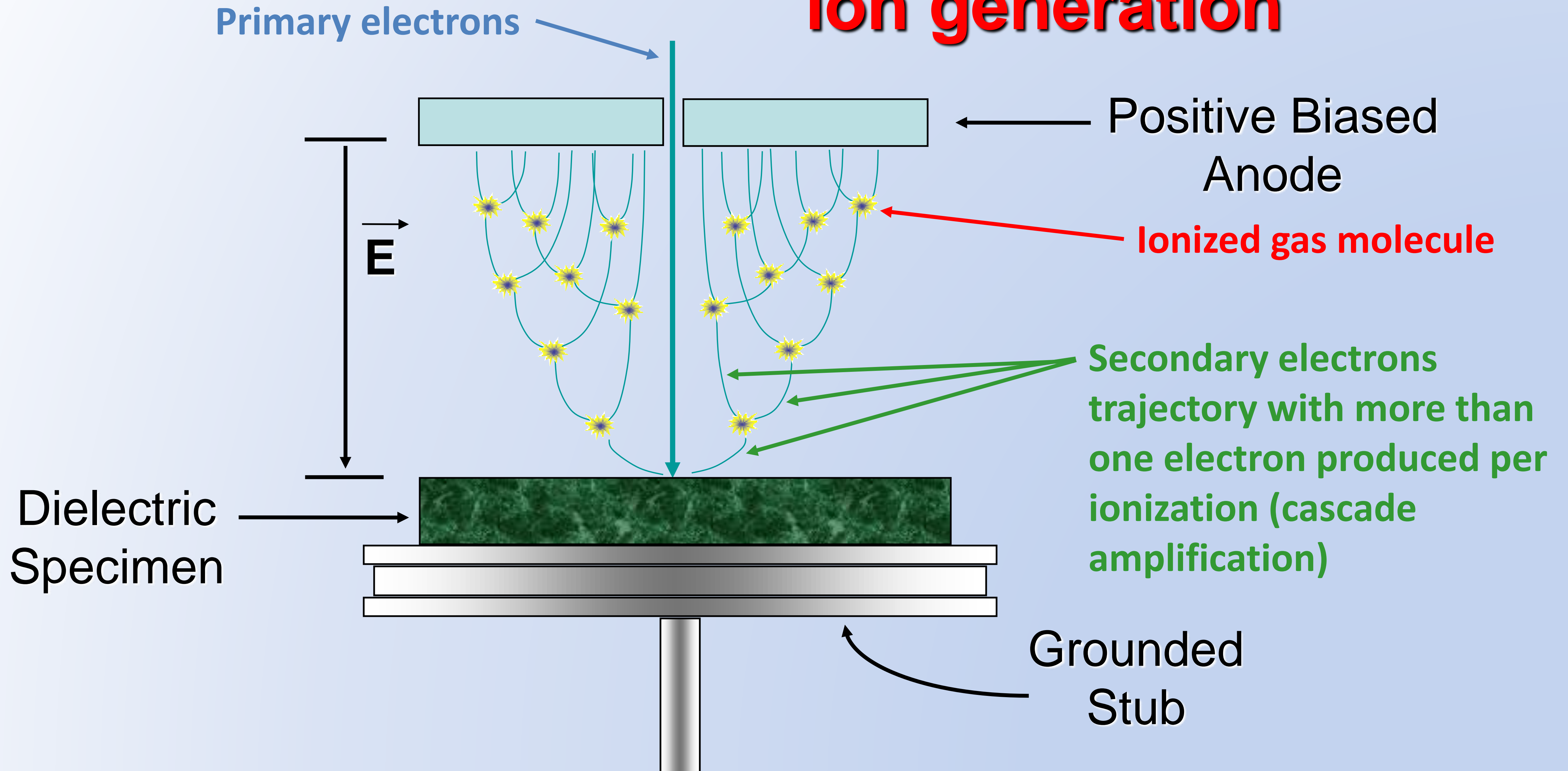
10
8
6
4
2
0

0 5 10 15 20 25 30

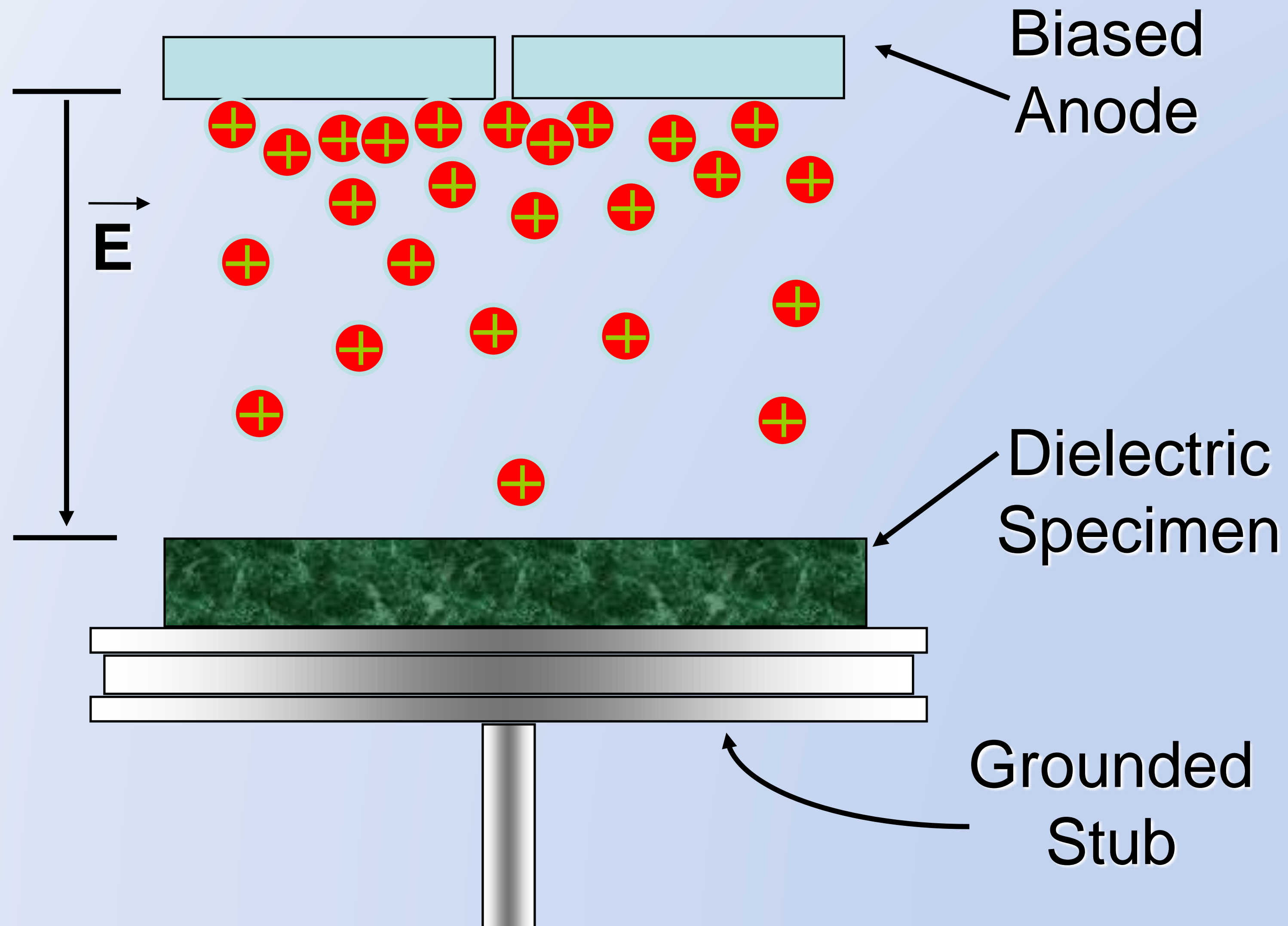
1 torr
5 torr
10 torr

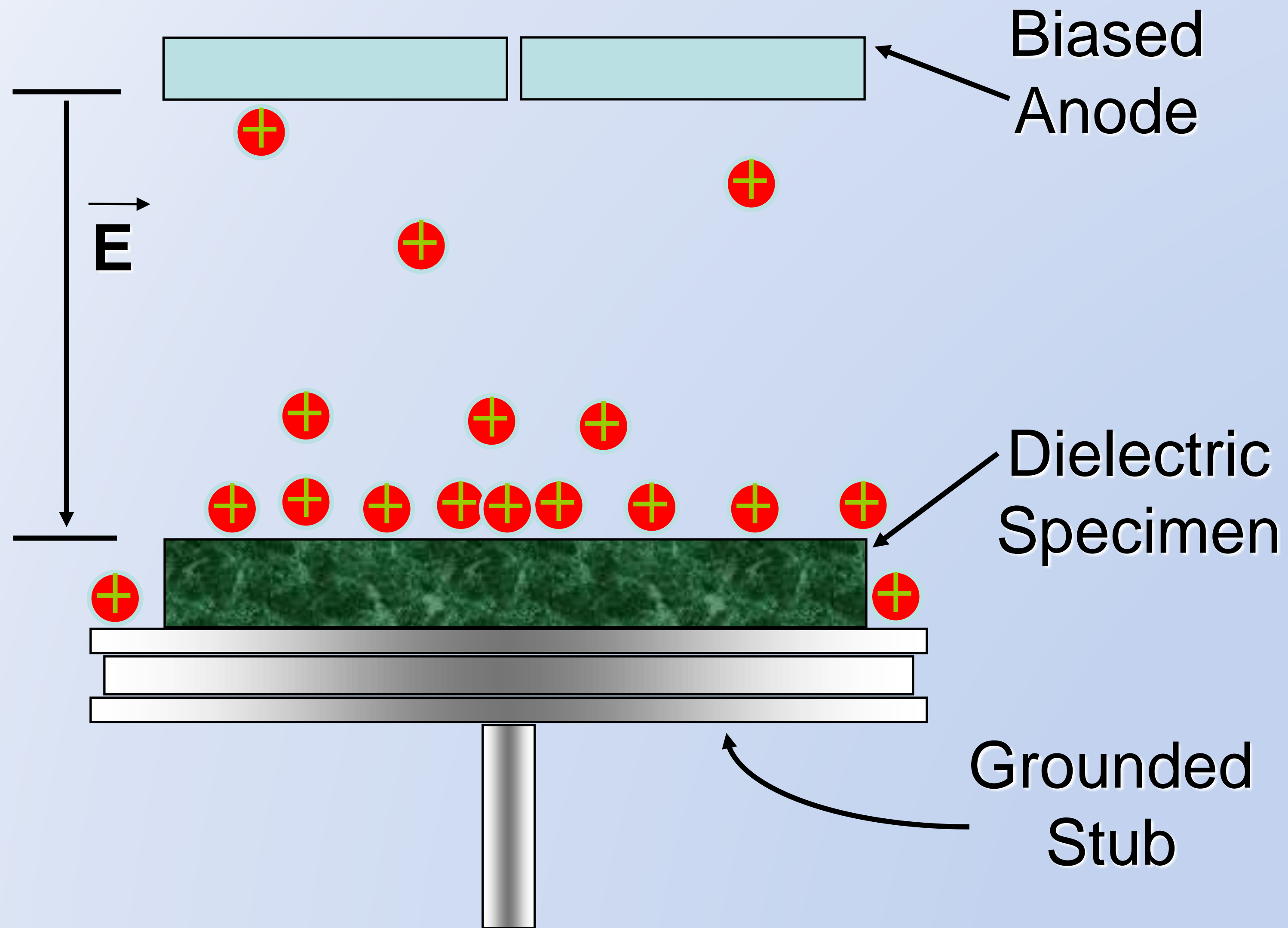


ESEM: cascade amplification – ion generation



ESEM: ion generation




Biased Anode
E
Dielectric Specimen
Grounded Stub

What if there are too many ions?

