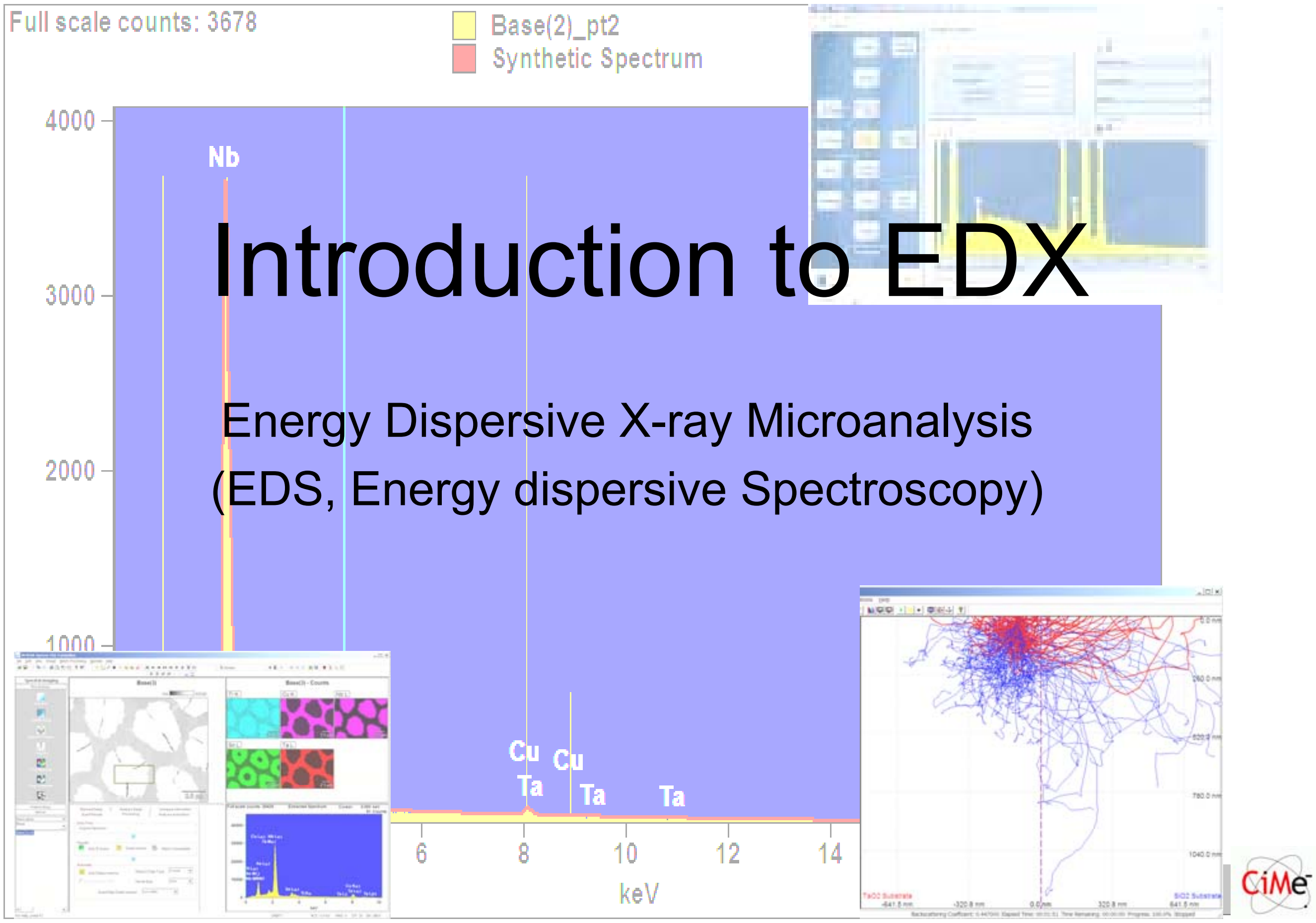


Introduction to EDX

Energy Dispersive X-ray Microanalysis
(EDS, Energy dispersive Spectroscopy)

Basics of EDX

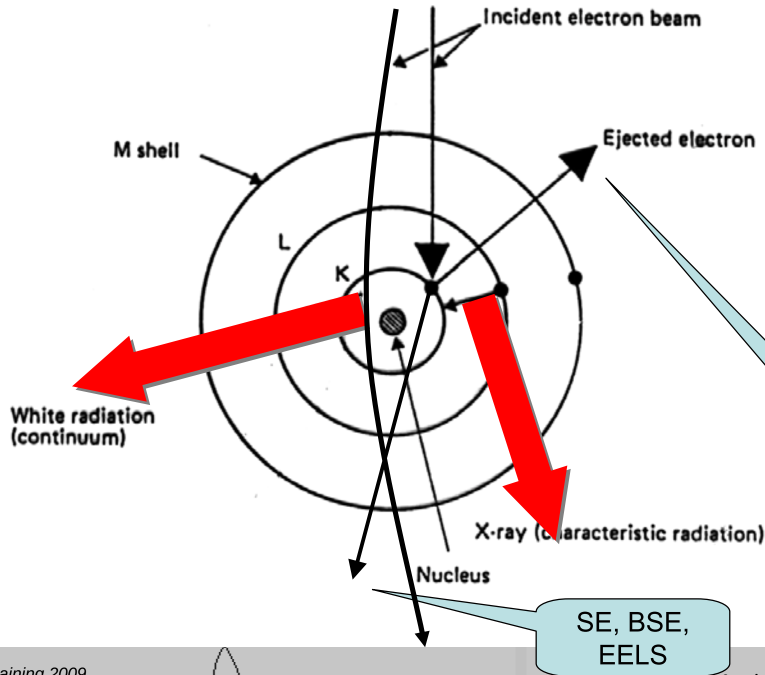
a) Generation of X-rays

b) Detection
Si(Li) Detector, SDD Detector, EDS (<-> WDS)

c) Quantification
EDX in SEM, Interaction volume
Monte-Carlo-Simulations
EDX in TEM

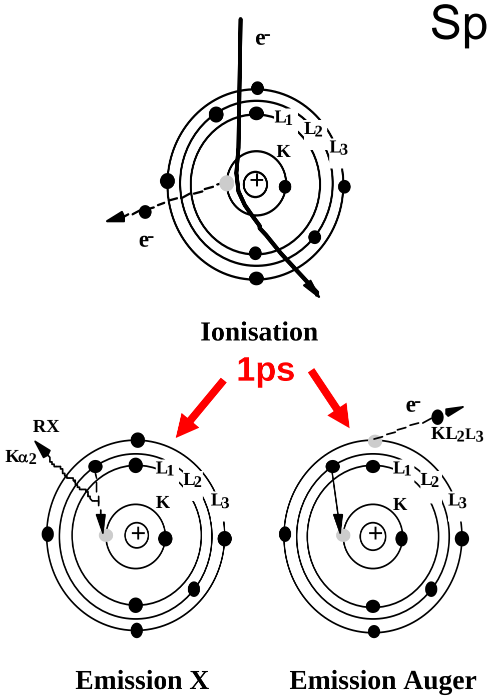
[d) EDX in SEM-STEM]

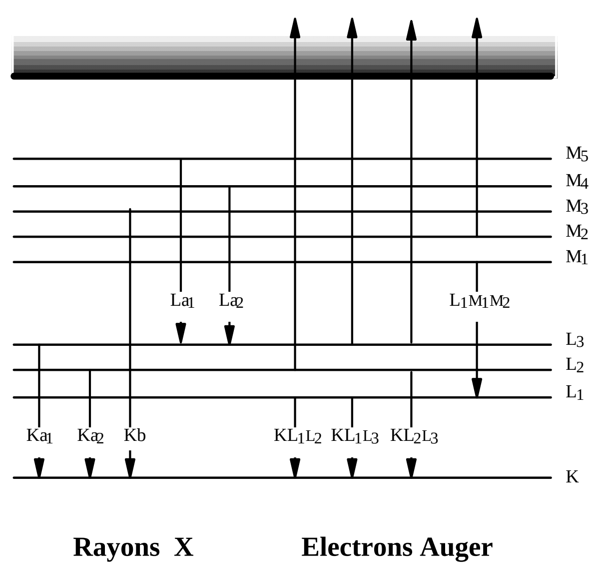
Inelastic scattering of electrons at atoms
$E_{electron\_in} > E_{electron\_out}$



- **Continuum X-ray production (Bremsstrahlung, Synchrotron)**
- **Inner shell ionization**

Core shell ionisation: chemical microanalysis by X-ray, Auger electrons and Electron Energy Loss Spectrometries





Emission of characteristic X-ray and Auger electron

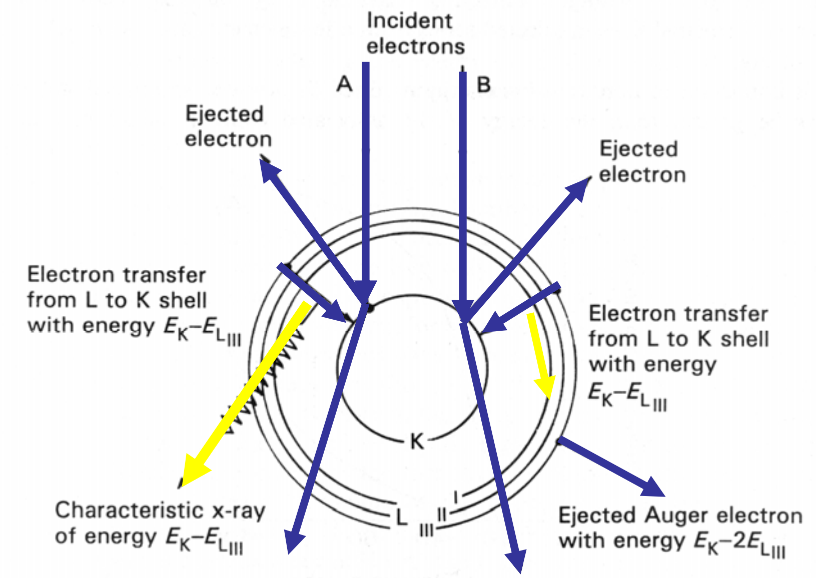


Fig. 2.3. Schematic diagram showing emission of characteristic x-ray by electron A and emission of Auger electron by electron B.

Designation of x-ray emission lines

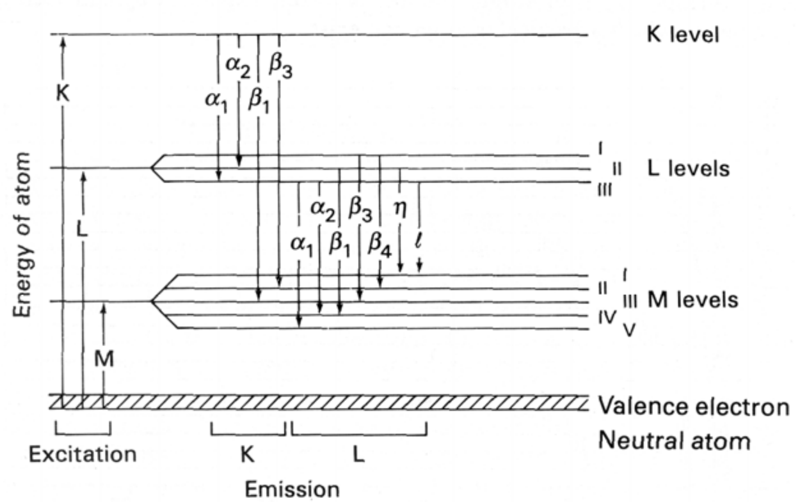


Fig. 2.2. Schematic diagram showing common x-ray emission lines with their designation for an element with atomic number (Z), where $29 < Z < 37$.

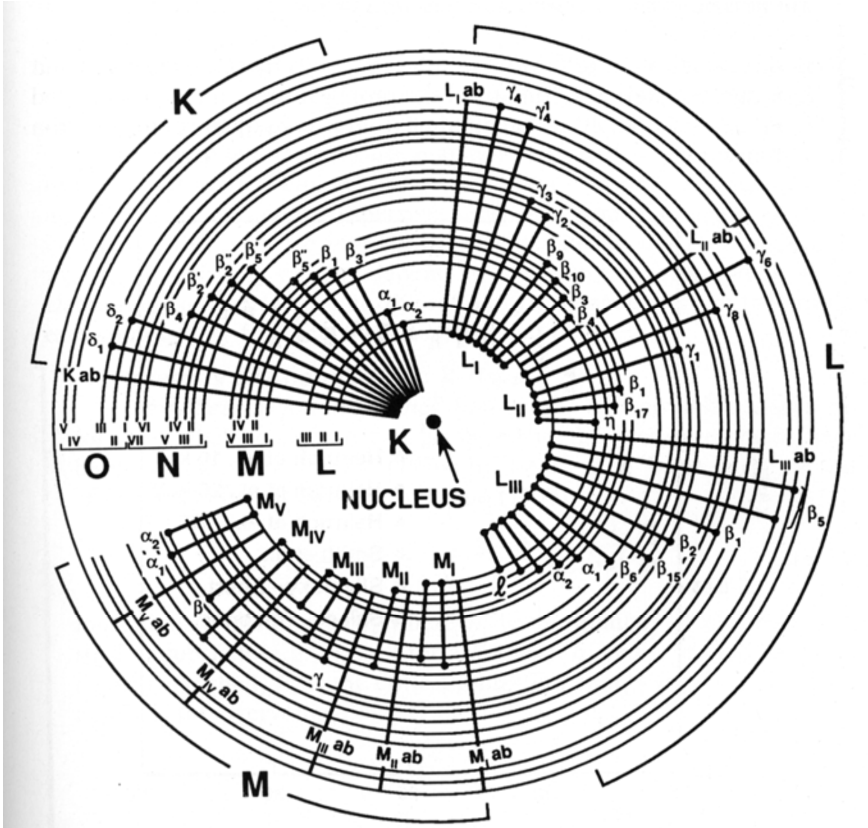
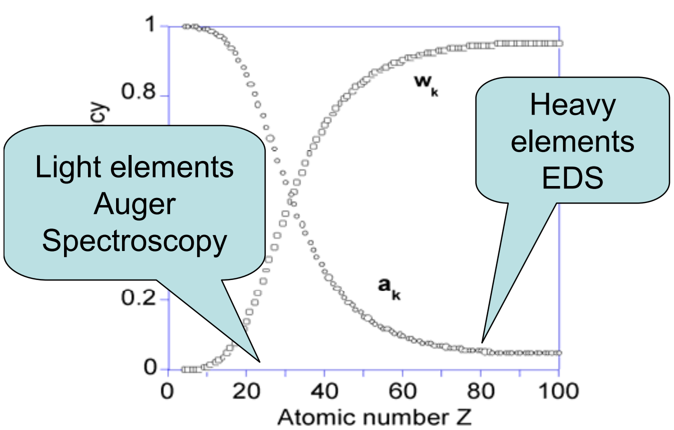


Figure 3.37. Comprehensive energy-level diagram showing all electron transitions which give rise to *K*, *L*, and *M* x rays (Woldseth, 1973).

Efficiency of X-ray generation

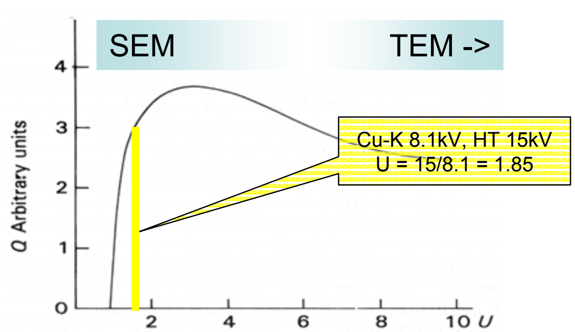
Relative efficiency of X-ray and Auger emission vs. atomic number for K lines



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.

Ionization cross-section vs. overvoltage U=Eo/Eedge

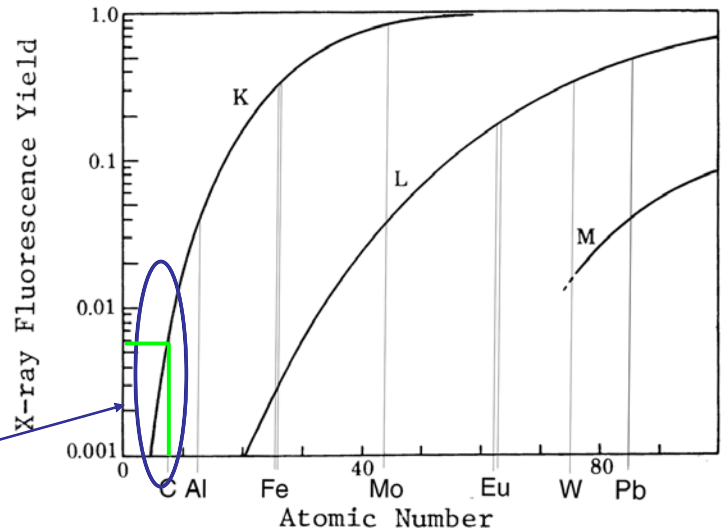
(electron in -> X-ray out)



To ionized 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.

