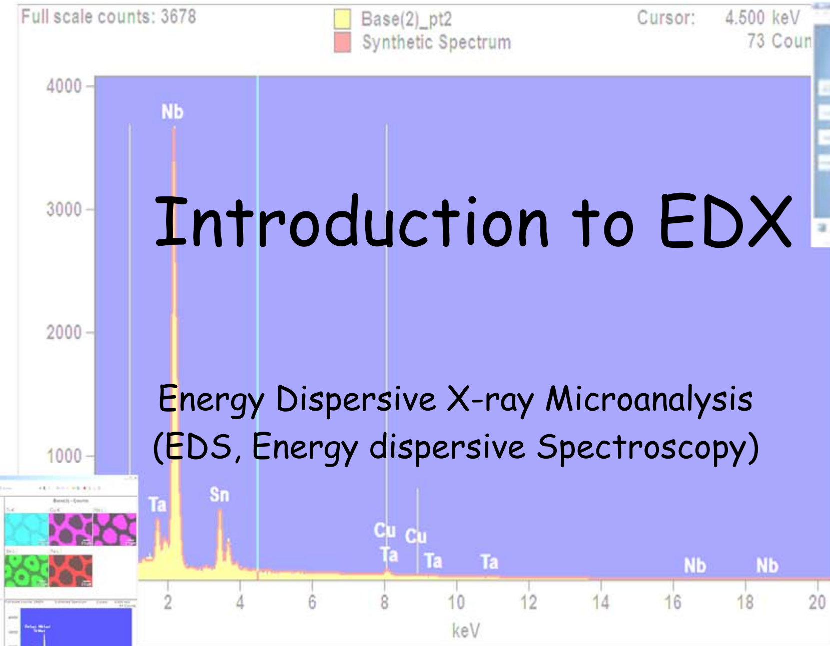
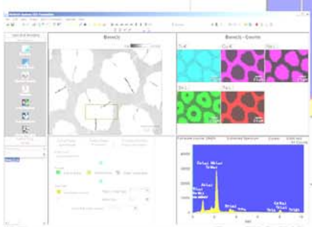
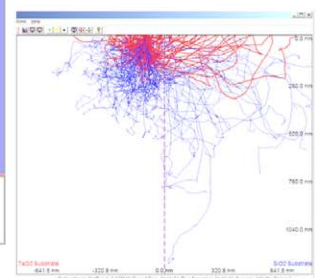






Introduction to EDX

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

summary

Energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of XRF. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing x-rays that are characteristic of an element's atomic structure to be identified uniquely from each other.

To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

Basics of EDX

a) Generation of X-rays

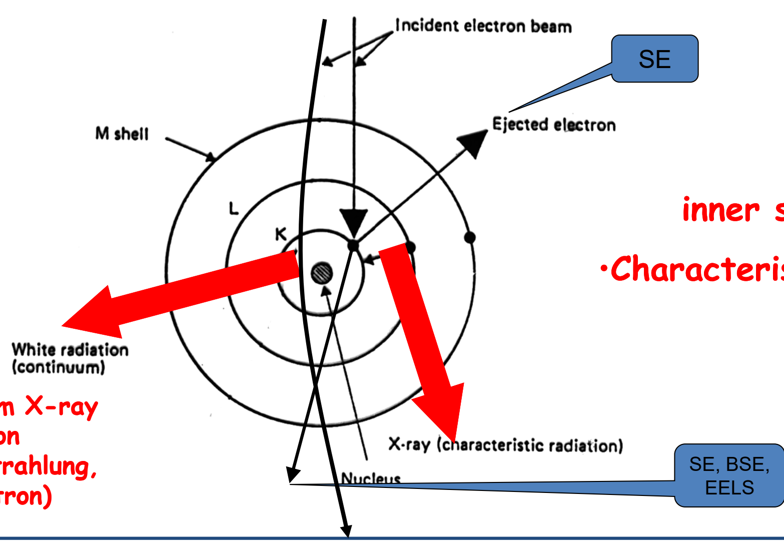
b) Detection
Si(Li) Detector, SDD (silicon drift detector)

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

d) Examples

X-ray generation: Inelastic scattering of electrons at atoms

$E_{electron\_in} > E_{electron\_out}$

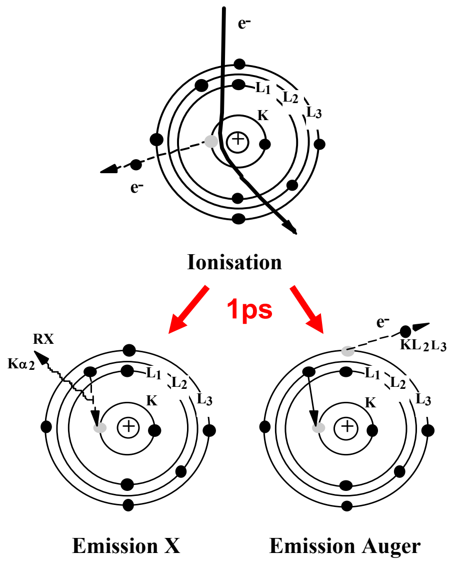


inner shell ionization

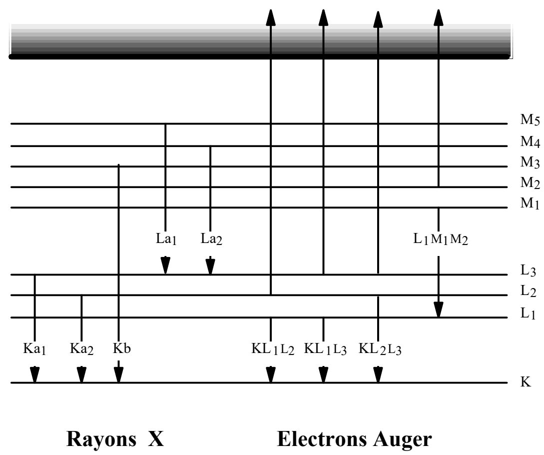
•Characteristic X-ray emission

- Continuum X-ray production (Bremsstrahlung, Synchrotron)

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



Designation of x-ray emission lines



Forbidden transitions !
quantum mechanics:
conservation of angular momentum

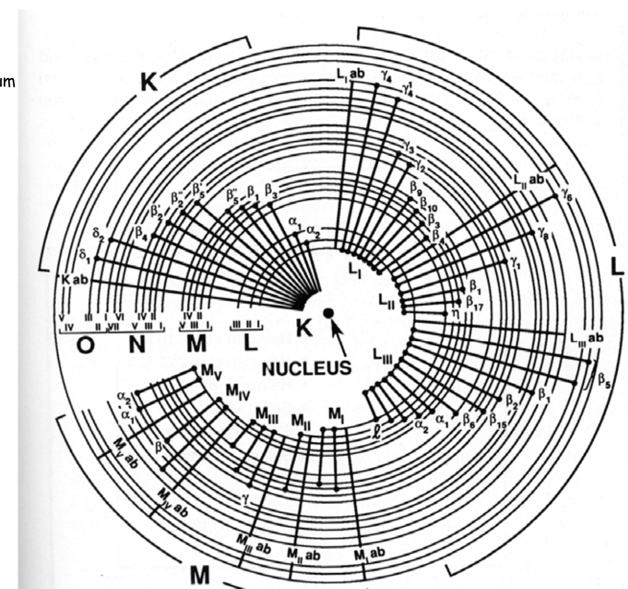
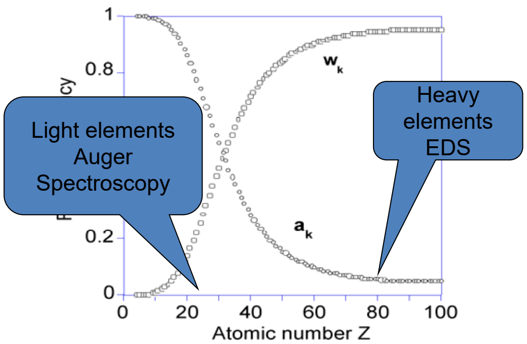


Figure 3.37. Comprehensive energy-level diagram showing all electron transitions which give rise to *K*, *L*, and *M* x rays (Woldseth, 1973).

Efficiency of X-ray generation

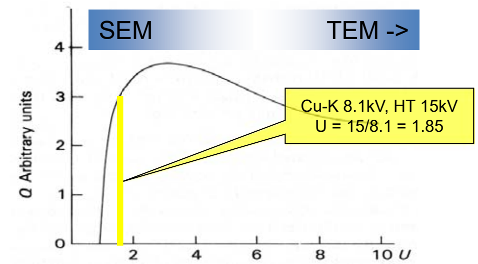
Relative efficiency of X-ray and Auger emission vs. atomic number for K lines



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.

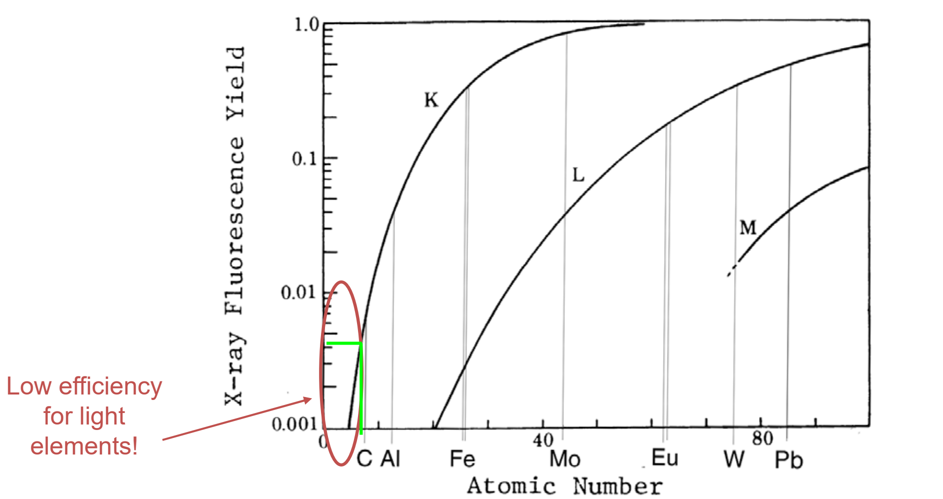
Ionization cross-section vs. overvoltage $U=E_o/E_{ionization}$

(electron in -> X-ray out)



To ionize an atom the incident electron MUST have an energy larger than the core shell level this means: U>1. To be efficient, it should have about twice the ionization energy U>2.

X-ray production yield vs. atomic number Z



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

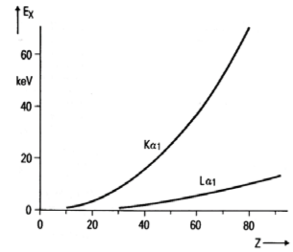
Characteristic lines: Moseley's Law

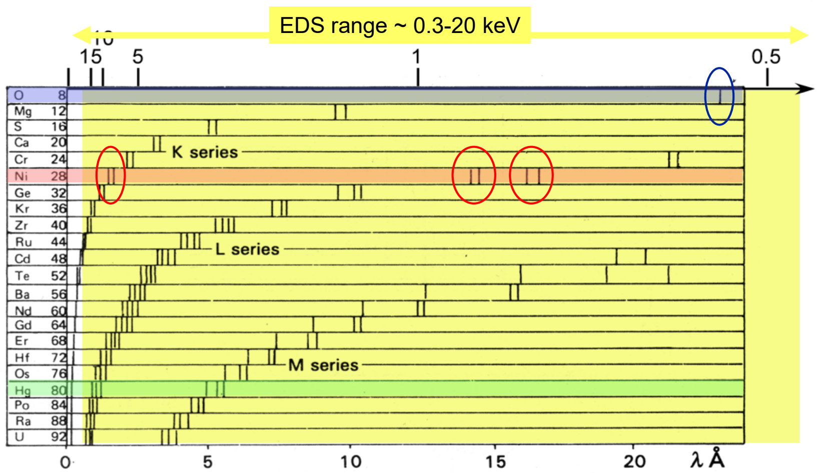
Frequency ν of X-rays emitted from K-level vs. atomic number

E= hν et λ=c/ν

$$\nu = 2.48 10^{15}(Z-1)^2$$

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



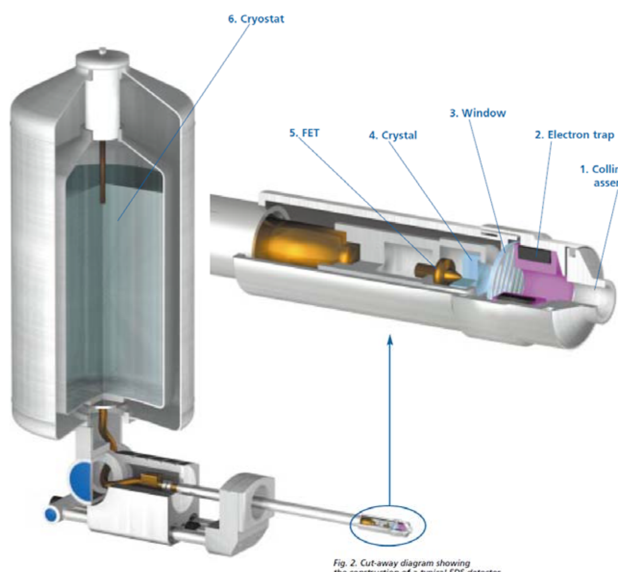


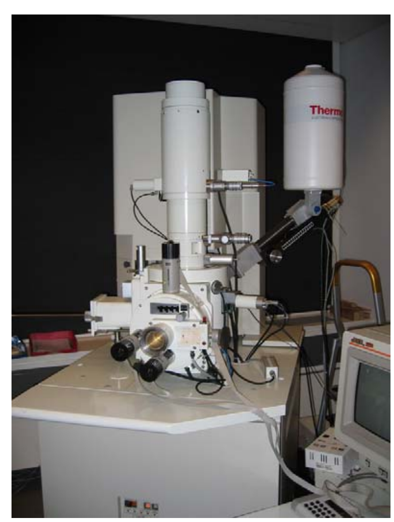
To assess an element all detectables lines MUST be present!!!