Surface potential can float positive.

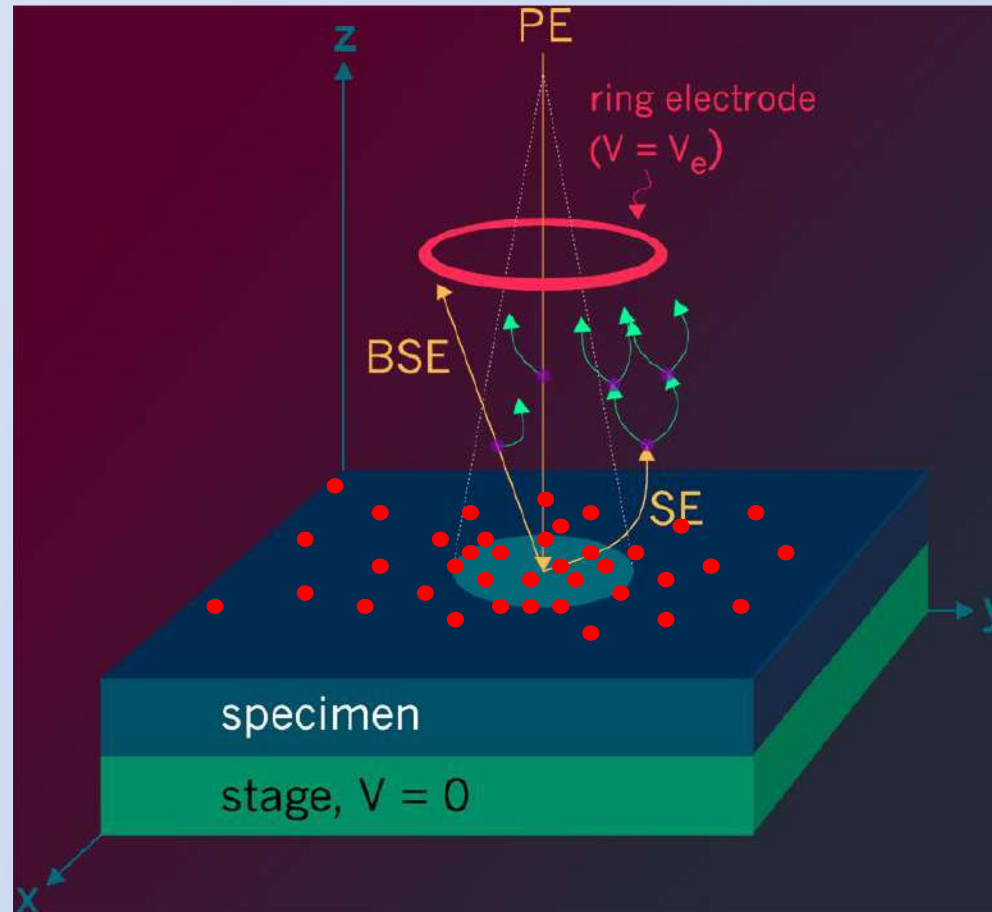
Reduces gas gain.

Can compromise x-ray microanalysis.

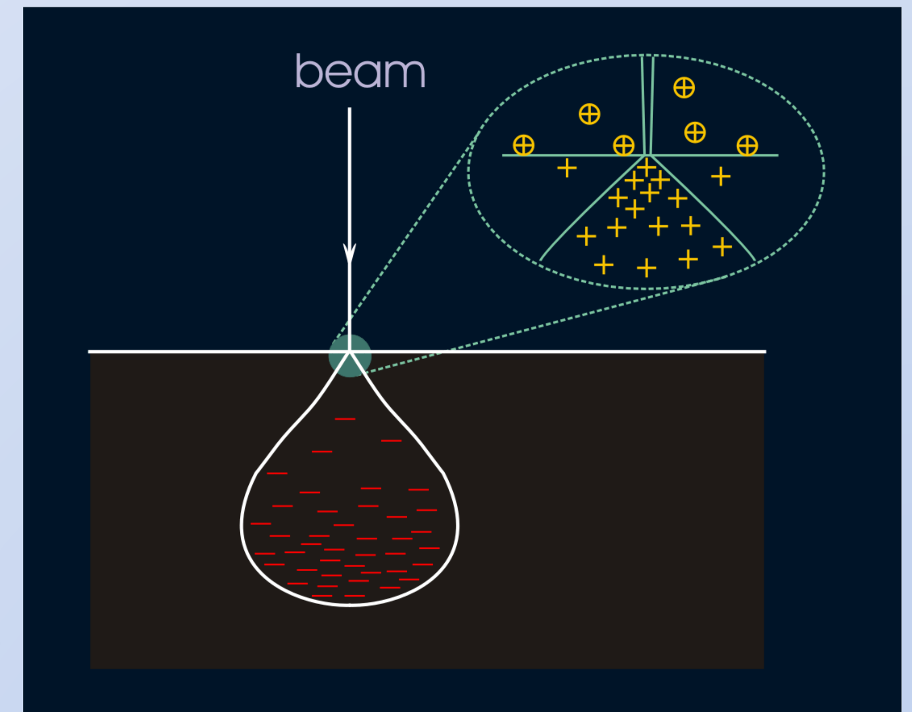
SEs can be “scavenged”.

Reduces SE signal intensity.

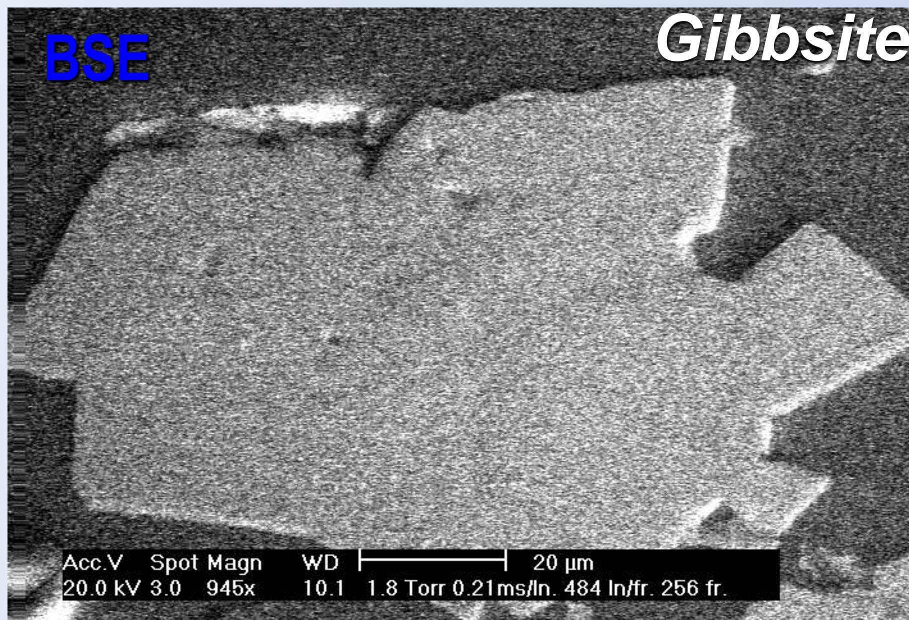
Can remove some contrast mechanisms.

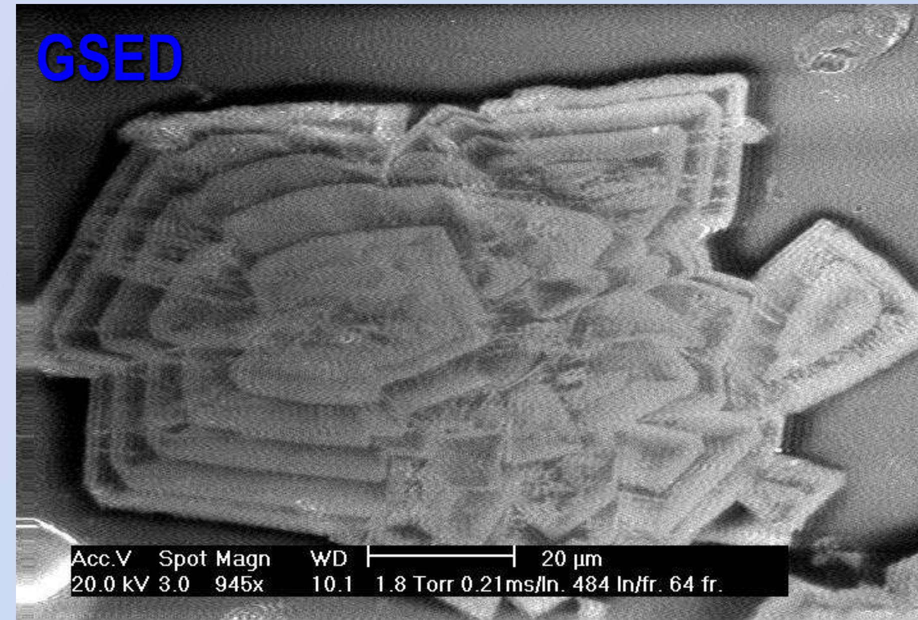


Differential charging: charge-induced SE image contrast

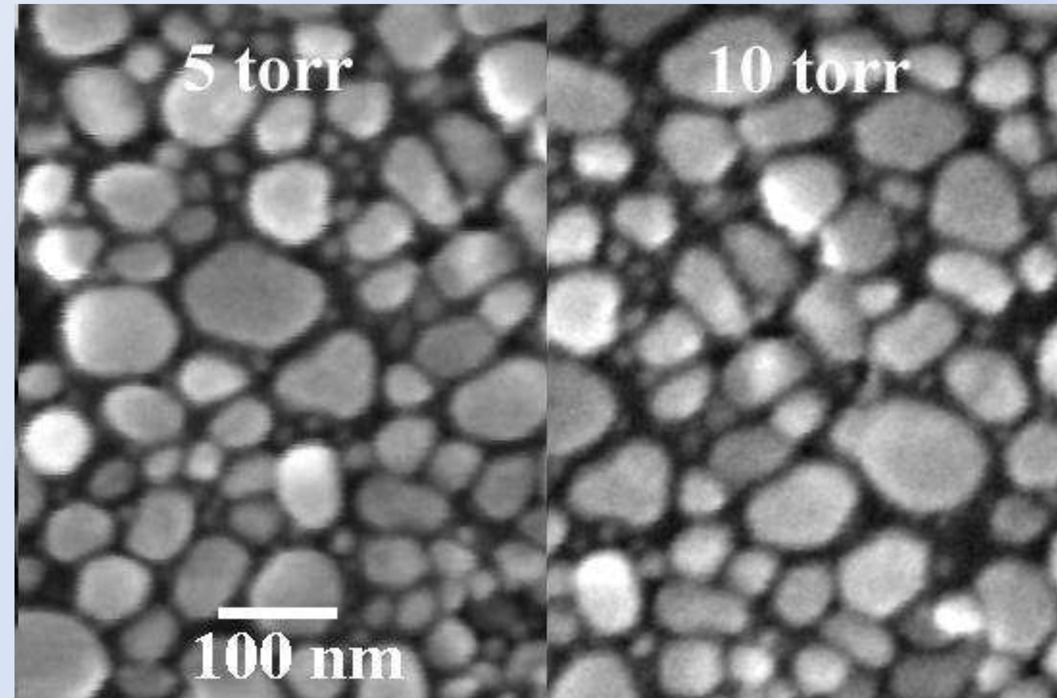


Absence of metallic coating:
SEs come from the sample, not the coating.
Charge-induced contrast is present in SE images.