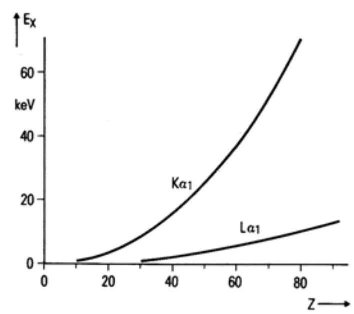
X-ray production vs. atomic number Z

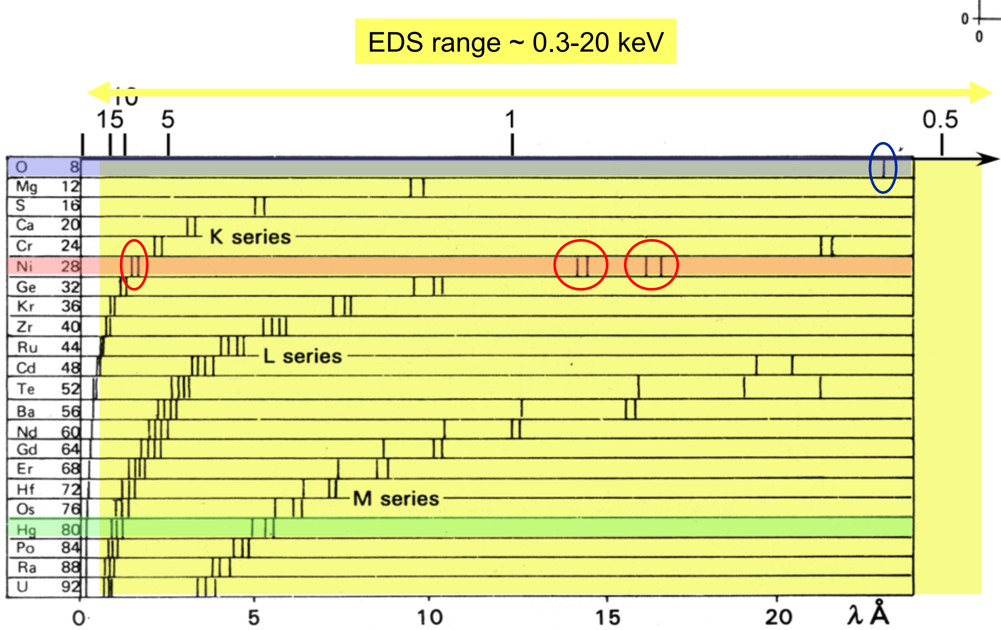
Low efficiency for light elements!



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

Characteristic lines: Moseley's Law





To assess an element all detectables lines MUST be present!!!

known ambiguities:

Al Kα = Br Ll

S Kα = Mo Ll

Moseley‘s law for K-series

Frequency ν of X-rays emitted from K-level vs. atomic number

$$\nu = 2.4810^{15}(Z-1)^2$$

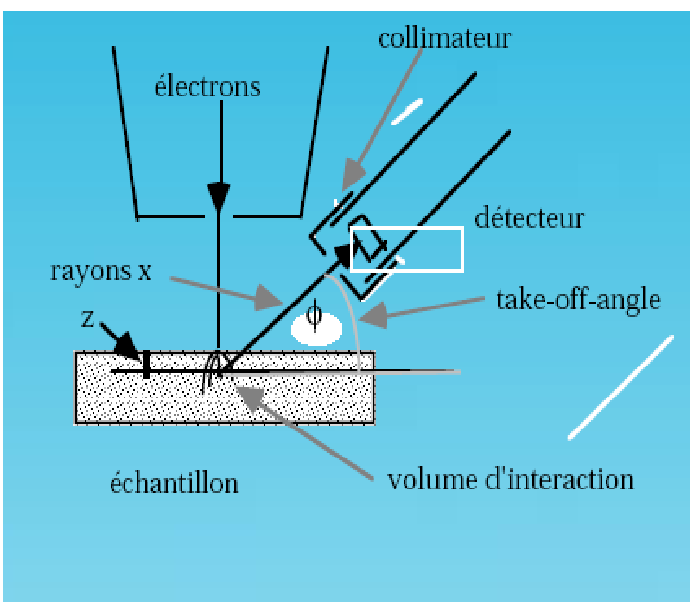
E= hν et λ=c/ν

with the Planck constant:h=6.626 068 76(52) × 10^{-34} J·s
and 1eV = 1.6 10^{-19} J

Energy of characteristic X-ray
-> Element
Qualitative EDX-Analysis

So, lets measure the X-rays emitted from my sample and determine the composition ! But how to detect it ?

b) Detection of X-rays (EDX)



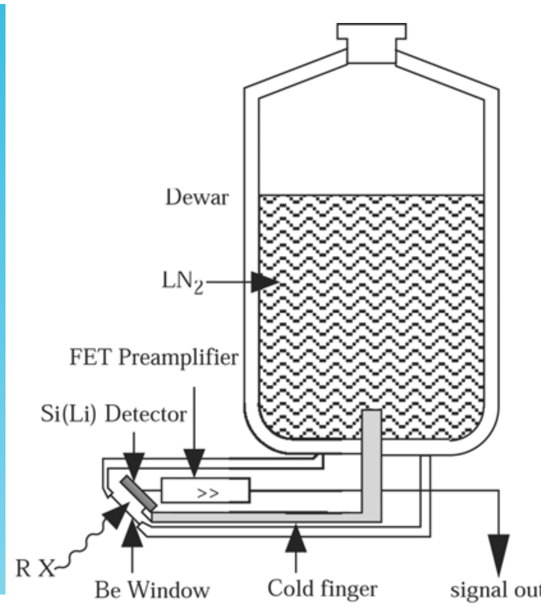
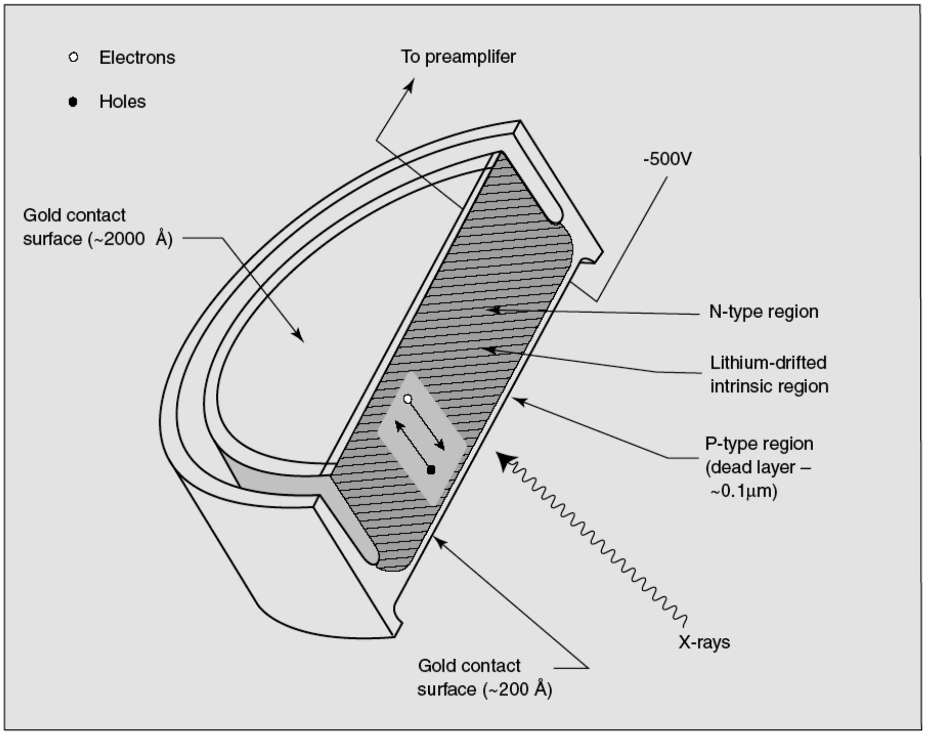
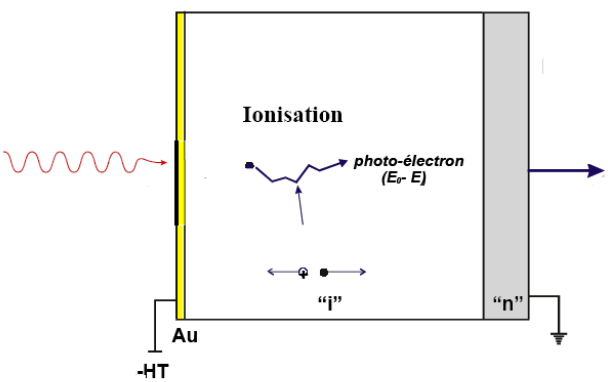
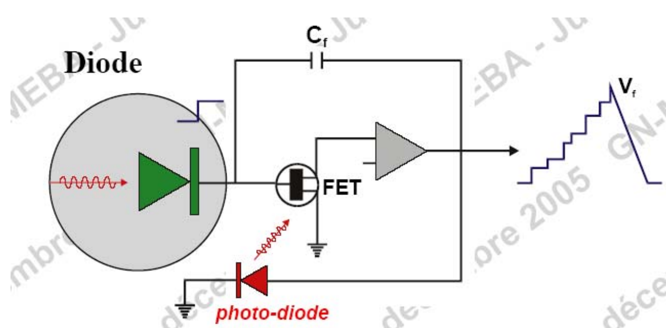


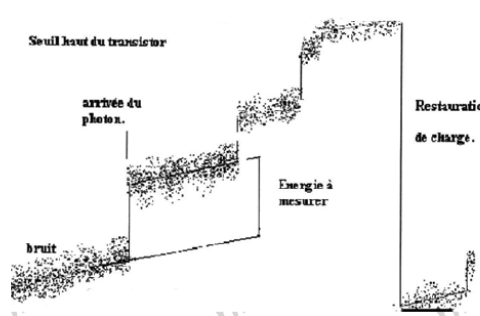
Figure 4-2. Cross section of a typical lithium-drifted silicon detector. X-rays create electron-hole pairs in the intrinsic region of the semiconductor; these charge carriers then migrate to the electrodes under the influence of an applied bias voltage.





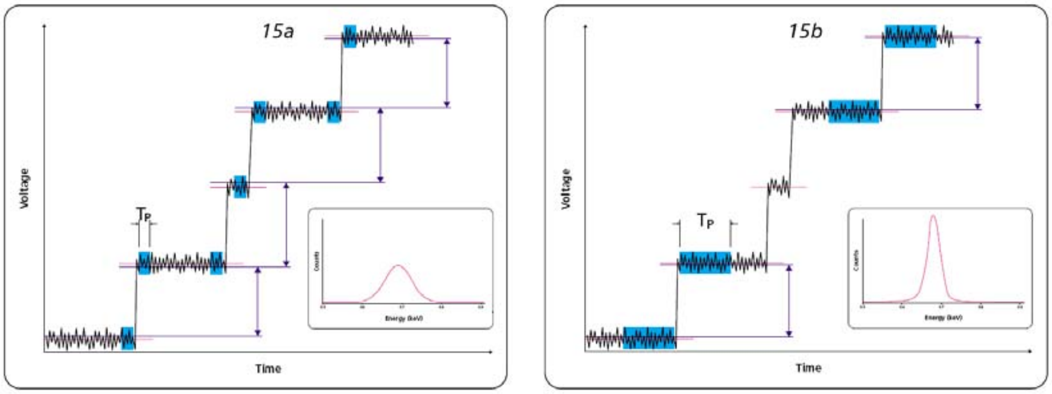


X-Ray energy conversion to electrical charges:
3.8eV / electron-hole pair in average
electronic noise+ imperfect charge collection:
130 eV resolution / Mn Ka line



- Detector acts like a diode: at room temperature the leak current for 1000V would be too high !
- The FET produces less noise if cooled !
- Li migration at room temperature !
- ->Detector cooling by L-N

Pulse detection and analysis



Pulse detection: Charge ~ energy

Shorter time constant = process time to analyze voltage
-> peak broadening (lower energy resolution)

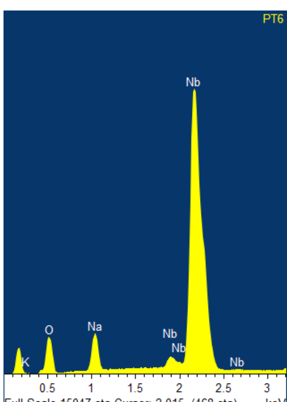
Longer time constant (higher energy resolution)

->pulse rejection (dead time)

Process time time constant

resolution peak identification

beam current count rate



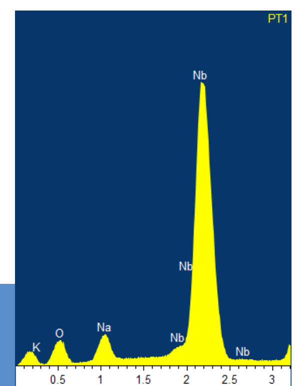
Long

low count rate

Higher dead time

narrow peaks

Time const. (μsec.)	Count rate, cts/sec. (30% dead time)
4	~30'000
15	~11'000
30	~4'500
50	~2'000

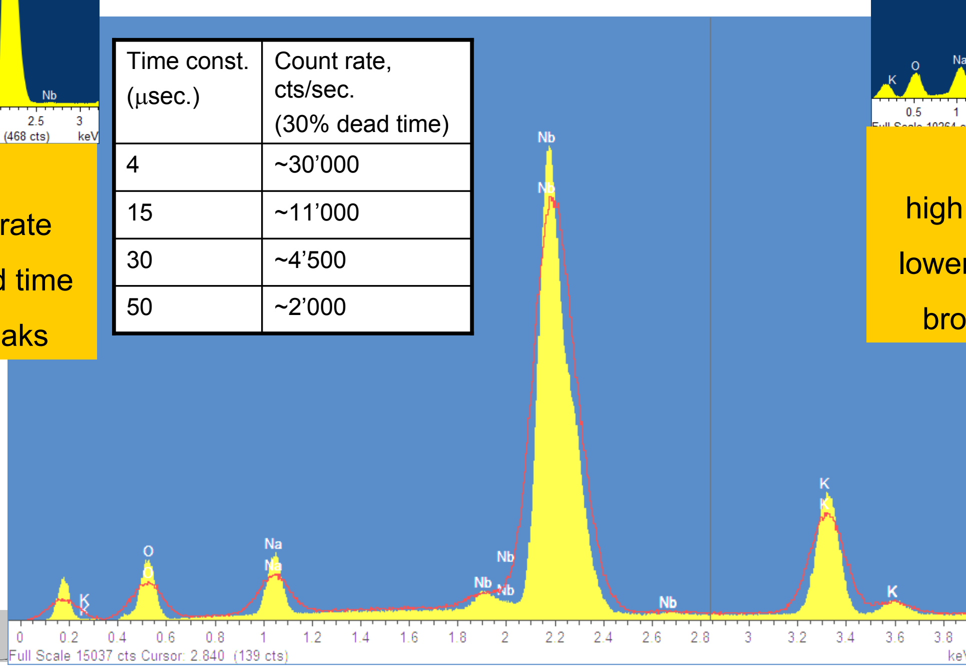


short

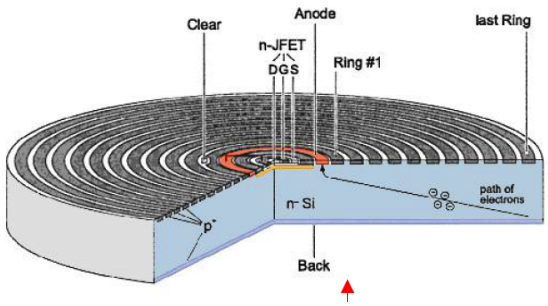
high count rate

lower dead time

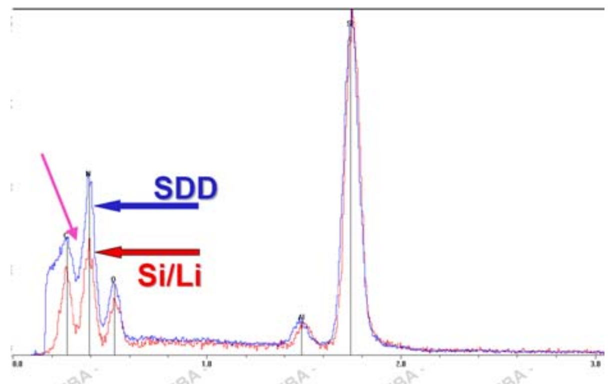
broad peaks



Silicon Drift Detectors



Extremely fast (up to 100’000 counts/sec.)
No L-N cooling required
Similar priced as Si/Li detectors



Peak tail at lower energies

Lower resolution for light elements

Detection and artifacts

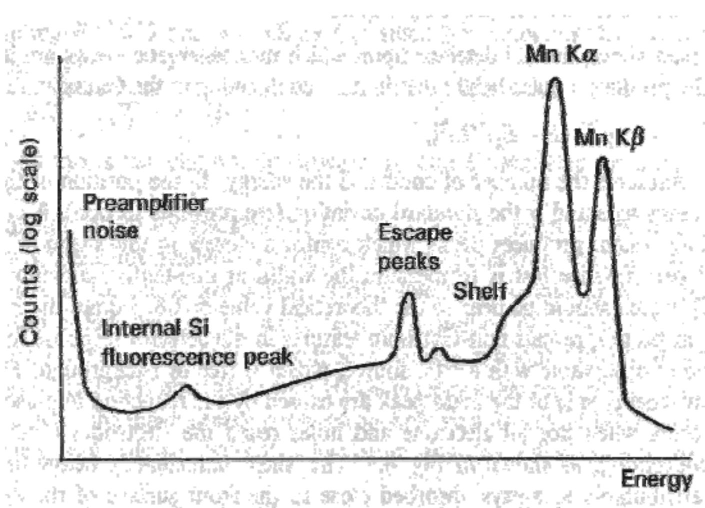
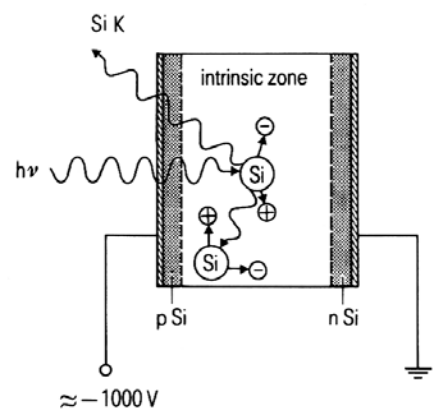


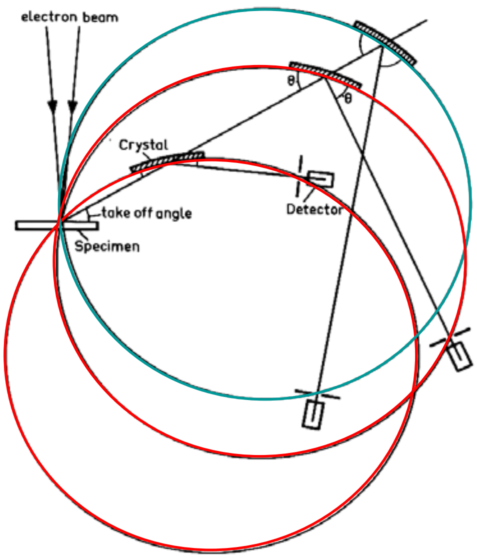
Fig. 4.9. Detector response for Mn K x-rays from ^{55}Fe source.