known ambiguities:

Al Kα = Br Ll
S Kα = Mo Ll

b) Detection of X-rays (EDX)





collection solid angle

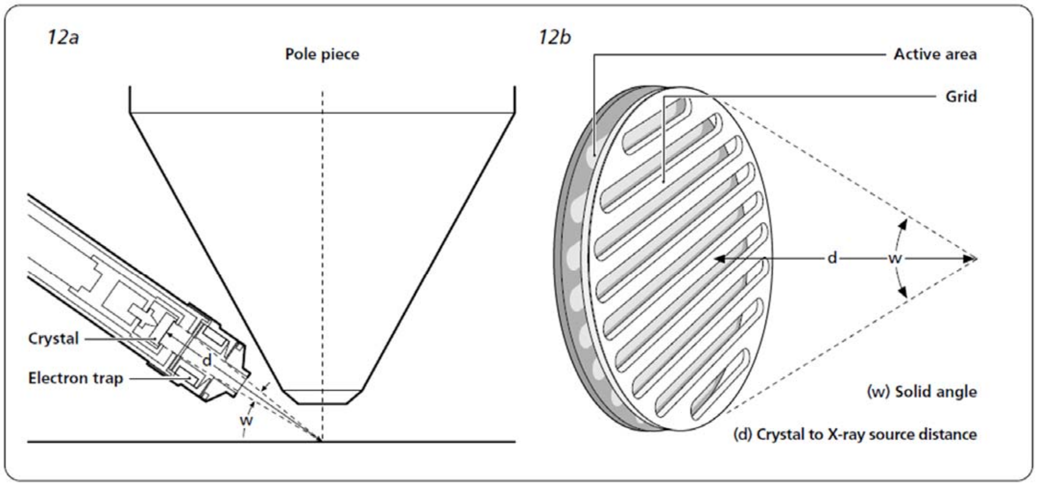
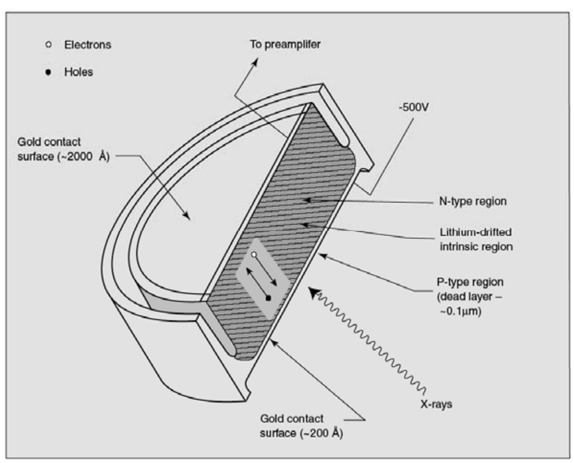
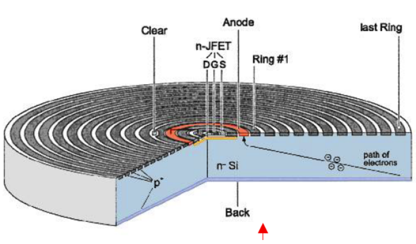


Fig. 12. Calculation of the solid angle of an EDS detector. (a) The detector size and the geometry of the microscope control the distance between X-ray source and crystal. (b) The solid angle is proportional to the active area of the crystal, rather than its actual area, and inversely proportional to the square of the distance.

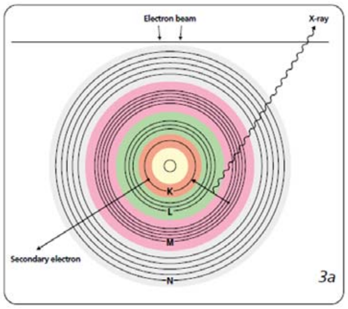
Figure 4-2. Cross section of a typical lithium-drifted silicon detector. X-rays create electron-hole pairs in the intrinsic region of the semiconductor; these charge carriers then migrate to the electrodes under the influence of an applied bias voltage.

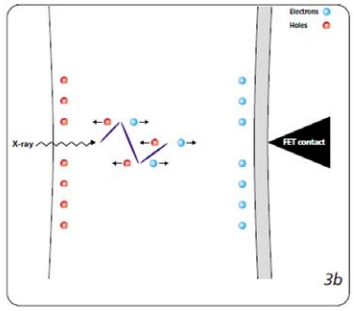
Right: Si(Li) detector
Cooled down to liquid nitrogen temperature

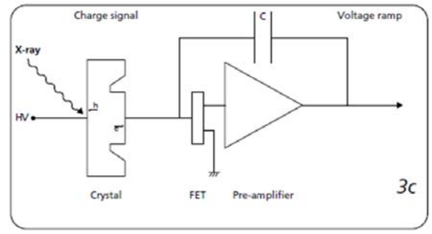




modern silicon drift (SDD) detector:
no LN cooling required

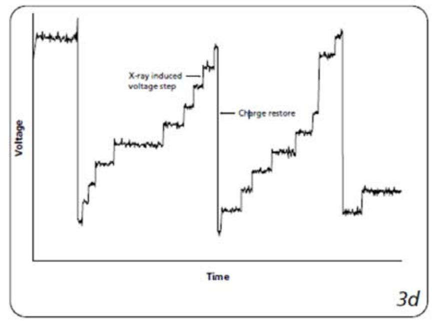






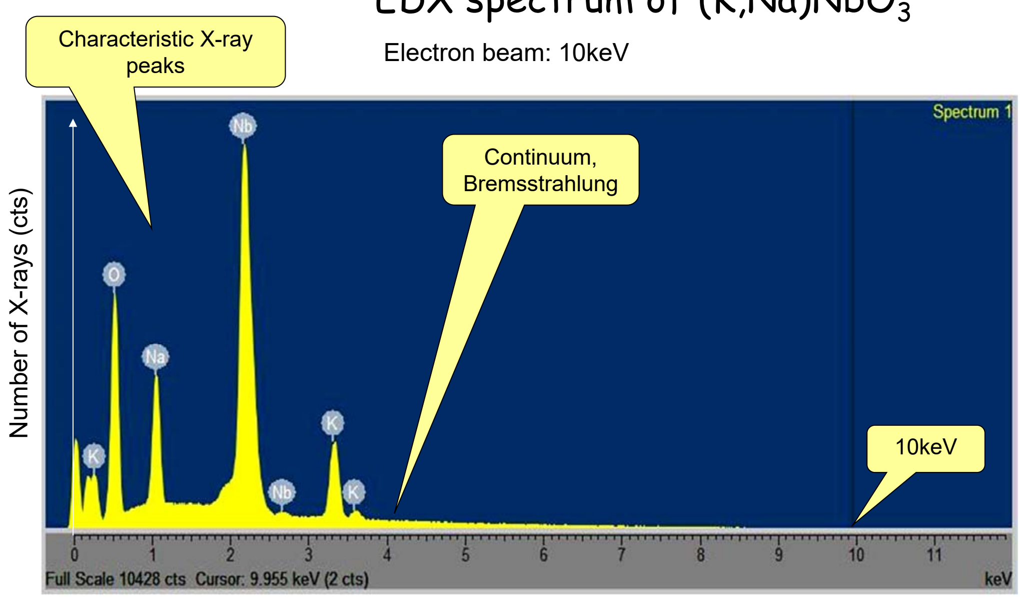
X-Ray energy conversion to electrical charges:
3.8eV / electron-hole pair in average
electronic noise+ imperfect charge collection:
130 eV resolution / Mn Ka line

- 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



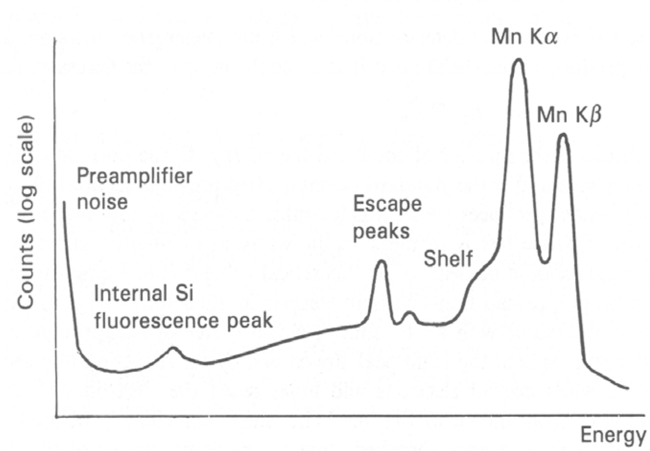
EDX spectrum of (K,Na)NbO_3

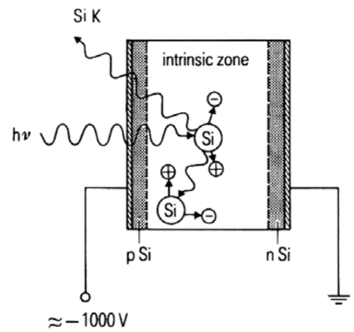
Electron beam: 10keV



Duane-Hunt limit

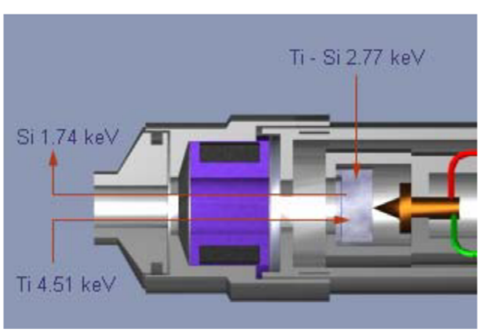
Detection and artifacts

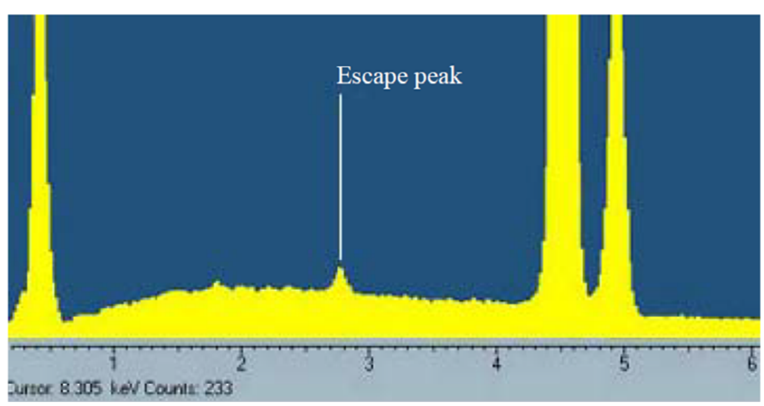




Take care when looking for "trace" elements (low concentrations). Don't confuse small peaks with escape peaks !