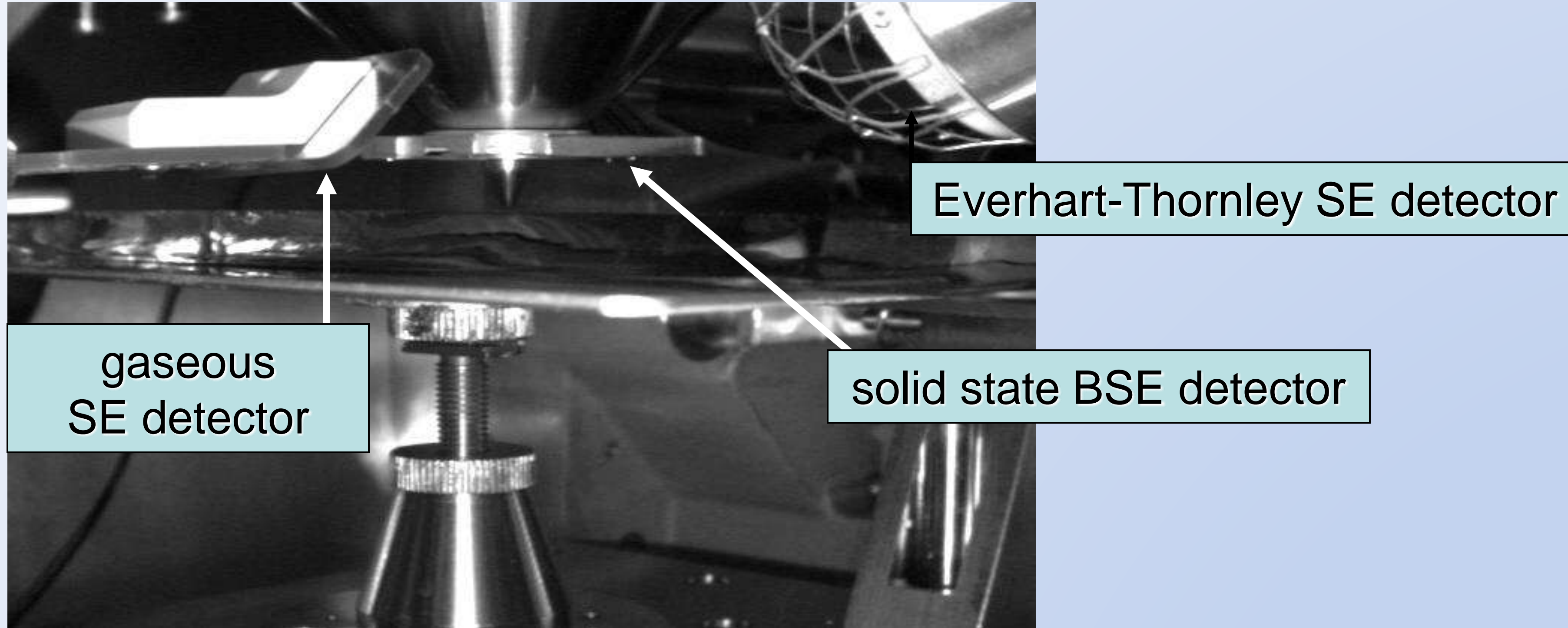


ESEM: resolution test
SE image



Gold-on-Carbon resolution standard
30 keV, Water Vapour

ESEM: electron imaging



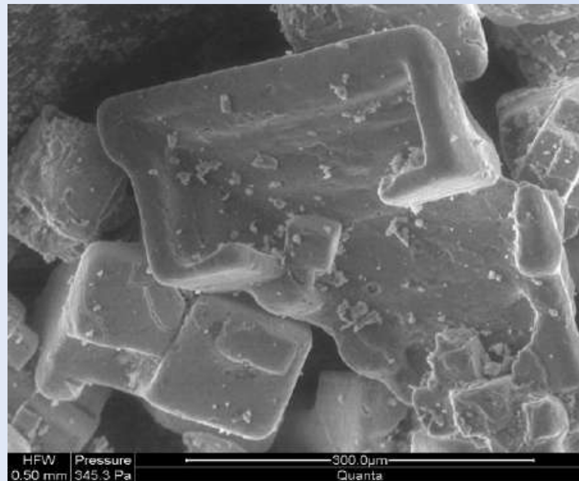
BSE imaging

The same of conventional SEM.

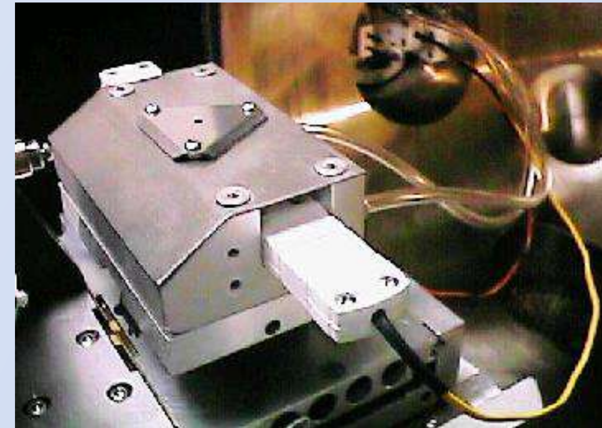
SE imaging

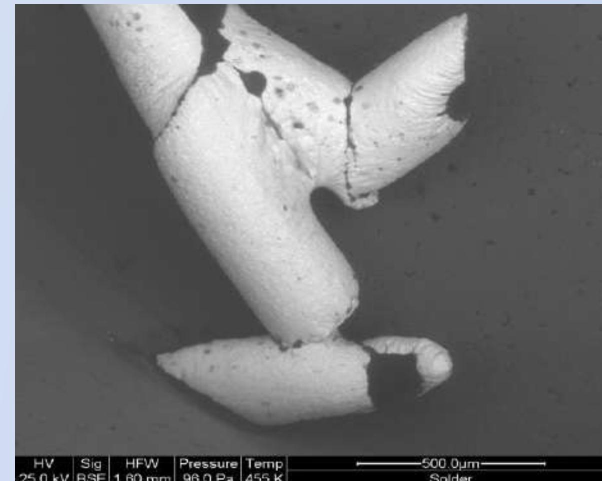
The conventional Everhart-Thornley detector does not work in a low vacuum environment...

