EDS – Energy Dispersive Spectrometry – Energo-disperzná röntgenová spektrometria

WDS – Wave Dispersive Spectrometry – Vlnovo-disperzná röntgenová spektrometria

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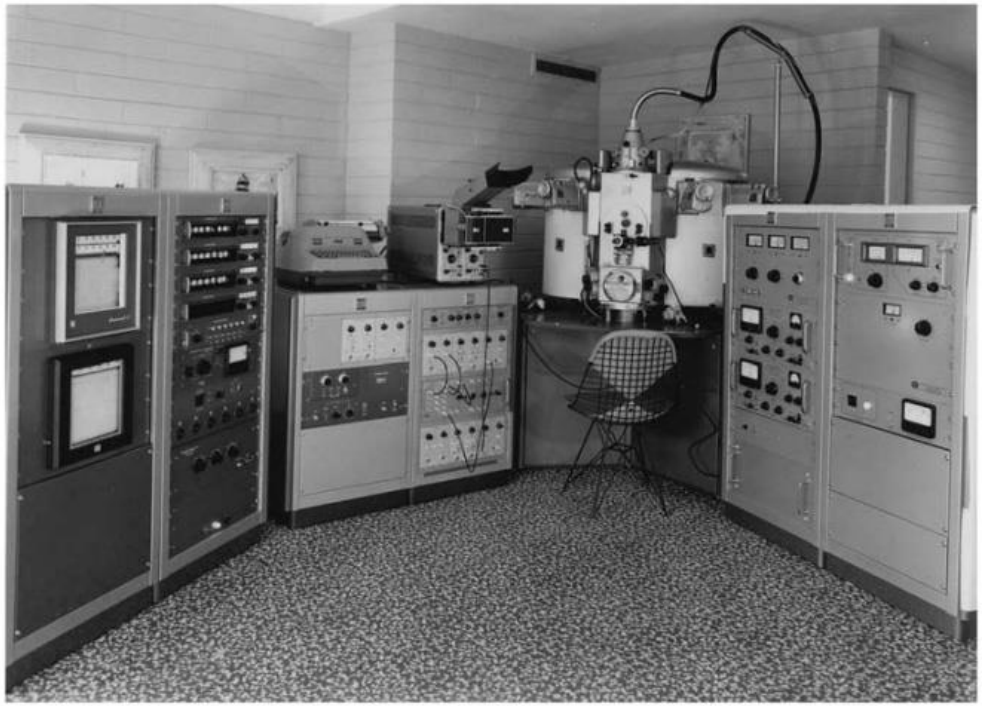
Recommended literature:

J.I. Goldstein et al: Scanning Electron Microscopy and X-Ray Microanalysis

CASINO: D. Druin, Sanning **29** (2007) 92-101.
and http://www.gel.usherbrooke.ca/casino/index.html

EDS – EDX - EDAX versus EPMA

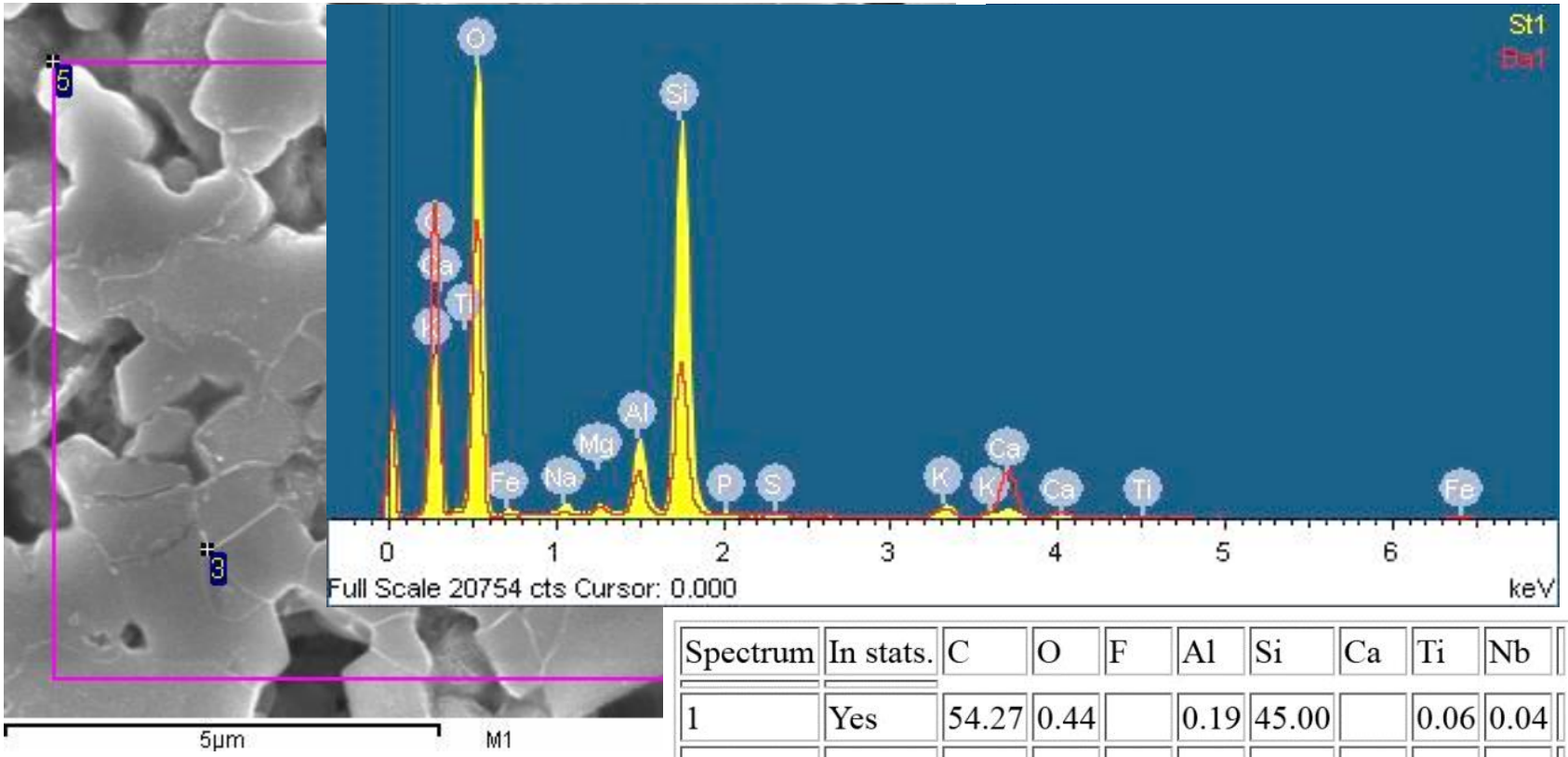
EPMA – electron probe microanalysis – special equipment with much higher electron beam intensity as in SEM – started about 70 years ago



- With new electron sources and X-ray detectors – EDS (from 1968) and lately WDS in SEM
- In present time – EPMA is a specialized SEM for precise and rapid WDS with several WDS systems

ARL EMX-SM equipement for EPMA of the mid -1960s. [R. Rinaldi and X.Llovet, Microsc. Microanal. 21 (2015) 1053]

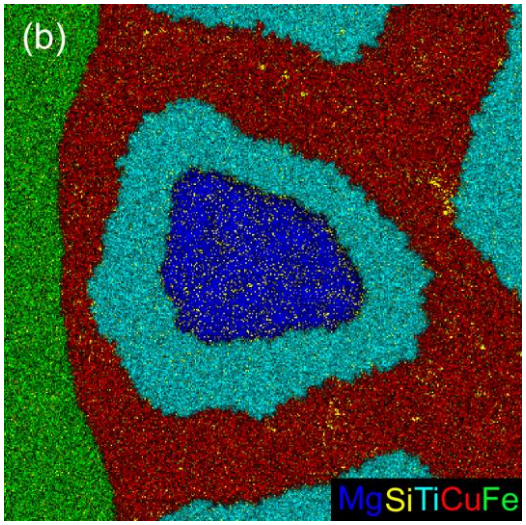
EDS – EDX - EDAX - As you know it….



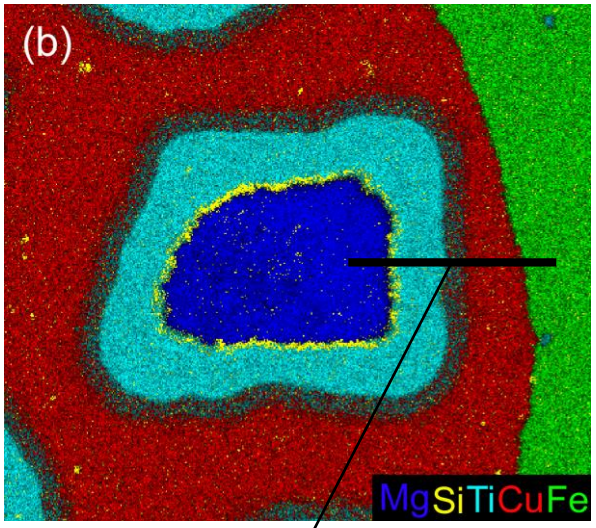
- qualitative elemental analysis
- quantitative elemental analysis

Spectrum	In stats.	C	O	F	Al	Si	Ca	Ti	Nb
1	Yes	54.27	0.44		0.19	45.00		0.06	0.04
2	Yes	53.90	0.78	0.43	0.30	44.50		0.03	0.07
3	Yes	54.10	1.34	0.54	0.52	43.02		0.27	0.21
4	Yes	58.54	1.46	1.71	0.26	37.68		0.19	0.16
5	Yes	53.40	1.53	1.90	0.28	42.24	0.16	0.25	0.25
Max.		58.54	1.53	1.90	0.52	45.00	0.16	0.27	0.25
Min.		53.40	0.44	0.43	0.19	37.68	0.16	0.03	0.04