artifact: escape peak



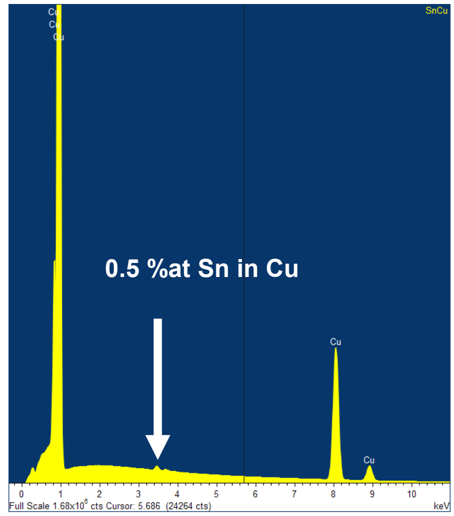


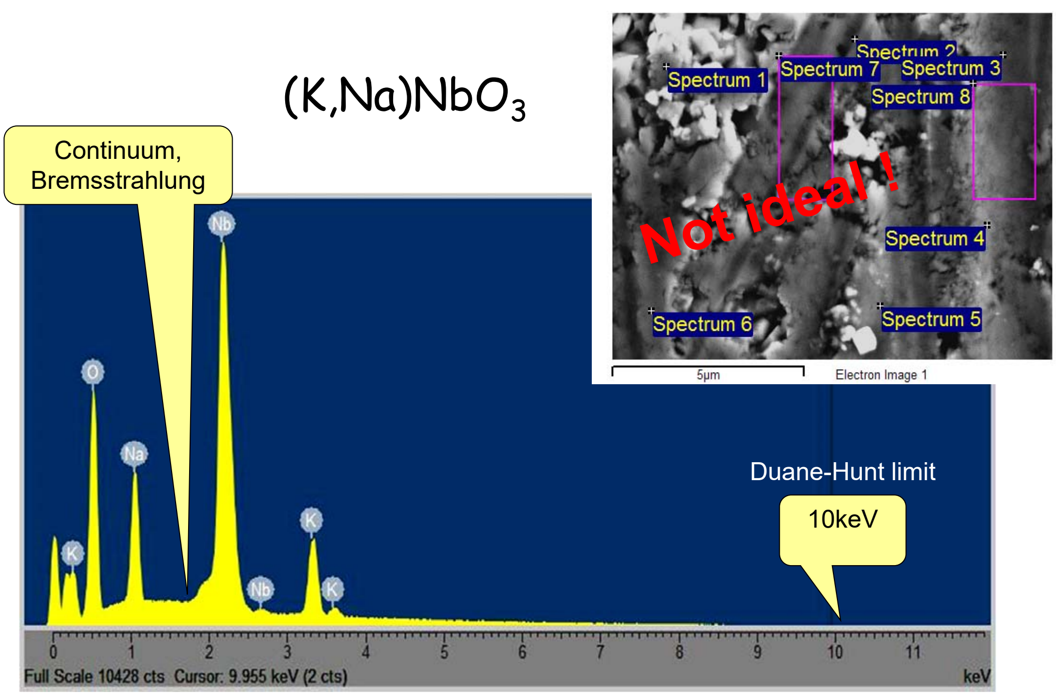
detection limit EDS in SEM

Acquisition under best conditions

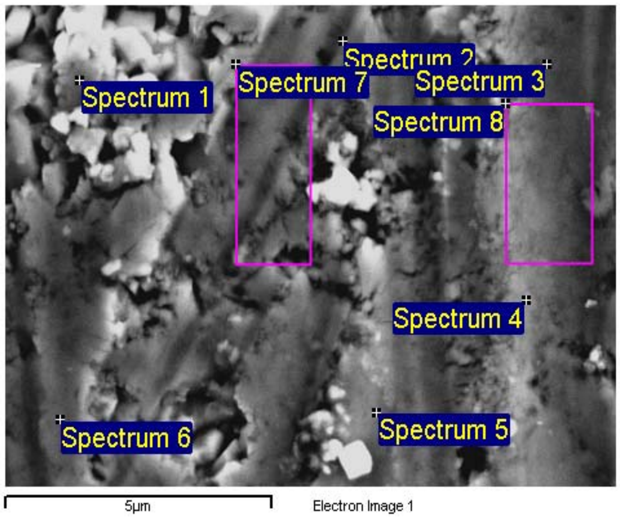
- Flat surface without contamination (no Au coating, use C instead)
- Sample must be homogenous at the place of analysis (interaction volume !!)
- Horizontal orientation of the surface
- High count rate
- Overvoltage U=Eo/Ec >1.5-2

For acquisition times of 100sec. : detection of ~0.5at% for almost all elements





(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)

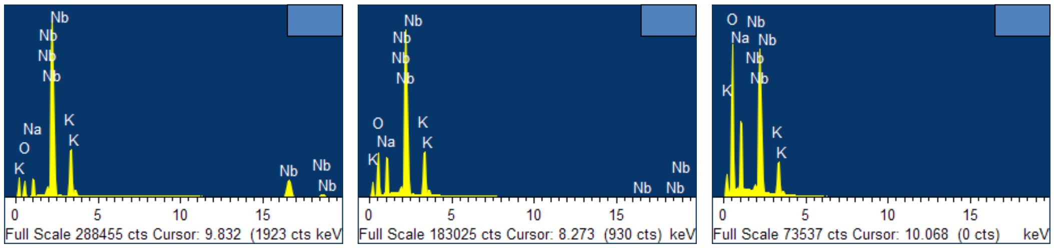
c_i: wt concentration of element i

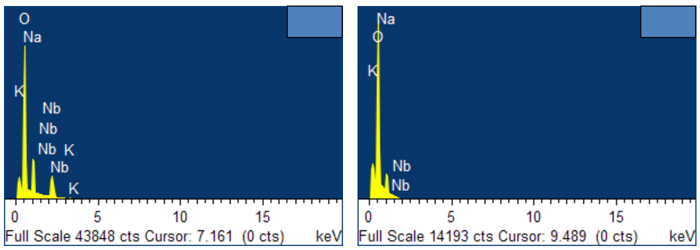
I_i: X-ray intensity of char. Line

k_i: concentration ratio

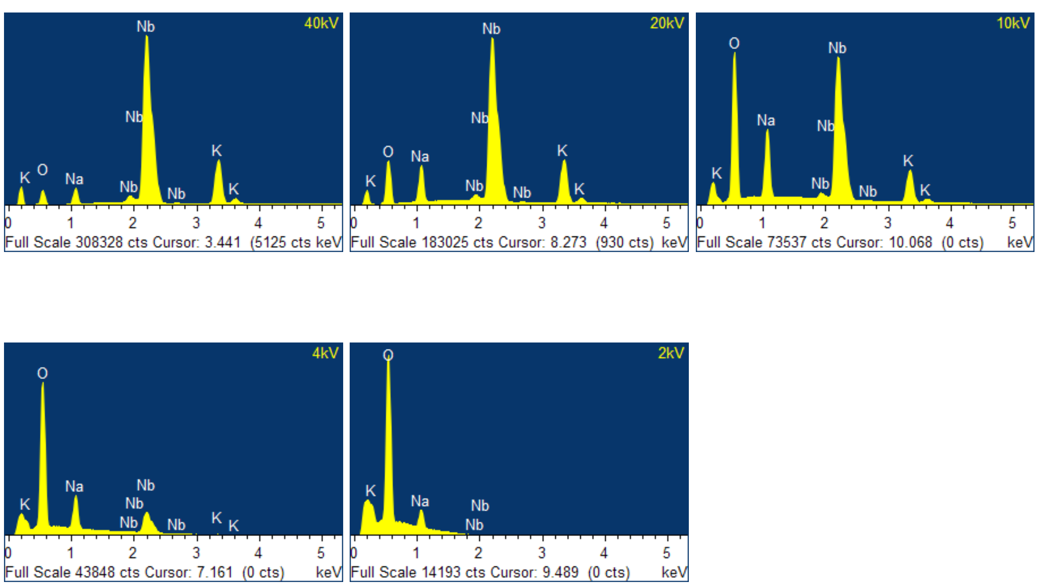
$$\frac{c_i}{c_i^{std}} = \frac{I_i}{I_i^{std}} = k_i$$

Intensity ~ Concentration…?

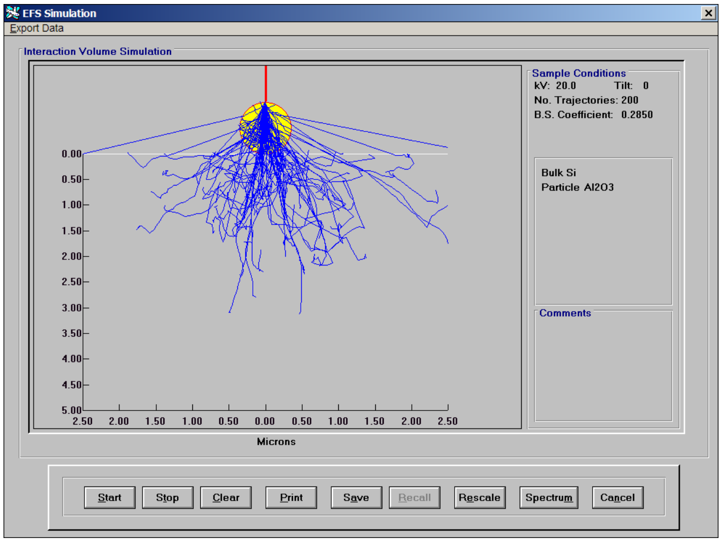




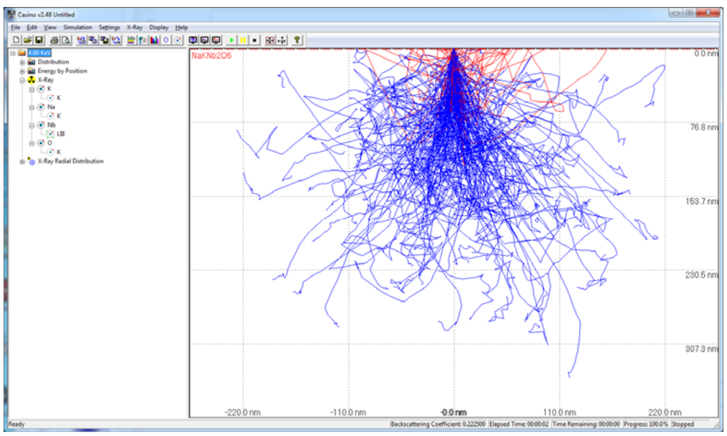
How many different samples…?