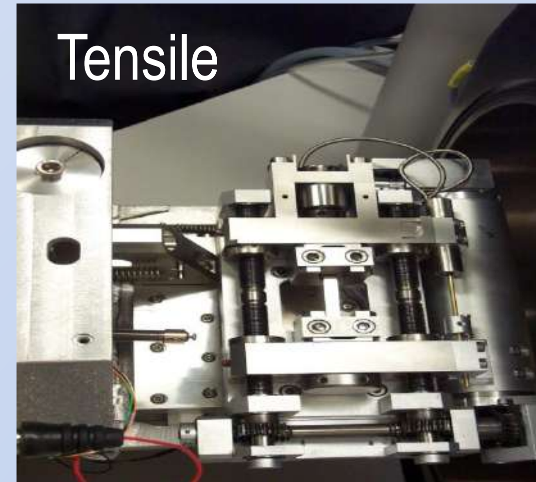
In-situ dynamic experiments

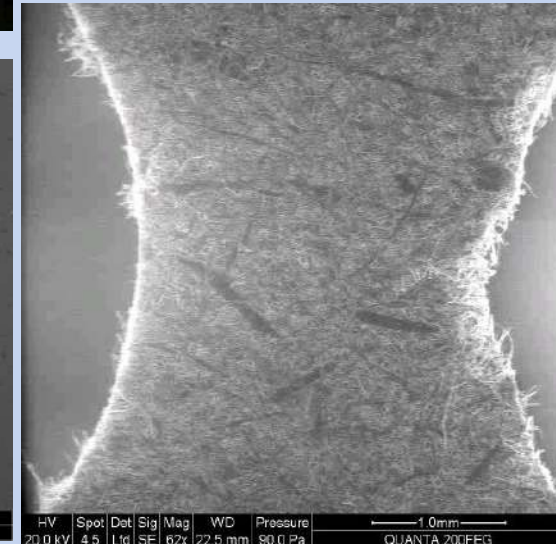


Heating





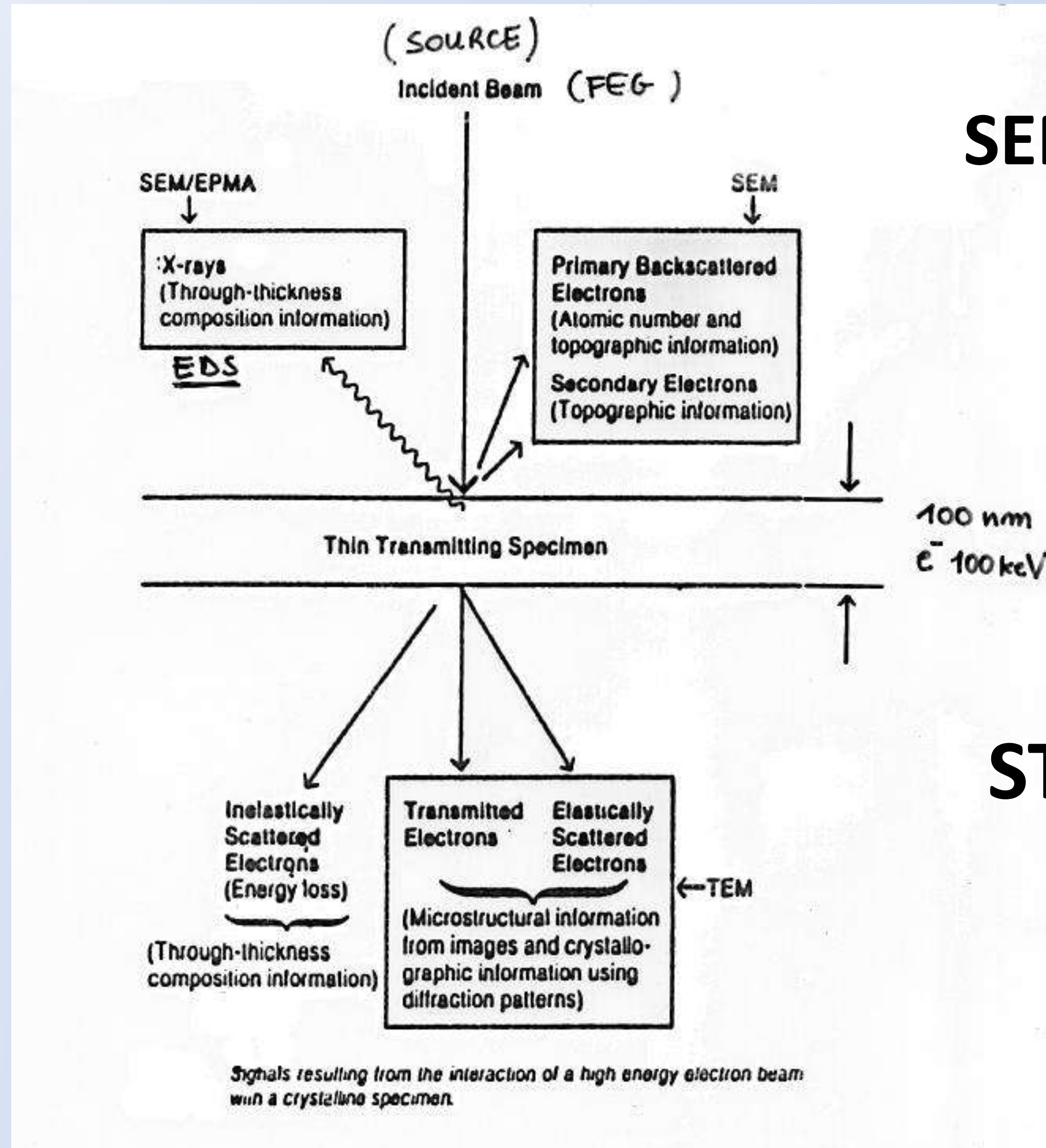




X-ray Microanalysis

Electrons-matter interaction

EDS microanalysis in SEM-ESEM - STEM



Signals resulting from the interaction of a high energy electron beam with a crystalline specimen.

SEM-ESEM

STEM

EDS Si-Li detector

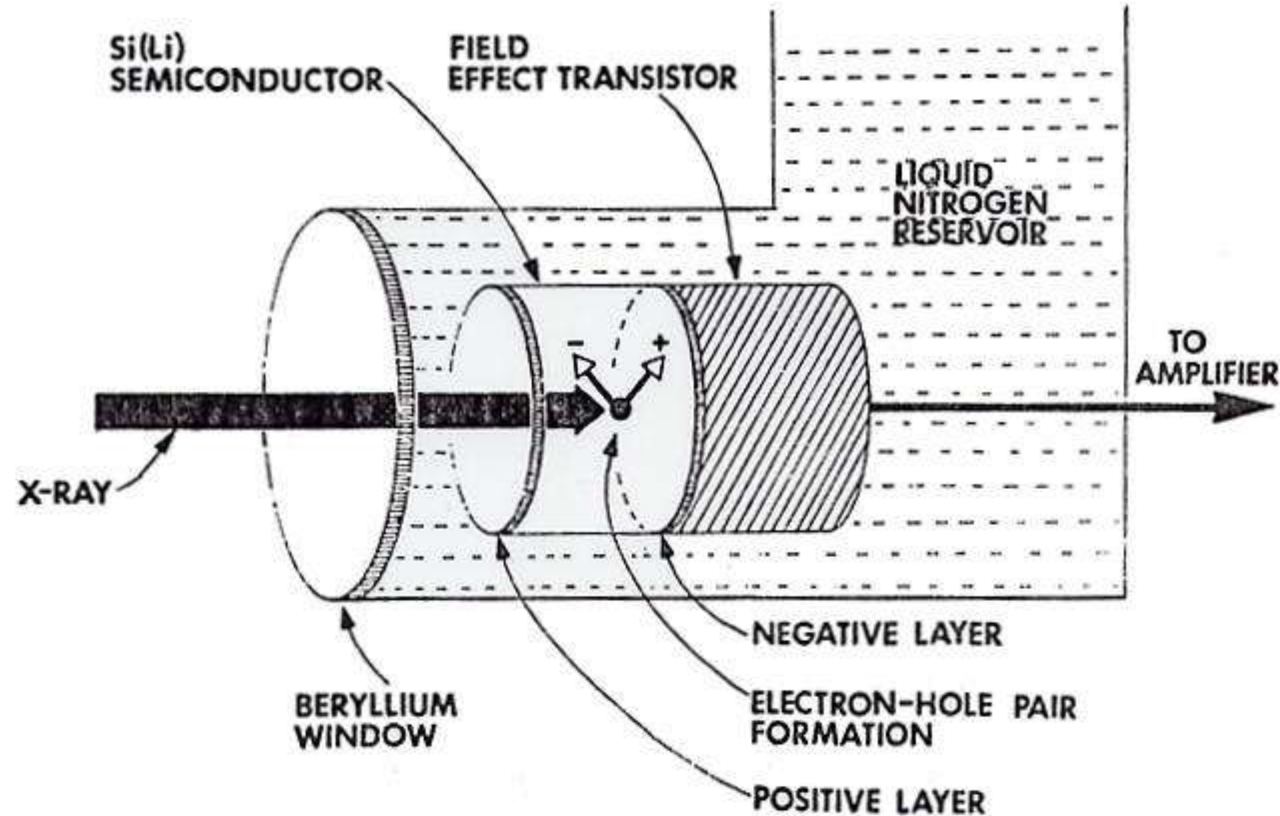
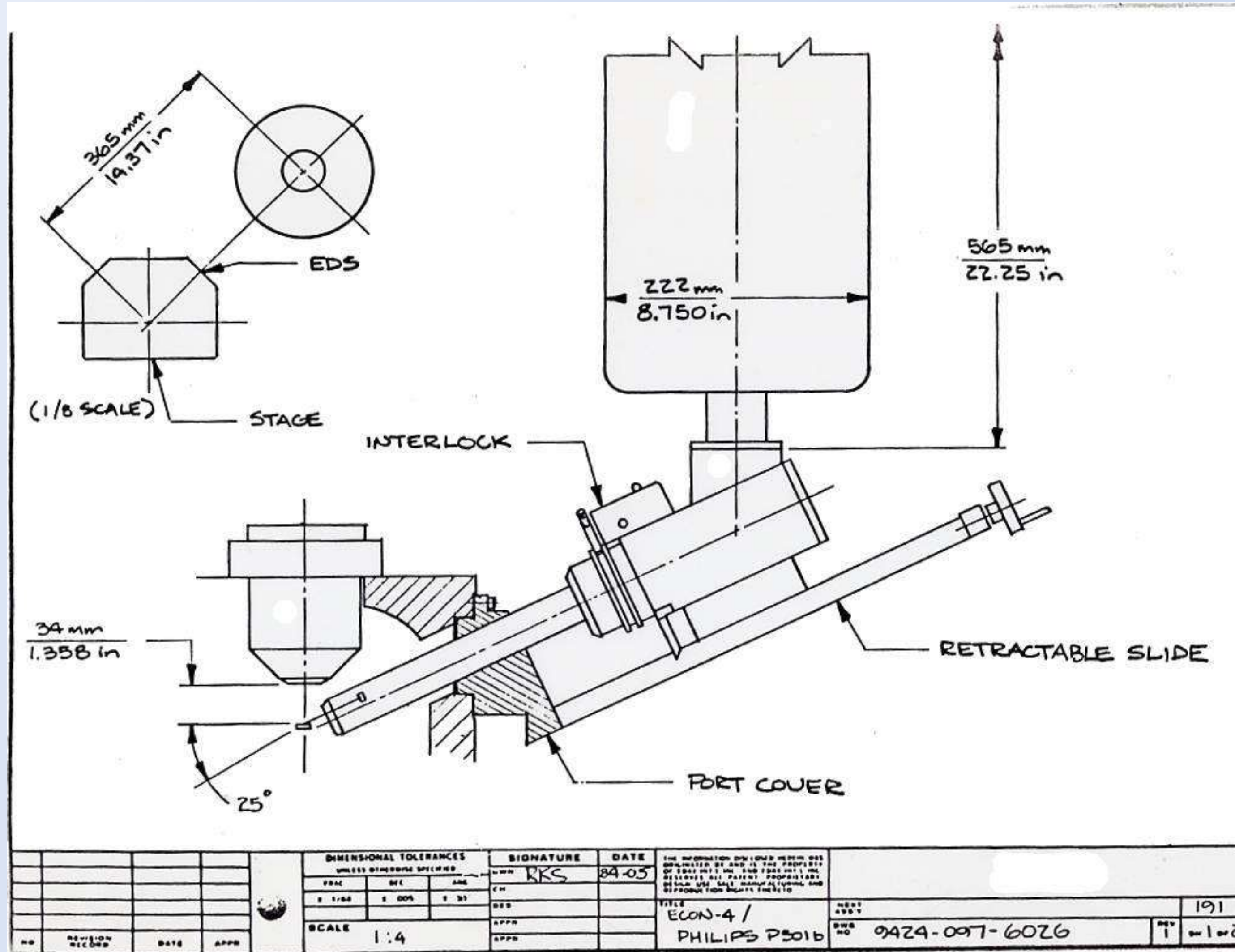


Fig. 3.8. Schematic representation of a solid state detector (SSD). X-rays enter the detector through a thin beryllium window and produce electron-hole pairs within the semi-conductor crystal. The ionisations produce pulses which are amplified by a field effect transistor (FET) built into the rear of the crystal. (Courtesy of John Wiley and Sons Inc., New York.)