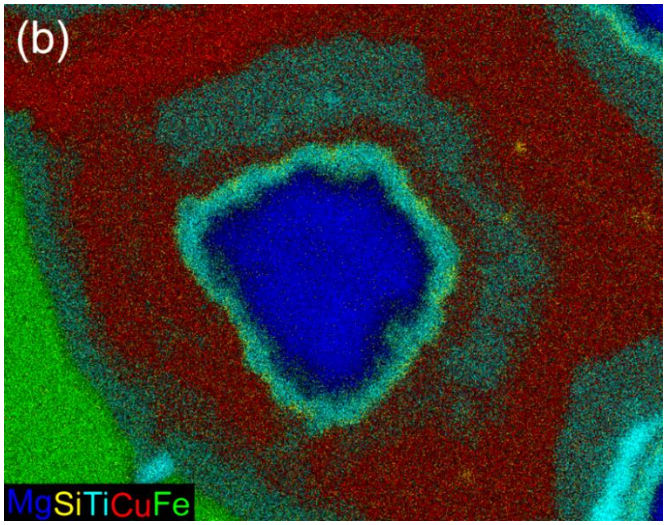
X-ray elemental mapping



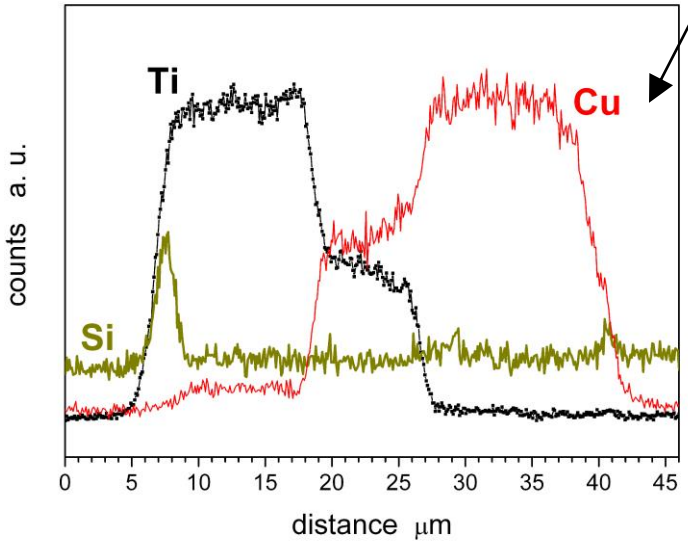
Before annealing



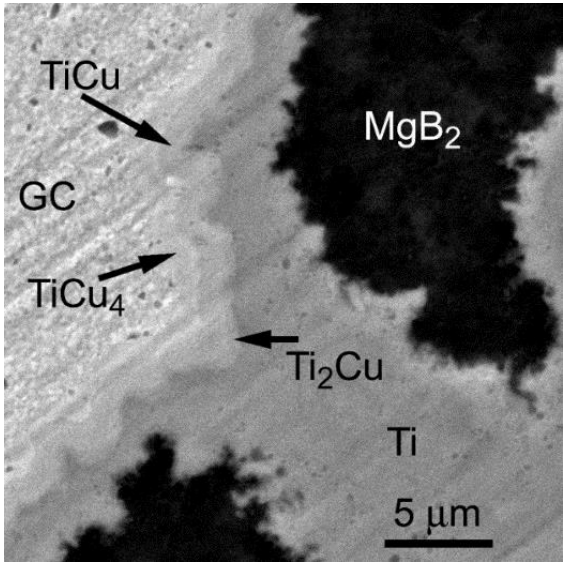
After optimal annealing



After excessive anealing



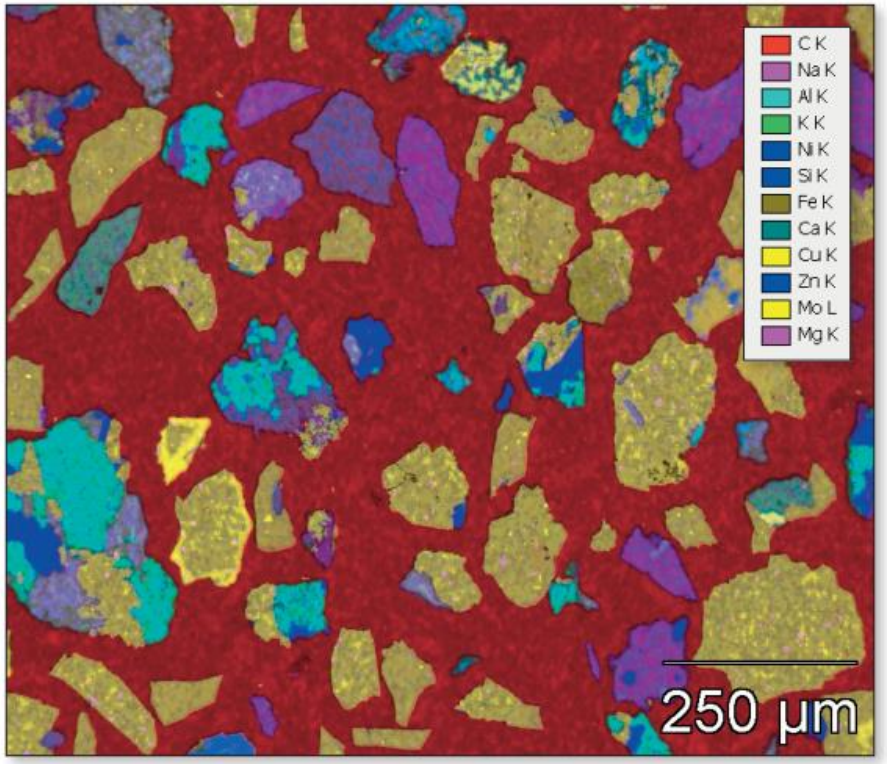
EDS line-scan

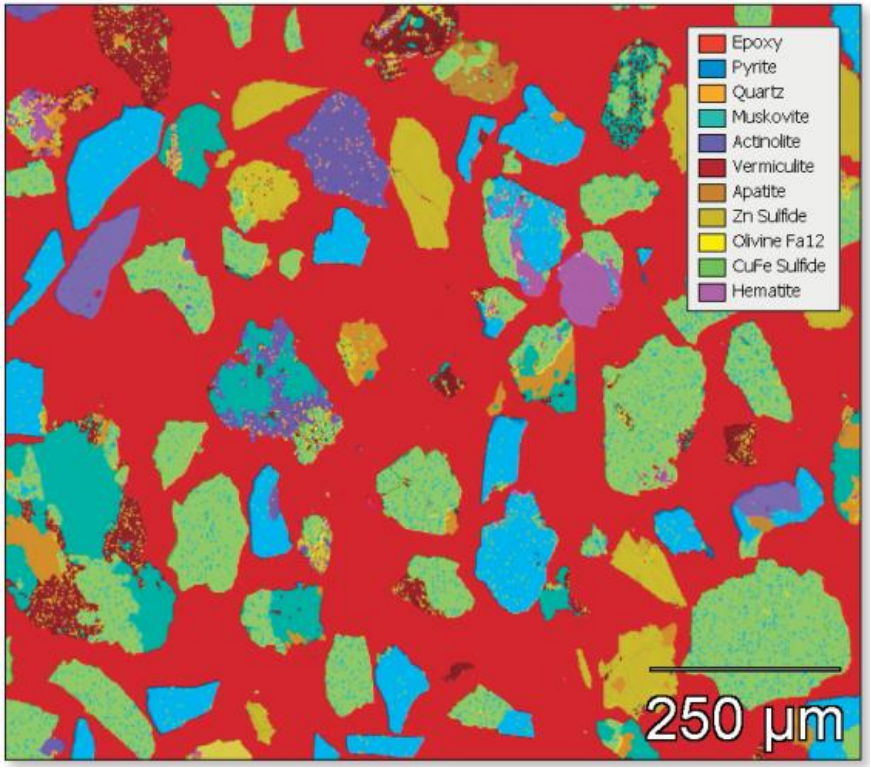


[A. Rosová et al, J. Alloys Comp. 509 (2011) 7961]

+ composition

Phase mapping



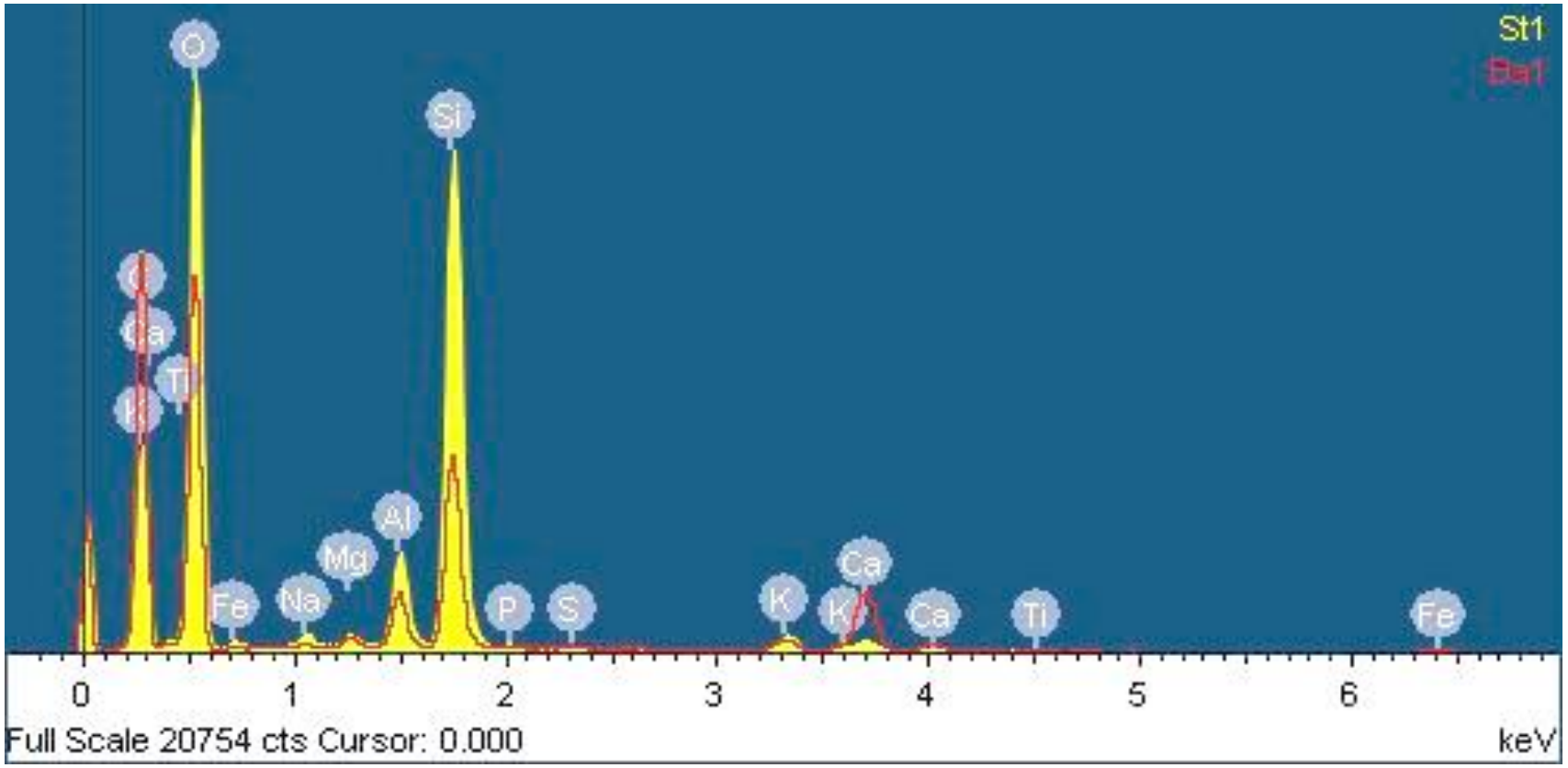


Chemical element map
It shows the distribution of X-ray counts for all identified elements in the acquisition.

Phase map
It groups together pixels with statistically similar X-ray spectra, performs a quantitative analysis of each phase, identifies the phases and compare them with a database to name them.

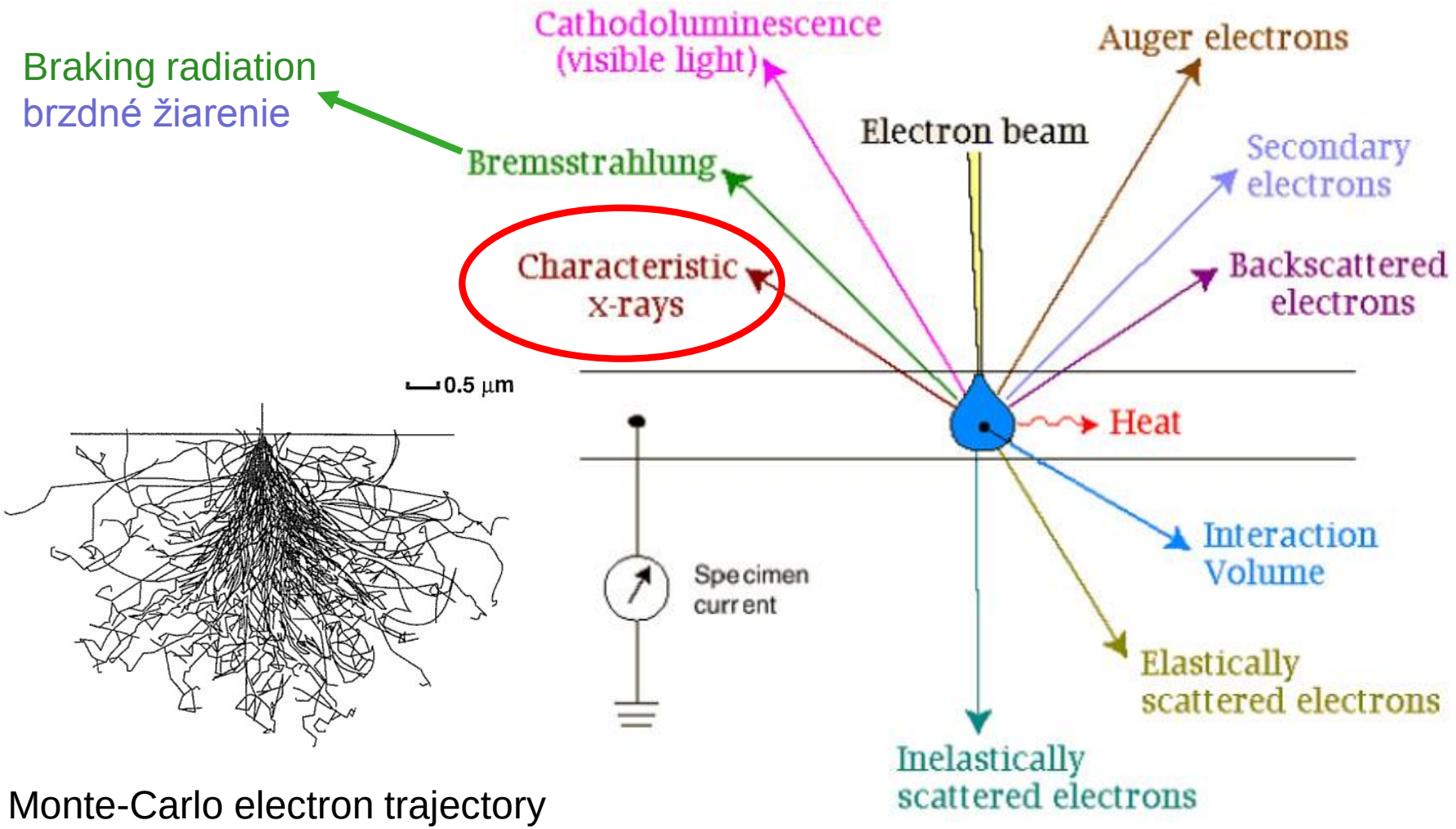
[EDS Mapping Routines by Thermo Scientific]

The goal of this session



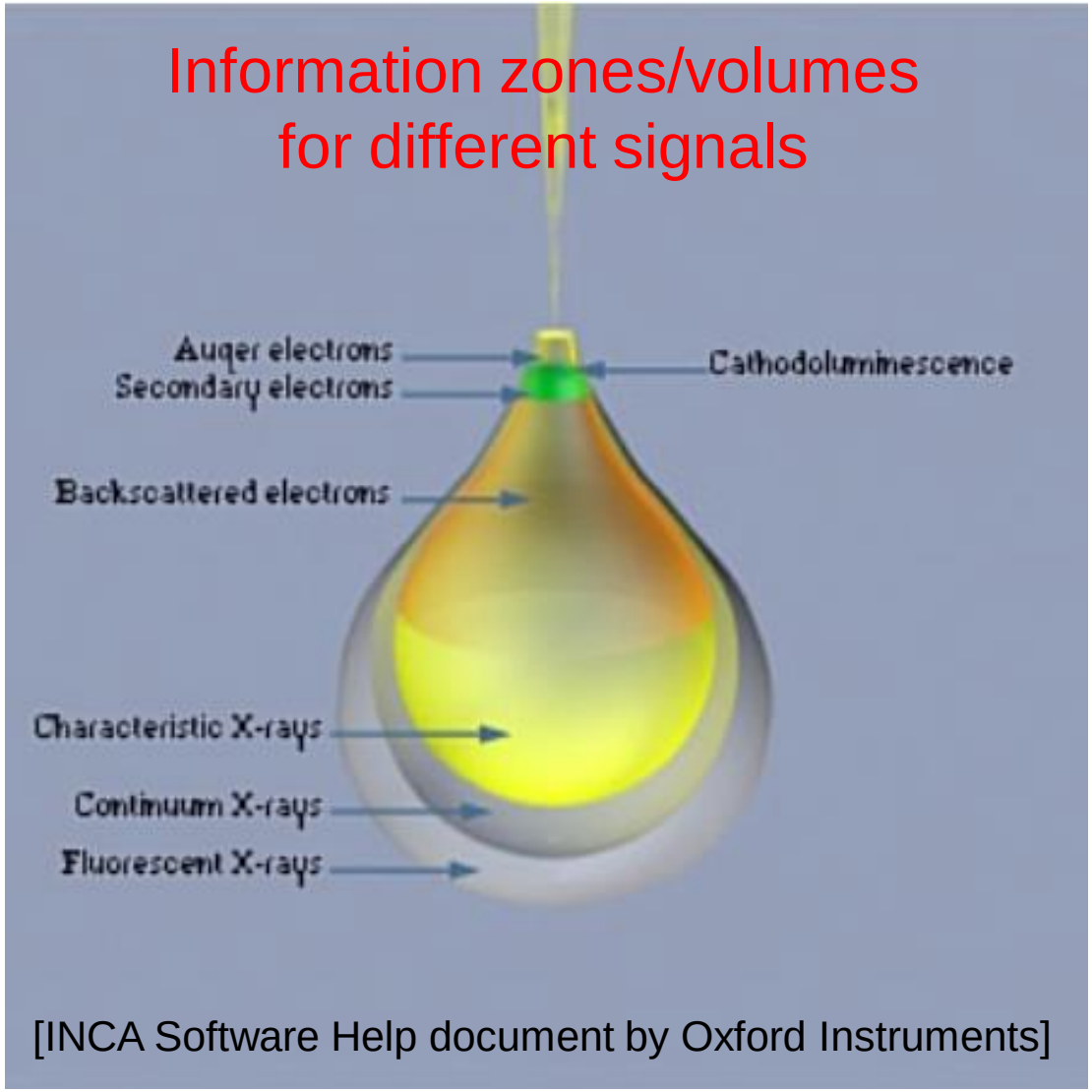
- To understand the origin and character of measured EDS spectra
- What information could be retired from
- What are the limits of spectra measurement and analysis
- How to optimize the measurements to obtain the optimal accuracy

SEM – electron beam interaction with a sample



Monte-Carlo electron trajectory simulations - CASINO

Interaction versus information volume



[INCA Software Help document by Oxford Instruments]

Interaction zone/volume - zone/volume in which electron beam can excite atoms

Information zone/ volume - from which we measure relevant signal – for EDS it is different for every atom and every X-ray energy.