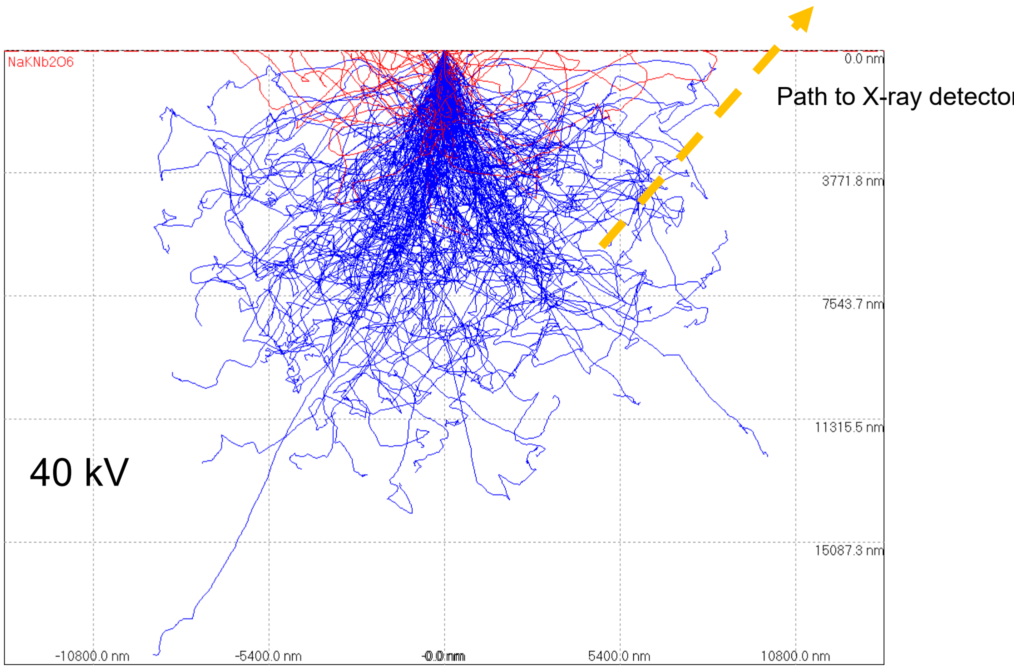


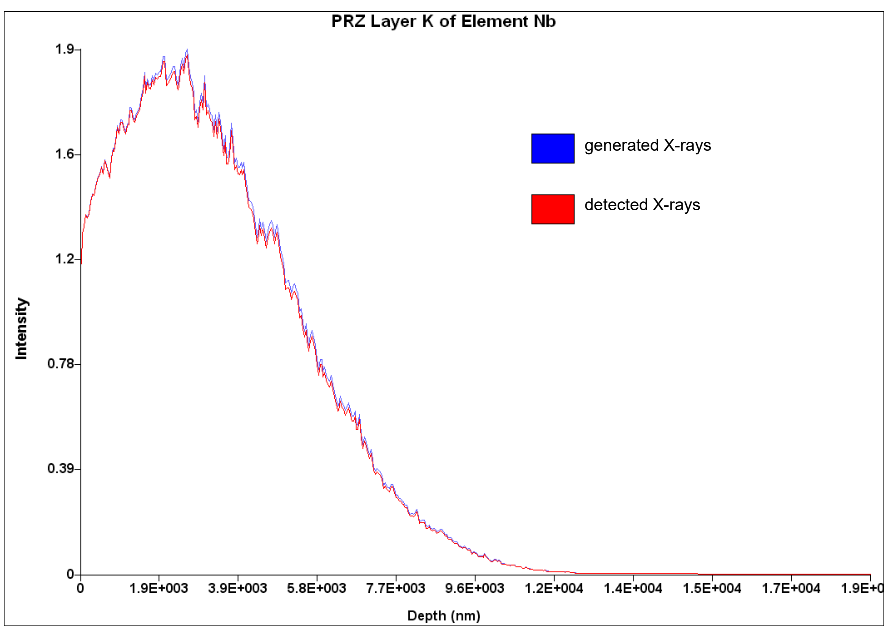
Electron Flight Simulator

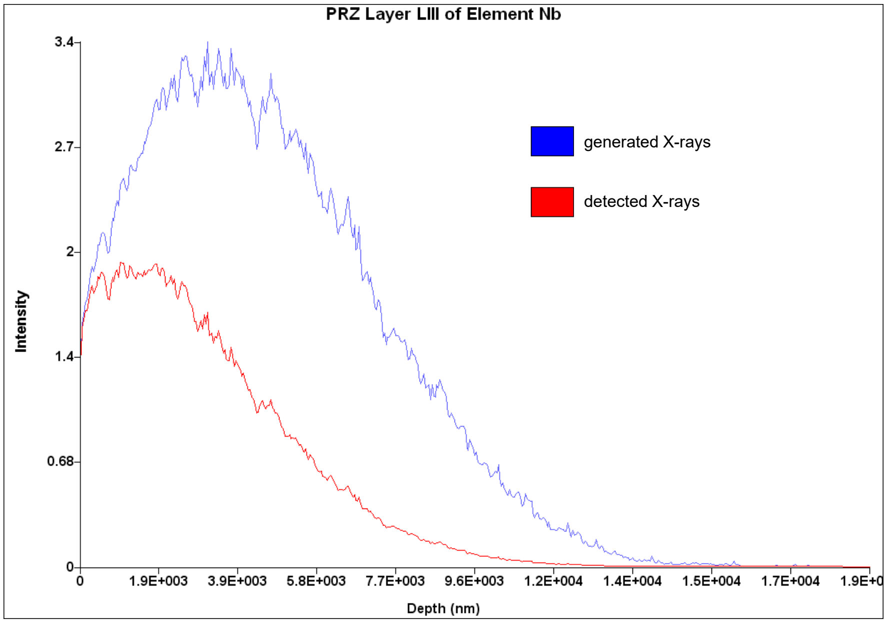


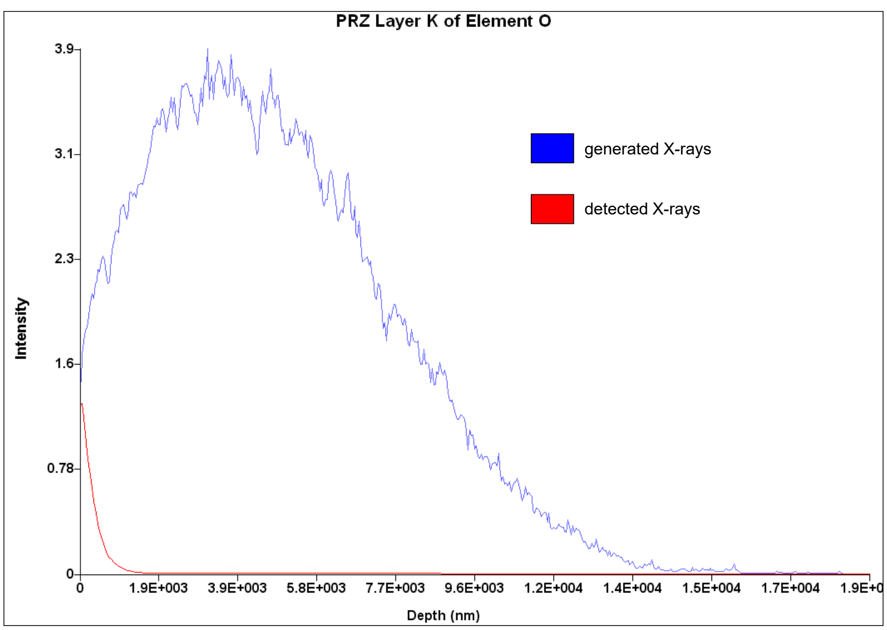
Monte-Carlo Simulation with CASINO

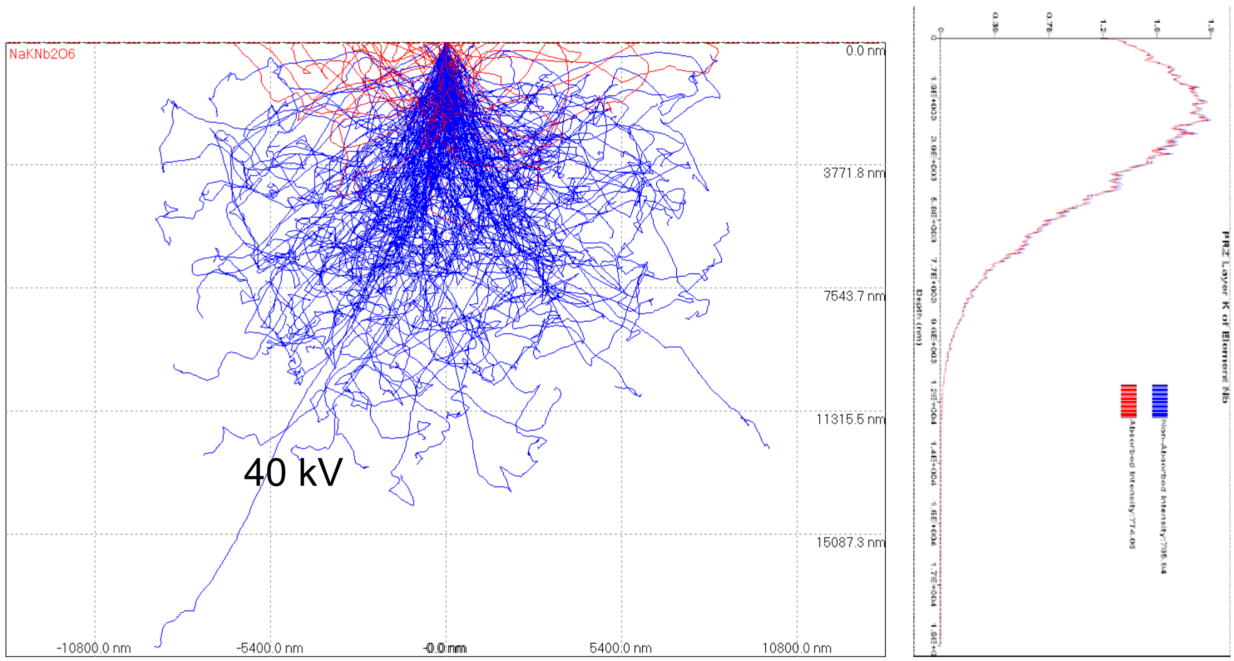


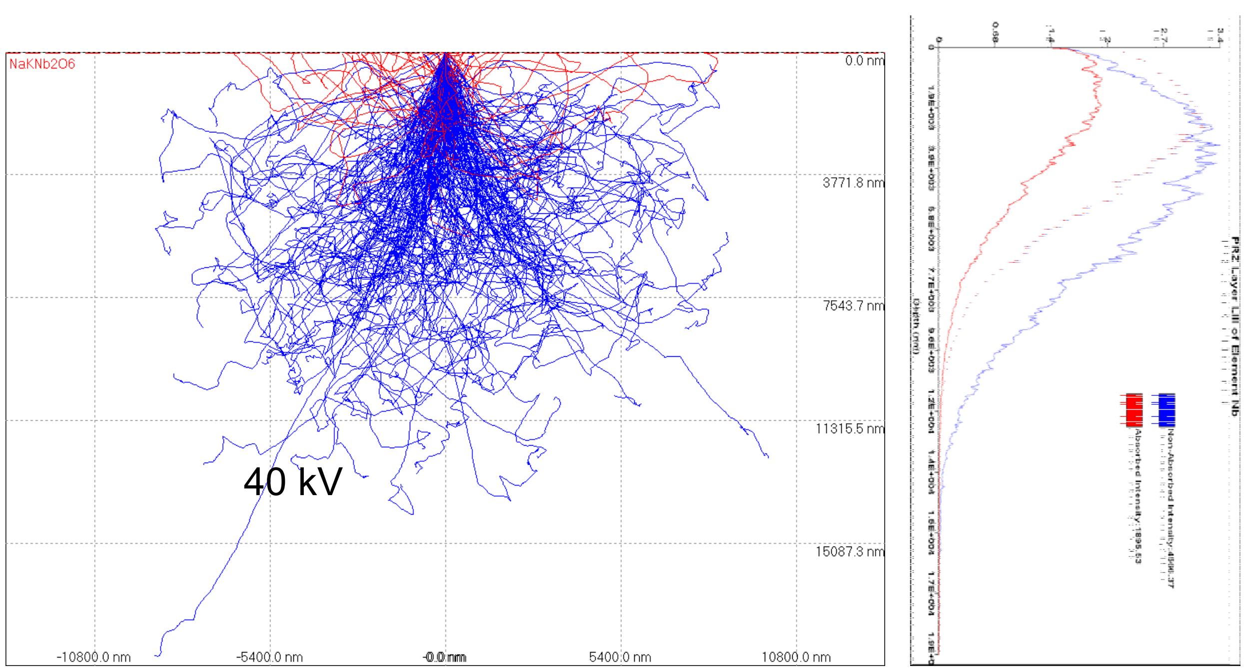

NaKNb2O6
0.0 nm
3771.8 nm
7543.7 nm
11315.5 nm
15087.3 nm
-10800.0 nm
-5400.0 nm
-0.0 nm
5400.0 nm
10800.0 nm
40 kV
Path to X-ray detector

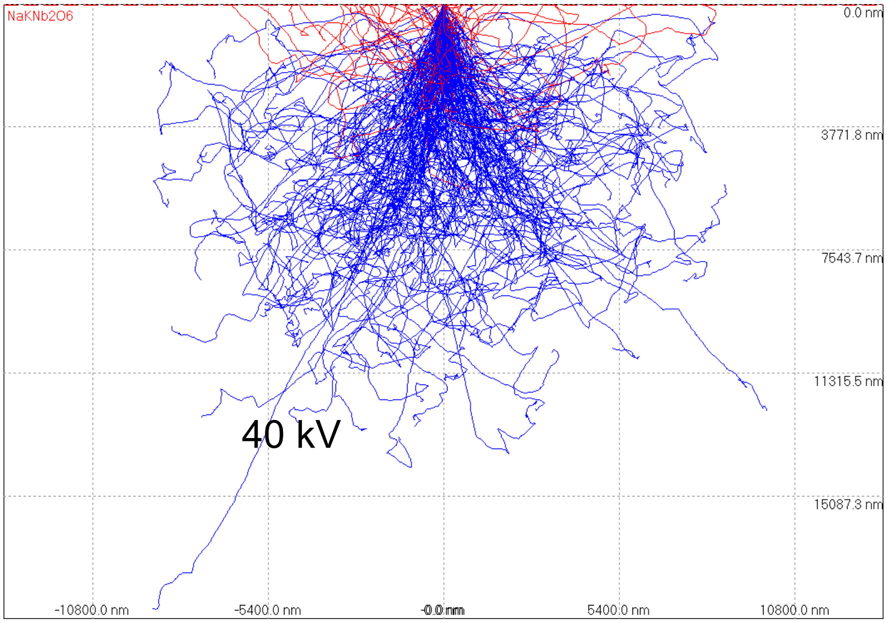

PRZ Layer K of Element Nb
generated X-rays
detected X-rays
Intensity
Depth (nm)
1.9
1.6
1.2
0.78
0.39
0
1.9E+003
3.9E+003
5.8E+003
7.7E+003
9.6E+003
1.2E+004
1.4E+004
1.5E+004
1.7E+004

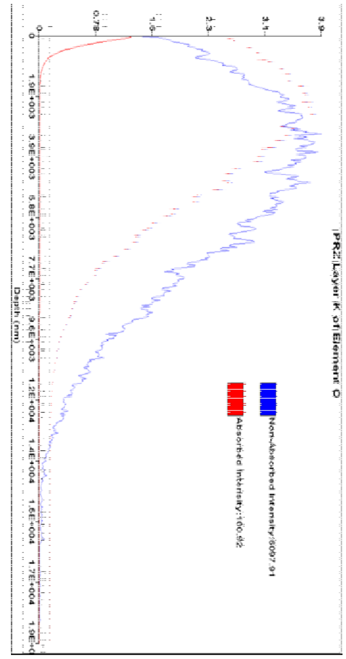

PRZ Layer LIII of Element Nb
generated X-rays
detected X-rays
Intensity
3.4
2.7
2
1.4
0.68
0
0
1.9E+003
3.9E+003
5.8E+003
7.7E+003
9.6E+003
1.2E+004
1.4E+004
1.5E+004
1.7E+004
1.9E+0
Depth (nm)

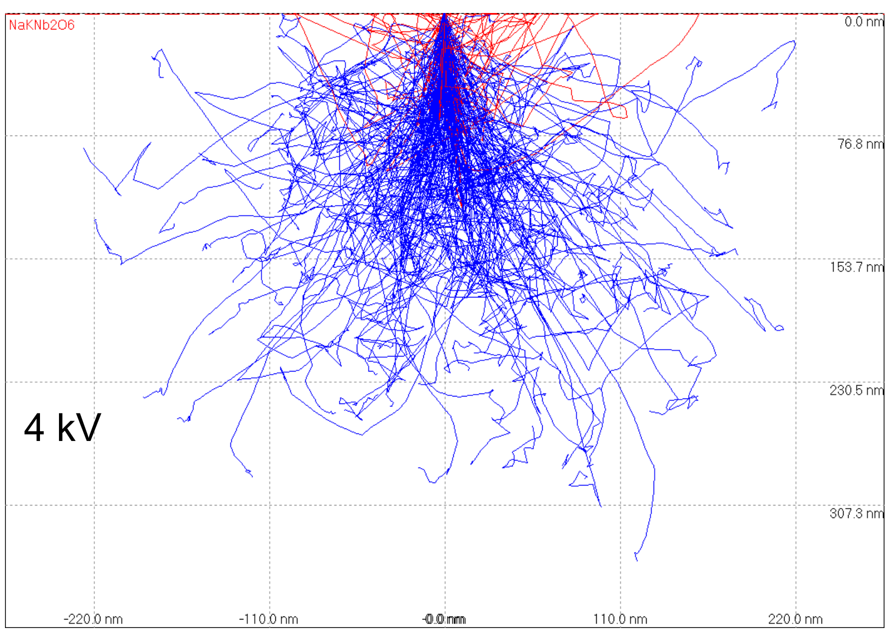

PRZ Layer K of Element O
generated X-rays
detected X-rays
Intensity
3.9
3.1
2.3
1.6
0.78
0
0
1.9E+003
3.9E+003
5.8E+003
7.7E+003
9.6E+003
1.2E+004
1.4E+004
1.5E+004
1.7E+004
1.9E+0
Depth (nm)