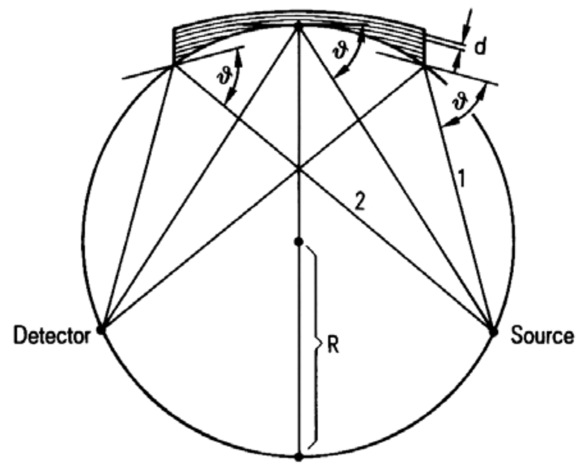


X-Ray energy conversion to electrical charges:
3.8eV / electron-hole pair in average
electronic noise+ imperfect charge collection:
130 eV resolution / Mn Ka line

Take care when looking for “trace” elements (low concentrations). Don’t confuse small peaks with escape peaks !

Wavelength Dispersive Spectroscopy (WDS)

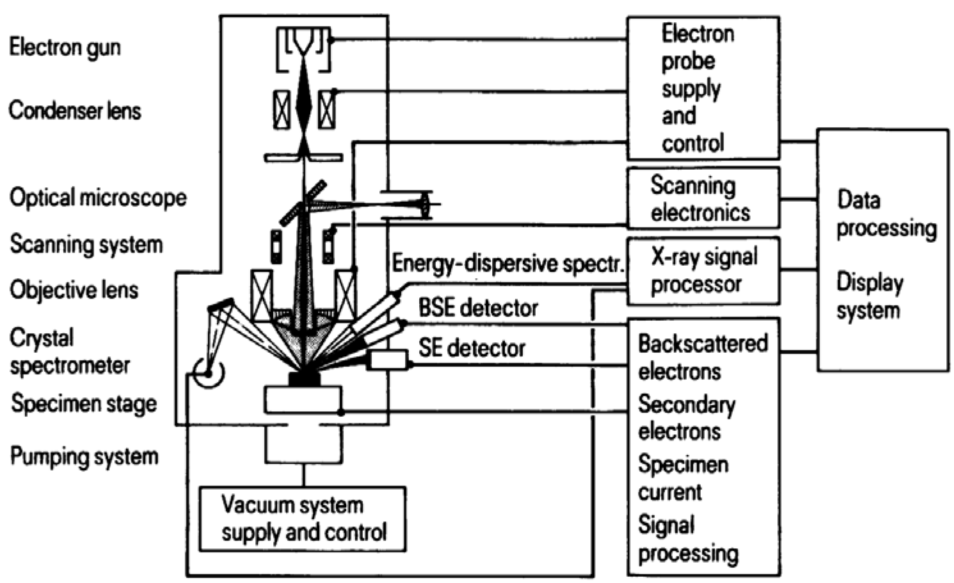


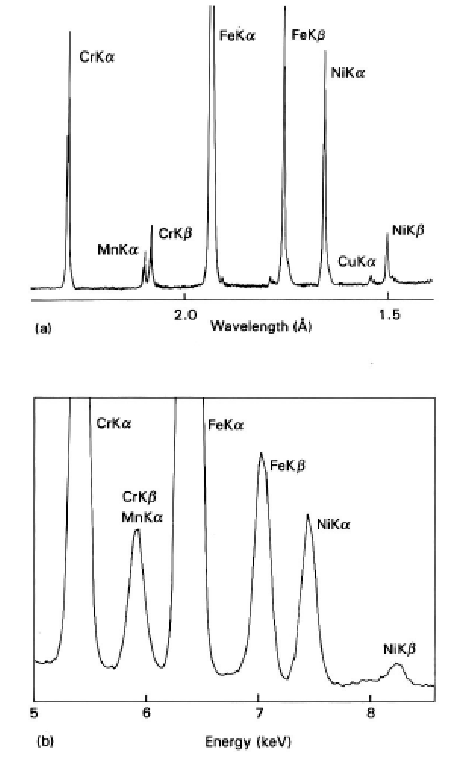


The specimen, the diffracting crystal and the detector stay on the Rowland circle. To scan the wavelength, this circle rotates around the specimen to satisfying the Bragg law

Johansson focusing spectrometer:
The diffracting crystal is bent with a curvature radius double of that of the Rowland circle
The crystal surface is cylindrically ground to the radius of the Rowland circle

Electron Microprobe EPMA (Electron Probe MicroAnalyser) with WDS



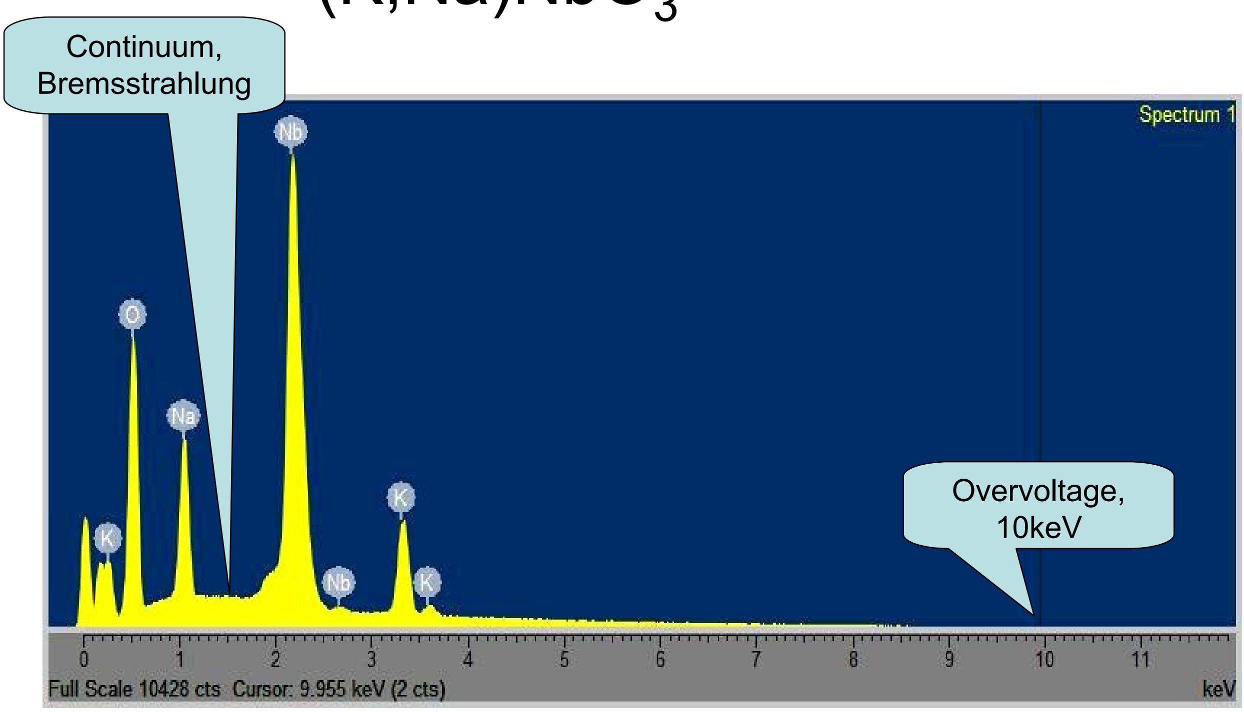


g. 6.7. Comparison of spectra from a steel (1.7 wt% Mn) at 20 kV recorded by (a) WDS and (b) EDS; note the Mn Kα peak is not resolved with EDS.

EDS <-> WDS

	EDS	WDS
Energy Resolution	80-180eV	≈5eV
Acquisition time	1 min.	5-30min.
Use	Easy	difficult
Standardless Analysis	++	difficult
Peak to background ratio	100:1	1000:1

(K,Na)NbO_3

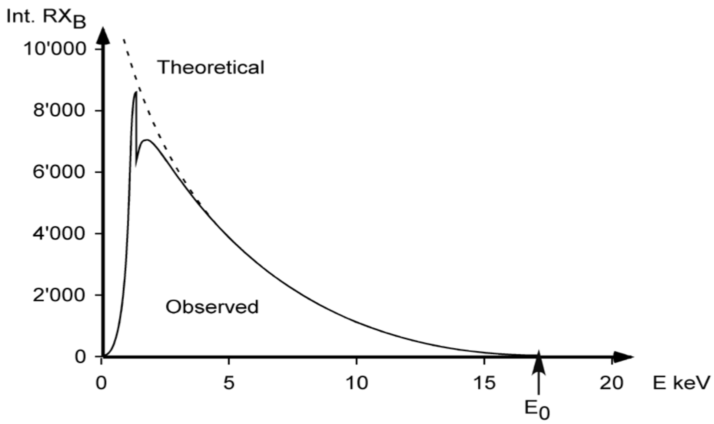


Electron beam: 10keV

Duane-Hunt limit

Bremstrahlung (background)

- when a charged particle (des-) accelarates or changes direction, it emits an electromagnetic wave.
  - This is widely used to produce synchrotron radiation
- On a bulk sample of atomic number Z:
  - N(E) is the number of photons of energy E, E0 the energy of the incident electron and K the Kramers constant

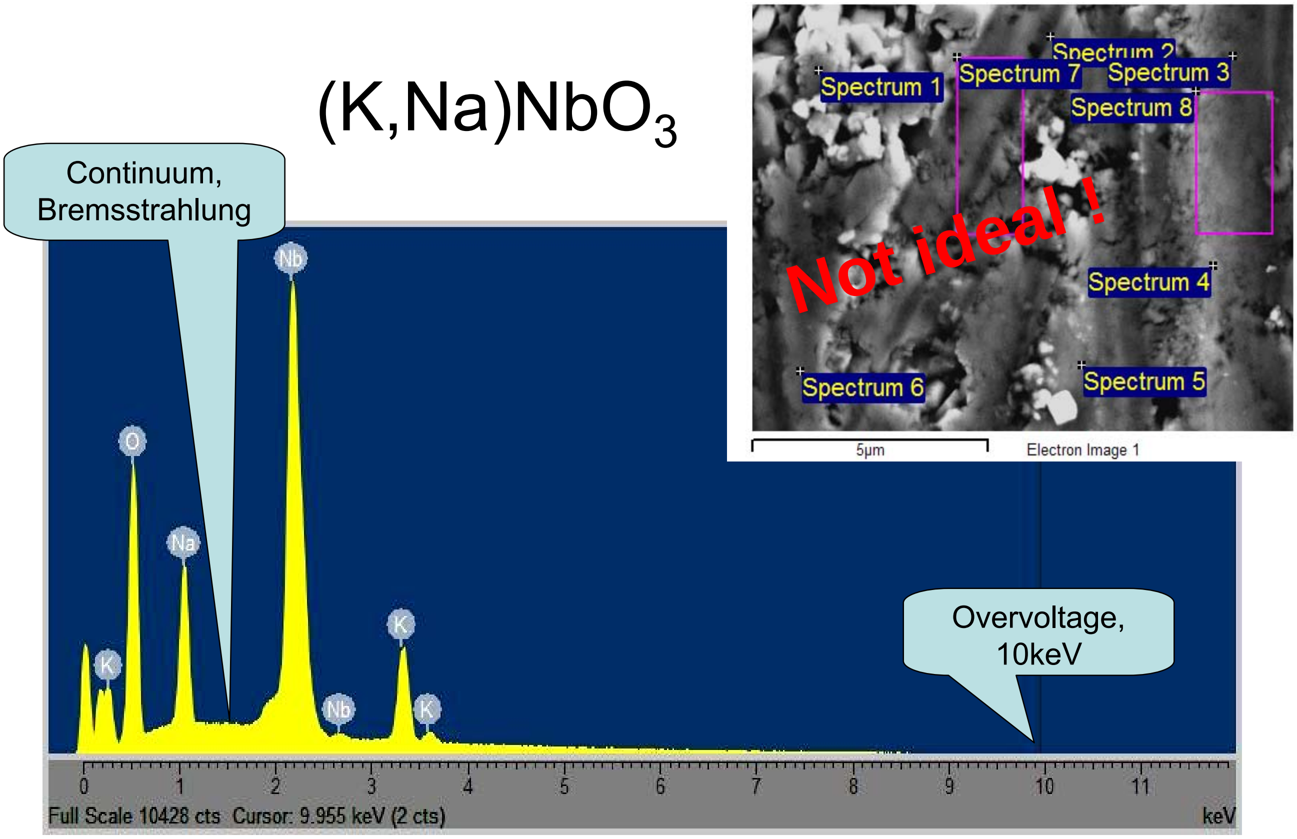


$$N(E) = \frac{KZ(E_0 - E)}{E}$$

EDS in SEM

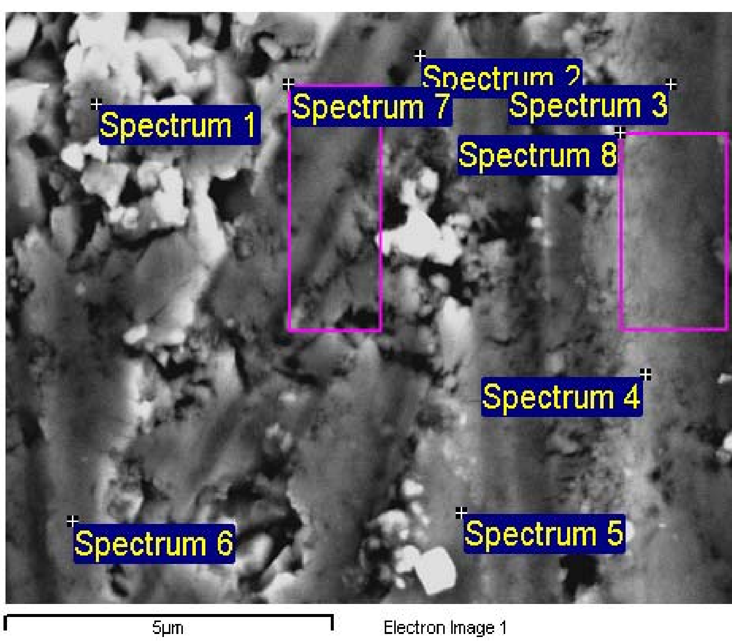
- Acquisition under best conditions
  - Flat surface without contamination (no Au coating, use C instead)
  - Sample must be homogenous at the place of analysis (interaction volume !!)
  - Horizontal orientation of the surface
  - High count rate (but dead time below 30%)
  - Overvoltage U=Eo/Ec >1.5-2
- For acquisition times of 100sec. : detection of ~0.5at% for almost all elements

(K,Na)NbO_3



Duane-Hunt limit

(K,Na)NbO3



Spectrum	Na	K	Nb	O	Total
Spectrum 1	8.19	10.18	20.70	60.93	100.00
Spectrum 2	9.59	8.66	20.75	61.00	100.00
Spectrum 3	7.82	9.54	21.13	61.51	100.00
Spectrum 4	9.79	9.37	20.36	60.48	100.00
Spectrum 5	8.86	9.35	20.77	61.02	100.00
Spectrum 6	9.46	9.07	20.63	60.84	100.00
Spectrum 7	8.89	10.25	20.37	60.49	100.00
Spectrum 8	8.60	9.40	20.86	61.14	100.00
Max.	9.79	10.25	21.13	61.51	
Min.	7.82	8.66	20.36	60.48	

c) Quantification

Yes, but…..

- First approach:
  compare X-ray intensity with a standard (sample with known concentration, same beam current of the electron beam)

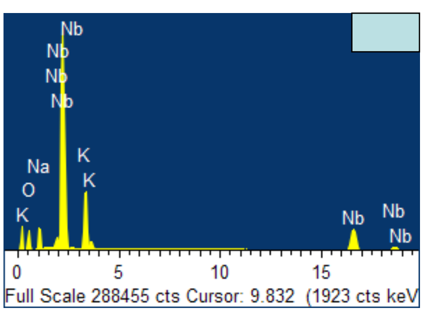
c_i: wt concentration of element i

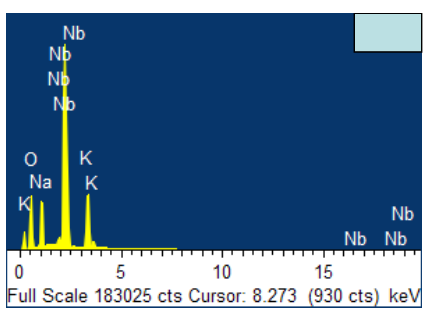
I_i: X-ray intensity of char. Line

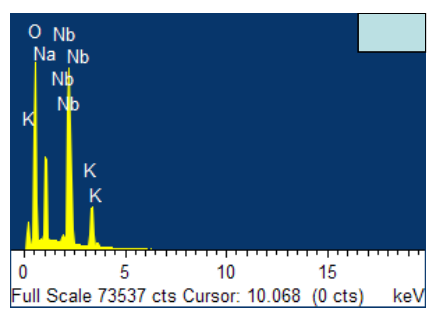
k_i: concentration ratio

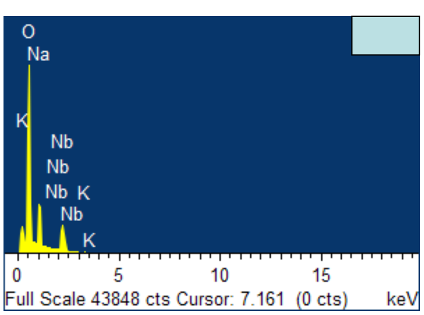
$$\frac{c_i}{c_i^{std}} = \frac{I_i}{I_i^{std}} = k_i$$

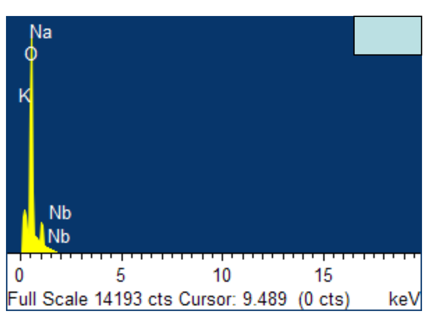
Intensity ~ Concentration…?