Design scheme of detector in SEM chamber



Cut-off of the window of the detector

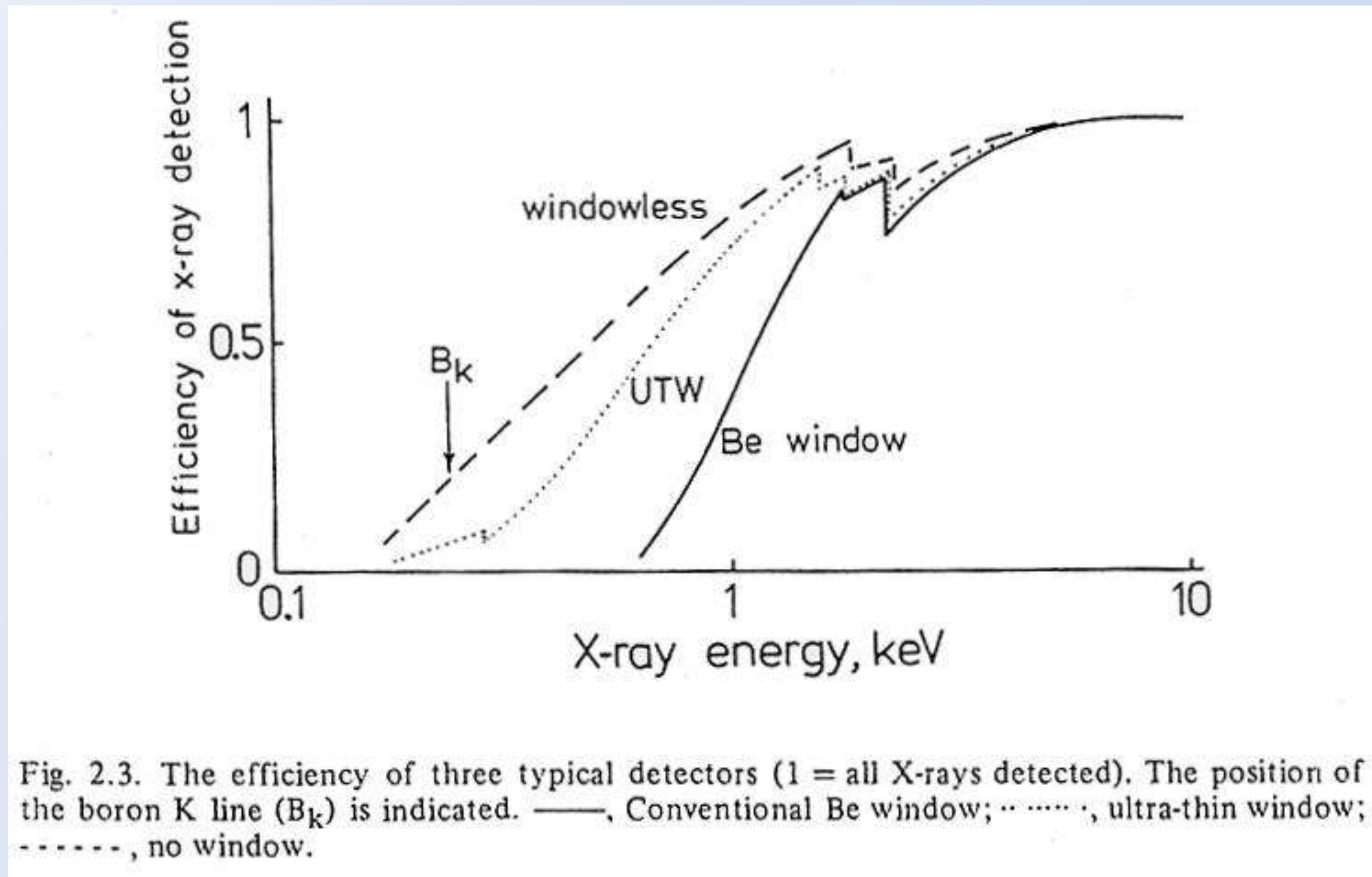
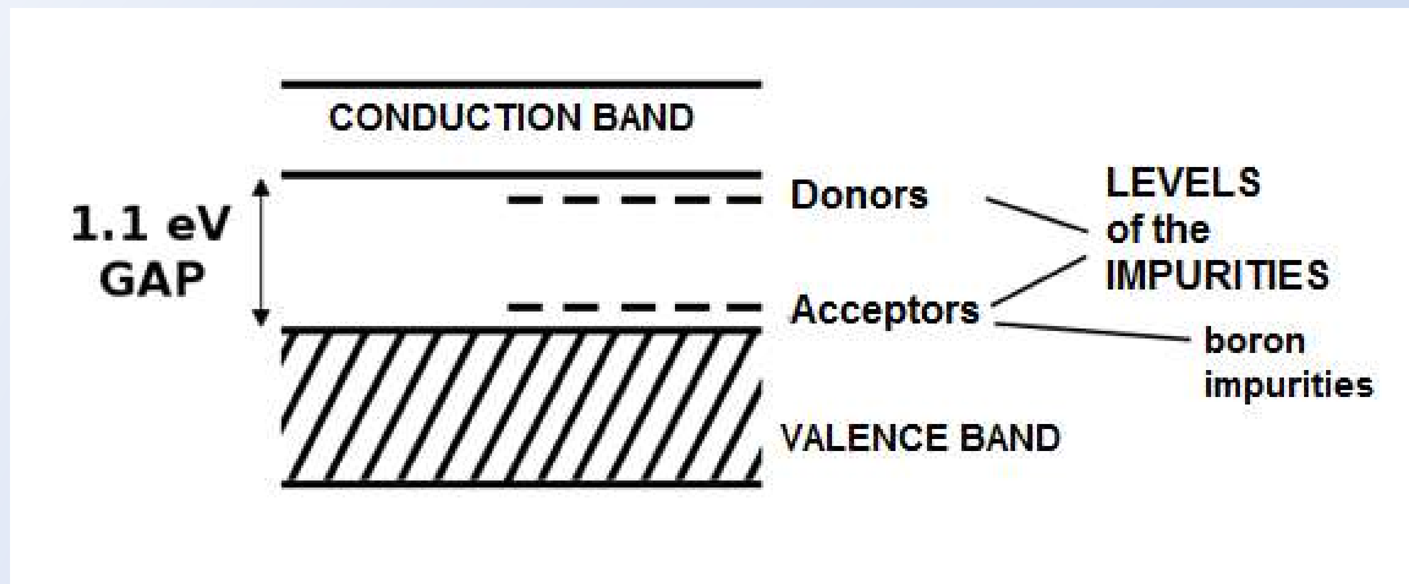


Fig. 2.3. The efficiency of three typical detectors (1 = all X-rays detected). The position of the boron K line (B_k) is indicated. ——, Conventional Be window; ·· ····· ·, ultra-thin window; - - - - - - , no window.



Incident X-rays move electrons from the valence band to the conduction band => a hole is produced in the valence band.
If a polarization is applied between the faces of the Si crystal, the carriers are collected, producing a voltage signal proportional to the energy of the incident X-ray:
<u>1 pair (e-h) for 3.8 eV.</u>

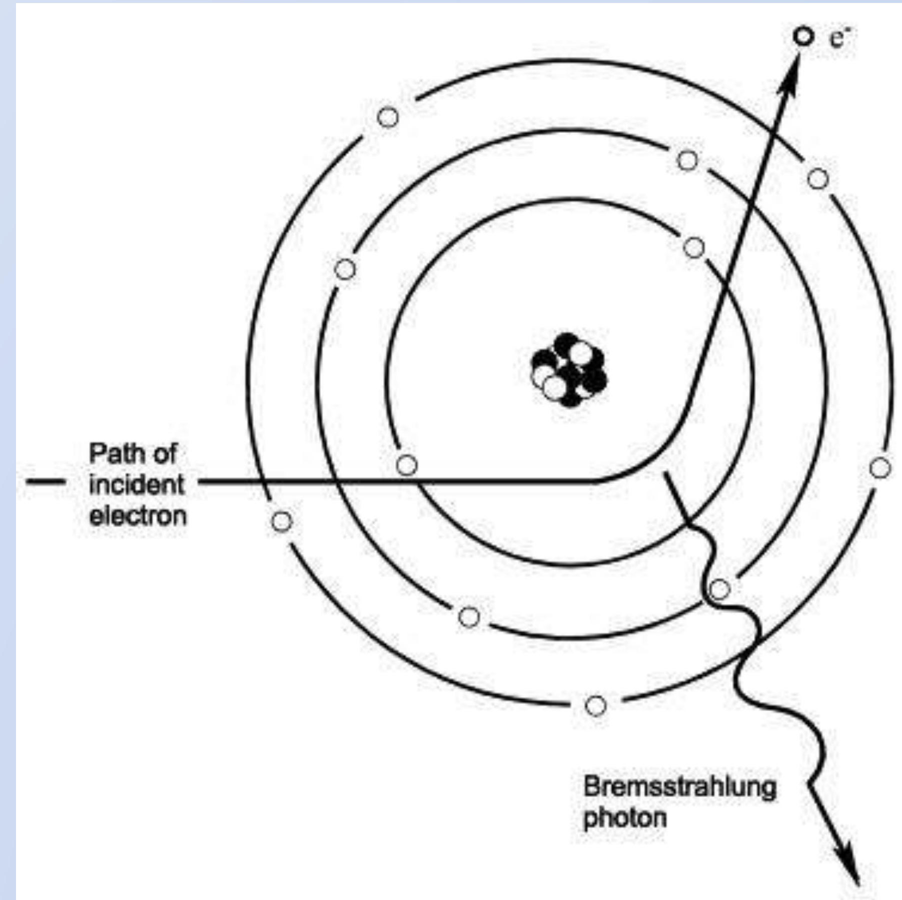
To keep electronic noise and disturbances low => low current losses => high resistivity silicon.
Unfortunately, perfectly pure silicon cannot be found: usually p-type boron impurities are present which give rise to acceptor levels just above the valence band, so that a small thermal excitation is enough to occupy them (statistical thermal noise).
This is obviated by adding donor atoms to neutralize acceptors: lithium is used for
1) small atomic radius (0.06 nm) 2) good conductor.

X-ray continuum spectrum

$$I_c = i_b Z \frac{(E_0 - E)}{E}$$

Kramer's equation

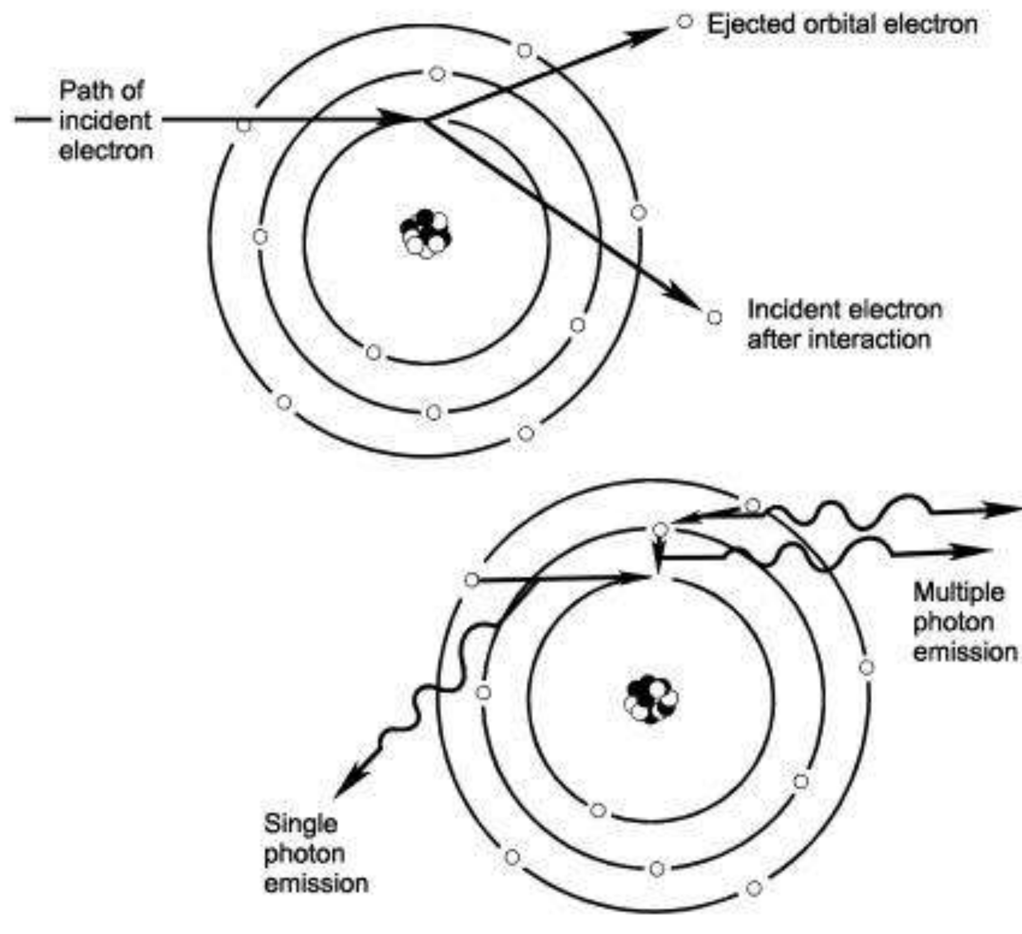
I_c = intensity of the continuum
I_b = beam current
Z = mean atomic number
E_0 = beam energy
E = energy of interest