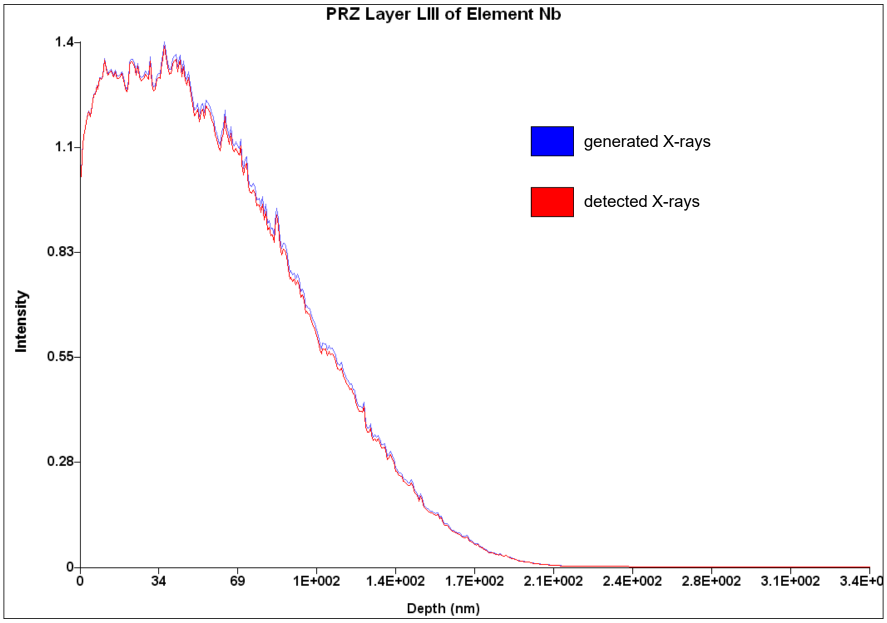

NaKNb2O6
0.0 nm
3771.8 nm
7543.7 nm
11315.5 nm
15087.3 nm
-10800.0 nm
-5400.0 nm
-0.0 nm
5400.0 nm
10800.0 nm
40 kV
PRZ Layer K of Element Nb
Depth (nm)

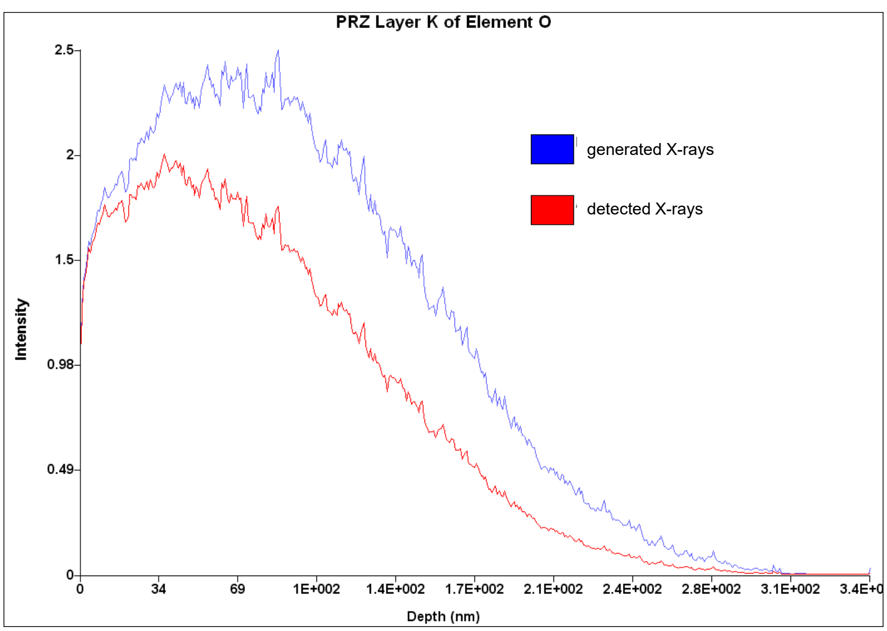

NaKNb2O6
0.0 nm
3771.8 nm
7543.7 nm
11315.5 nm
15087.3 nm
-10800.0 nm
-5400.0 nm
-0.0 nm
5400.0 nm
10800.0 nm
40 kV
PRZ Layer LIII of Element Nb
Depth (nm)

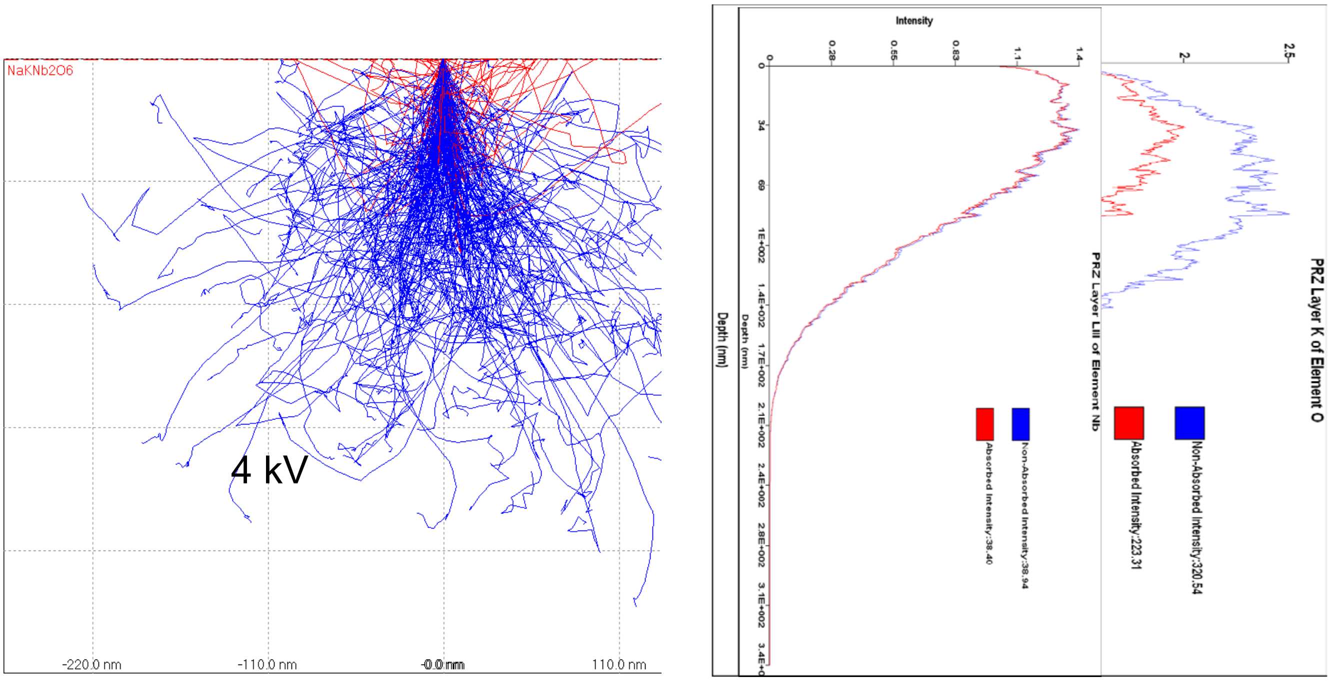

NaKNb2O6
0.0 nm
3771.8 nm
7543.7 nm
11315.5 nm
15087.3 nm
40 kV
-10800.0 nm
-5400.0 nm
-0.0 nm
5400.0 nm
10800.0 nm

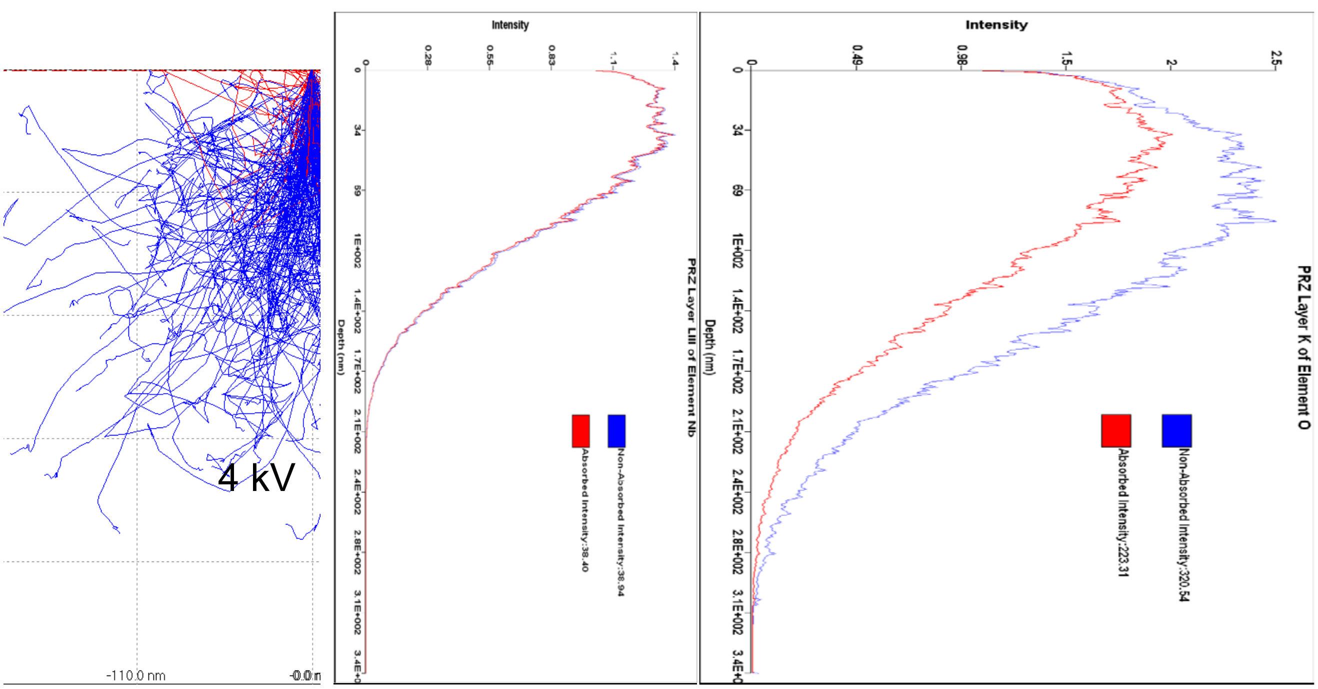

Depth (nm)

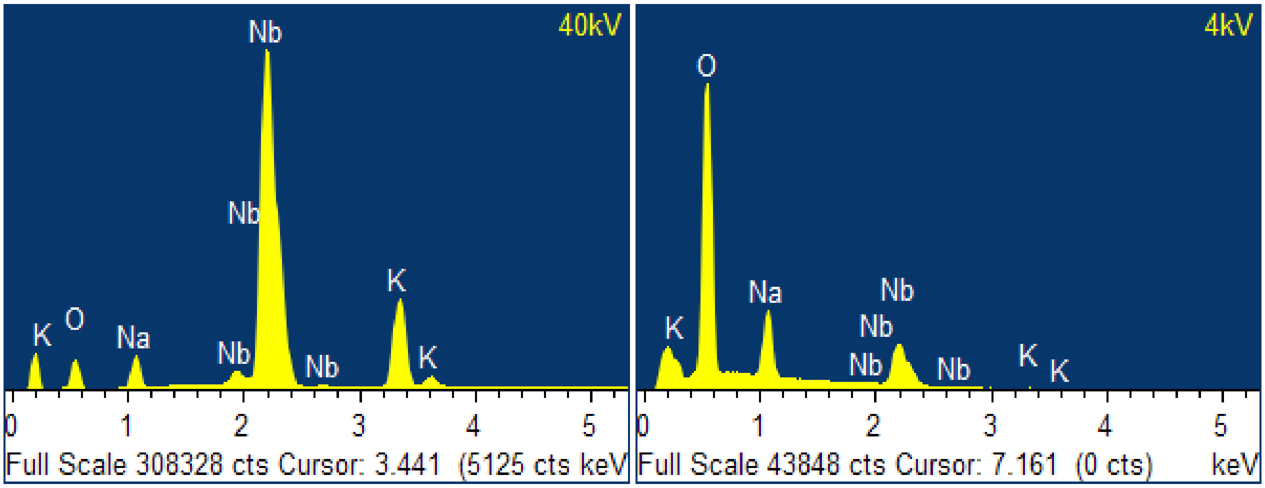

NaKNb2O6
0.0 nm
76.8 nm
153.7 nm
230.5 nm
307.3 nm
4 kV
-220.0 nm
-110.0 nm
-0.0 nm
110.0 nm
220.0 nm


PRZ Layer LIII of Element Nb
generated X-rays
detected X-rays
Intensity
1.4
1.1
0.83
0.55
0.28
0
0
34
69
1E+002
1.4E+002
1.7E+002
2.1E+002
2.4E+002
2.8E+002
3.1E+002
3.4E+0
Depth (nm)


PRZ Layer K of Element O
generated X-rays
detected X-rays
Intensity
2.5
2
1.5
0.98
0.49
0
0
34
69
1E+002
1.4E+002
1.7E+002
2.1E+002
2.4E+002
2.8E+002
3.1E+002
3.4E+0
Depth (nm)


NaKNb2O6
4 kV
-220.0 nm
-110.0 nm
-0.0 nm
110.0 nm
PRZ Layer K of Element O
Non-Absorbed Intensity:320.54
Absorbed Intensity:223.31
PRZ Layer LIII of Element Nb
Non-Absorbed Intensity:38.94
Absorbed Intensity:38.40
Intensity
Depth (nm)

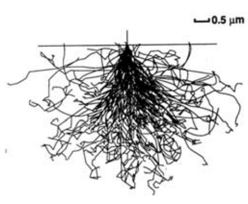

4 kV
-110.0 nm
-0.0 n
PRZ Layer LIII of Element Nb
Non-Absorbed Intensity:38.94
Absorbed Intensity:38.40
PRZ Layer K of Element O
Non-Absorbed Intensity:320.54
Absorbed Intensity:223.31
Intensity
Depth (nm)



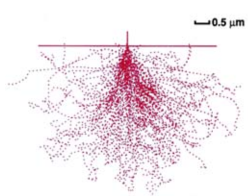
Quantification

When the going gets tough…..