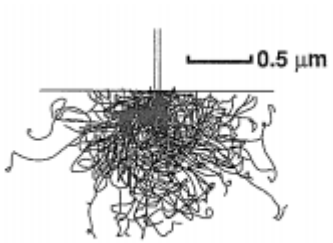
- necessary to know what processes are active in the zones

Interaction volume – atom excitation

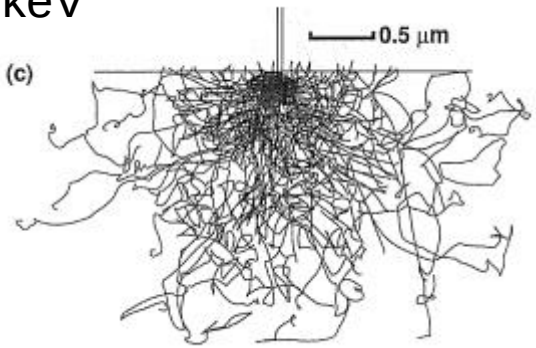
Iron Fe

10 keV

20 keV

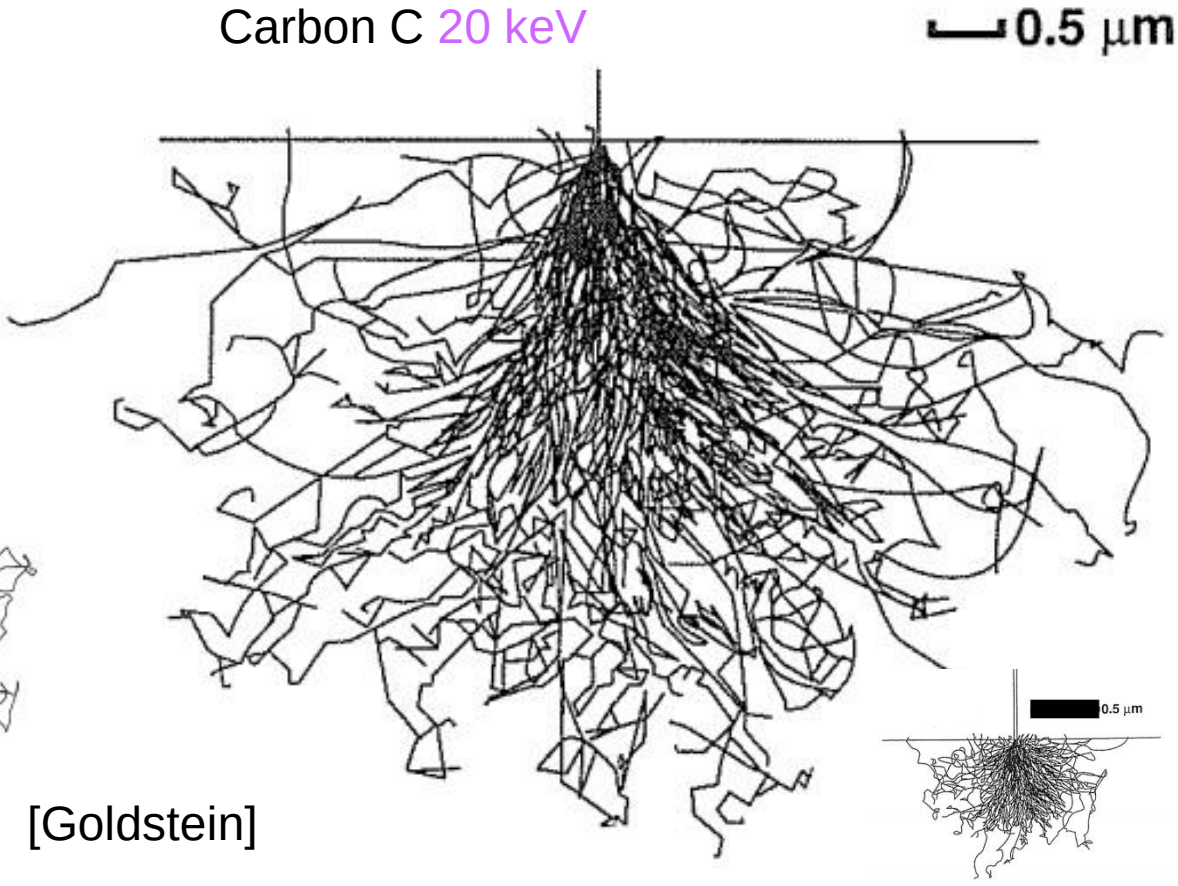


30 keV



For atom excitation $E_e > E_c$

Carbon C 20 keV

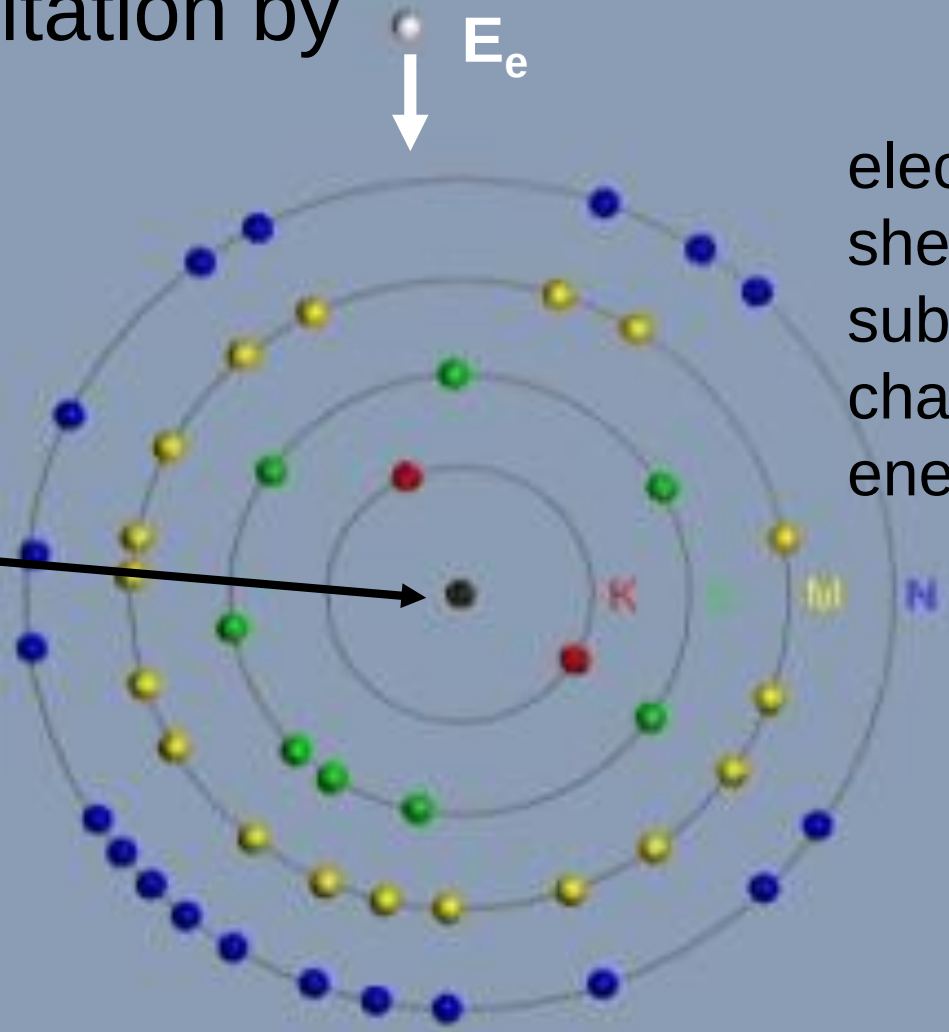


[Goldstein]

Monte-Carlo electron trajectory simulations - CASINO

Silver Ag 20 keV

Atom excitation by electron



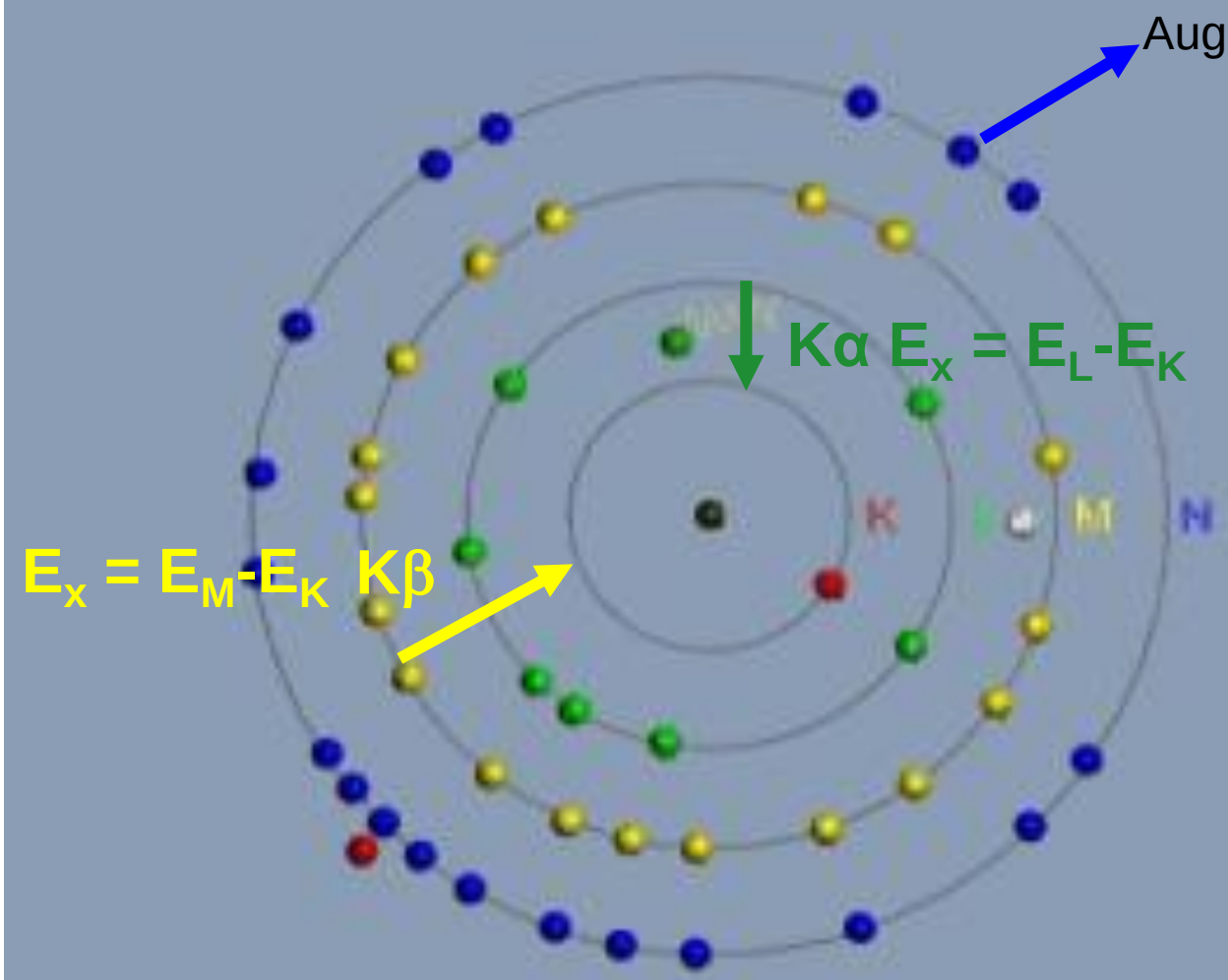
electron energy shells (and subshells) with characteristic energy levels

nucleus

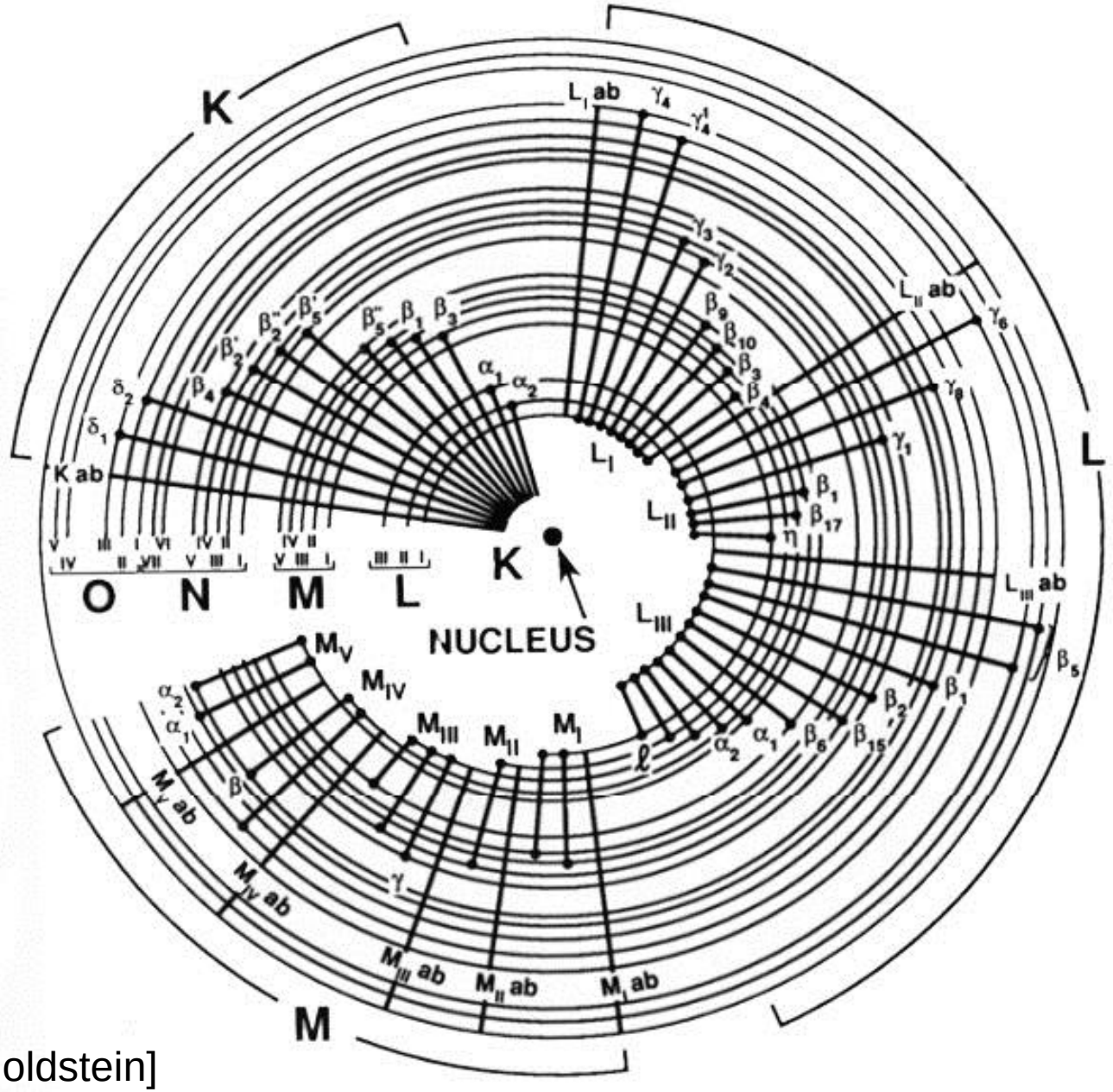
Electron energy - $E_e > E_c$ – critical ionization or excitation energy