Characteristic radiation

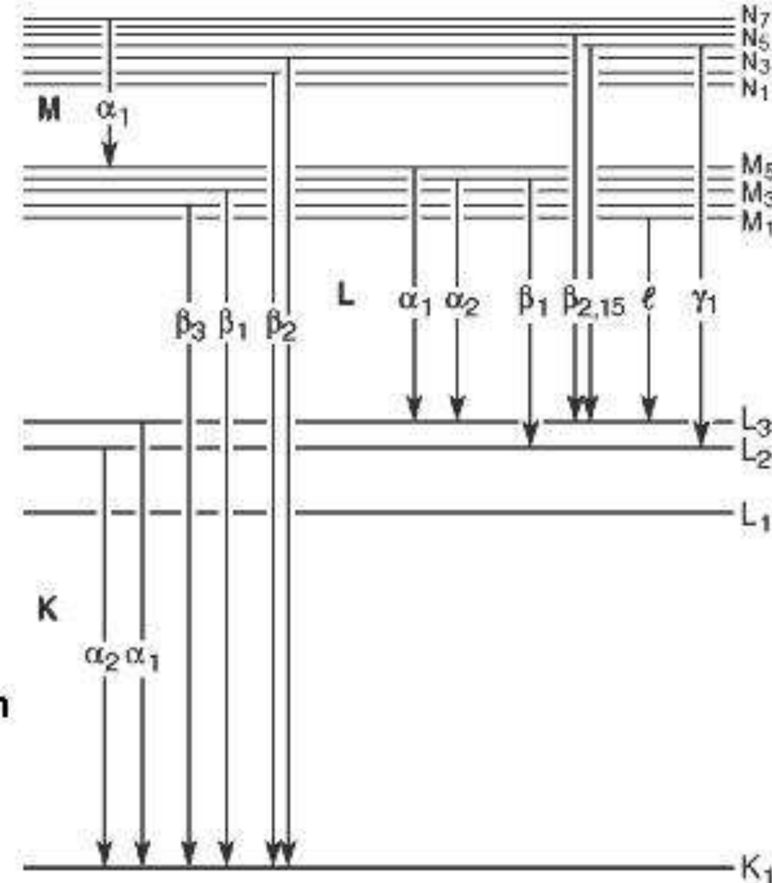
$$\Delta E = h\nu$$

$$\nu = c/\lambda$$



Siegbahn notation

Karl Manne Georg Siegbahn



THE SIGNAL

a) EXCITATION (ionization)

The cross section Q for the excitation (knocking-out) of an internal level by an electron incident with energy E_0 is:

$$Q = \frac{cZ \ln(E_0/E_C)}{E_0 E_C} \qquad [m^2]$$

E_c = ionization energy of the level under examination;
Z = atomic number of the element;
c = constant of the level (K, L, M, etc);

Since $E_0 \propto Z^2$, the cross section is larger for elements of low atomic number.

The average number of atoms n excited by an incident electron passing through a sample of thickness t is:

$$n = Qt\rho \, {}^{N}\!/_{A}$$

(usually a small number)

ρ = density
N = Avogadro's number
A = atomic weight

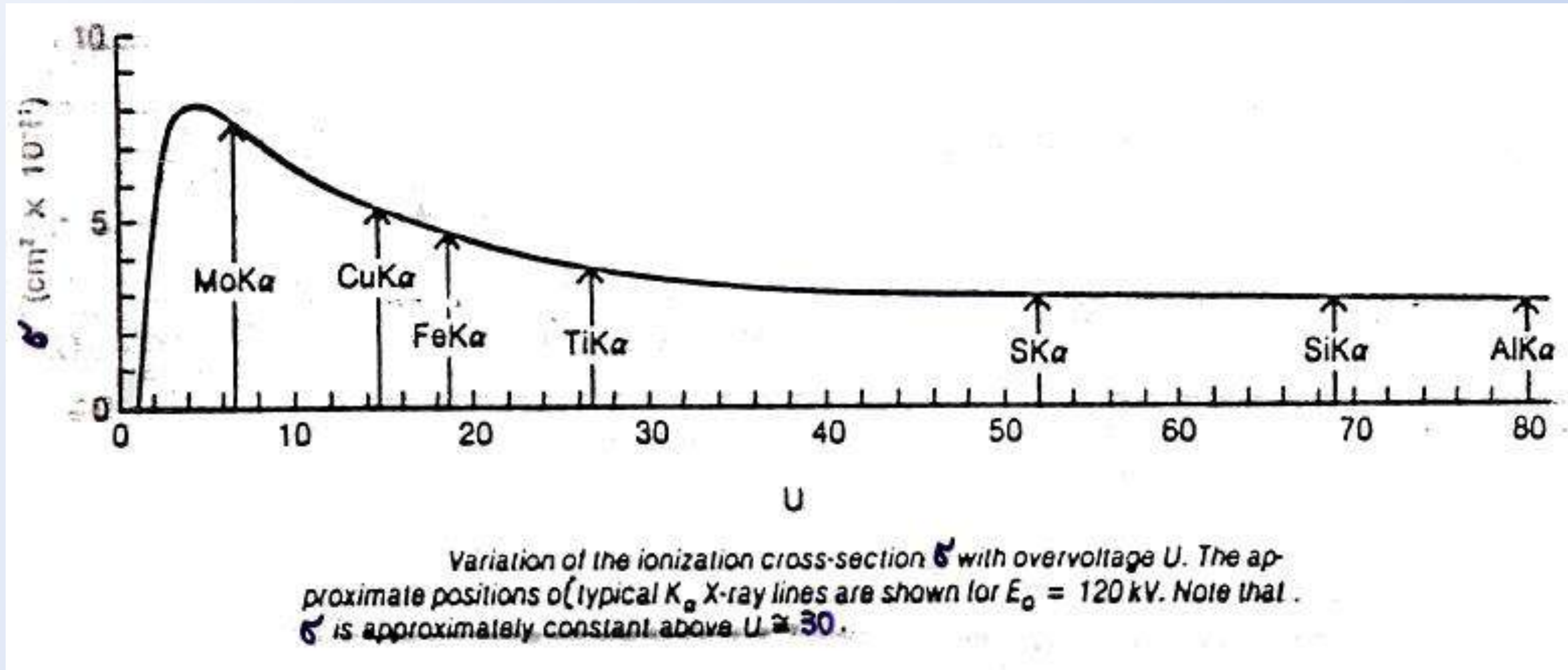
Example: for K-shell

10 nm thickness of Cu (100% Cu)
E_0 = 100 keV
n = 2.5 x 10^{-4}

b) <u>DE-EXCITATION: e^- AUGER or X-RAY</u>

Return of the excited atom to the ground state through a Z-dependent competition mechanism between e^- Auger and X-rays.

Ionization cross section as a function of U (overvoltage E_0/E_C)

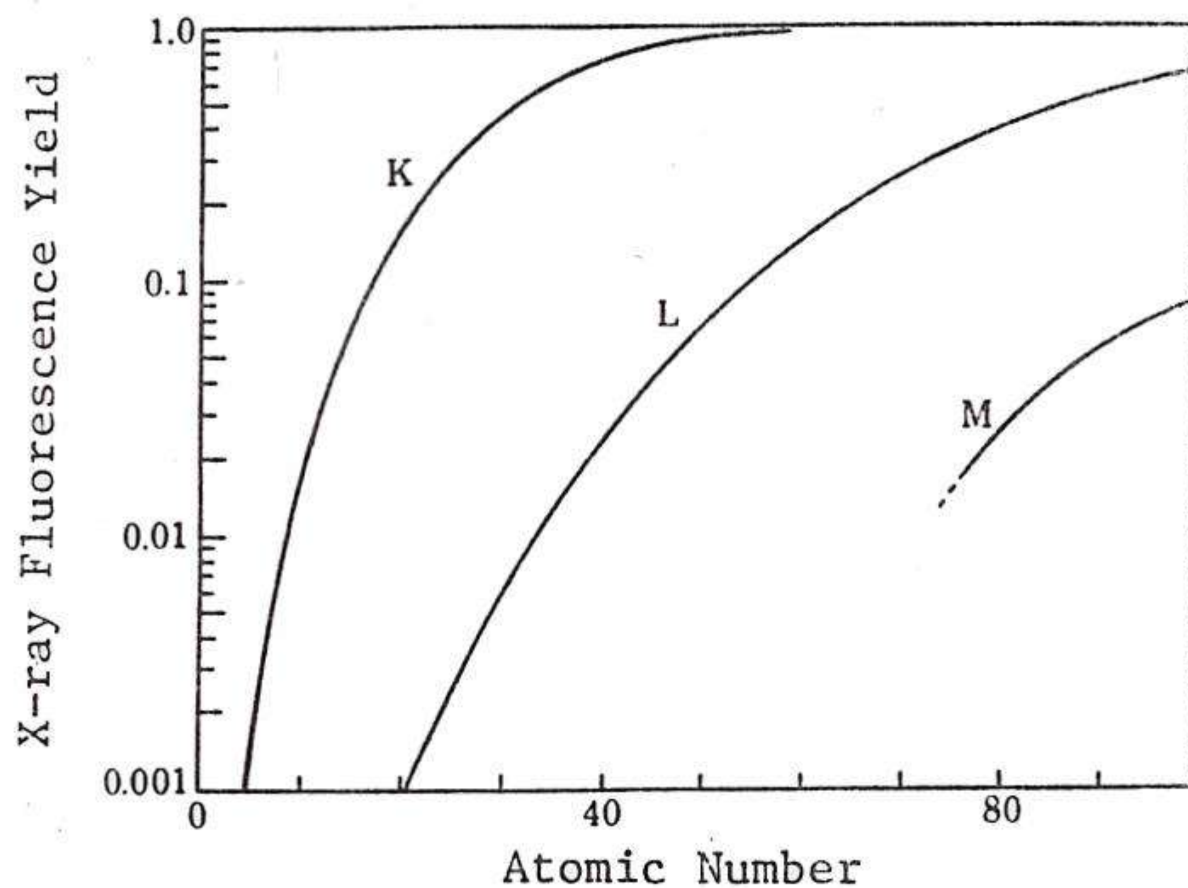


Variation of the ionization cross-section σ with overvoltage U. The approximate positions of typical K_α X-ray lines are shown for E_0 = 120 kV. Note that σ is approximately constant above U ≥ 30.

$$\sigma = \frac{cZ\ln(E_0/E_C)}{E_0 E_C} \quad [m^2]$$

E_0 energy of incident electrons, E_c ionization energy of the element, c level constant (K, L, M, etc)

There is poor X-ray production for low Z elements, despite the ionization cross sections are favourable: almost all de-excitations go to Auger electrons.
Hence, EDS limitation to high atomic numbers.
High EELS capacity for low atomic numbers.