Correction matrix



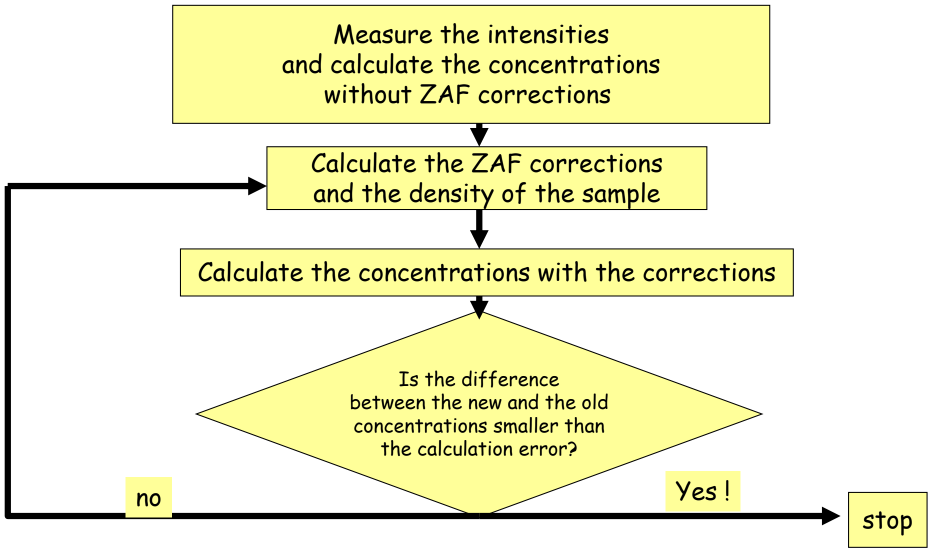
c



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

- "Z" describe how the electron beam penetrates in the sample (Zdependant 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 quantification

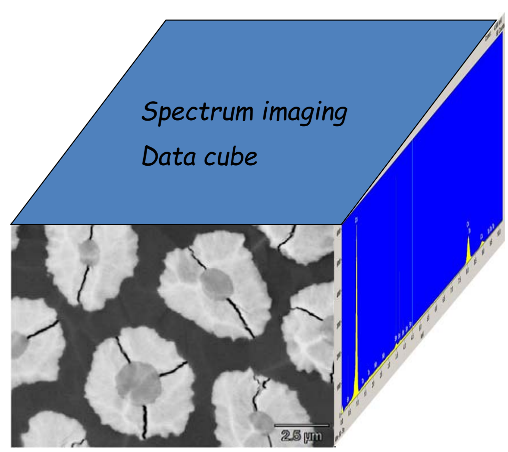
possible with high accuracy (intensities of references under the given conditions can be calculated for a great range of elements), test with samples of known composition, light elements (like O) are critical…

Spatial resolution depends strongly on HT and the density of the sample

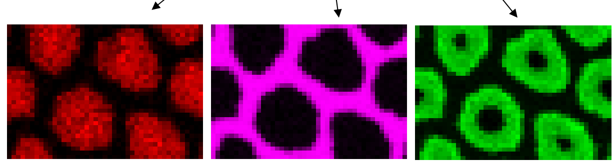
EDX mapping

Data cube:
In each pixel a spectrum is recorded and stored

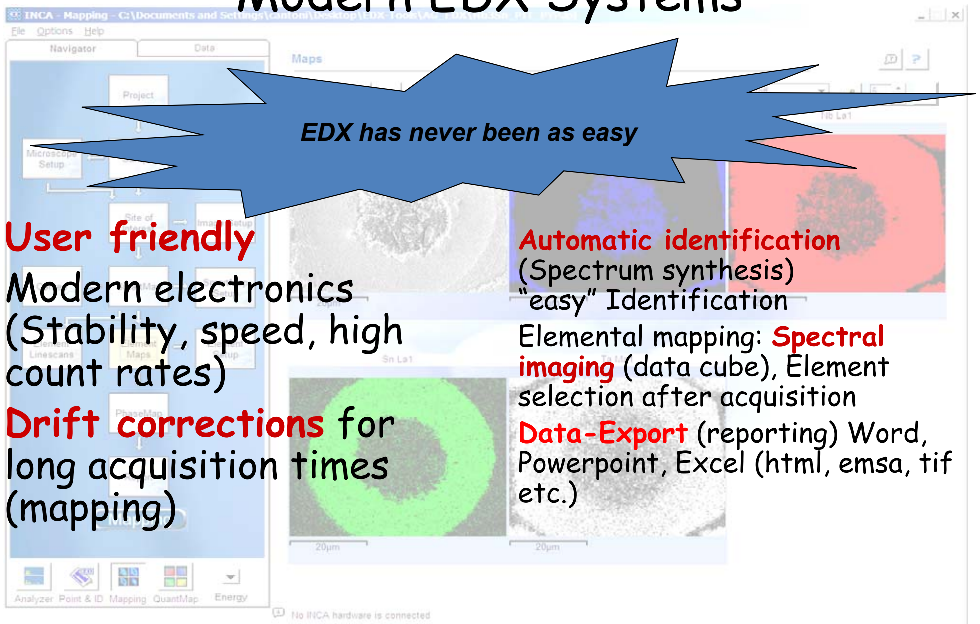
Post-acquisition Analysis:
Each spectrum can be analyzed and quantified off-line



Extraction of element maps



Modern EDX Systems



User friendly

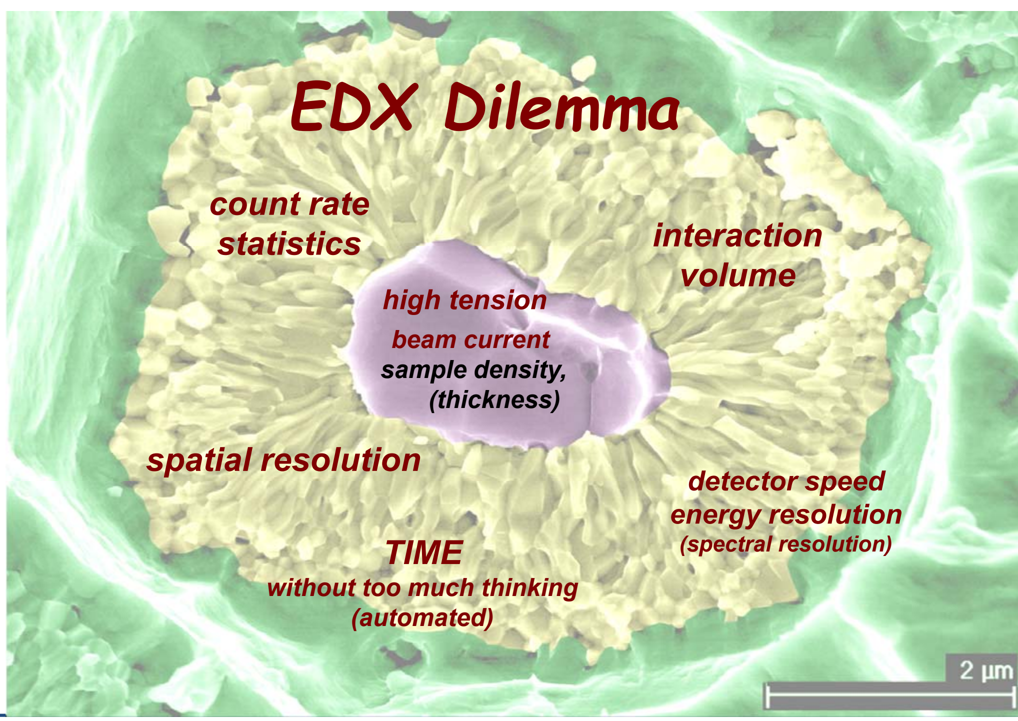
Modern electronics (Stability, speed, high count rates)

Drift corrections for long acquisition times (mapping)

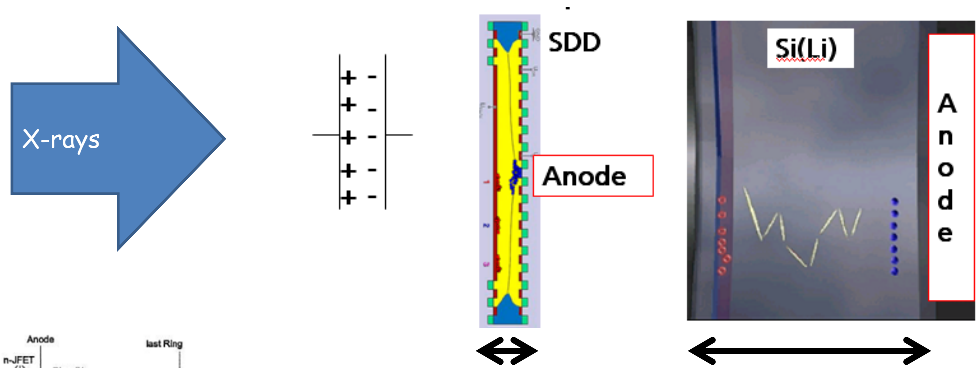
Automatic identification (Spectrum synthesis) "easy" Identification

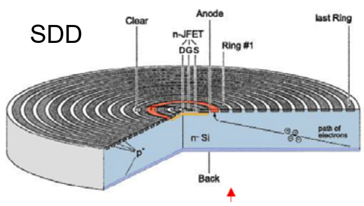
Elemental mapping: **Spectral imaging** (data cube), Element selection after acquisition

Data-Export (reporting) Word, Powerpoint, Excel (html, emsa, tif etc.)



New possibilities due to SDD (silicon drift detector) technology



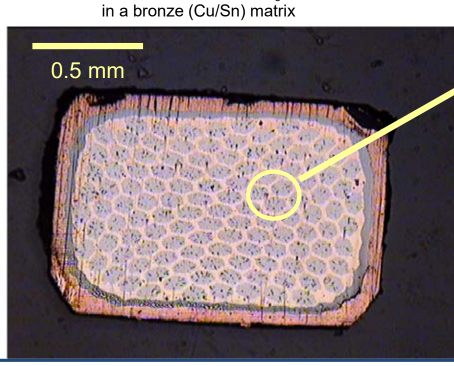


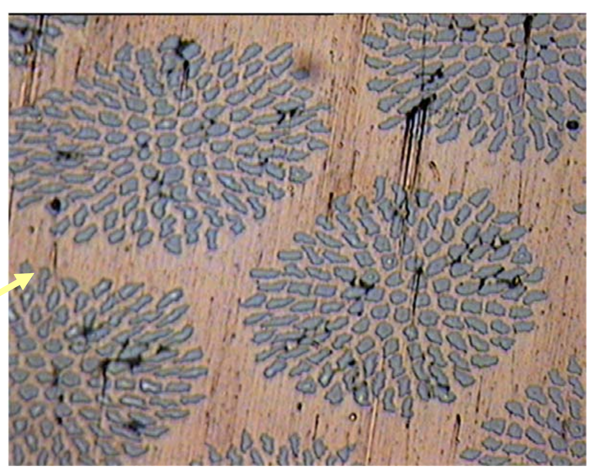
	SDD	Si(Li)
Thickness	300-400µm	3mm
Area	30,50,80,150mm^2	30mm^2
Det. Interval	4-10µsec.	50-100µsec.
Speed	100'000cps	10'000cps
Cooling	Peltier	Liq. N

Nb_3Sn multifilament superconducting cables

Superconducting Nb_3Sn cables for high magnetic fields 10-20T:
increase current density, lower cost
Potential Applications:
NMR, Tokamak fusion reactors
Large Hadron Collider (LHC), CERN