[INCA Software Help document by Oxford Instruments]

De-excitation

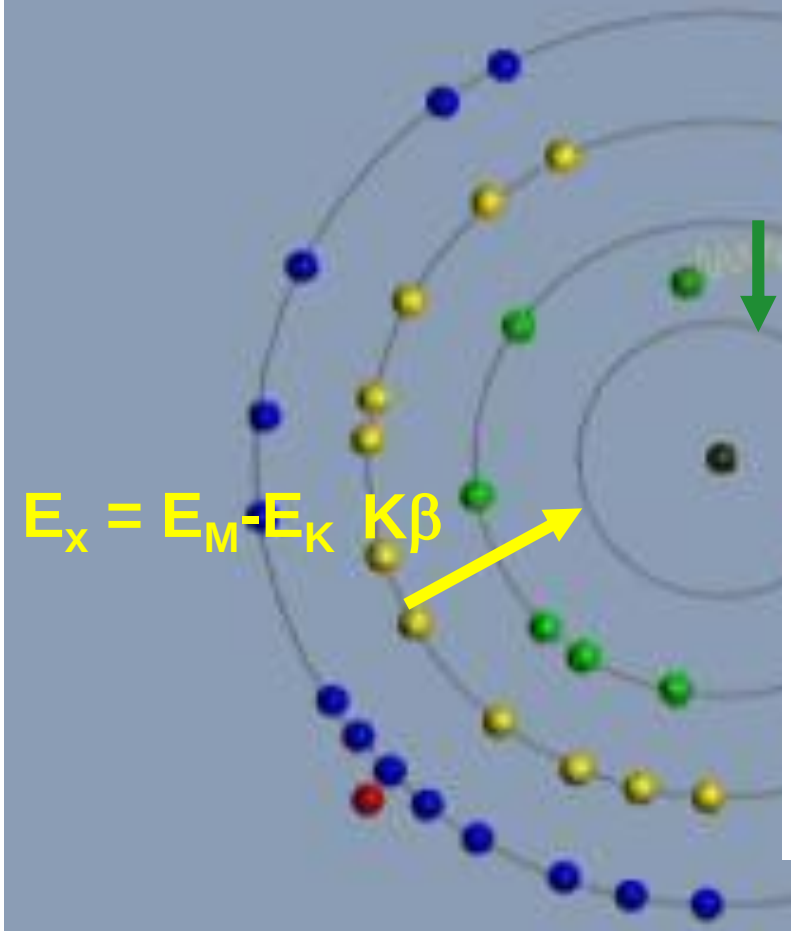


$E_x < E_c$

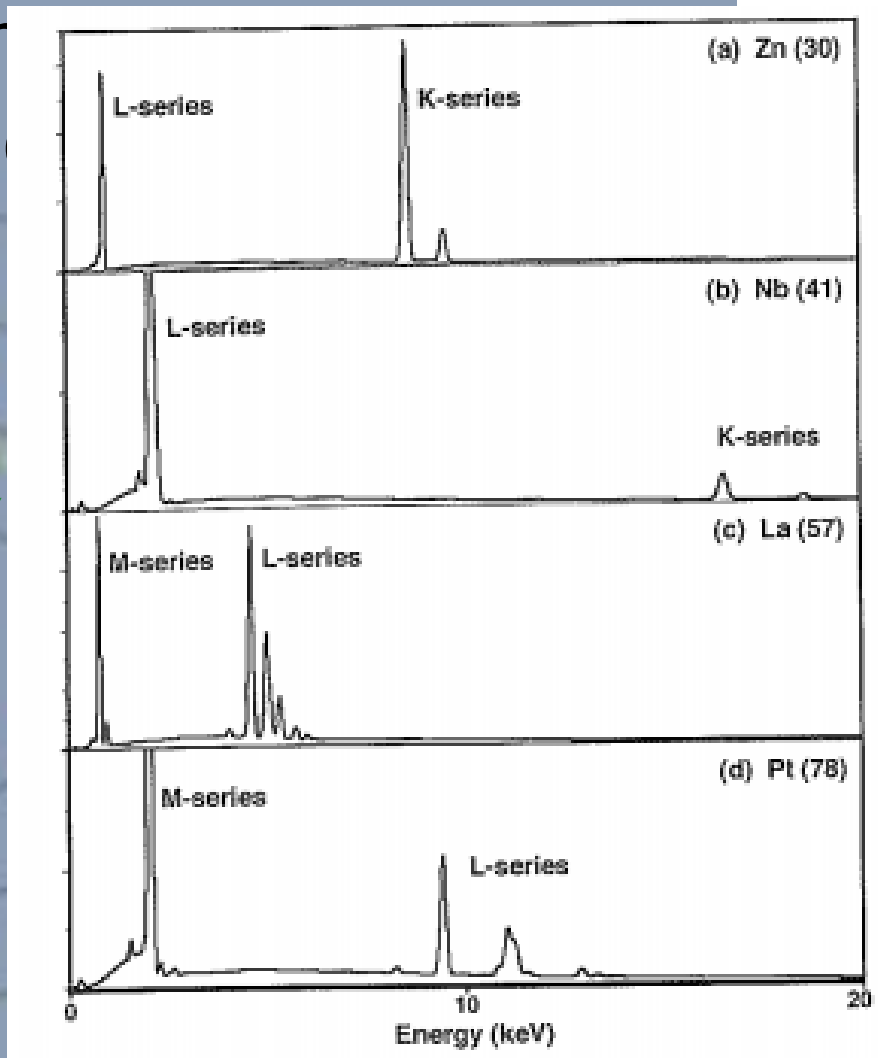

K
L
M
O
N
M
L
K
NUCLEUS
K ab
L I ab
L II ab
L III ab
M V ab
M IV ab
M III ab
M II ab
M I ab

[Goldstein]

De-excitation by ch
produ



$E_x = E_M - E_K$ Kβ



All vacancies should be filled to obtain equilibrium => all higher level transformations should run => the full family of characteristic lines should appear according to the number of electrons in the atom electron orbital

$E_x < E_c$

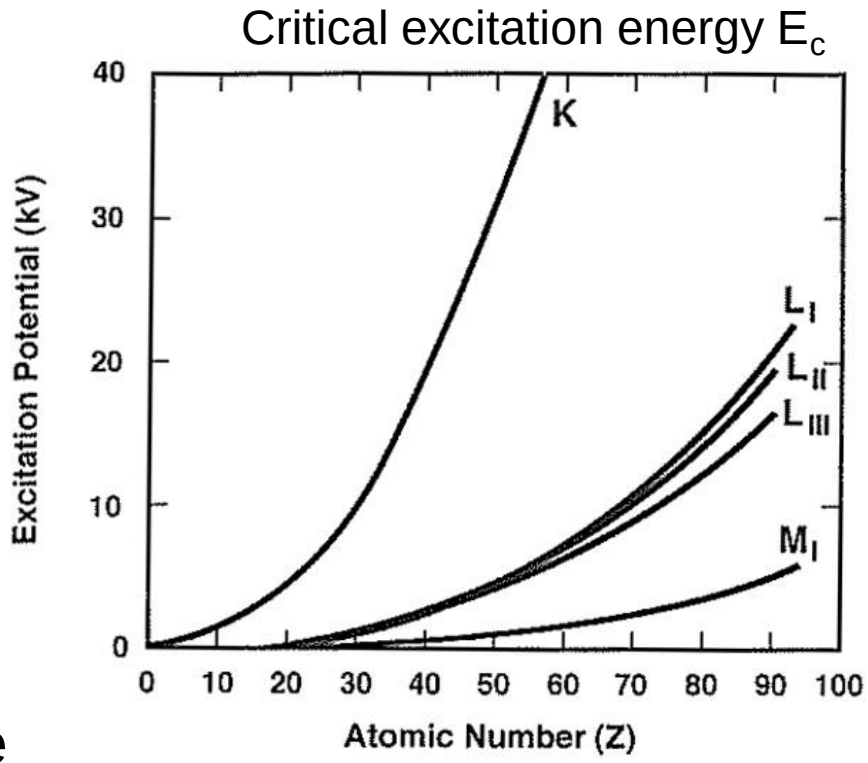
Families of characteristic lines

$E_X < E_c$

all $E_X < E_c$!!

$E_{K\alpha} = E_K - E_L$

$E_{K\beta} = E_K - E_M \ (less\ probable)$



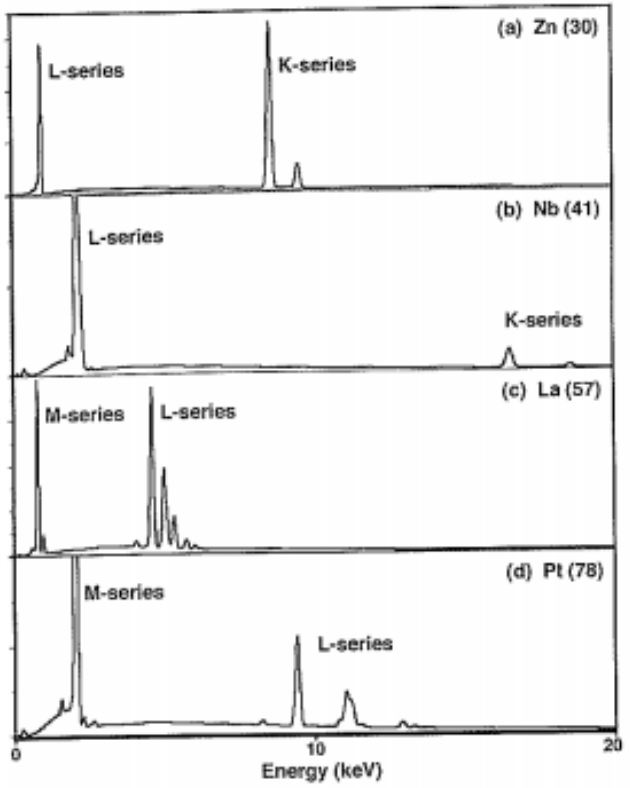
- The greater energy difference, the less probable and less intense X-ray line
- Table – **approximate** line weights for one element

Families of characteristic lines

Table 6.3. Weights of Lines

Family	Approximate line weights for K, L, or M shells
K	$K\alpha = 1, K\beta = 0.1$
L	$L\alpha = 1, L\beta_1 = 0.7, L\beta_2 = 0.2, L\gamma_1 = 0.08, L\gamma_3 = 0.03, L_l = 0.04$
M	$M\alpha = 1, M\beta = 0.6, M\zeta = 0.06, M\gamma = 0.05, M_{II}N_{IV} = 0.01$

- It is impossible to compare lines of different elements
- Useful guideline for qualitative and quantitative analysis – **all lines should be present** (they can overlap -> deconvolution)



[Goldstein]

Cross section for inner shell ionization Q

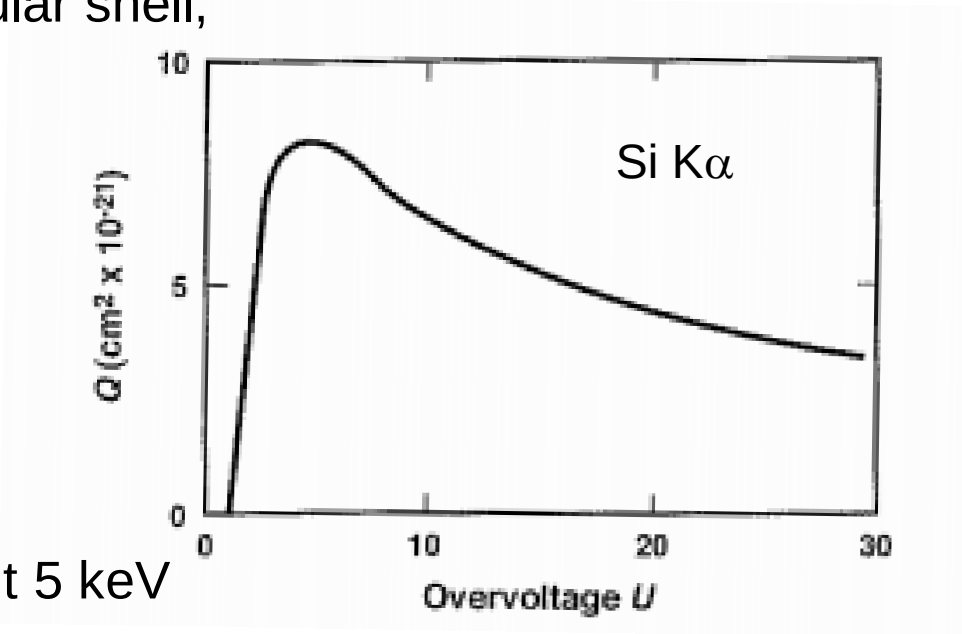
$$Q = 6.51 \times 10^{-20} \frac{n_S b_S}{U E_c^2} \log_e(c_S U),$$

Účinný ionizačný prierez

Where n_S the number of electrons in shell or subshell,
E_C is the critical ionization energy,
$b_S \; and \; c_S$ are constants for the particular shell,
U is the overvoltage

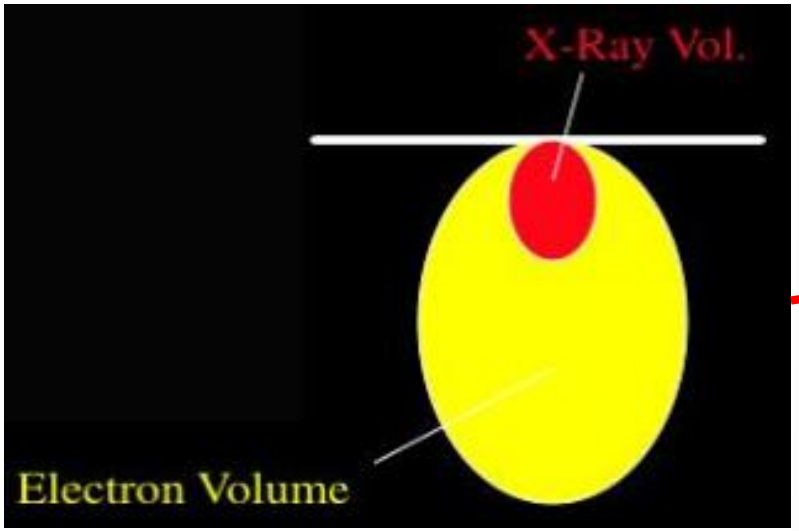
$$U = {}^{E}\!/_{E_c} \approx {}^{E}\!/_{E_{x\,max}}$$