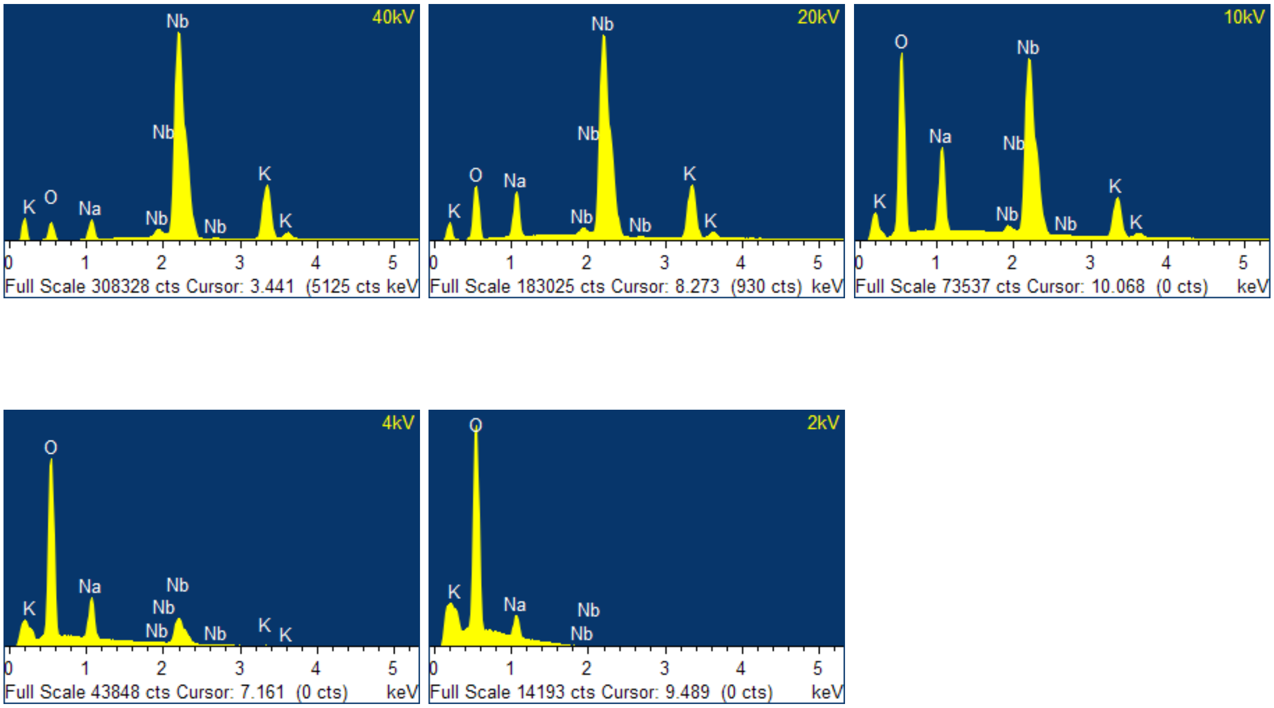




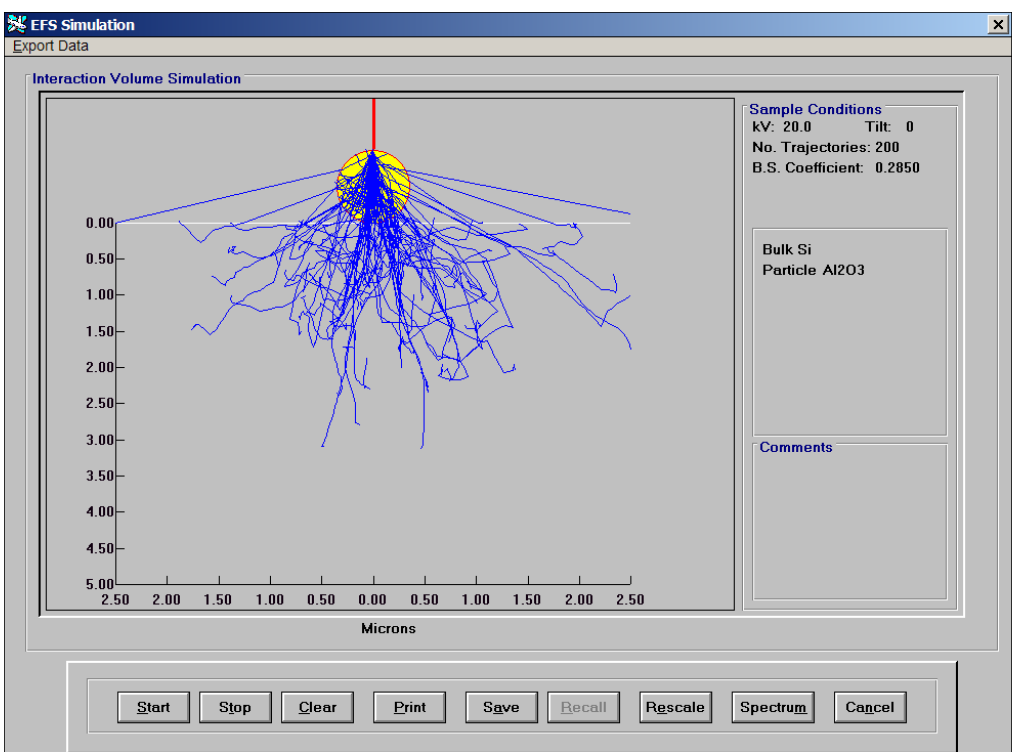




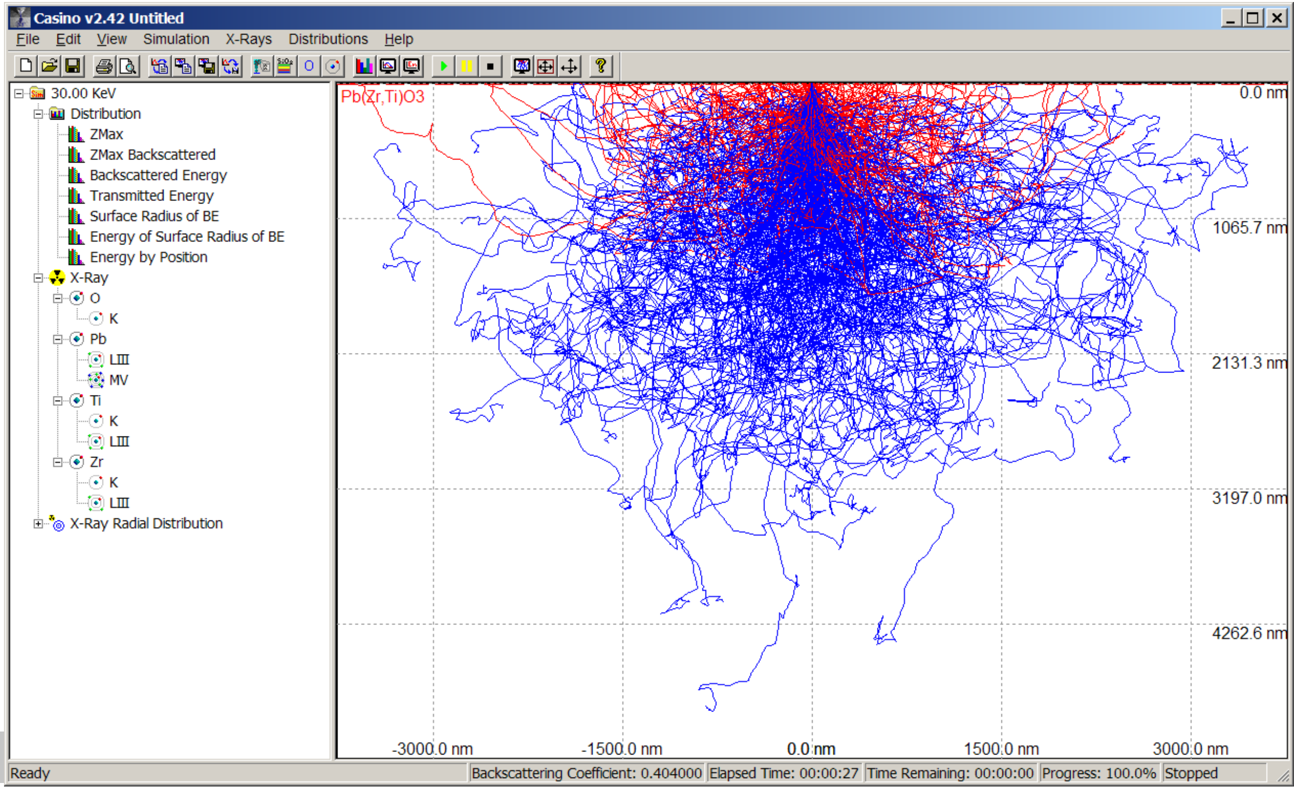
How many different samples…?

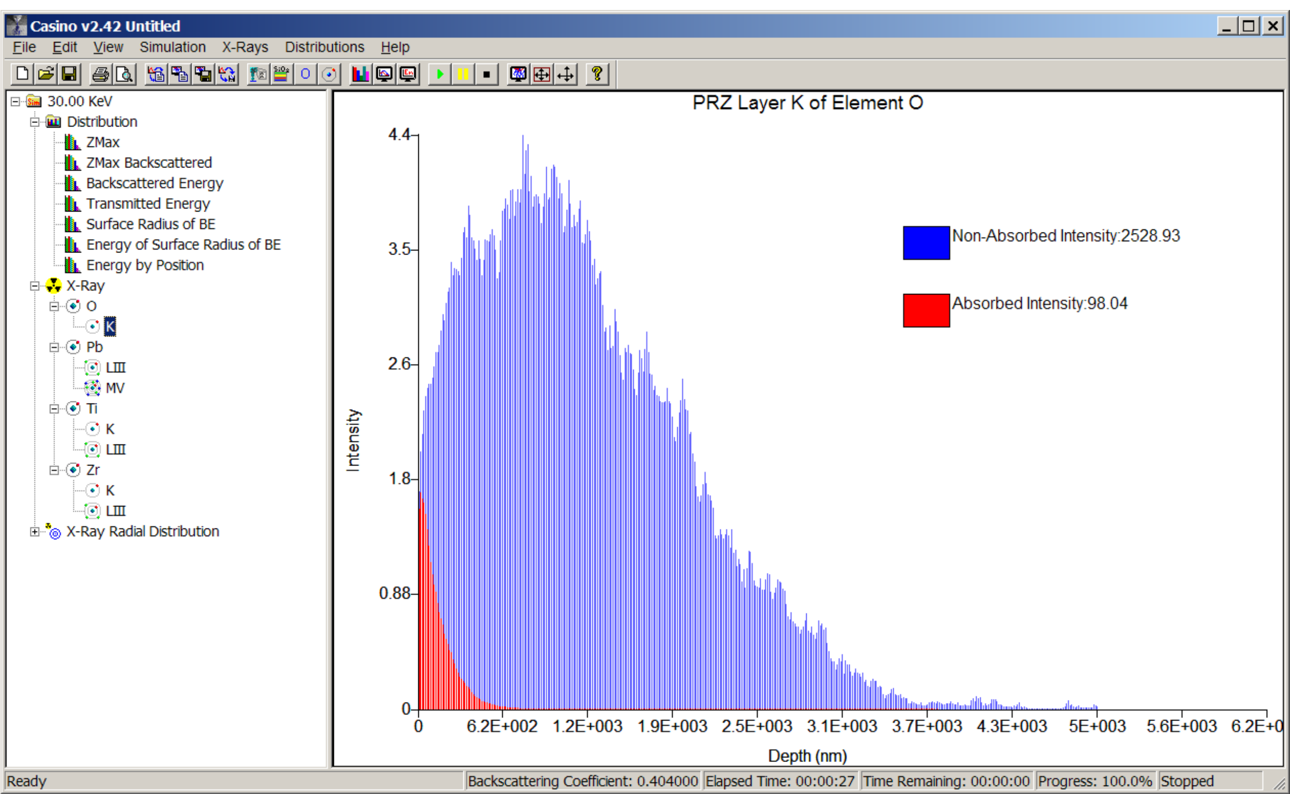


Electron Flight Simulator



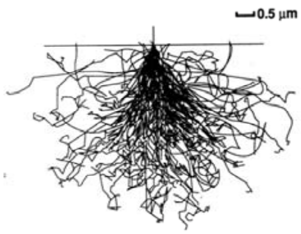
Casino


Casino v2.42 Untitled
File Edit View Simulation X-Rays Distributions Help
30.00 KeV
Distribution
ZMax
ZMax Backscattered
Backscattered Energy
Transmitted Energy
Surface Radius of BE
Energy of Surface Radius of BE
Energy by Position
X-Ray
O
K
Pb
LIII
MV
Ti
K
LIII
Zr
K
LIII
X-Ray Radial Distribution
Pb(Zr,Ti)O3
0.0 nm
1065.7 nm
2131.3 nm
3197.0 nm
4262.6 nm
-3000.0 nm
-1500.0 nm
0.0 nm
1500.0 nm
3000.0 nm
Ready
Backscattering Coefficient: 0.404000
Elapsed Time: 00:00:27
Time Remaining: 00:00:00
Progress: 100.0%
Stopped

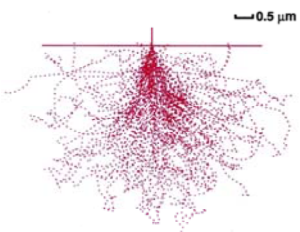

Casino v2.42 Untitled
File Edit View Simulation X-Rays Distributions Help
30.00 KeV
Distribution
ZMax
ZMax Backscattered
Backscattered Energy
Transmitted Energy
Surface Radius of BE
Energy of Surface Radius of BE
Energy by Position
X-Ray
O
K
Pb
LIII
MV
Ti
K
LIII
Zr
K
LIII
X-Ray Radial Distribution
PRZ Layer K of Element O
Non-Absorbed Intensity:2528.93
Absorbed Intensity:98.04
Intensity
4.4
3.5
2.6
1.8
0.88
0
0
6.2E+002
1.2E+003
1.9E+003
2.5E+003
3.1E+003
3.7E+003
4.3E+003
5E+003
5.6E+003
Depth (nm)
Ready
Backscattering Coefficient: 0.404000
Elapsed Time: 00:00:27
Time Remaining: 00:00:00
Progress: 100.0%
Stopped

When the going gets tough…..

Quantification



C

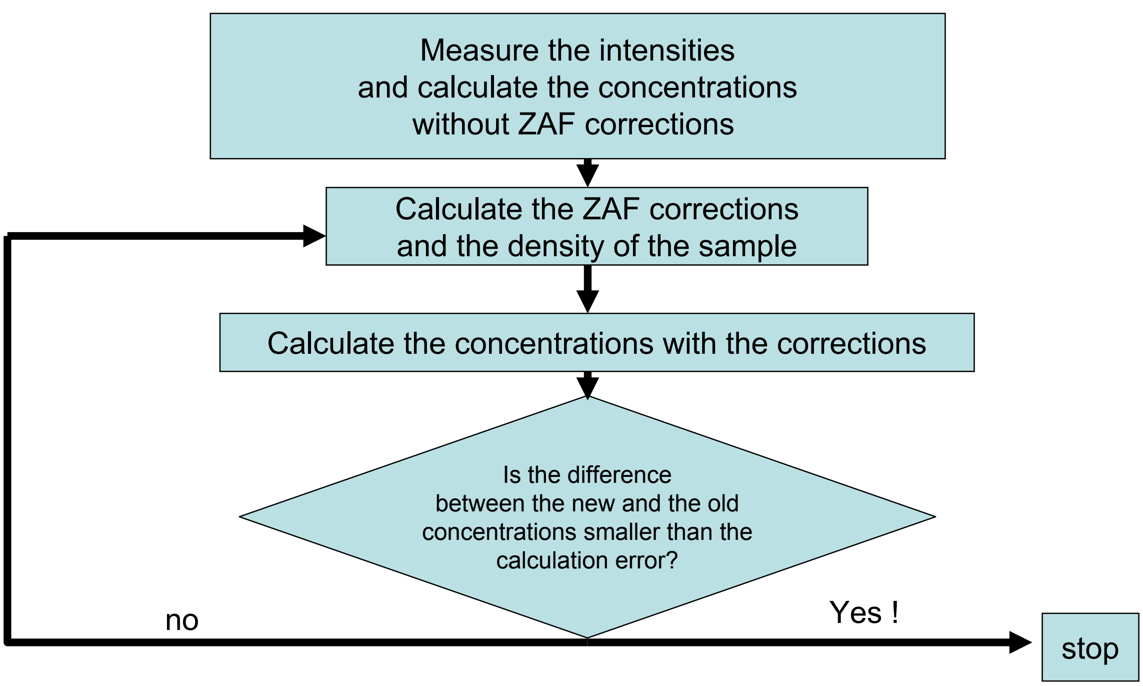


Correction matrix

$$[Z \times A \times F]\frac{c_i}{c_i^{std}} = \frac{I_i}{I_i^{std}} = k_i$$

- "Z" describe how the electron beam penetrates in the sample (Z-dependant and density dependant) and loose energy
- "A" takes in account the absorption of the X-rays photons along the path to sample surface
- "F" adds some photons when (secondary) fluorescence occurs

Flow chart of quantification



Correction methods:

- ZAF (purely theoretical)
- PROZA Phi-Rho-Z
- PaP (Pouchou and Pichoir)
- XPP (extended Puchou/Pichoir)

- with standards (same HT, current, detector settings)
- Standardless: theoretical calculation of I_{std}
- Standardless optimized: « hidden » standards, user defined peak profiles