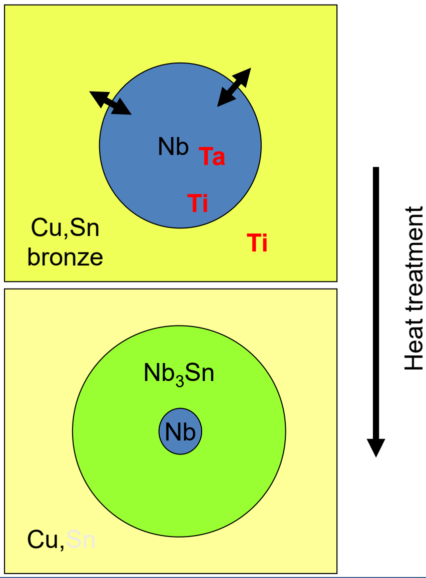
Typical cable:
1 x 1.5mm cross-section
121x121 filaments of Nb_3Sn
in a bronze (Cu/Sn) matrix





Prof. R. Flükiger, V. Abächerli, D. Uglietti, B. Seeber
Dept. Condensed Matter Physics (DPMC),
University of Geneva

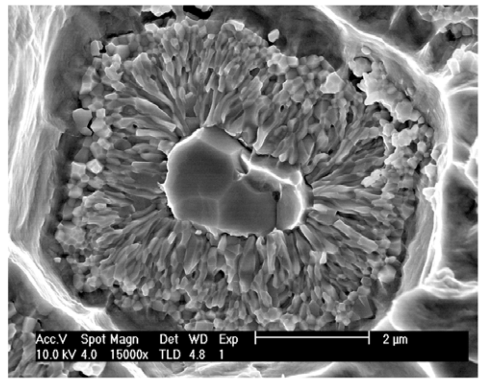
Processing „bronze route“



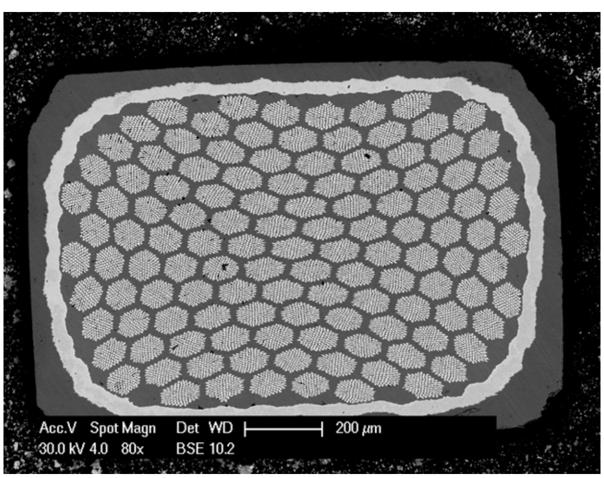
Cu and Ti are believed to play an important role at the grain boundaries (pinning)

Is the Nb3Sn phase homogenous?

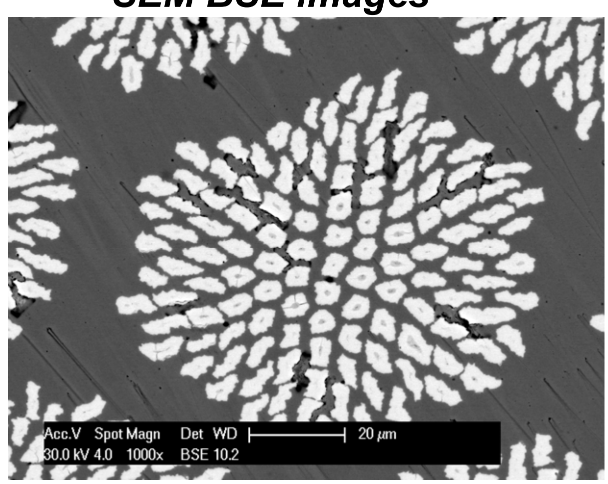
Is it possible to detect Cu and Ti at the grain boundaries ?



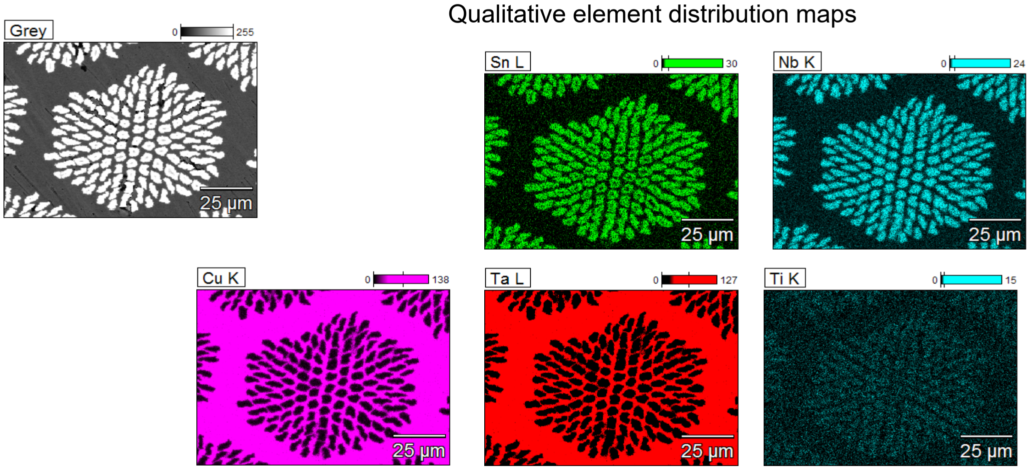
SEM: reacted filament



SEM BSE images



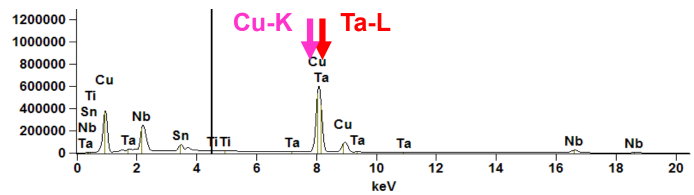
Qualitative element distribution maps



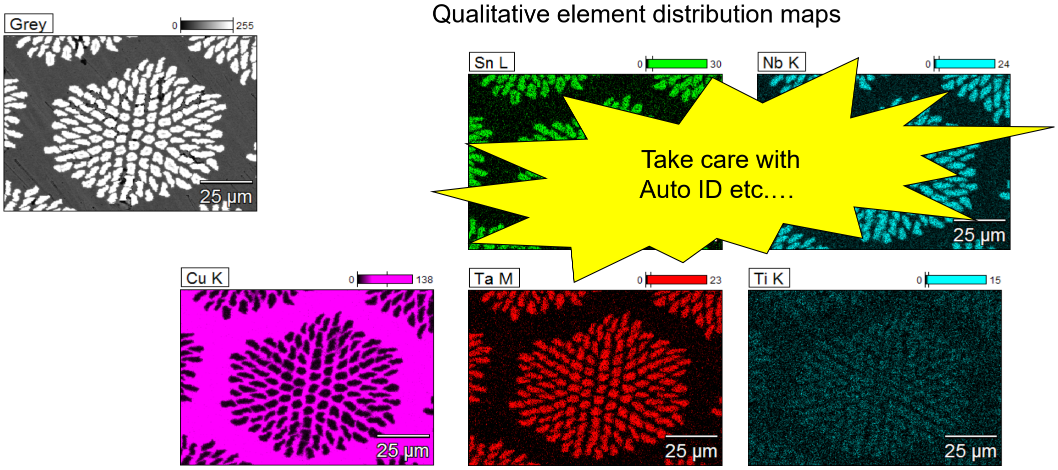
20 keV

30 min.

Auto ID

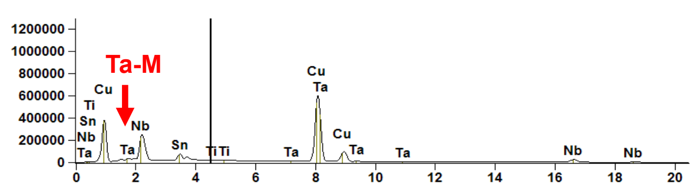


Qualitative element distribution maps

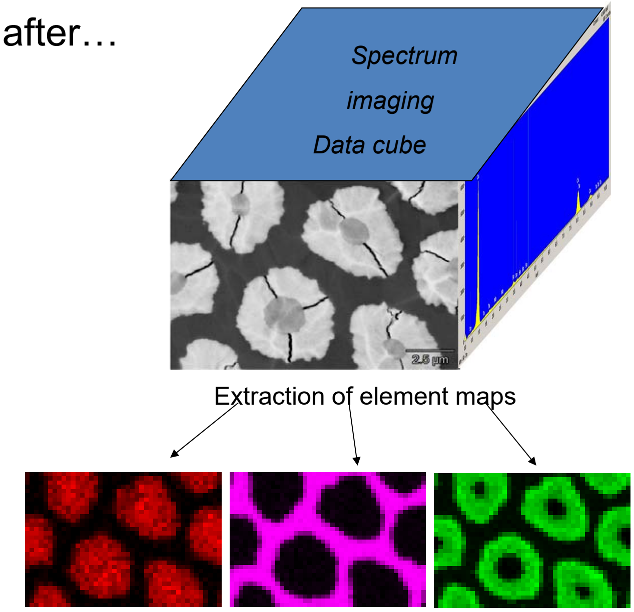


20 keV

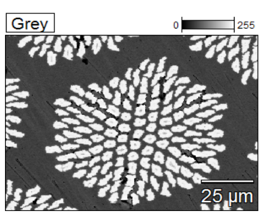
Manual ID

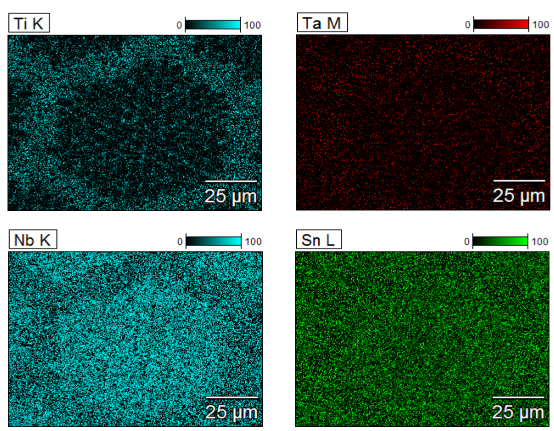


- Acquire first
- Analyze after…



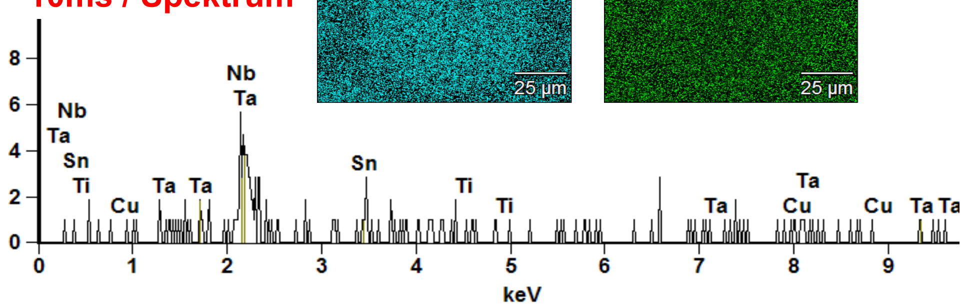
Quantification



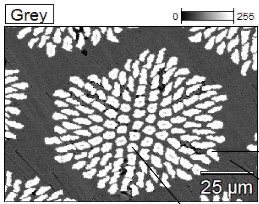


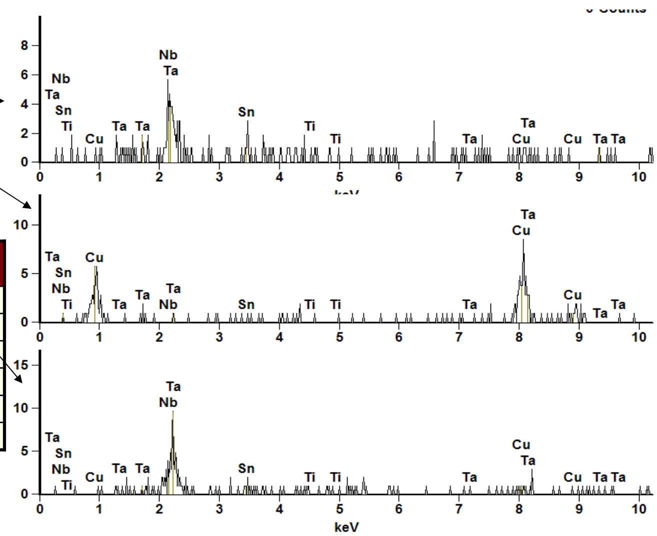
30min. / 512x384 Datapoints

~10ms / Spektrum



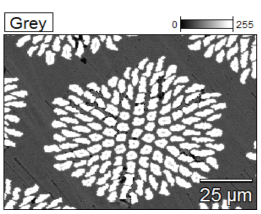
« Quantify »…?