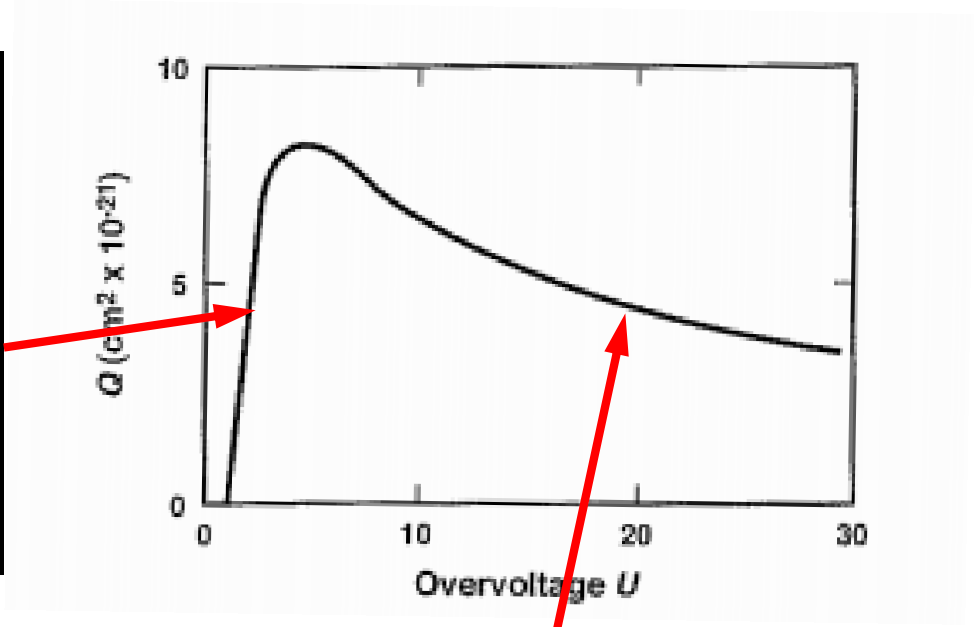
$E_{x\,max}$ - the maximum energy of line which we want to analyze

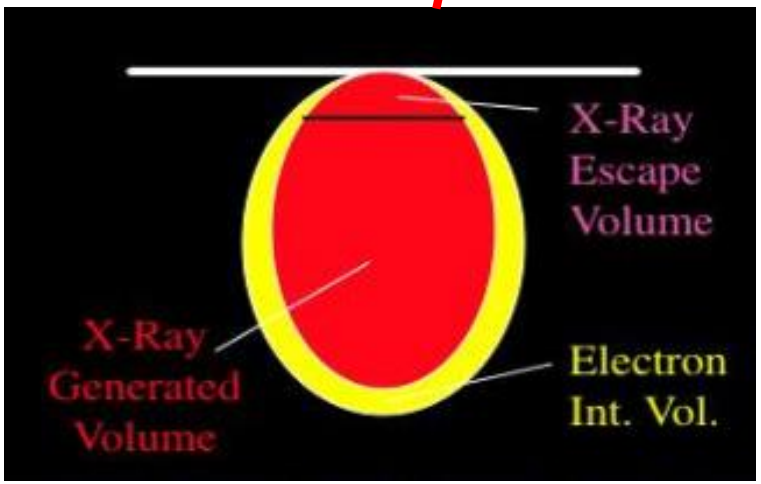


=> For Si Kα (1.739 keV) E_{opt} is about 5 keV

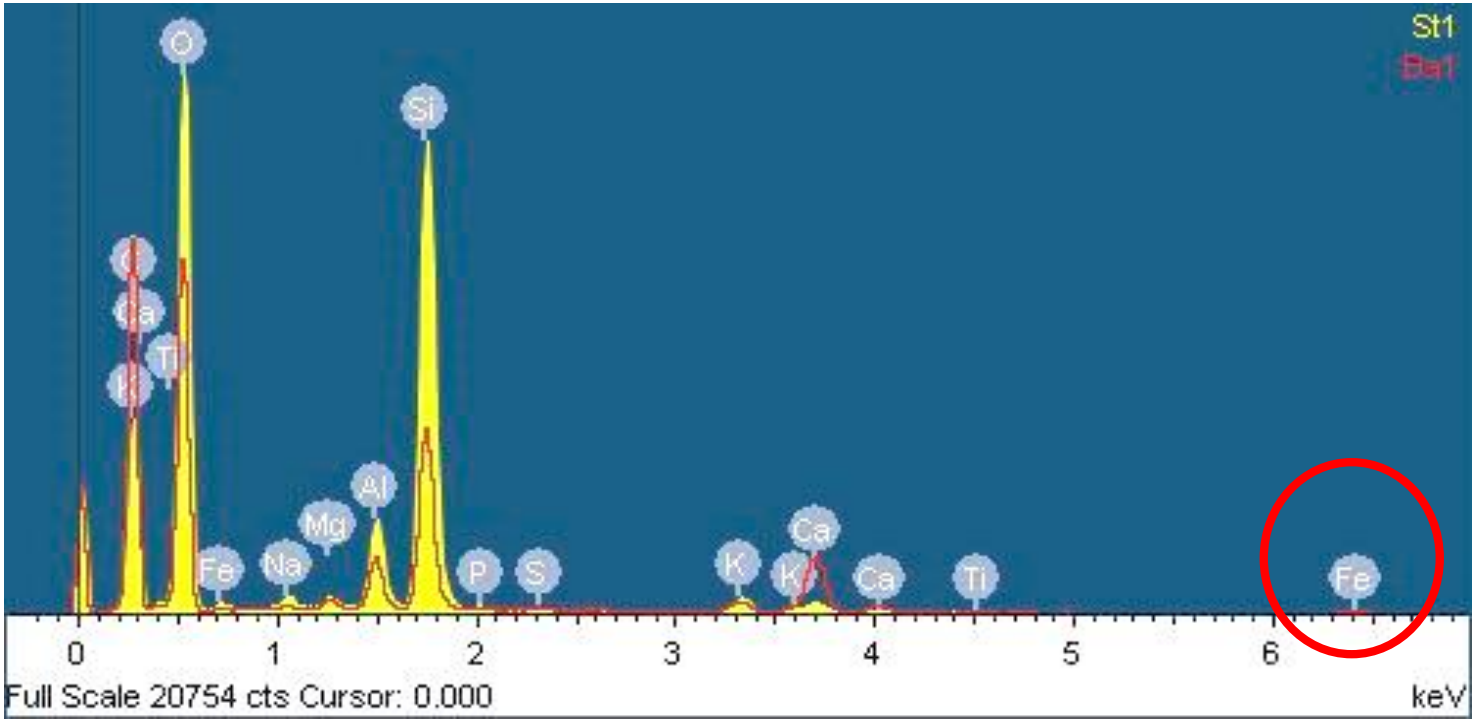
Overvoltage





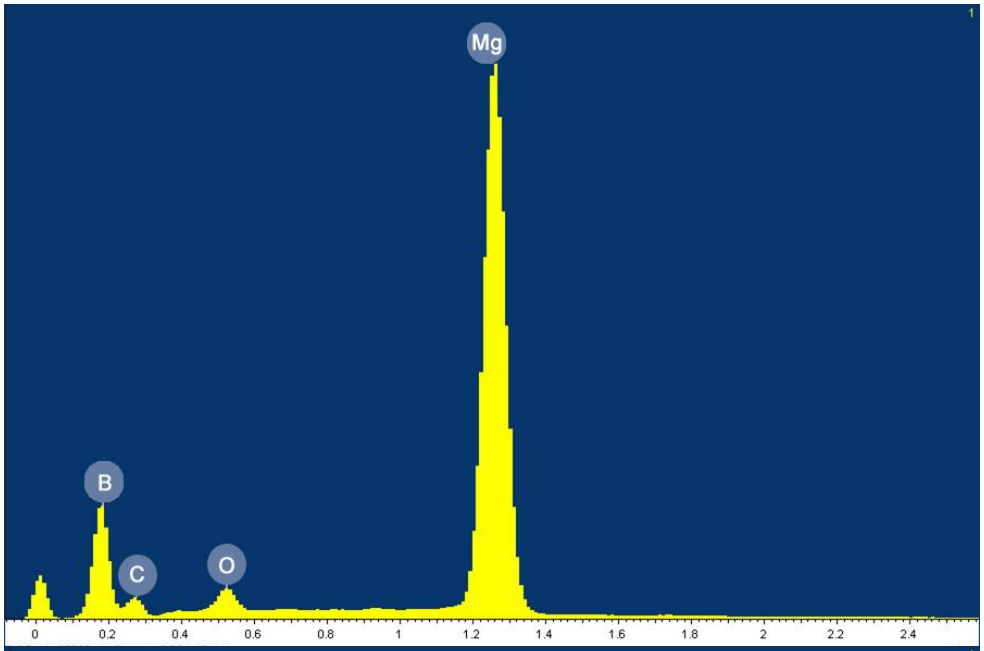


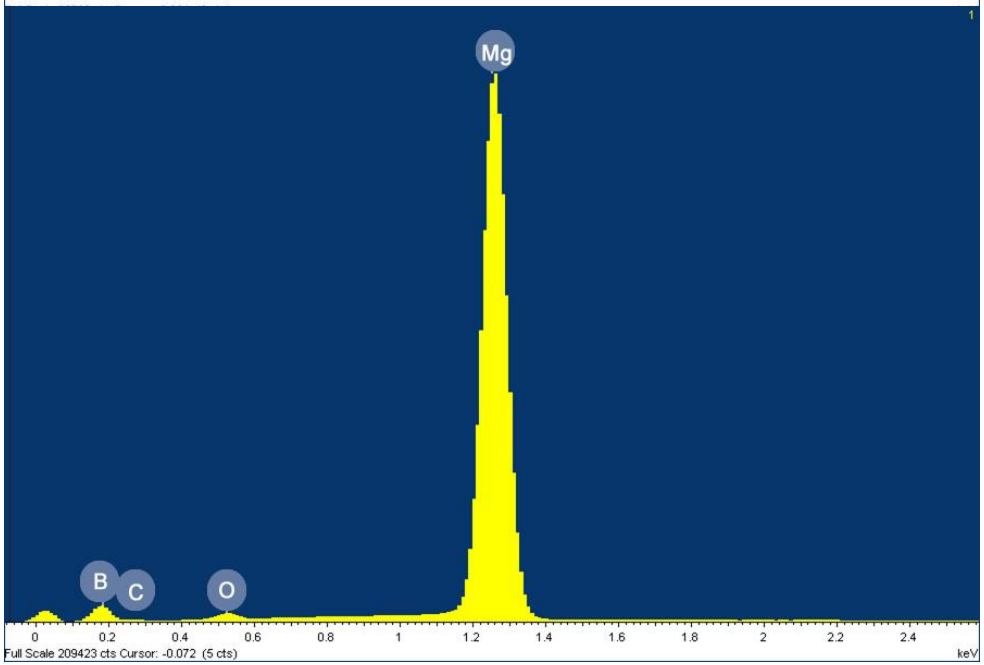
U = 2 - 3 is appropriate
for the maximal ionization
U $\leq$ **10-20** for the lowest peak
of interest



For used acceleration voltage = 10 kV E = 10 keV,

Ideal overvoltage U = 3, obviously used ~ 2 - 2.5





Overvoltage

E (Mg Kα) = 1.2536 keV
E (B Kα) = 0.1833 keV

MgB_2 E = 5 keV
U (Mg Kα) ≅ 4
U (B Kα) ≅ 27

MgB_2 E = 10 keV
U (Mg Kα) ≅ 8
U (B Kα) ≅ 55

=> It decreases the accuracy of light element quantification

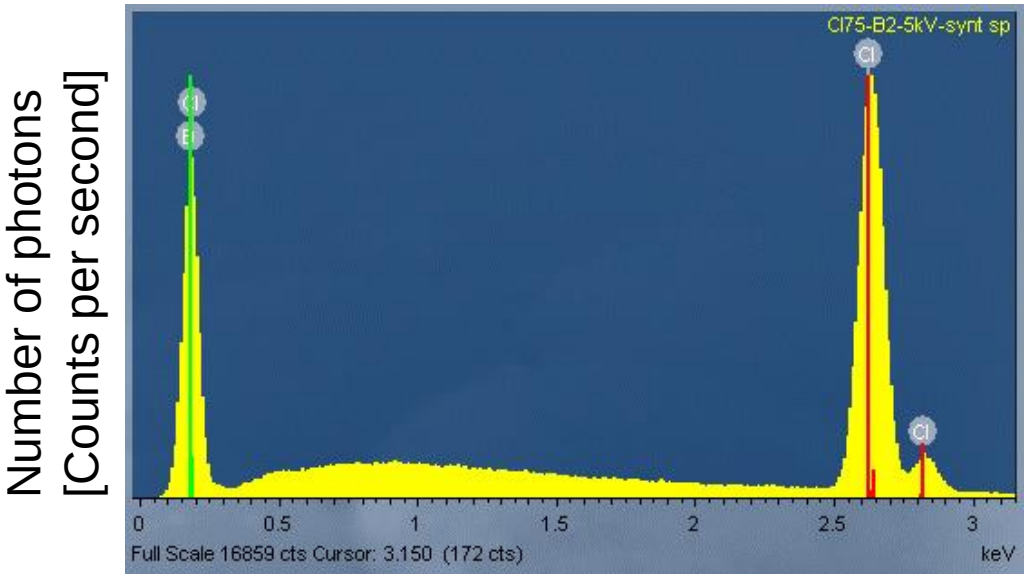
X-ray generation

e-beam interaction with:

- electrons on inner energetic shells in atoms → X-ray photons with energies specific for emitting atoms