Quantitative EDX in SEM

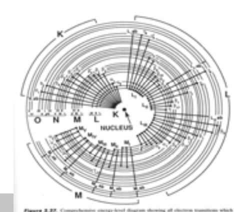
- Acquisition under best conditions
  - Flat surface without contamination, horizontal orientation of the surface (no Au coating, use C instead)
  - Sample must be homogenous at the place of analysis (interaction volume !!)
  - High count rate (but dead time below 30%)
  - Overvoltage U=Eo/Ec >1.5-2
- For acquisition times of 100sec. : detection of ~0.5at% possible for almost all elements
- Standardless acquisition possible with high accuracy (intensities of references under the given conditions can be calculated for a great range of elements), test with samples of known composition, light elements (like O) are critical…
- Spatial resolution depends strongly on HT and the density of the sample

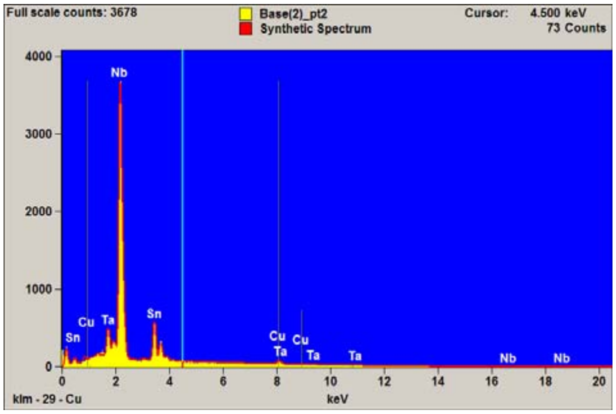
Demo NSS/INCA

- Peak finding, synthetic spectrum
- Spectrum imaging (extraction of elements)

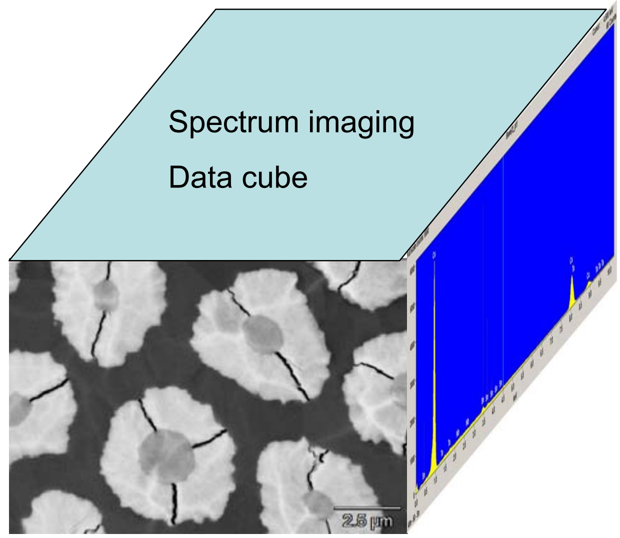
Modern EDX systems:

- **User friendly** interfaces
- New and more **powerful electronics** (stability of calibrations, higher count rate)
- **Drift compensation** for long acquisition times (element mapping on CM300 at high mag, “sitelock”)
- **Synthesized spectra** (spectrum overlay) easier identification
- Advanced element mapping: **Spectral imaging** (data cube), selection of elements and regions post-acquisition
- Powerfull **reporting** and Export tools (Word, Powerpoint, html, tif etc.)

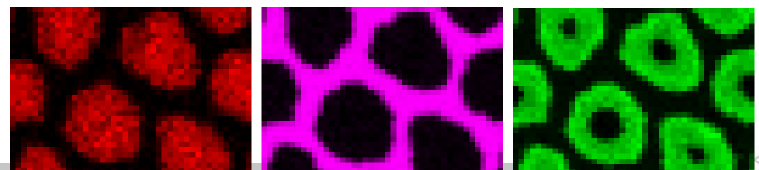




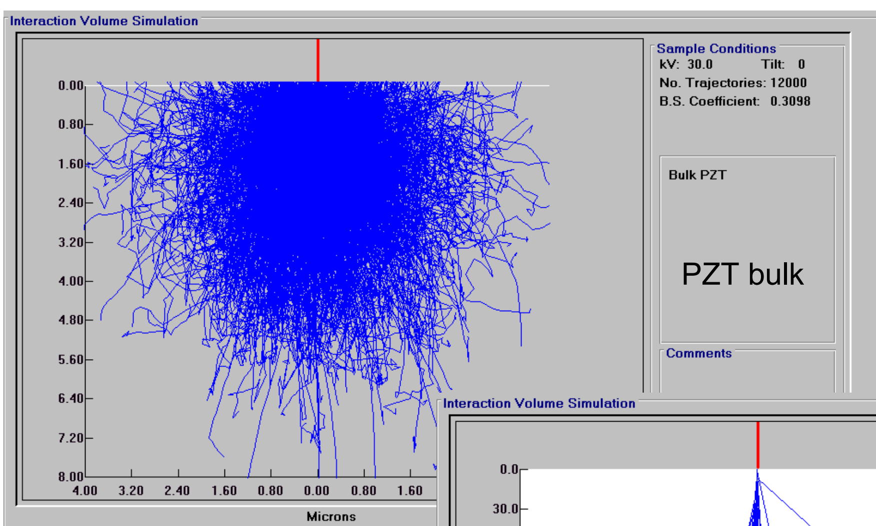
Synthesized spectrum

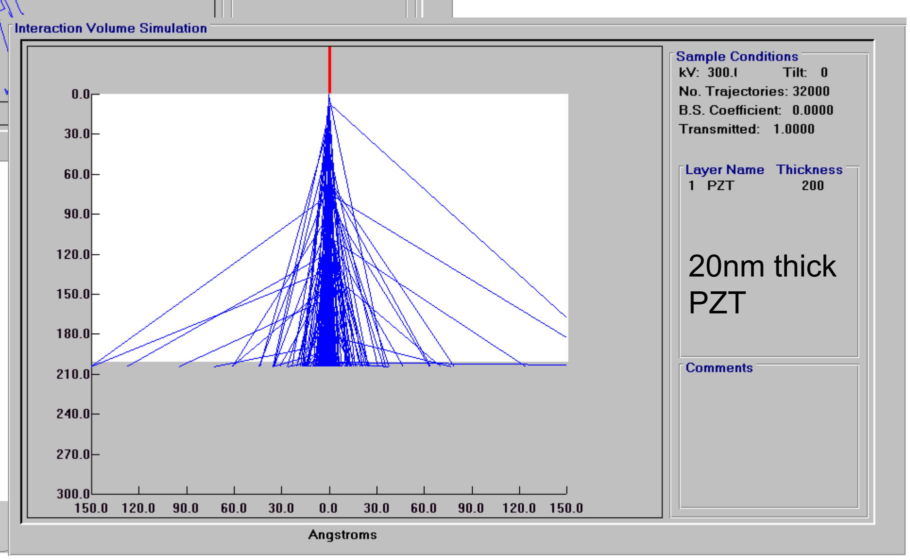


Extraction of element maps



EDS in TEM

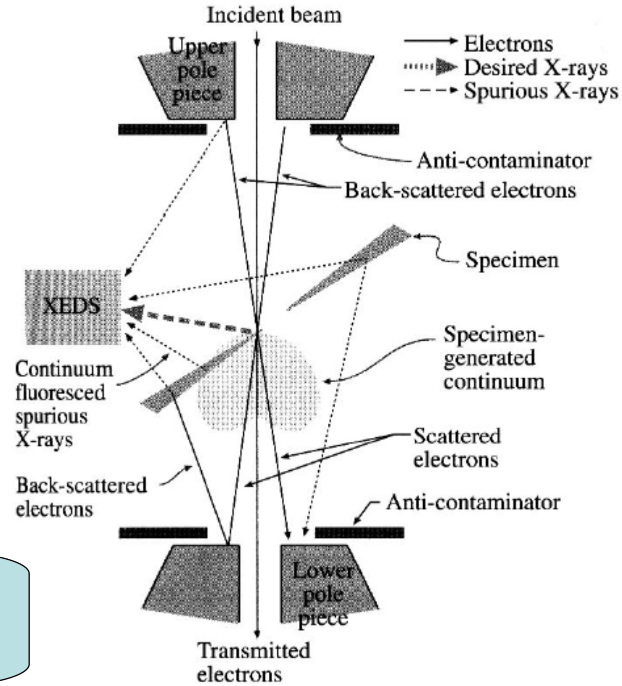




High spatial resolution !

EDS in TEM

- Thin samples -> correction factors weak (A and F can be neglected)
- Very weak beam broadening -> high spatial resolution ~ beam diameter (~nm)



High energy: artifacts !

If only there wasn't this specimen preparation……

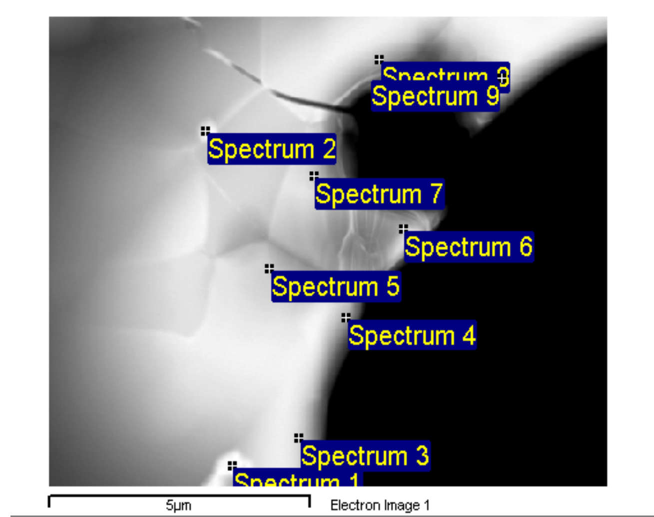
STEM point analysis

$PbMg_{1/3}Nb_{2/3}O_3$ (bulk)

Processing option : Oxygen by stoichiometry (Normalised)

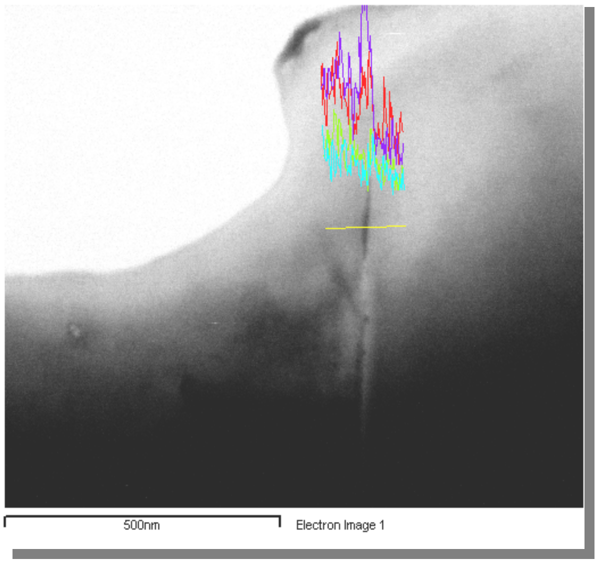
Spectrum	Mg	Si	Nb	Pb	O	Total
Spectrum 1	30.02	13.32			56.66	100.00
Spectrum 2	19.15	7.96	4.11	11.72	57.06	100.00
Spectrum 3	6.01		12.49	22.13	59.37	100.00
Spectrum 4	5.65		12.39	22.67	59.29	100.00
Spectrum 5	5.63		12.48	22.52	59.36	100.00
Spectrum 6	5.98		13.66	20.11	60.25	100.00
Spectrum 7	5.55		12.45	22.66	59.34	100.00
Spectrum 8	5.49		12.96	21.84	59.72	100.00
Spectrum 9	5.63		12.19	23.04	59.14	100.00
Max.	30.02	13.32	13.66	23.04	60.25	
Min.	5.49	7.96	4.11	11.72	56.66	

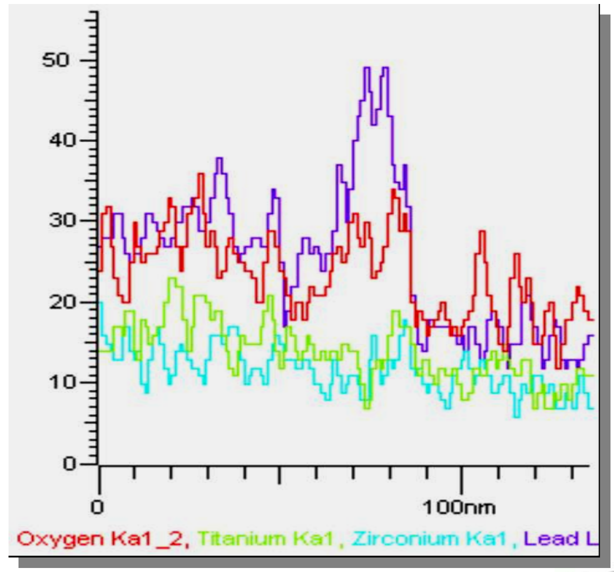
All results in Atomic Percent



STEM linescan

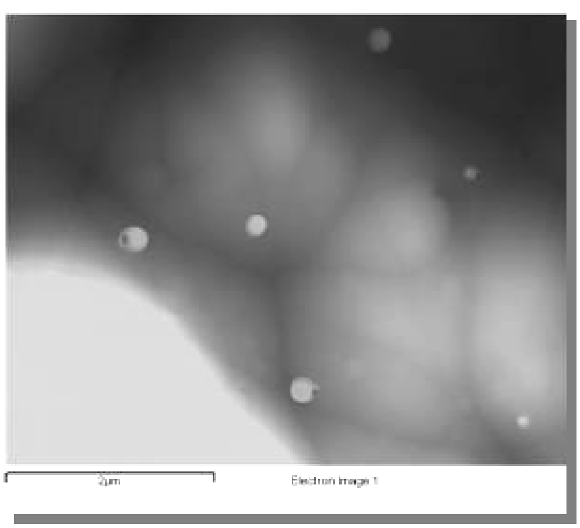
Pb(Zr,Ti)O_3 (thick film), slight Pb excess

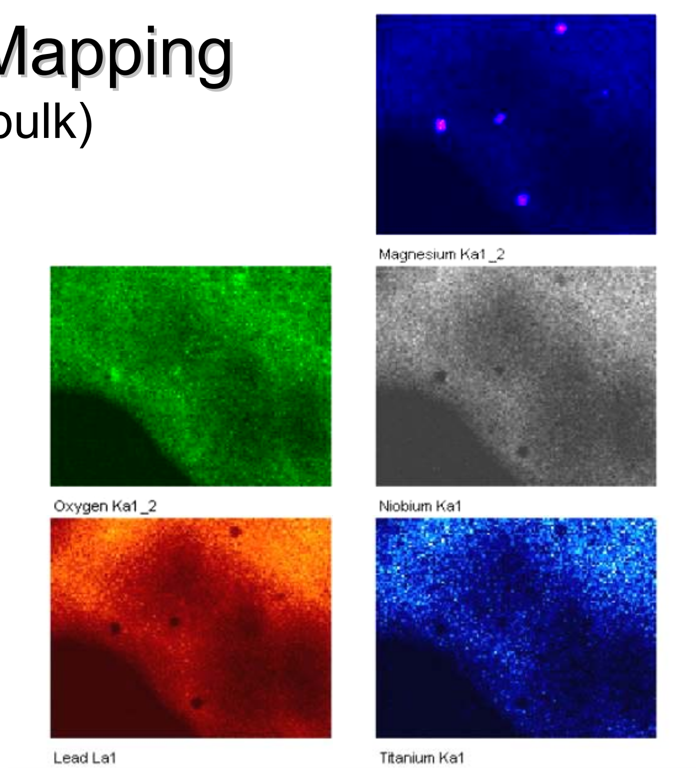




STEM Element Mapping

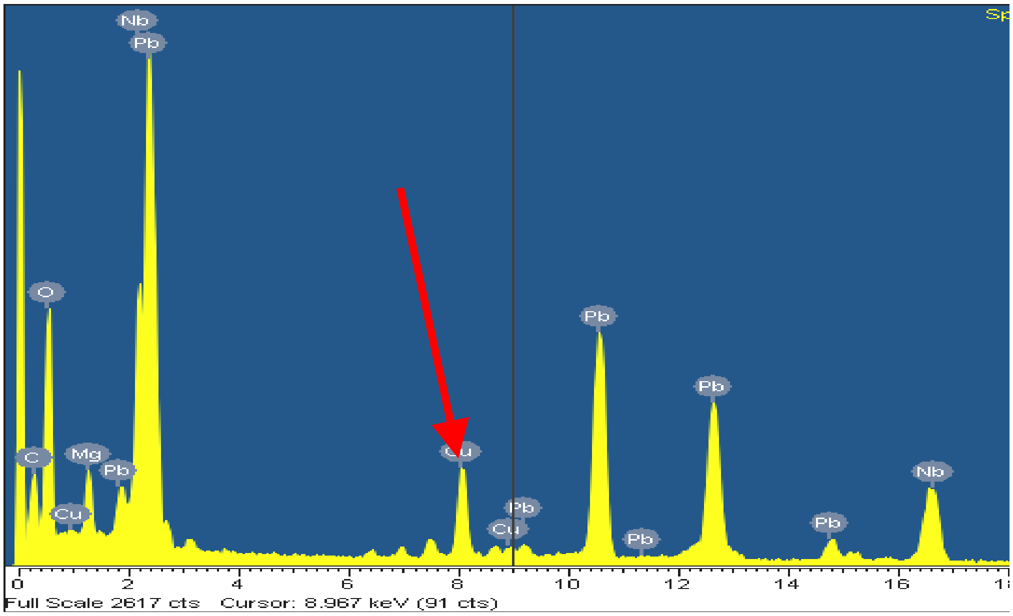
PMN/PT 90/10 (bulk)