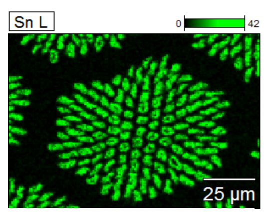


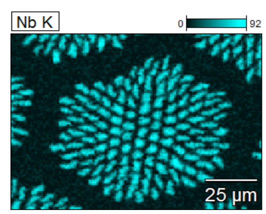


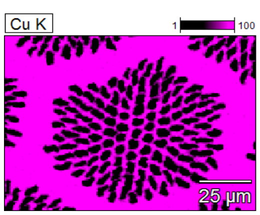
Element Line	Net Counts	ZAF	Weight %	Weight % Error	Atom %	Atom % Error
Ti K	0	1.584	0.00	---	0.00	+/- 0.00
Cu K	2	1.010	10.88	+/-38.08	18.46	+/-64.60
Nb K	1	0.963	25.20	+/-226.79	29.24	+/-263.16
Sn L	8	1.428	45.49	+/-39.80	41.32	+/-36.15
Ta M	2	1.679	18.43	+/-36.86	10.98	+/-21.96
Total			100.00		100.00	

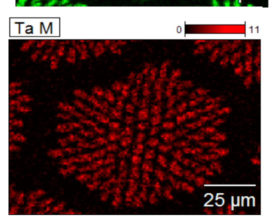
Improved statistics: 5x5 pixel binning

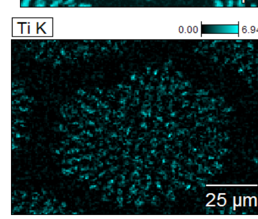




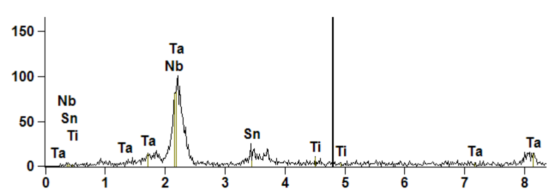




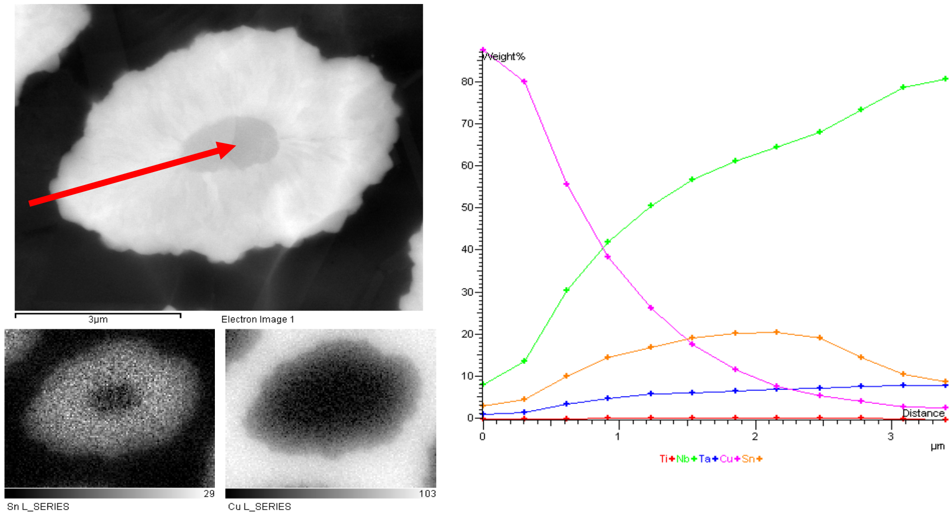




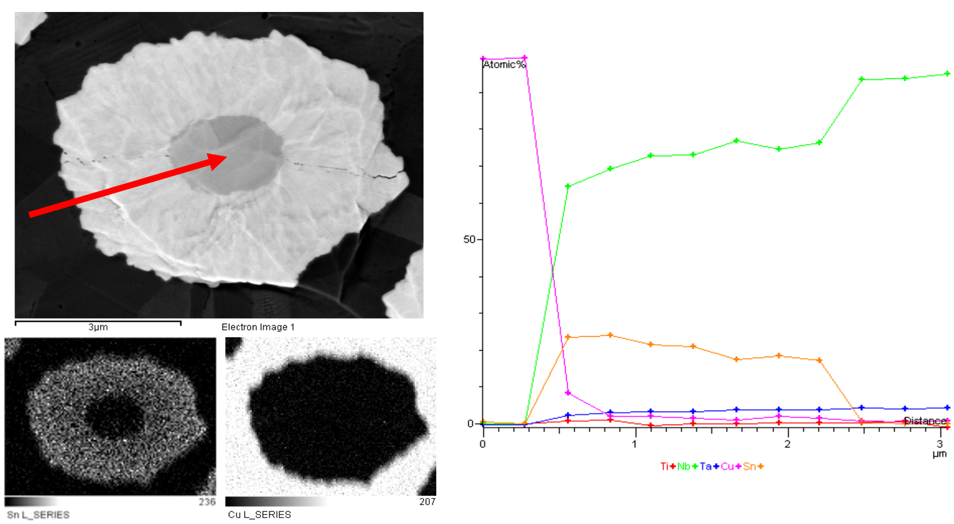
Element Line	Net Counts	ZAF	Weight %	Weight % Error	Atom %	Atom % Error
Ti K	36	1.584	2.14	+/- 0.95	4.42	+/- 1.97
Nb K	124	0.981	66.95	+/-30.24	71.27	+/-32.19
Sn L	305	1.722	25.87	+/- 3.48	21.56	+/- 2.90
Ta M	57	1.351	5.04	+/- 2.21	2.75	+/- 1.21
Total			100.00		100.00	



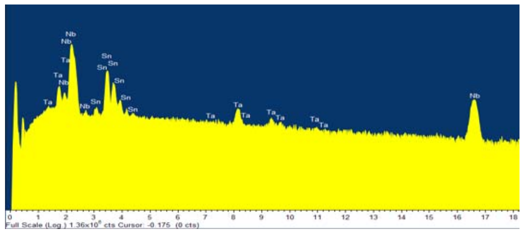
Spatial resolution @ 30kV

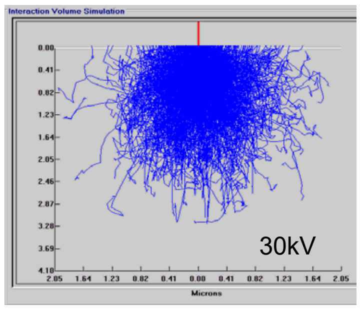


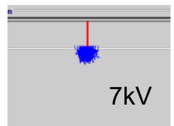
Spatial resolution @ 7kV

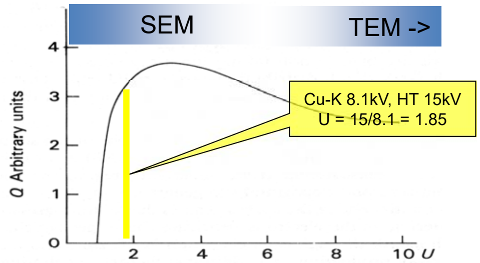


Overvoltage and penetration depth !



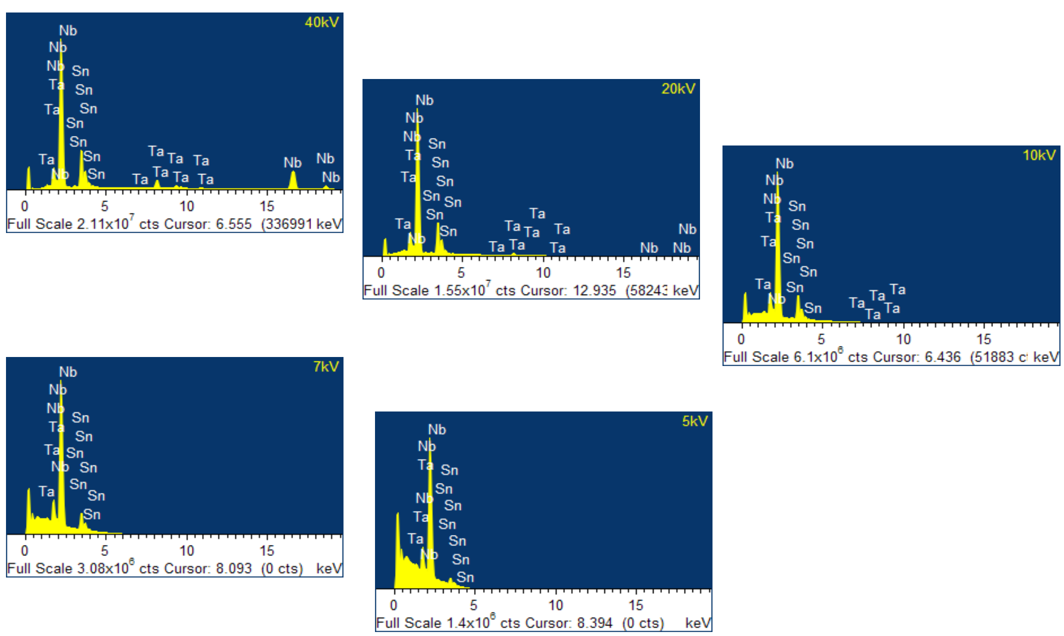


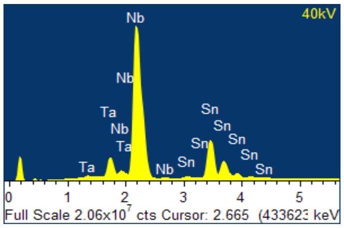


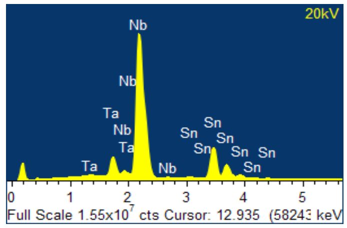


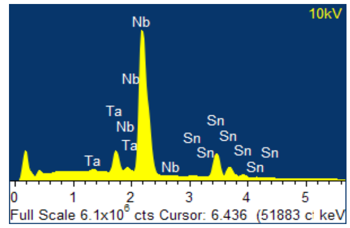
To ionized the incident electron MUST have an energy larger than the core shell level U>1. To be efficient, it should have about twice the edge energy U>2.

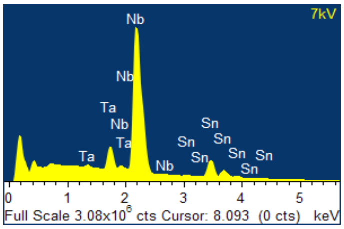
- Nb Ka1 16.6 keV
  Nb La1 2.14 keV
- Cu Ka1 8.1 keV
  Cu La1 0.93 keV
- Sn Ka1 25.2 keV
  Sn La1 3.44 keV
- Ta La1 8.14 keV
  Ta Ma1 1.71 keV
- Ti Ka1 4.51 keV
  Ti La1 0.45 keV

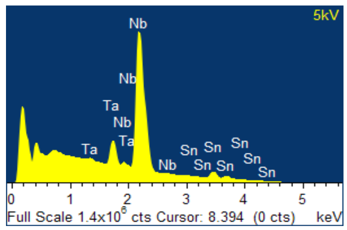












Monte-Carlo Simulations

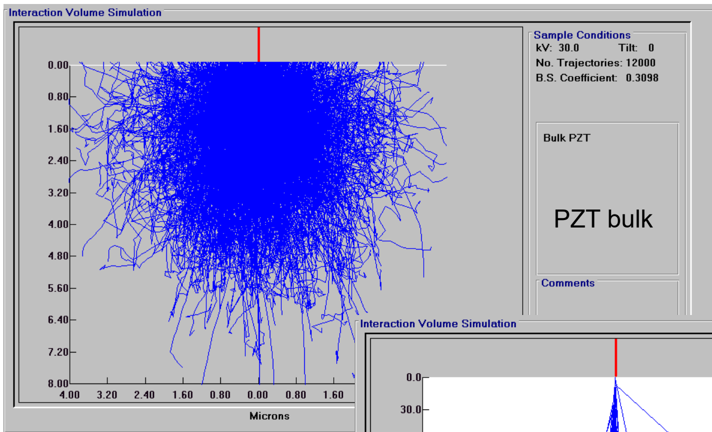
CASINO (free)

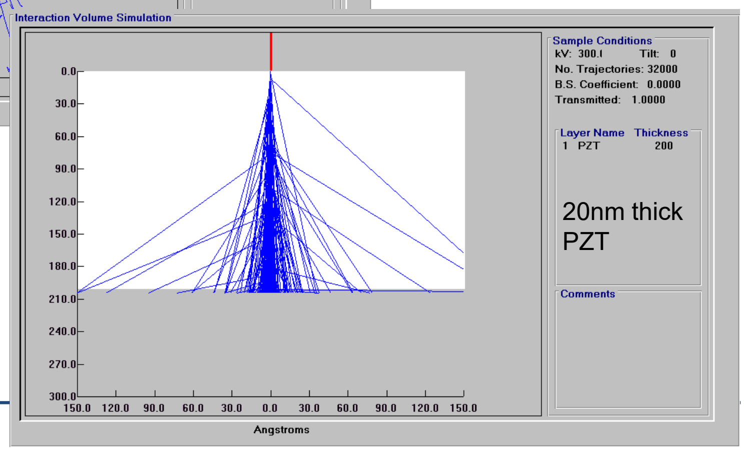
http://www.gel.usherbrooke.ca/casino/What.html

DTSA-II (free), NIST

http://www.cstl.nist.gov/div837/837.02/epq/dtsa2/index.html

EDS in TEM





High spatial resolution !