  → characteristic X-rays

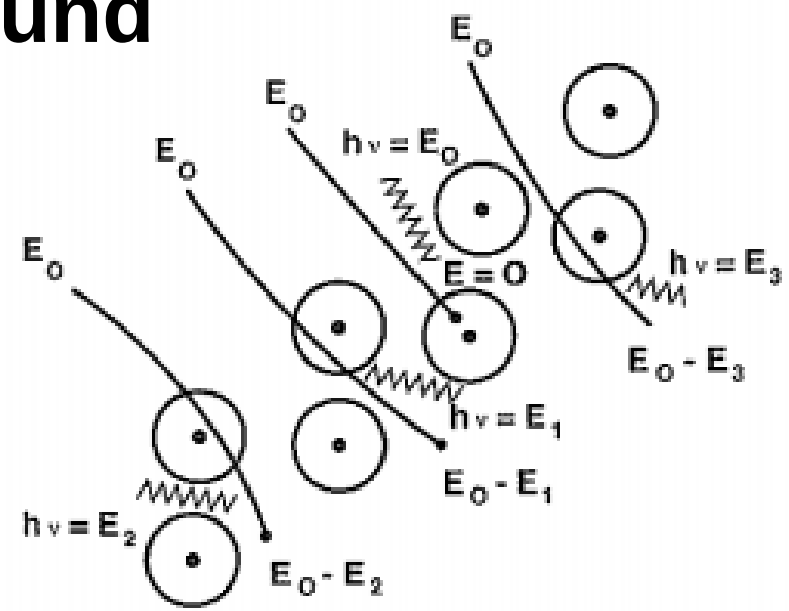
- Coulombic fields of the specimen atoms → continuous spectrum background



Spectrum background

- Bremsstrahlung = braking radiation = brzdné žiarenie
- Inelastic interaction – deceleration of e^- in the Coulombic field of atoms

$\Delta E = E_p = h\nu \qquad \lambda = h / E_p$



$$I_{cm} \approx i_p \bar{Z} \frac{E_o - E_\nu}{E_\nu}$$

- Spectrum background – intensity

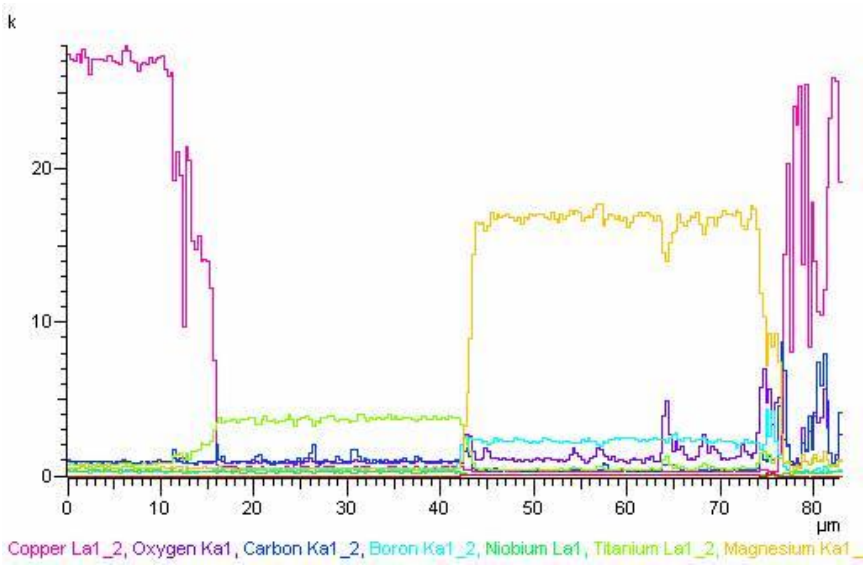
(i_p - current, $\bar{Z}$ - mean atomic number, E_o - incident beam energy, E_ν - continuum photon energy)

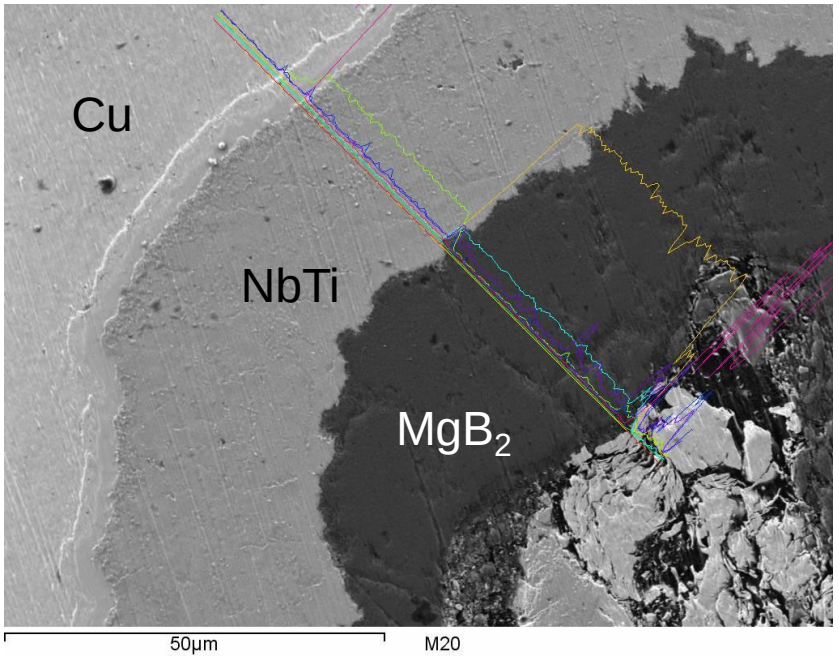
Effect of spectrum background on line-scans

Line-scans of measured signals at corresponding photon energies

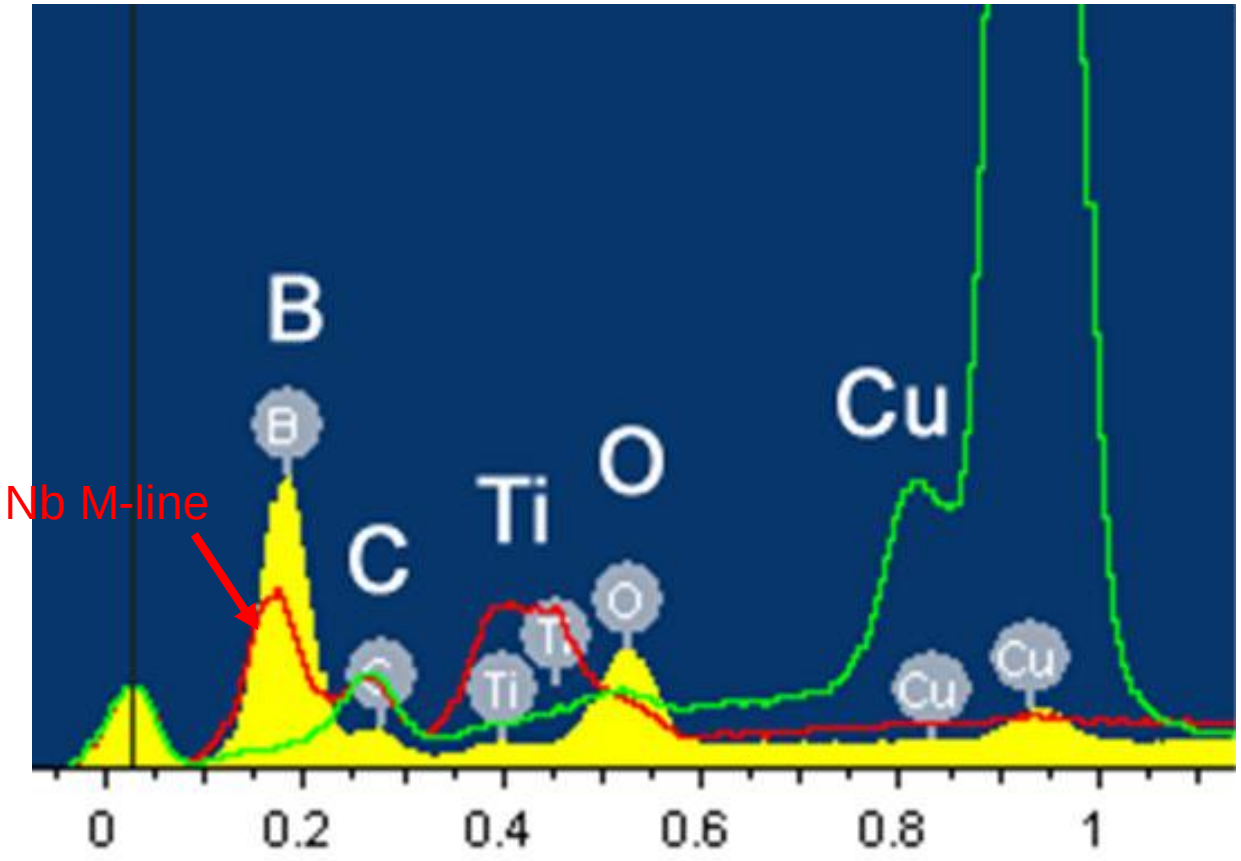
– no background or overlapping maxima correction !!!!

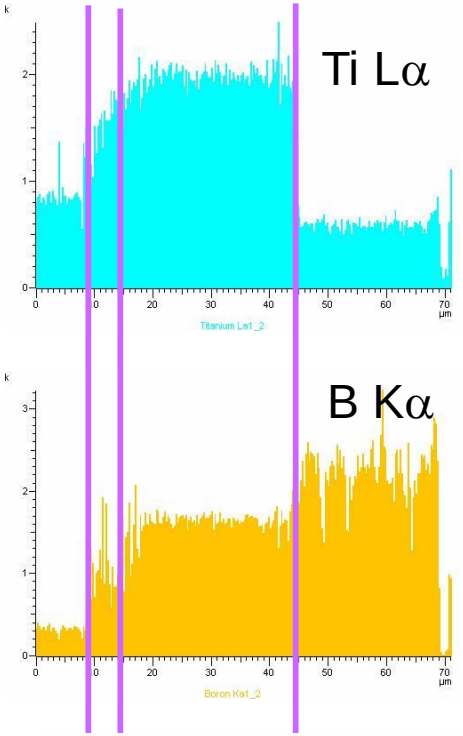
– no quantitative relation between scans of different atoms !!!!

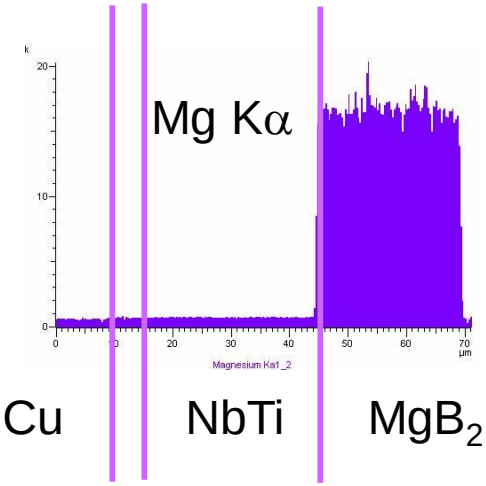


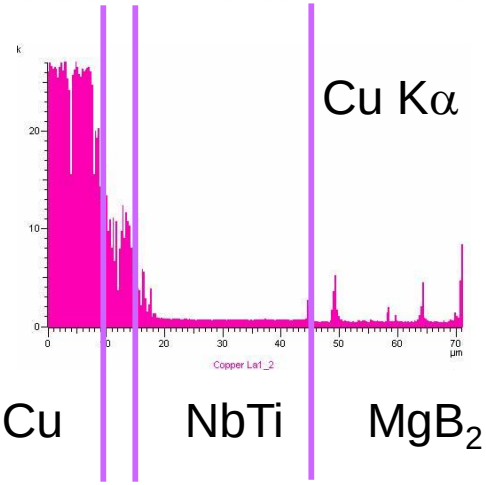


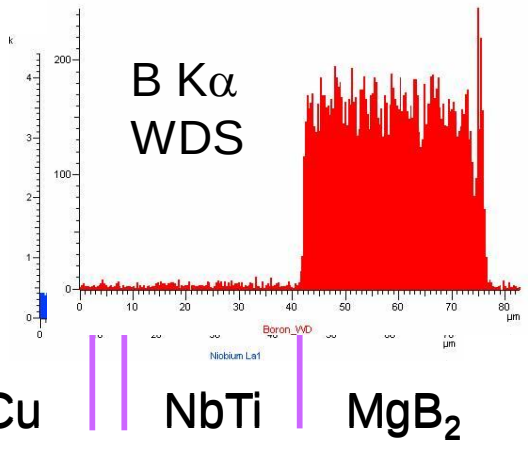
MgB_2/NbTi/Cu


B
C
Ti
O
Cu
Nb M-line
0
0.2
0.4
0.6
0.8
1


Ti Lα
B Kα


Mg Kα
Cu
NbTi
MgB2


Cu Kα
Cu
NbTi
MgB2


B Kα
WDS
Cu
NbTi
MgB2

X-ray absorbtion

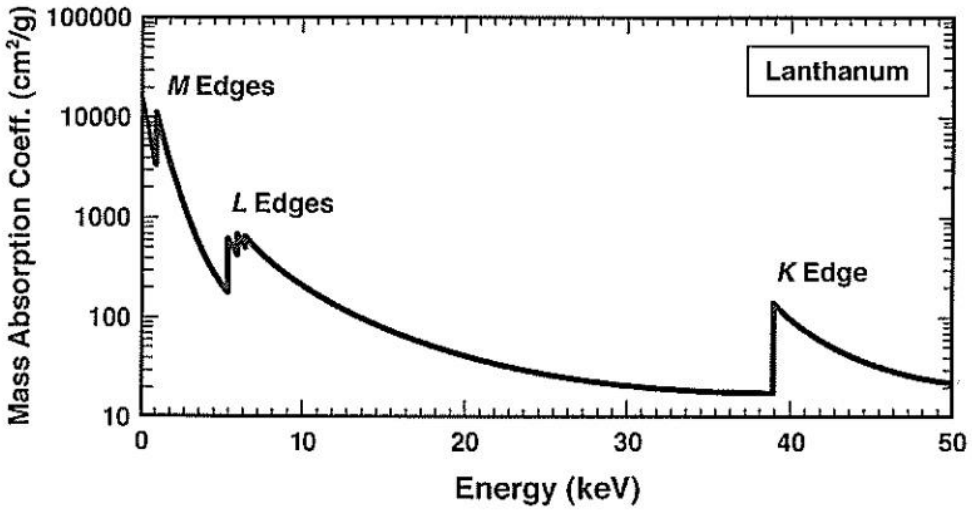
Photons loose their energy on their path from the sample – by photoelectric absorbtion - transfering **the whole energy** to orbital electrons – the signal loses its intensity **but not its energy** - fortunately!!!