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

Fluorescence yield $\omega = \frac{\text{de-excitation emitted X-rays}}{\text{number of excitations}}$, 1-ω = fraction of emitted e^- Auger

$$\omega = \frac{Z^4}{Z^4 + C}$$

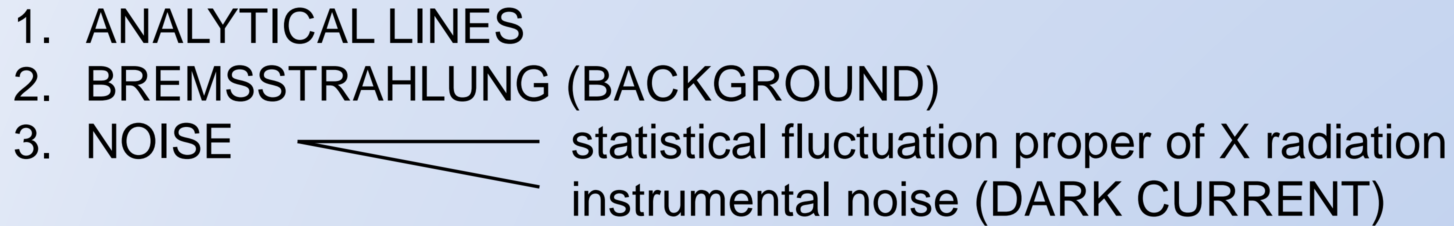
C ~
- 10^6 for excitations of level K
- 10^8 for excitations of level L
- 10^9 for excitations of level M

Low X-ray emission for low Z
E.g. C (Z=6); ω = 1‰ (K)
Zr (Z=40); ω = 72% (K)

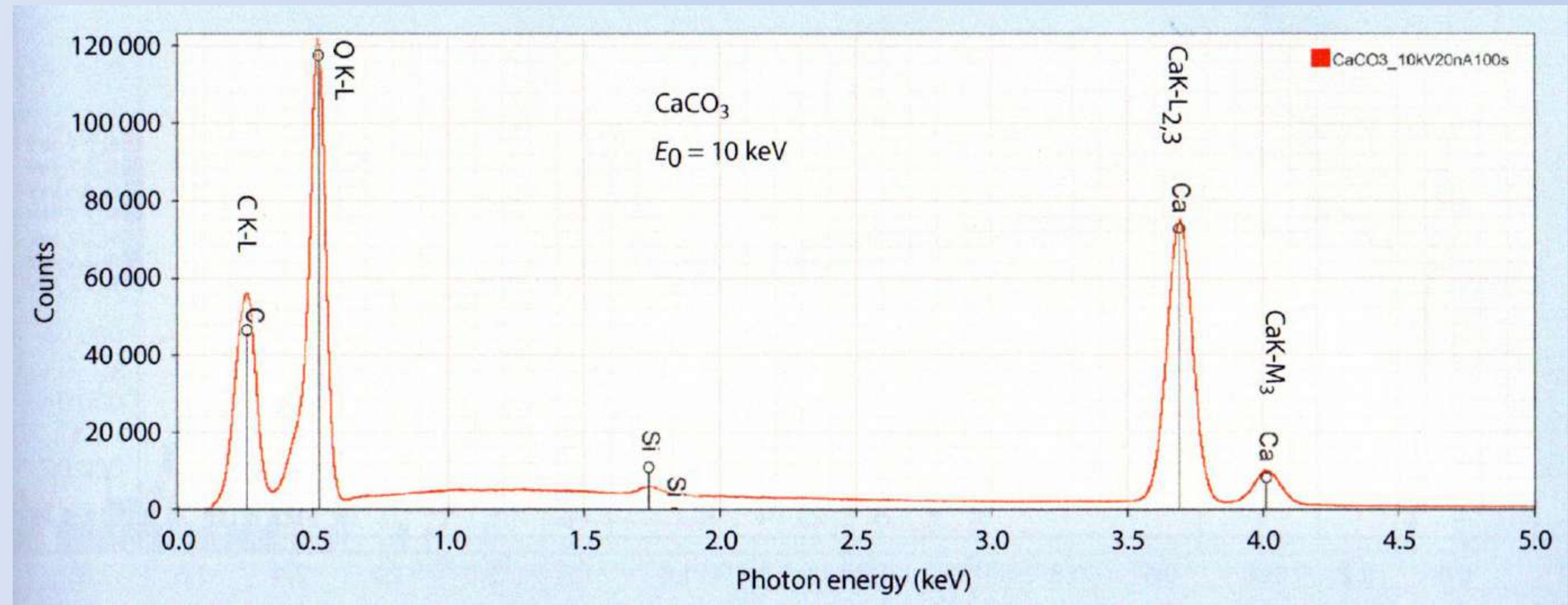
PROCESSING OF EDS SPECTRA

Necessity of spectra processing for qualitative and quantitative purposes.
Because it can occur:

1. PARTIAL OVERLAPPING of ANALYTICAL LINES
2. CALCULATION AND SUBTRACTION of the BACKGROUND



SPECTRUM EDS
=> HISTOGRAM



Thus free from electronic noise problems, the efficiency of the detection system and the geometric arrangement, the MEASURED INTENSITY becomes the TOTAL EMITTED INTENSITY.

To TRACE BACK TO THE CONCENTRATION OF THE ELEMENTS ANALYZED, WE MUST TAKE INTO ACCOUNT:

I) ABSORPTION and FLUORESCENCE — of the X radiation generated within the sample and subsequent

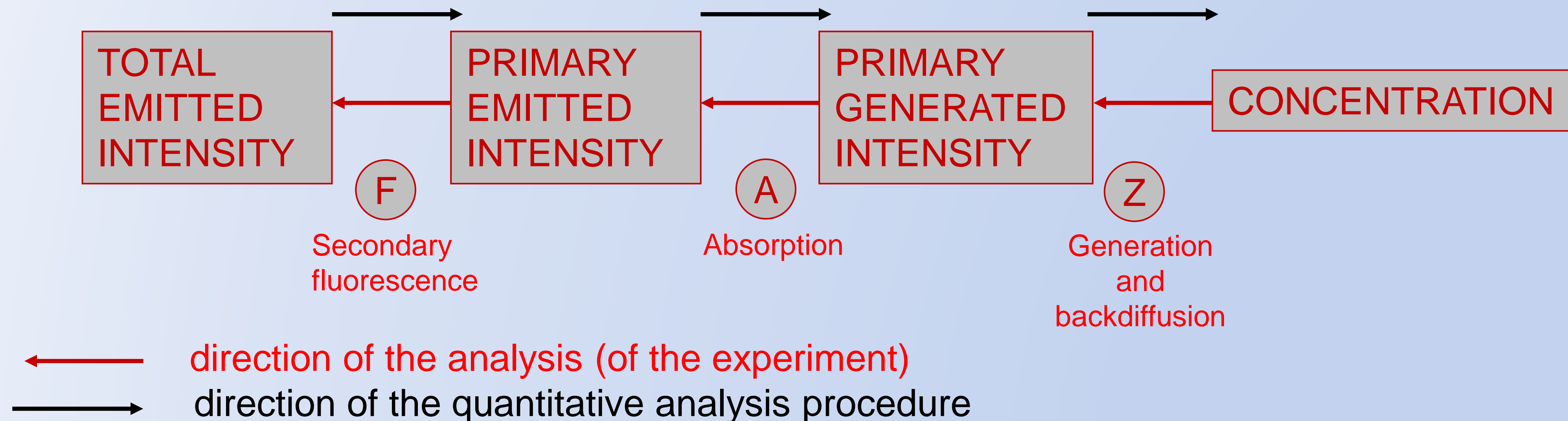
then

II) NECESSARY KNOWLEDGE OF THE PHYSICAL PHENOMENA OF RADIATION GENERATION AND ELECTRONIC BACKDIFFUSION OF THE PRIMARY BEAM TO ESTABLISH A CORRECT CORRESPONDENCE BETWEEN X RADIATION OF PRIMARY GENERATION AND CONCENTRATION OF THE ELEMENT ITSELF (NOT FORGETTING THE INTENSITY OF THE CURRENT OF THE ELECTRONIC BEAM).

GENERATION AND EMISSION of X RADIATION
(essential for quantitative analysis)

IMP. THE QUANTITATIVE ANALYSIS OF A SAMPLE IMPLIES ABOVE ALL THE KNOWLEDGE AND STUDY OF THE PHYSICAL, GEOMETRIC AND INSTRUMENTAL FACTORS THAT ALLOW TO TRACE BACK, FROM THE MEASUREMENT OF THE X INTENSITY DETECTED, TO THE MEASUREMENT OF THE X INTENSITY ACTUALLY GENERATED INSIDE THE SAMPLE AND FINALLY, TAKING INTO ACCOUNT THE PROCESS OF X GENERATION, TO THE COMPOSITION OF THE SAMPLE ITSELF. **

ALL THIS CAN BE SUMMARIZED FROM THE FOLLOWING SCHEME:



** TO THE COMPOSITION OF THE SAMPLE AREA PROBED BY THE BEAM

Microchemical quantitative analysis

Method of the continuous: (thin films)

THE X INTENSITY UNDER CONSIDERATION IS PROPORTIONAL TO THE MASS PER UNIT OF AREA OF THE ELEMENT UNDER EXAMINATION, WHEREAS THE INTENSITY OF THE CONTINUOUS RADIATION IS PROPORTIONAL TO THE MASS PER UNIT OF AREA OF THE ENTIRE SAMPLE IN THE IRRADIATED AREA. CONTINUOUS RADIATION DEPENDS ON THE AVERAGE ATOMIC NUMBER OF THE ANALYZED SAMPLE.

$$C_A = K\frac{I_A}{W}$$

$$I_A = K'\frac{m_A}{A}$$

$$W = K''\frac{M_T}{A}$$

$$\Rightarrow \quad \frac{m_A}{M_T} = C_A = K'''\frac{I_A}{W}$$

I_A = Intensity of the characteristic line of element A
W = continuous radiation
K = constant of proportionality calculated using a standard with known concentration C_A

$$K = \frac{C_{ASTd}W_{STD}}{I_{ASTd}}$$

Method commonly used in biology since the average atomic number of the samples is almost constant.