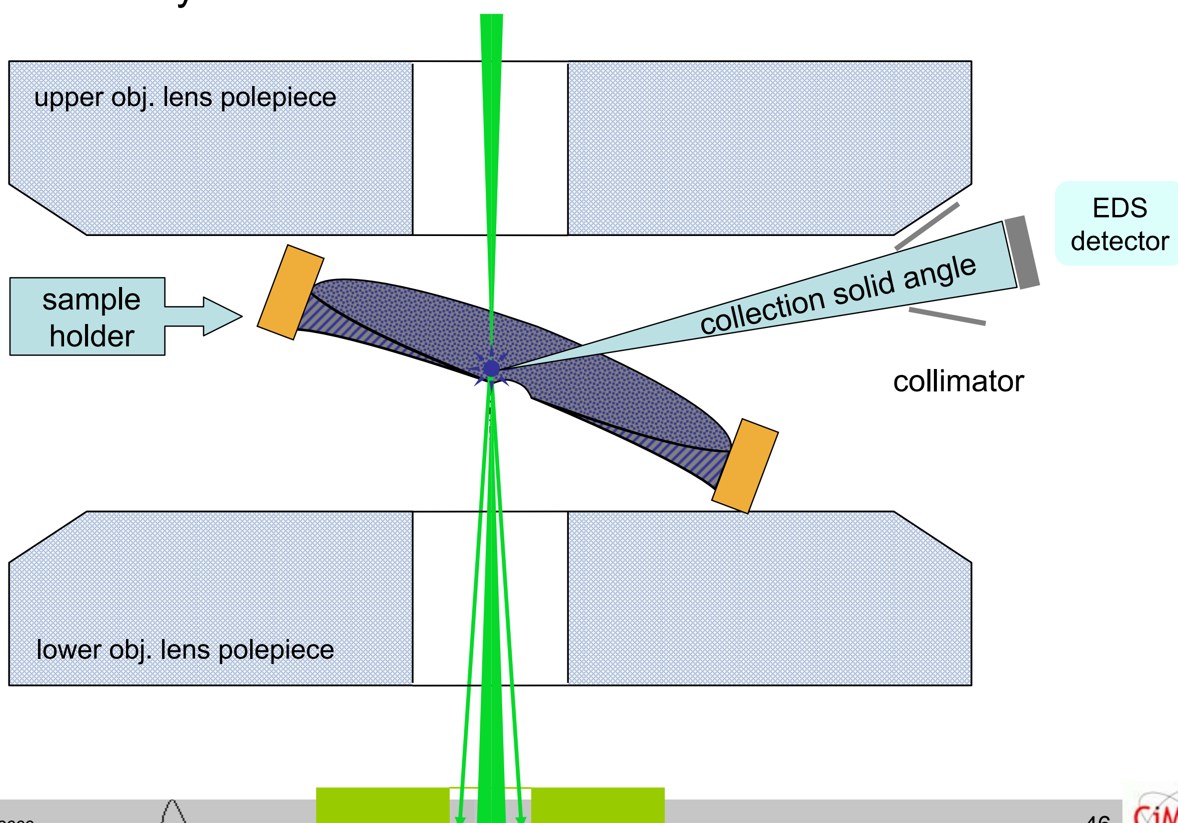


Artifacts

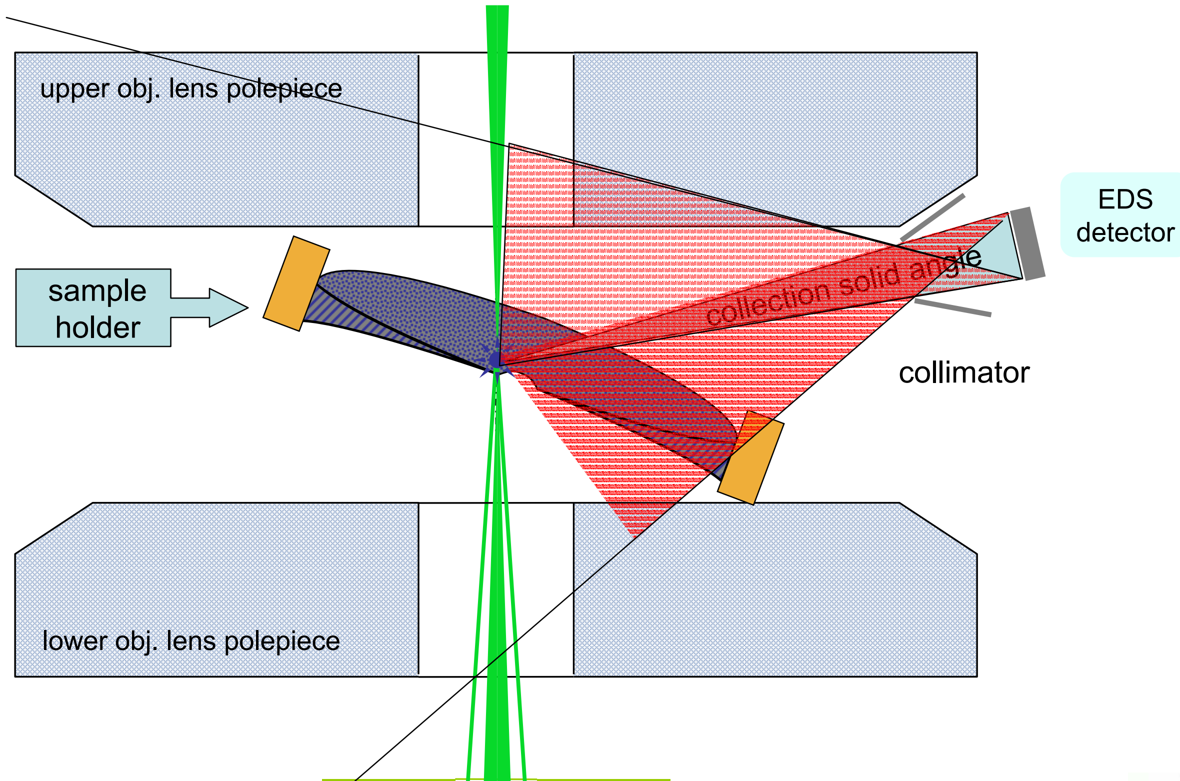
how to recognize/minimize them



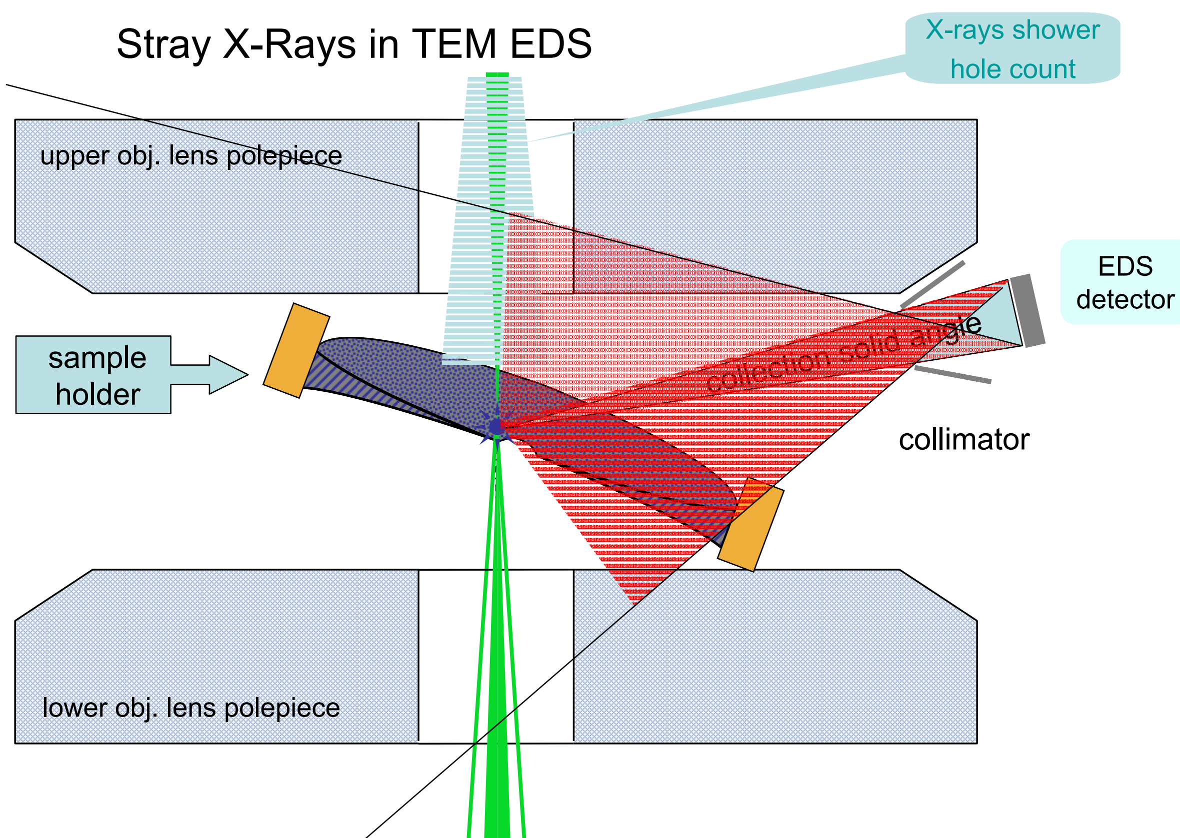
X-Ray collection in TEM EDS



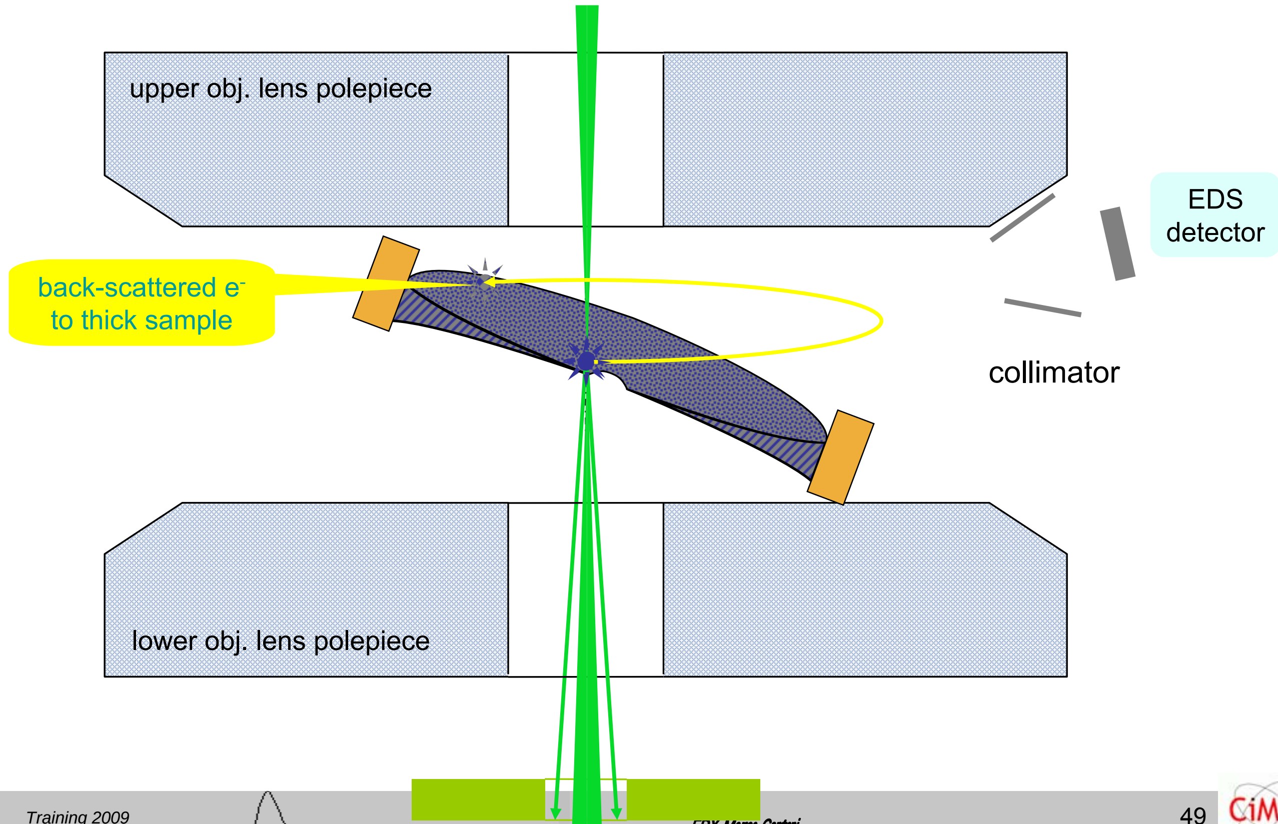
X-Ray collection in TEM EDS



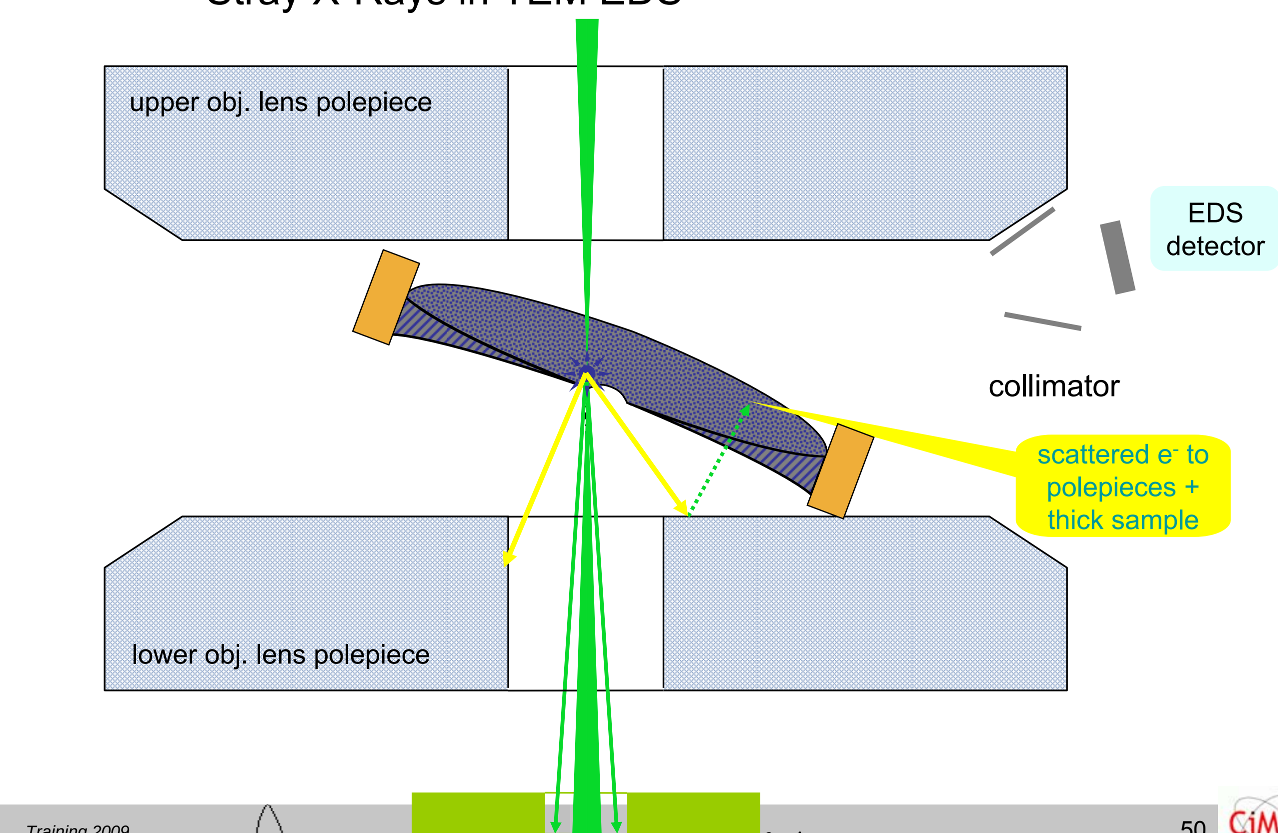
Stray X-Rays in TEM EDS



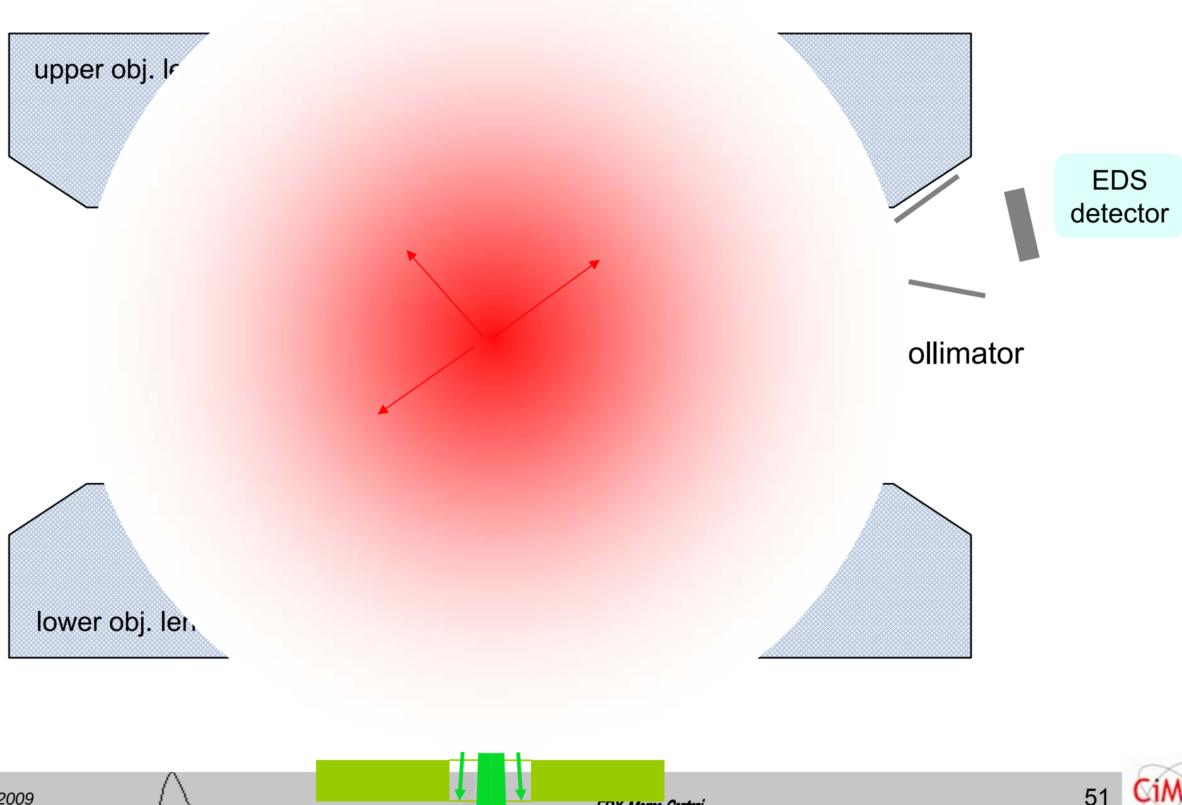
Stray X-Rays in TEM EDS



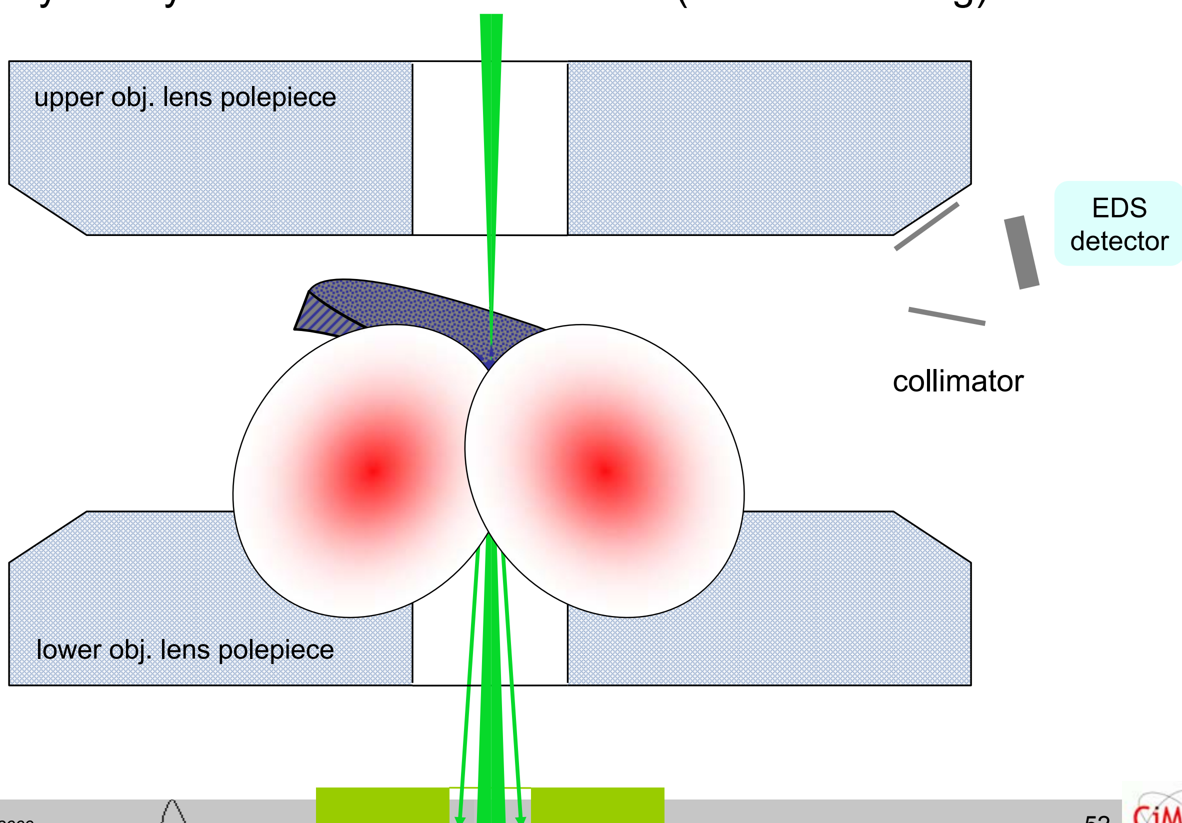
Stray X-Rays in TEM EDS



Stray X-R… …haracteristic x-rays



Stray X-Rays in TEM EDS: continuum (Bremsstrahlung)



Ideal samples:

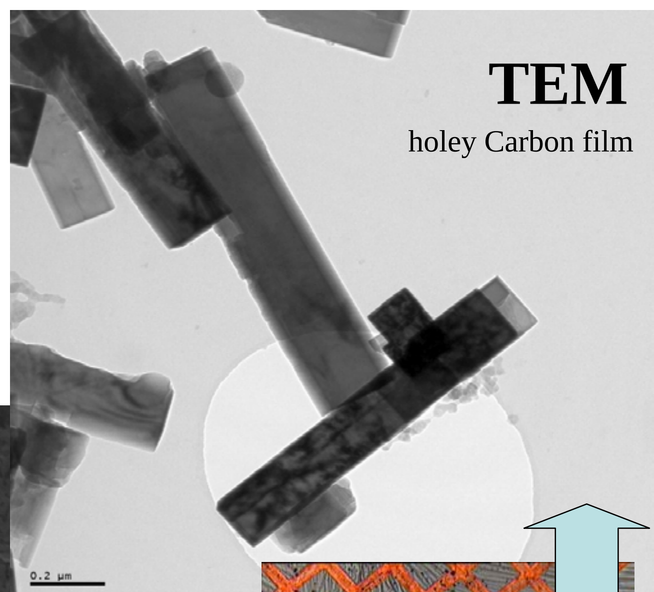