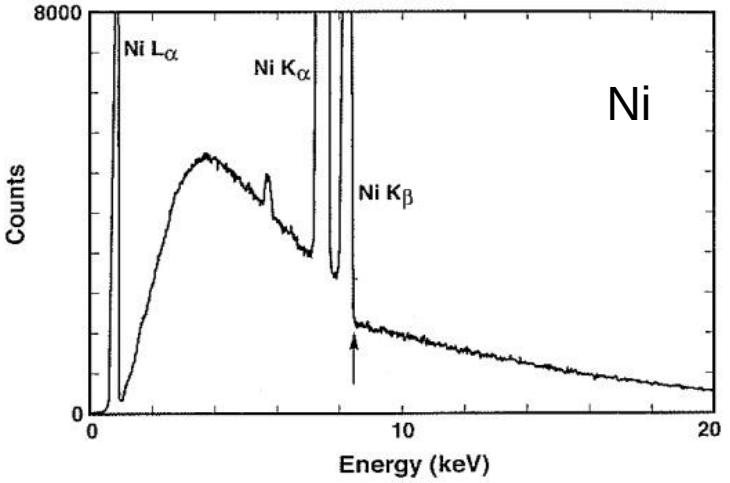
$$I = I_0 \exp\left[-\left(\frac{\mu}{\rho}\right)^{\text{x-ray}}_{\text{absorber}} (\rho t)\right]$$

density thickness

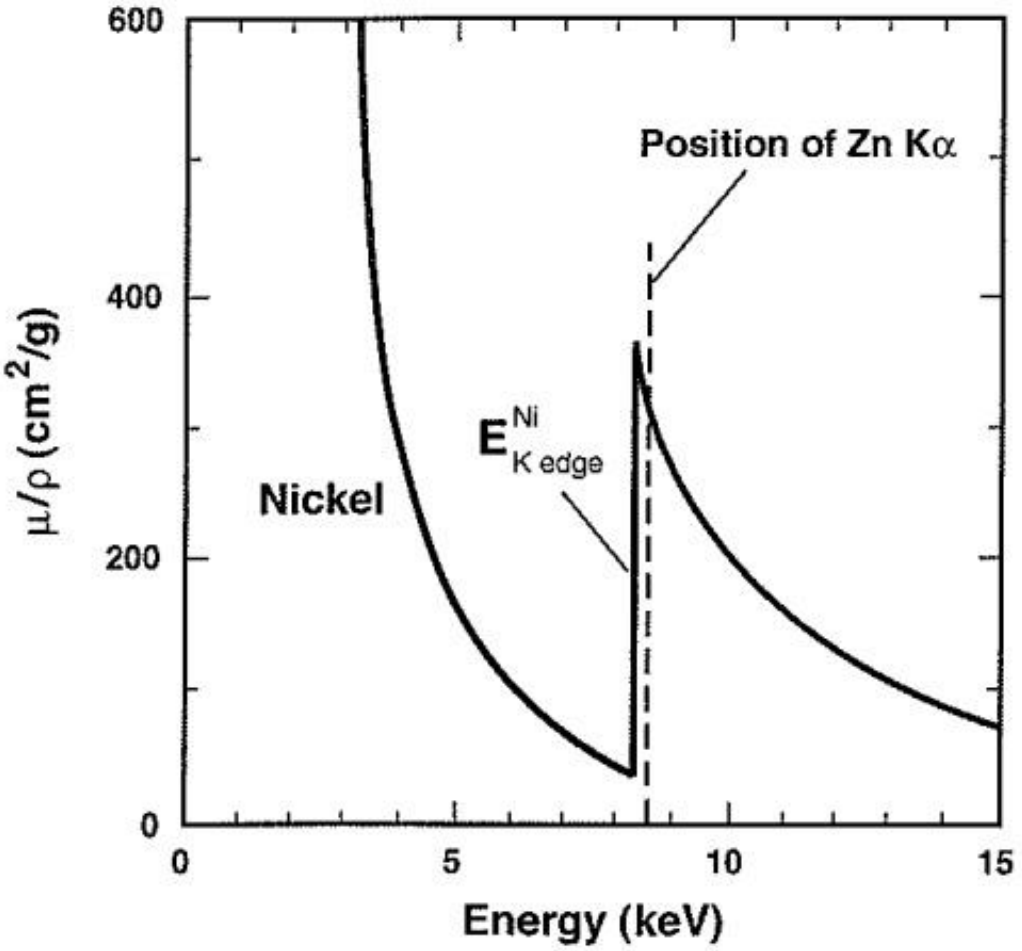
$$\left(\frac{\mu}{\rho}\right) = K Z^4 \left(\frac{1}{E}\right)^3$$

but with sharp jumps for energy just above Ec of absorber shells





X-ray absorbtion



For Zn in Ni –
as Zn Kα has energy a bit higher as Ni K absorbtion edge - thus it can eject electrons from K Ni shell (fluorescence) and it is strongly absorbed.

X-ray fluorescence

= X-ray induced emission of X-rays

- Consequence of X-ray absorption
- Photons with energy higher than Ec for a x-line can ionize atom and as a result a new photon can be emitted with Ex

- If primary photon is a part of characteristic X-ray radiation -> characteristic fluorescence – it is significant only if the primary photon energy is up to 3 keV higher
- If primary photon is a part o braking radiation -> continuum fluorescence – the extra intensity range is about several %

What does the “apparatus” really do?

A. An e-beam of chosen energy scans a selected zone and the detector collects the emitted photons, analyzes their energy and creates a spectrum

B. software analyze the peak positions and proposes possible element lines – the operator verifies them and verifies possible artifacts of measurement

   A+B – *qualitative analysis*

C. software subtracts the spectrum background and calculate peak areas - I_i - very often automatically, but we can control it

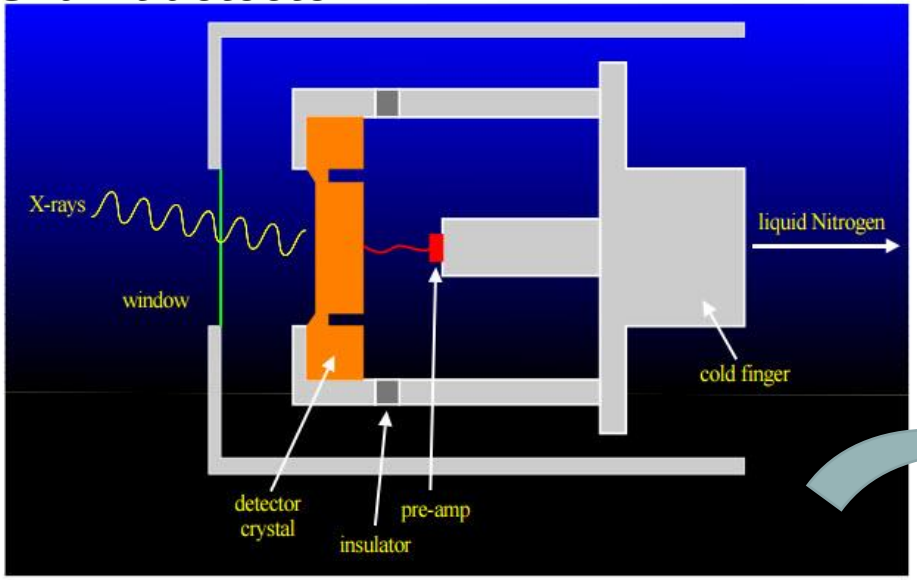
D. It calculates k-factor $k = {}^{I_i}/_{I_{(i)}}$ for each found element

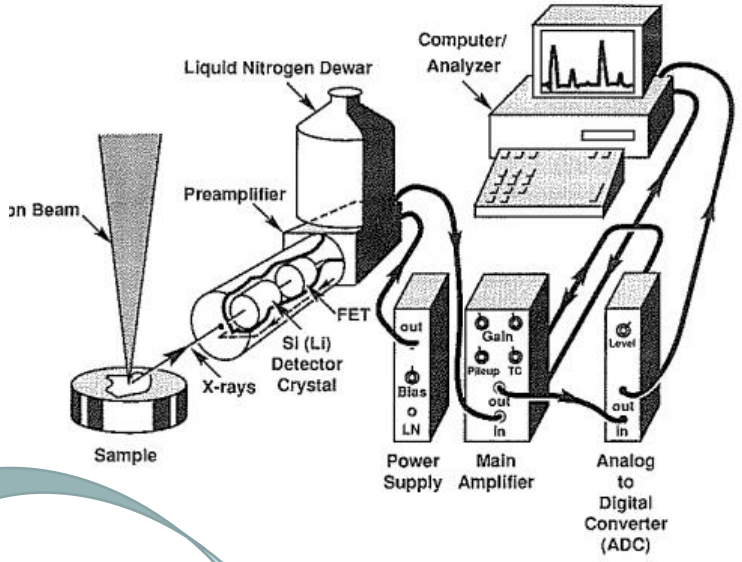
E. By iterative process it re-calculates composition considering different physically based corrections and normalizes the composition to 100%

   C - E – *quantitative analysis*

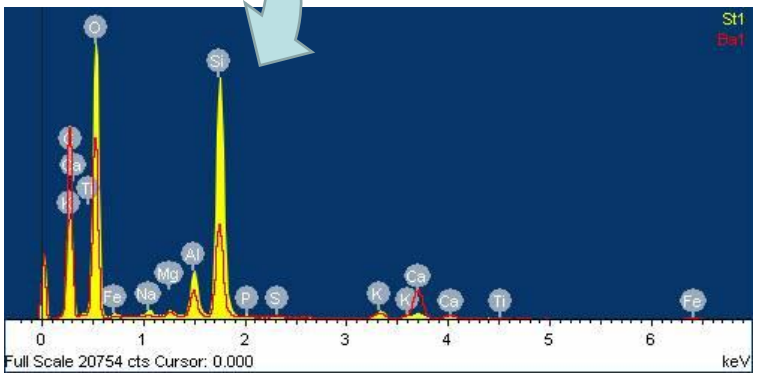
A. Spectrum acquirement

Si drift detector





X-ray photon -> photoelectron -> voltage pulse proportional to the photon energy -> **histogram of intensity by voltage** in counter and computer = spectrum – intensity [Cps – counts per second] dependance on energy [keV]



Spectral artifacts from detection process

- **Peak broadening** – natural width of x-ray peaks – FWHM 2-10 eV (dependant on energy) –> modern detector resolution of about 120-130 eV for Mn Kα (at 5.9 keV) – due to statistic character of detection
- **Peak distortion** – deviation from Gaussian shape and background increasing at energies below the peaks
- **"Sum" or "coincidence" or "pileup" peaks** with the sum energy (e.g. 2Kα) + background deformation => (decrease of X-ray signal by decreasing of e. beam current or increasing of detector distance or change of time constant)

real time = dead time + live time

Dead time – characterise the detection process – for quantification it is necessary to use similar conditions, thus the best value for any used equipment is estimated (e.g. 30-33% UMMS)

B. Qualitative analysis

- What do I want to analyze? Presence of major and minor elements
- Measuring conditions – voltage (appropriate overvoltage), current, process time, dead time
- Verifying of measured peaks (Presence of line families!!)
- Removing of spectra artifacts
- Only statistically significant peaks

  $P > 3 (N_B)^{1/2}$

  P – peak, N_B – background at peak energy
- Possible additive measurements if peak overlapping (change of voltage, process time, WDS, ...)

C. Quantitative analysis

- What do I want to measure?
- First – accurate qualitative analysis !
- Peak overlapping - deconvolution
- Background subtraction (modeling, filtering, interpolation or extrapolation from background near the peak)

Only 1.68 wt% of Mn in a steel

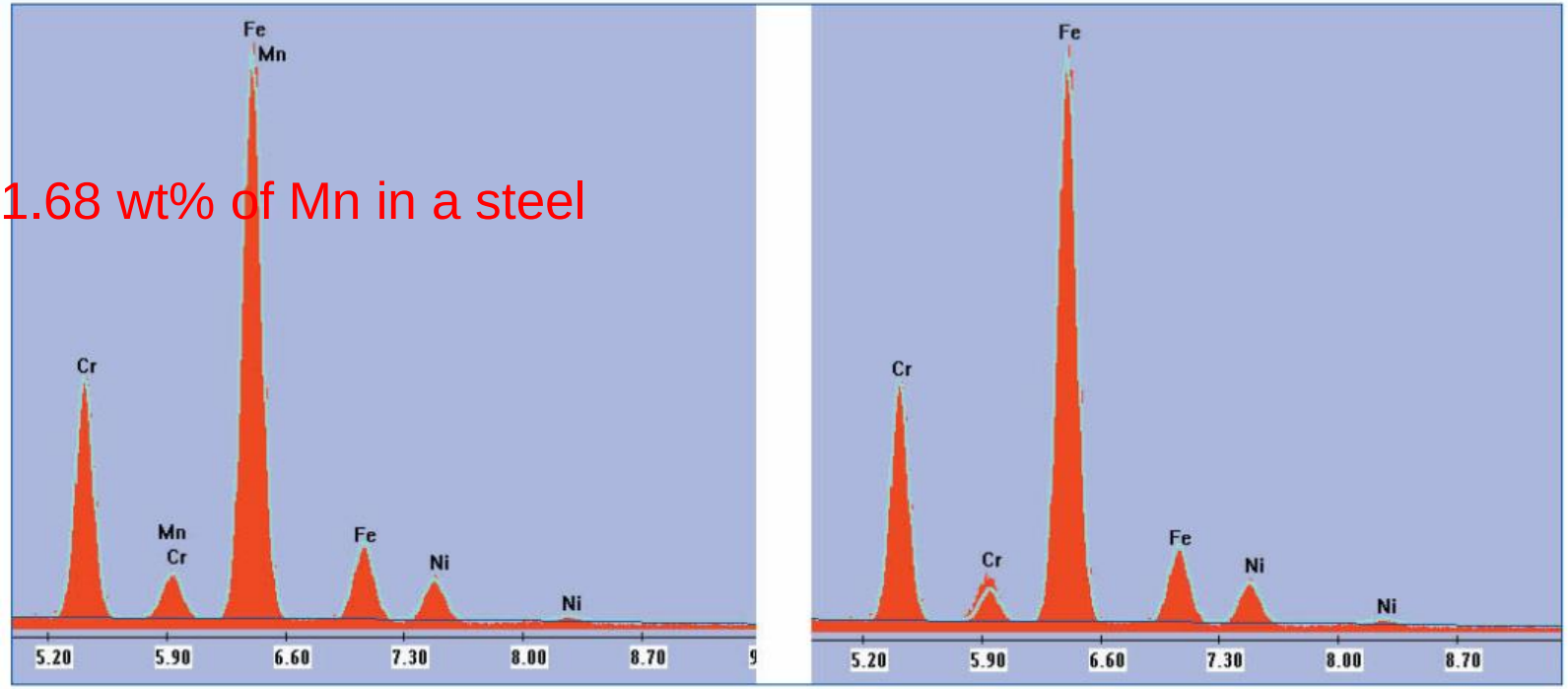


Figure 3 shows the correct and incorrect identification for the Cr and Mn overlap in stainless steel.