METHOD OF THE THIN STANDARD

Relative concentration of two elements A and B in a thin binary alloy can be directly calculated from the ratio of their characteristic X intensities,

$$\frac{C_A}{C_B} = K_S \frac{I_A}{I_B}$$

Ks = constant that takes into account the relative detection efficiency of the analysis system for the 2 elements A and B; easily deducible from a STD containing the 2 elements in known quantities.

STANDARDLESS METHOD

Theoretical calculation of the constant K_s.

According to RUSS: $K_S = Q(\omega r)\,{}^{T}/_{A}$

$$T = \delta e^{-C_1/E^3} \cdot \left(1 - e^{-C_2/E^3}\right)$$ (detector efficiency)

Q = ionization cross section → TABULATED
(ωr) = product of the fluor. yield
x relative intensity of the X line → TABULATED
A = atomic weight → is known
δ = detector solid angle → "
E = X photon energy → "
C_1 and C_2 = constants that depend on the thickness of the Detector and Be Windows

BULK STANDARDS

$$\frac{C_A}{C_B} = \left(\frac{I_A}{I_B}\right)_{spec.} \cdot \left(\frac{I_A}{I_B}\right)_{std} \cdot \frac{Q_B}{Q_A} \cdot ZAF$$

ZAF = appropriate function that takes into account the atomic number, absorption and fluorescence in the sample.

Q_B and Q_A = are the ionization cross sections of elements B and A.

EMPIRICAL REVEALABILITY LIMITS (Silicates)

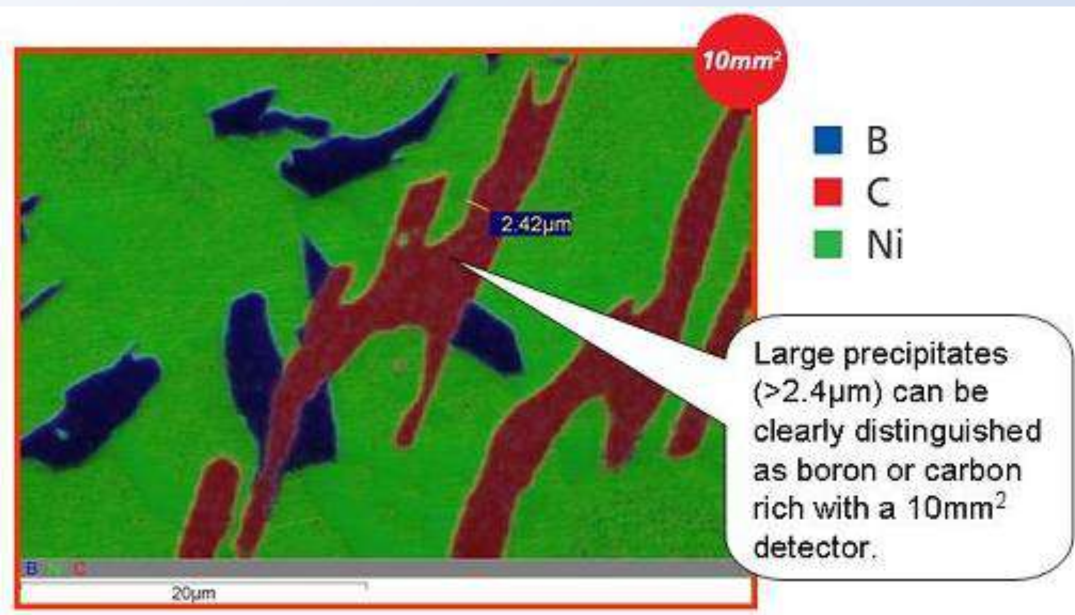
From: Dunham and Wilkinson
X-ray spectrometry, 7, n° 2, 1978

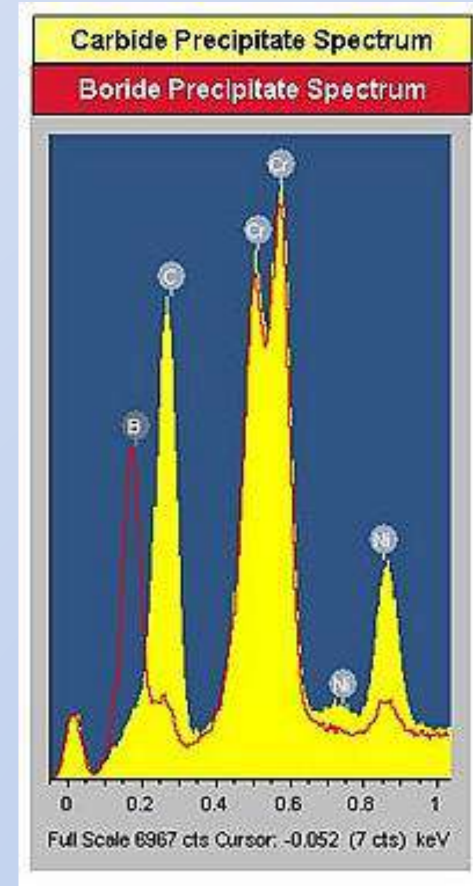
SEM

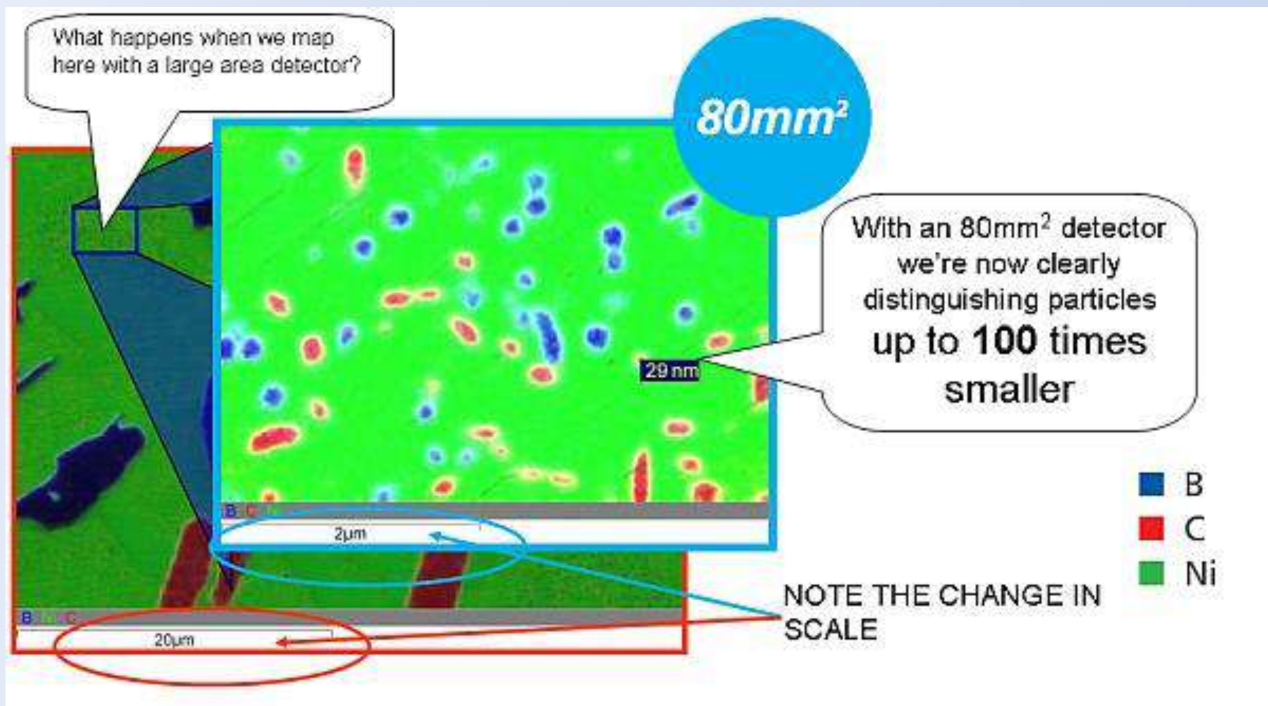
15 kV /100 Liveseconds -3 KCPS -bulk specimen > 10 μm

	Weight %
Na_2O	0.26
MgO	0.10
Al_2O_3	0.11
SiO_2	0.10
K_2O	0.10
CaO	0.12
TiO_2	0.12
Cr_2O_3	0.15
MnO	0.17
FeO	0.19
NiO	0.15

The values vary according to the atomic number, the type of sample, and the counting time (liveseconds).
Note that the values have been calculated for a beam acceleration potential of 15 kV (not ideal for all elements).


10mm²
B
C
Ni
2.42µm
Large precipitates (>2.4µm) can be clearly distinguished as boron or carbon rich with a 10mm² detector.
20µm


Carbide Precipitate Spectrum
Boride Precipitate Spectrum
B
C
Cr
Cr
Ni
Ni
0
0.2
0.4
0.6
0.8
1
Full Scale 6967 cts Cursor: -0.052 (7 cts) keV


What happens when we map here with a large area detector?
80mm²
With an 80mm² detector we're now clearly distinguishing particles up to 100 times smaller
29 nm
2µm
20µm
NOTE THE CHANGE IN SCALE
B
C
Ni

Electron probe x-ray microanalysis

Basic information. Elemental identification and quantification.

Specimen types:

- Ideal: bulk specimen (millimetre to centimetre dimensions) polished flat to mirror finish, conductive
- Special cases: particles, foils, film(s)-on-substrate, rough surfaces, beam-sensitive specimen (especially biological), nonconductors

Spectrometer types:

- Energy-dispersive x-ray spectrometer (130-eV resolution at Mn Kα)
- Wavelength-dispersive spectrometer (8-eV resolution at Mn Kα)

Signals detected:

- Characteristic x-rays (identify elements)
- Continuum x-rays (background)

Electron probe x-ray microanalysis

Speed:

• Qualitative analysis: 10-100 s (EDS)

• Quantitative analysis: 100-500 s

• Mapping: 1000-10000 s

Elements detected. $Z \geq 4$ (Be).

Accuracy (95% of analyses):

• Flat, bulk target: ± 5% relative for pure-element standards and matrix correction calculations, and ± 25% relative for "standardless" analysis

• Particles, rough surfaces: ± 50% relative

Limits of detection:

• WDS: 10-100 parts per million (ppm)

• EDS: 1000-3000 ppm

Analytical resolution (lateral):

• Low Z: 1-5 µm

• High Z: 0.2-1 µm