- FIB samples: almost uniform thickness, small sample size(less bulk material around)

EDS in TEM

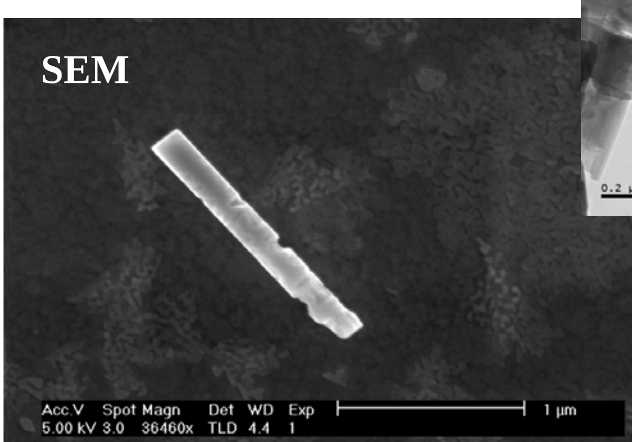
- Thin samples -> correction factors weak (A and F can be neglected), quantification “easy”
- Very weak beam broadening -> high spatial resolution ~ beam diameter (~nm)
- High energy -> artifacts
- Sample preparation, sample geometry……

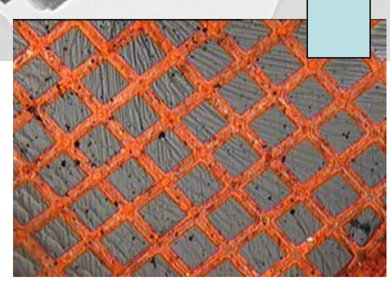
Bonus

EDX of Powders nano particles SEM or TEM ???



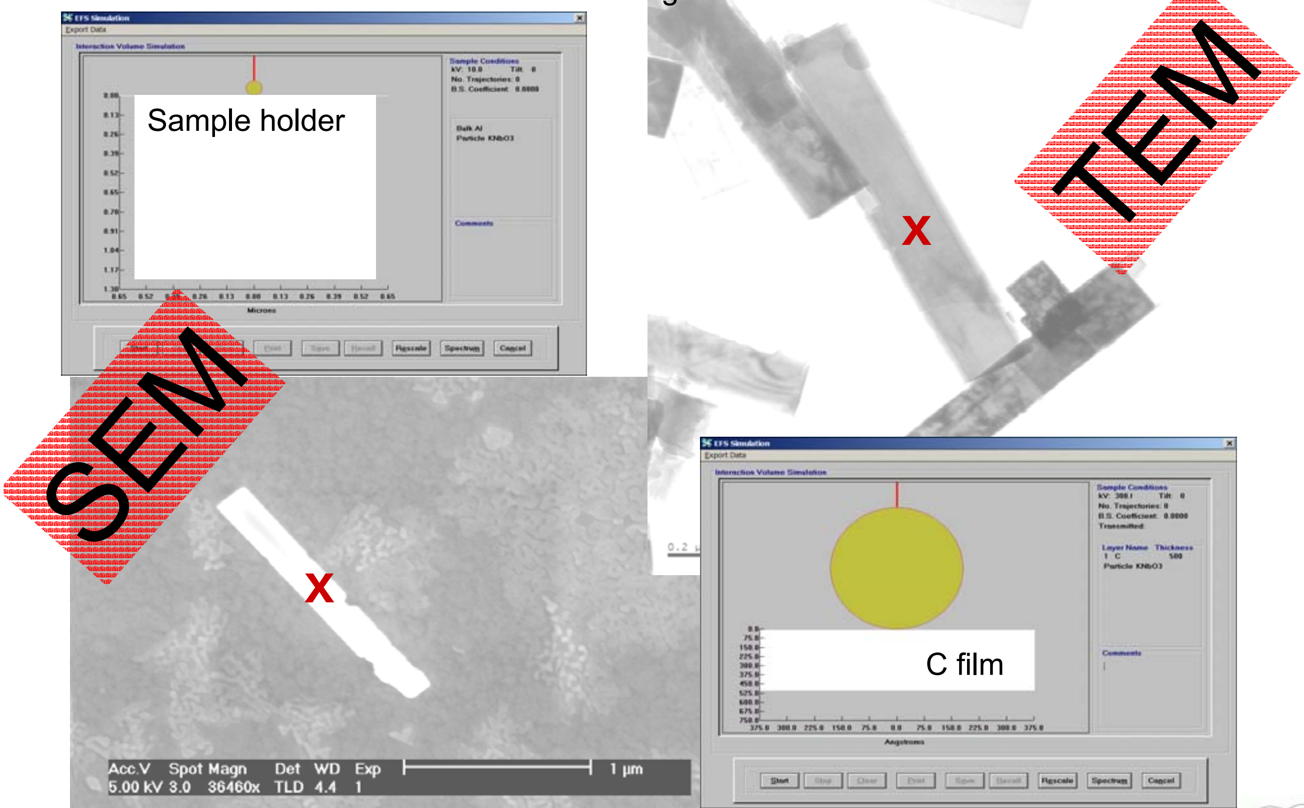
$KNbO_3$
Nano-rods



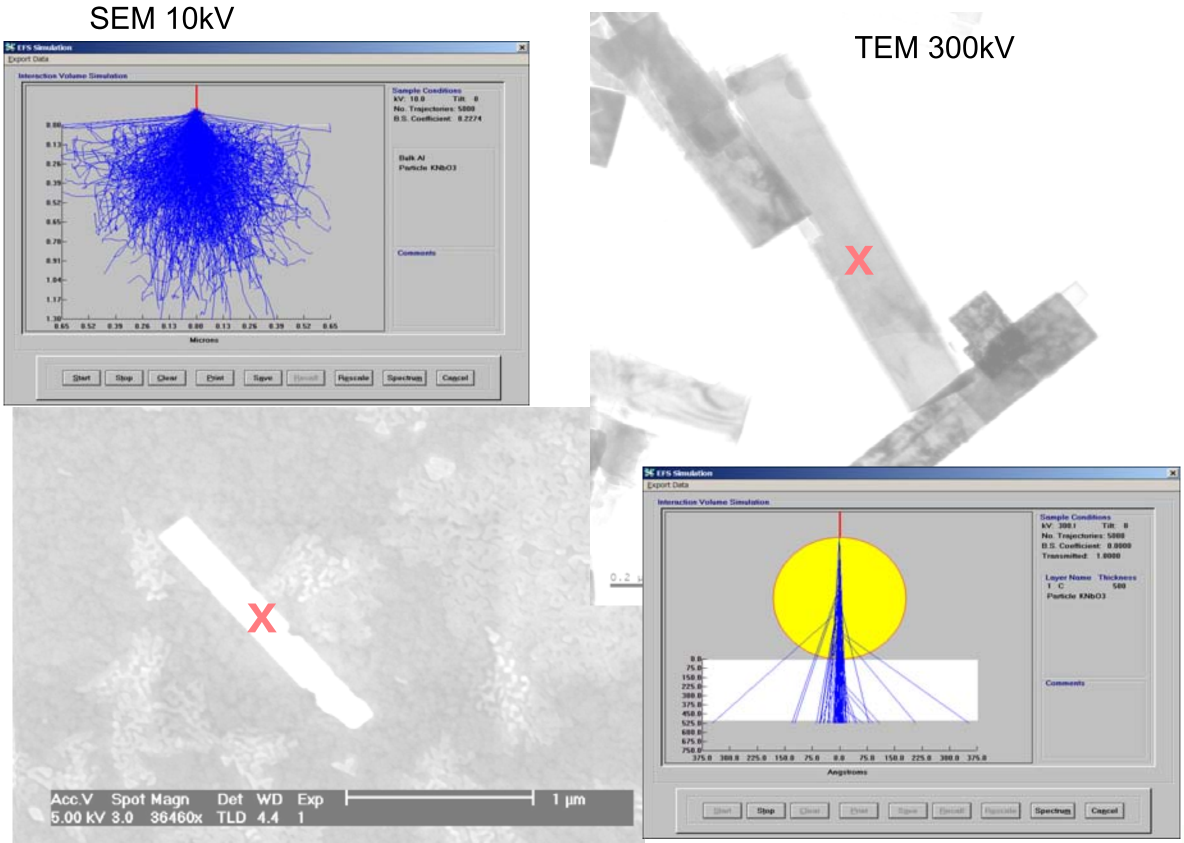


Optical microscope
reflected light

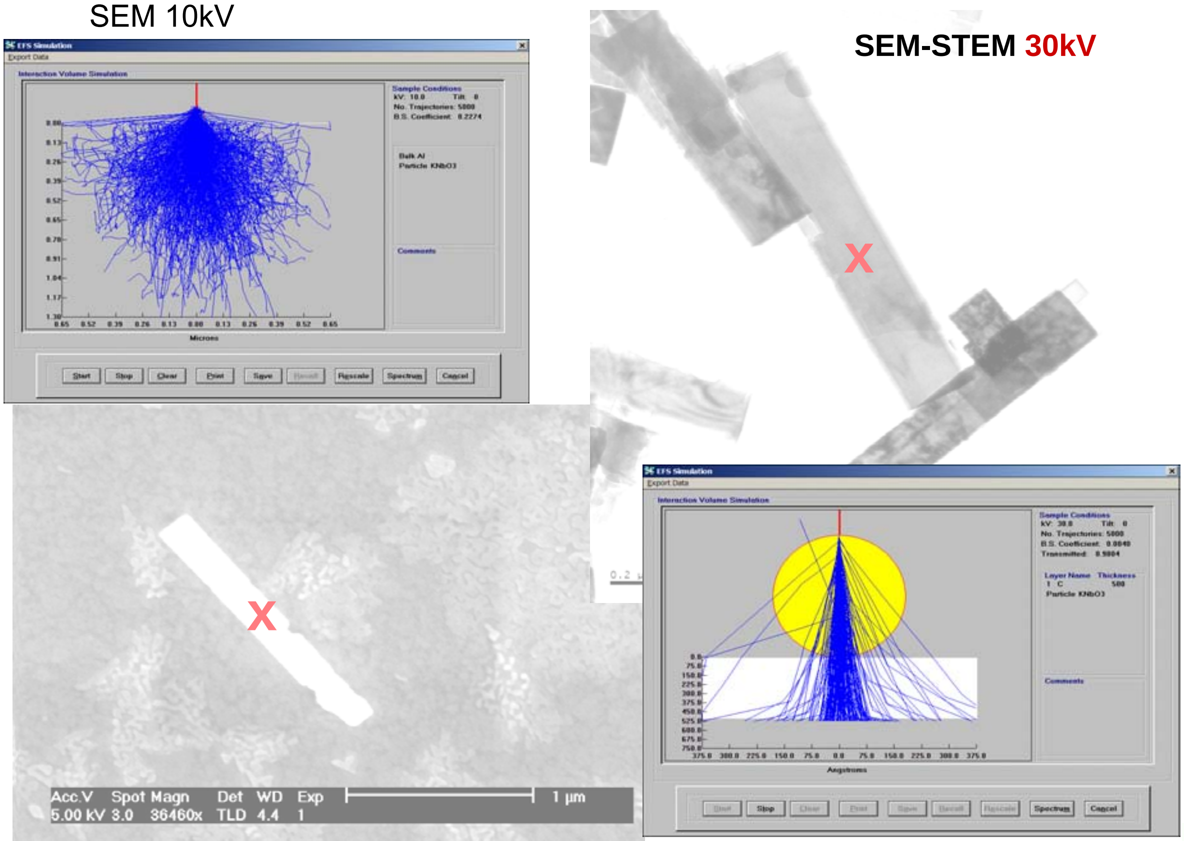
Simulation Electron Flight Simulator EFS



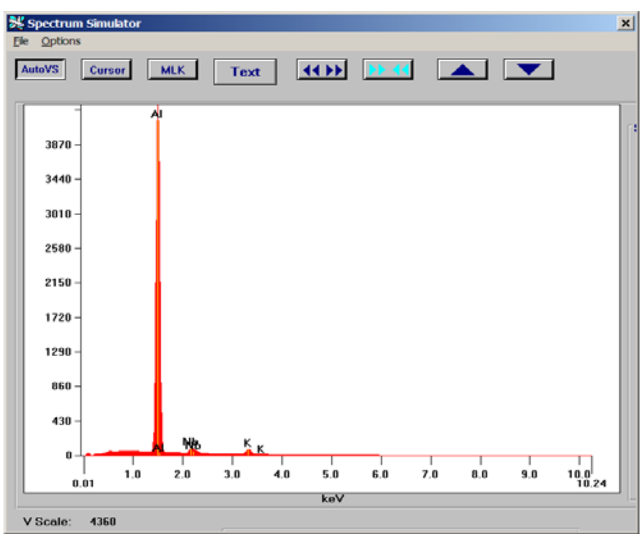
SEM 10kV



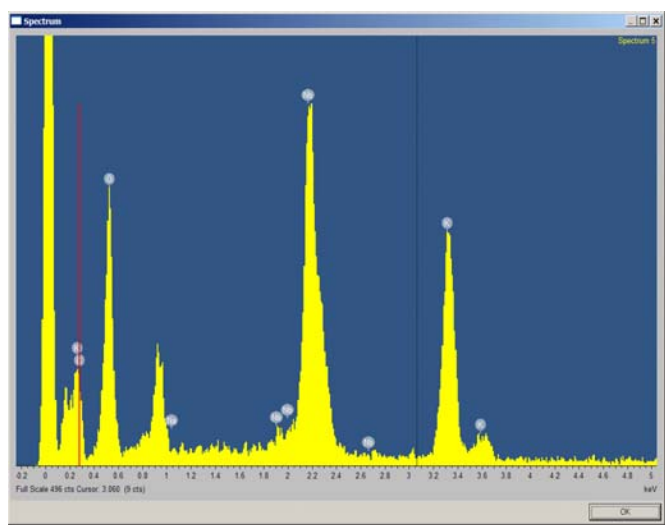
SEM 10kV



SEM 10kV

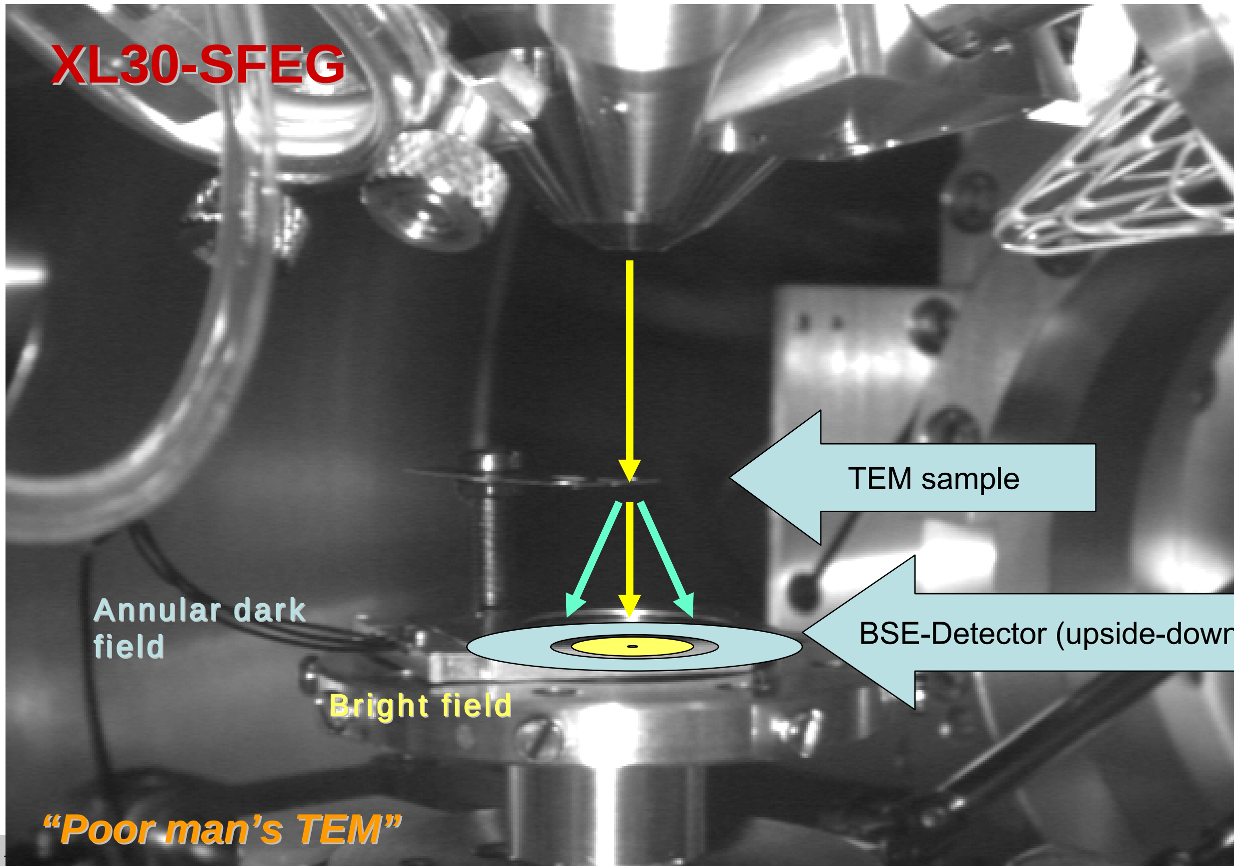


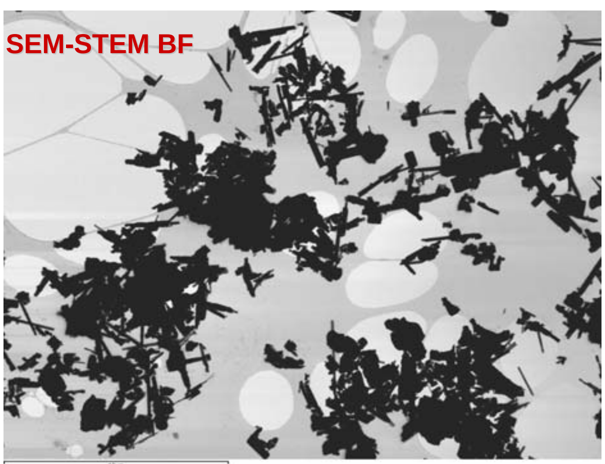
STEM 30kV

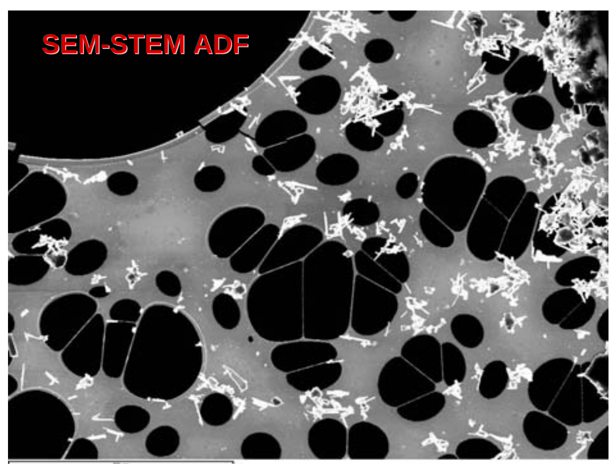


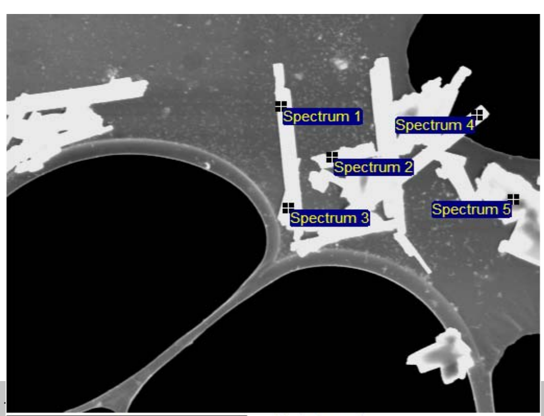
- Interaction volume >> particle size
- Sample holder analyzed
- No deconvolution possible
- Low HT = limited energy range for ionization energies

- Easy interpretation
  “no” contribution from substrate (C)
- MBTF corrections for quantification





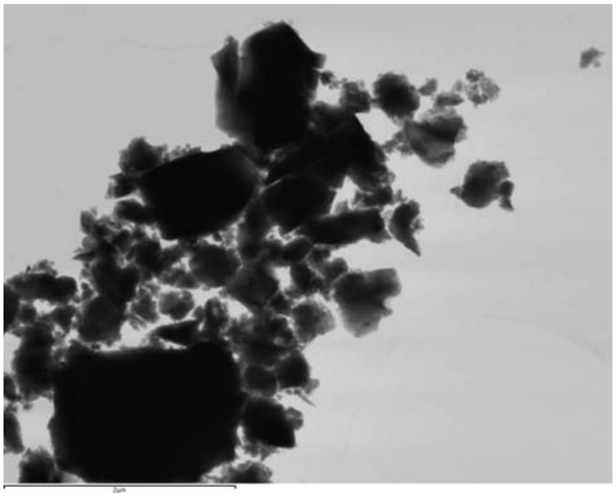




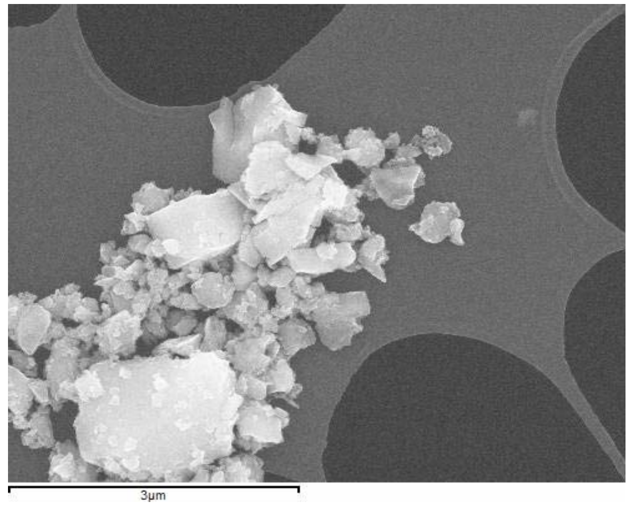
KNbO3

Processing option : All elements analysed (Normalised)

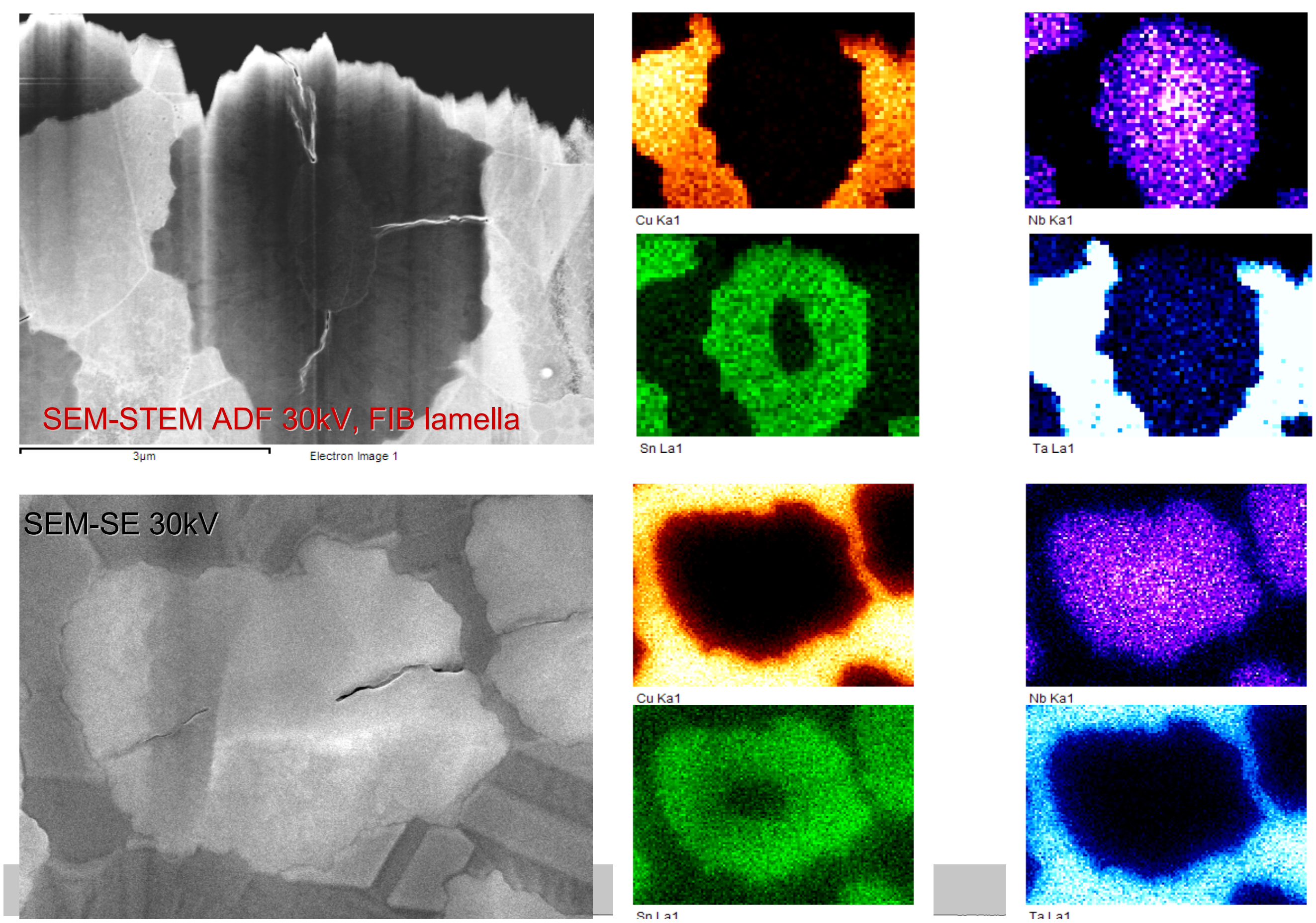
Spectrum	In stats.	O	K	Nb
Spectrum 1	Yes	56.00	21.88	22.12
Spectrum 2	Yes	58.89	19.01	22.10
Spectrum 3	Yes	43.22	27.24	29.54
Spectrum 4	Yes	67.41	16.23	16.36
Spectrum 5	Yes	56.23	20.82	22.95
Mean		56.35	21.04	22.61
Std. deviation		8.68	4.08	4.68
Max.		67.41	27.24	29.54
Min.		43.22	16.23	16.36

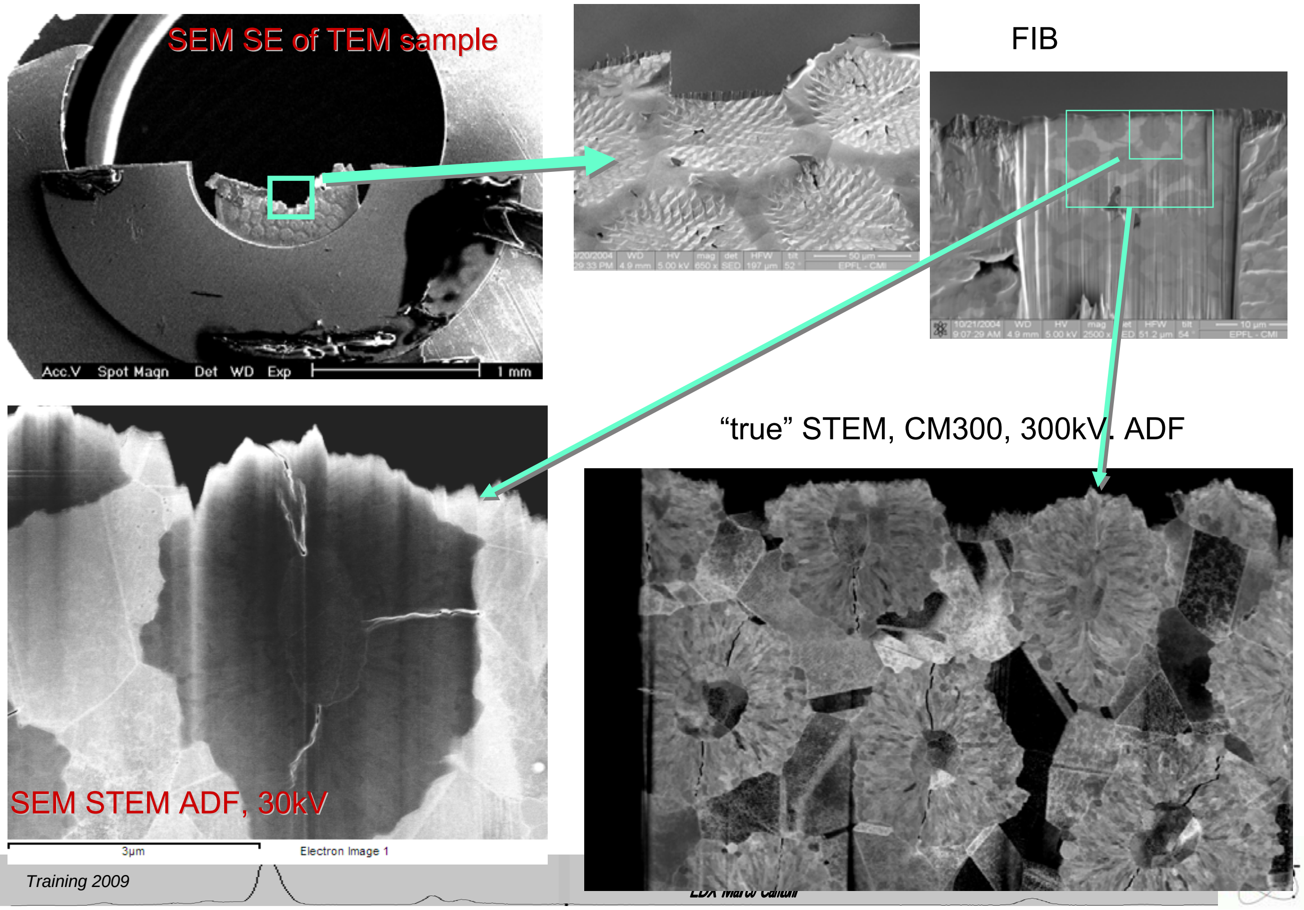


SEM-STEM BF



SE detector




SEM SE of TEM sample
Acc.V Spot Magn Det WD Exp 1 mm
FIB
"true" STEM, CM300, 300kV, ADF
SEM STEM ADF, 30kV
3µm
Electron Image 1