D. Quantitative analysis

- k - factors $k = {I_i}/{I_{(i)}} = {C_i}/{C_{(i)}}$

Castaing´s first approximation to quantitative analysis

I_i is measured “i“ peak intensity without background

$I_{(i)}$ is standard “i“ peak intensity without background

C_i is weight fraction of i-th element in the sample

$C_{(i)}$ is weight fraction of i-th element in the standard

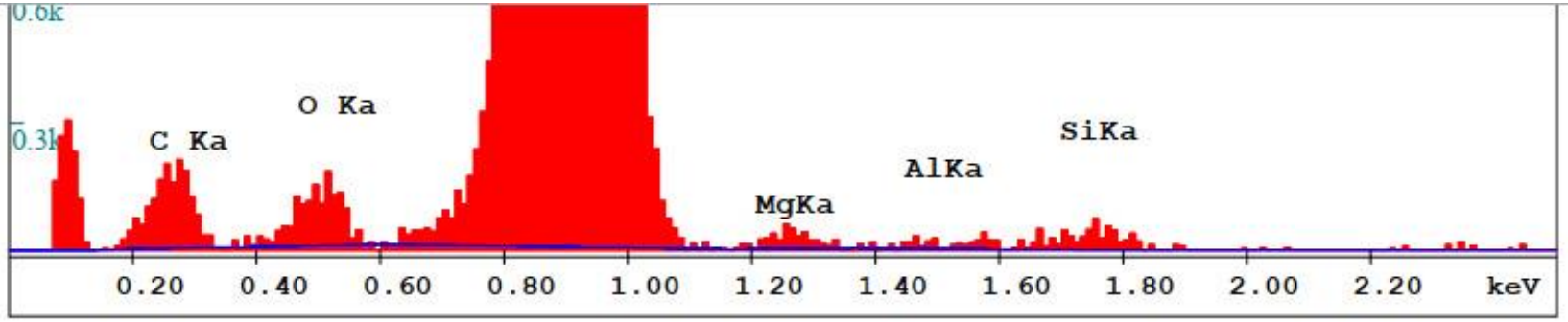
E. Matrix effect correction

Matrix effect can be divided into 3 effects:

- atomic number Z_i
- x-ray absorption A_i
- x-ray fluorescence F_i

$$C_i/C_{(i)} = [ZAF]_i \cdot I_i/I_{(i)} = [ZAF]_i \cdot k$$

ZAF correction



EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
C K	1.64	7.91	0.0110	1.3756	0.4867	1.0001
O K	0.60	2.17	0.0065	1.3494	0.8084	1.0016
CuL	97.40	89.04	0.9619	0.9891	0.9985	1.0000
MgK	0.37	0.88	0.0035	1.2489	0.7526	1.0000
Total	100.00	100.00				

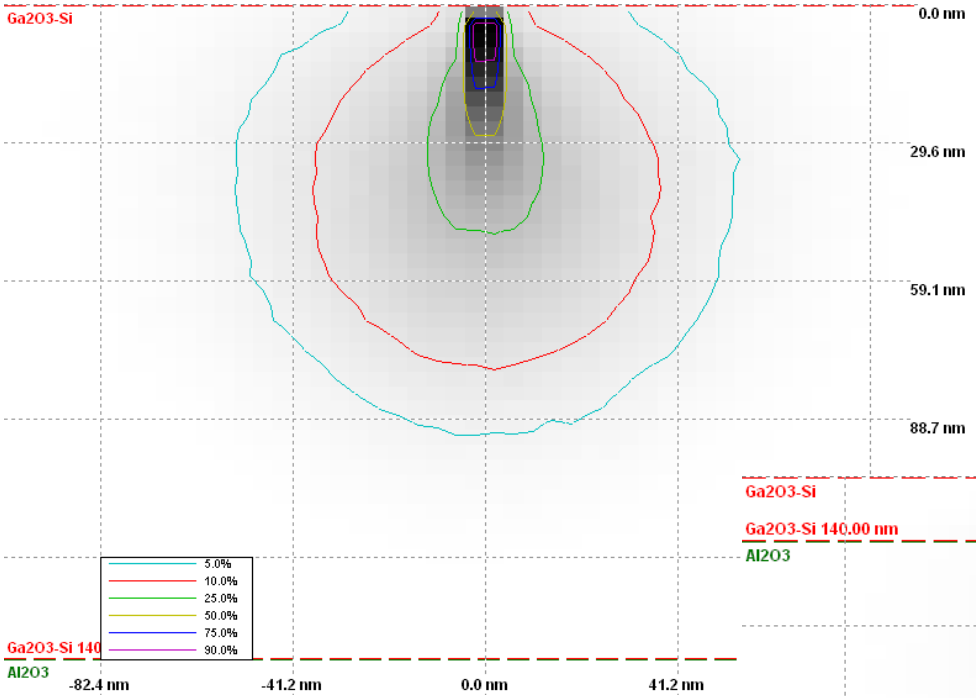
Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	2.78	0.09	2.93	32.63
O K	1.98	0.20	3.68	10.07
CuL	163.02	0.15	0.37	1120.45
MgK	0.70	0.06	6.18	10.72

C-D-E. Quantitative analysis

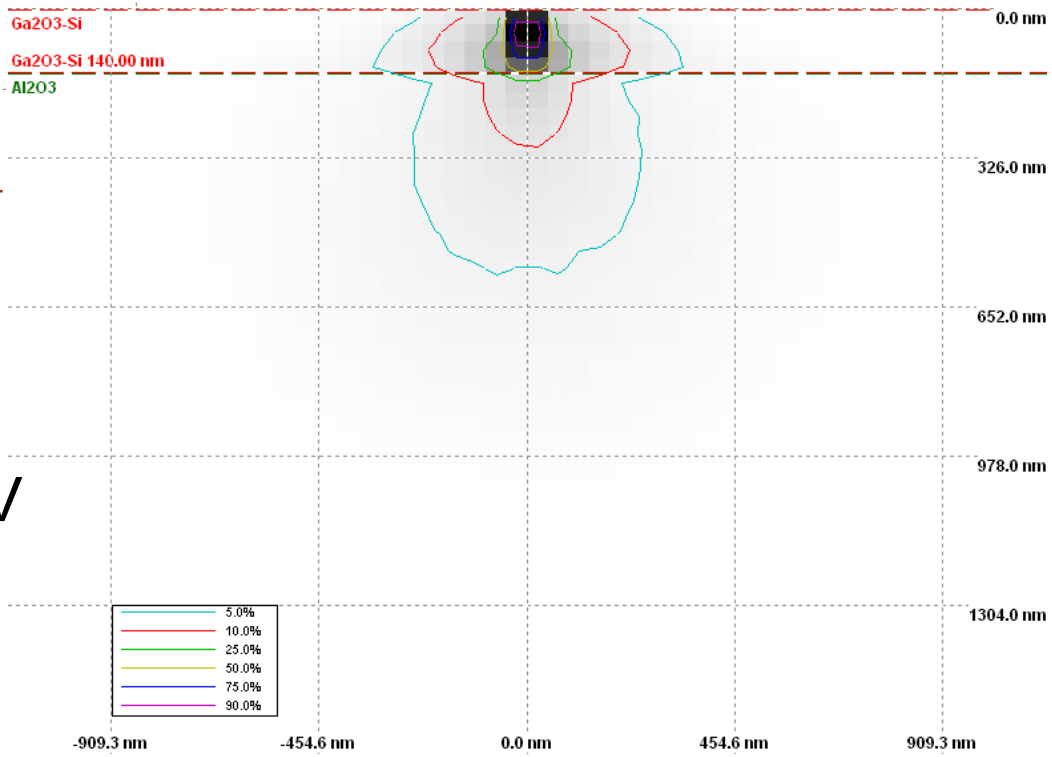
- Remember that the quantification routine is designed based on the three assumptions of microanalysis:

1. The sample is smooth and polished.
2. The sample is homogeneous (minimally in the actual information volume).
3. The sample is infinitely thick to the electron beam.

=> “Bulk method”



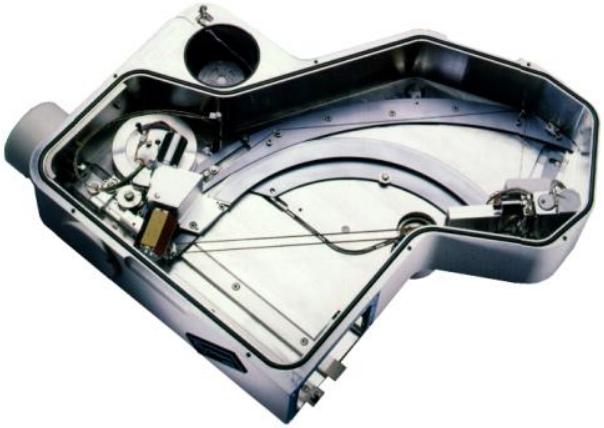
4 keV el. beam

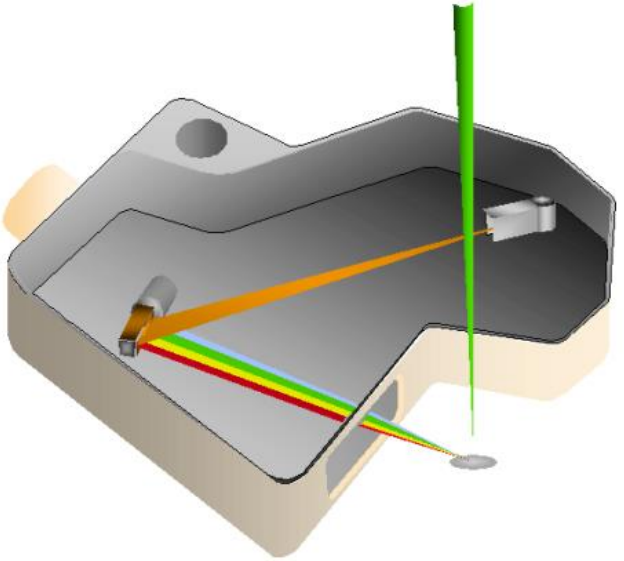


10 keV

Ga_2O_3(140 nm) on Al_2O_3 substrate

WDS



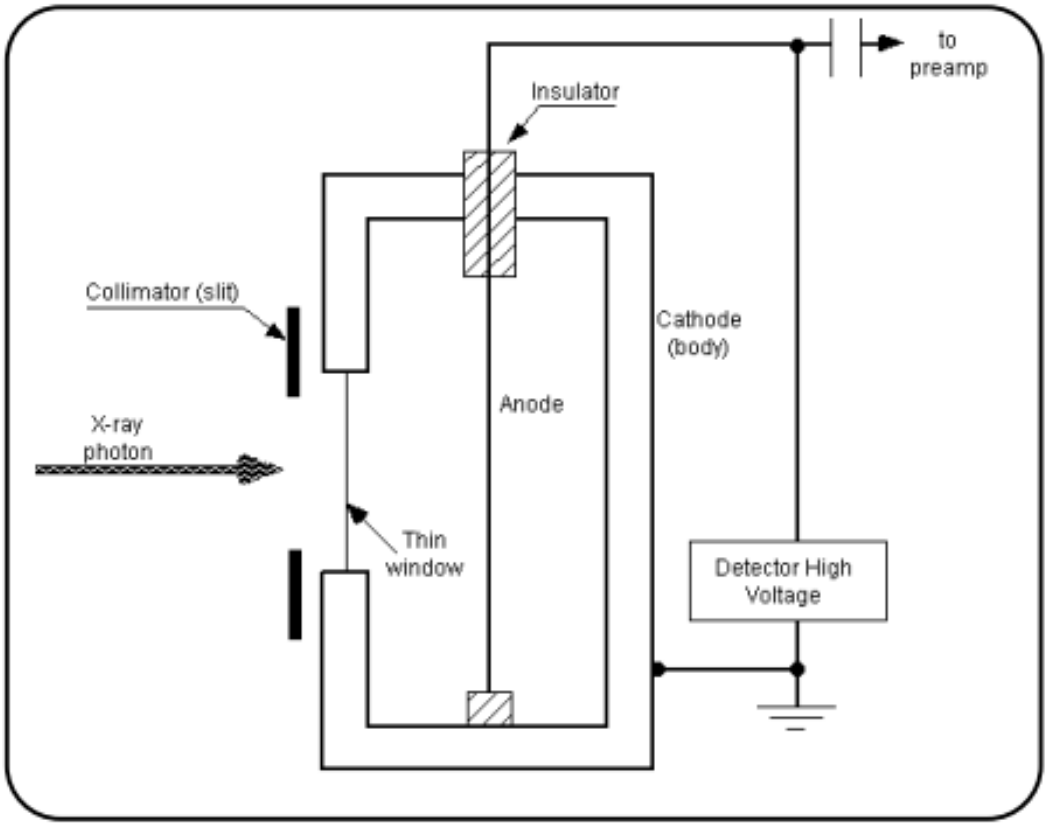


- The same physical concept based on characteristic X-ray detection
- the measured X-rays are selected by diffraction on build-in crystals to measure signal intensity with high energy resolution of 2 – 40 eV (120-130 eV for EDS)
- Gas proportional counter is used as detector of X-rays without artifacts present in semiconducting EDS detectors.

WDS – X-ray signal detection

gas proportional counter

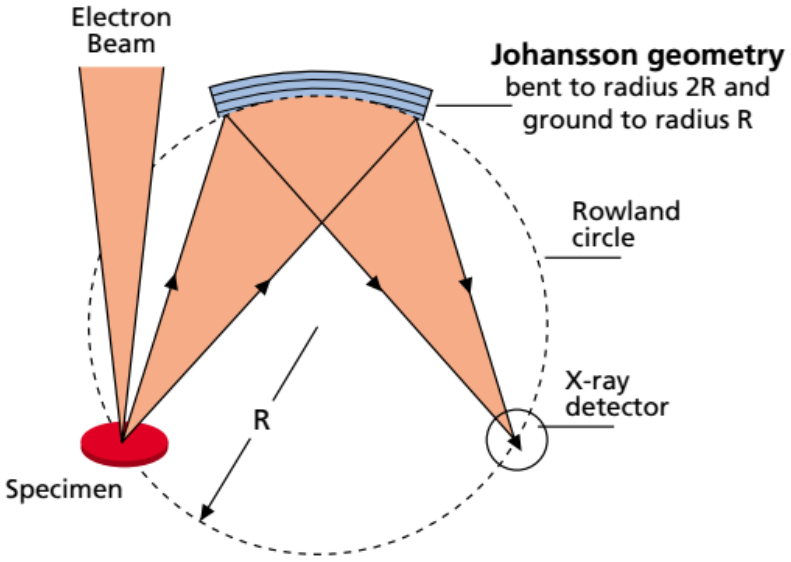
- Excelent dynamic range
  0 – 50000 cps or more
- Wide range of energies
- High collection efficiency



Diffraction on crystals

$$E = hF = \frac{hc}{\lambda}$$

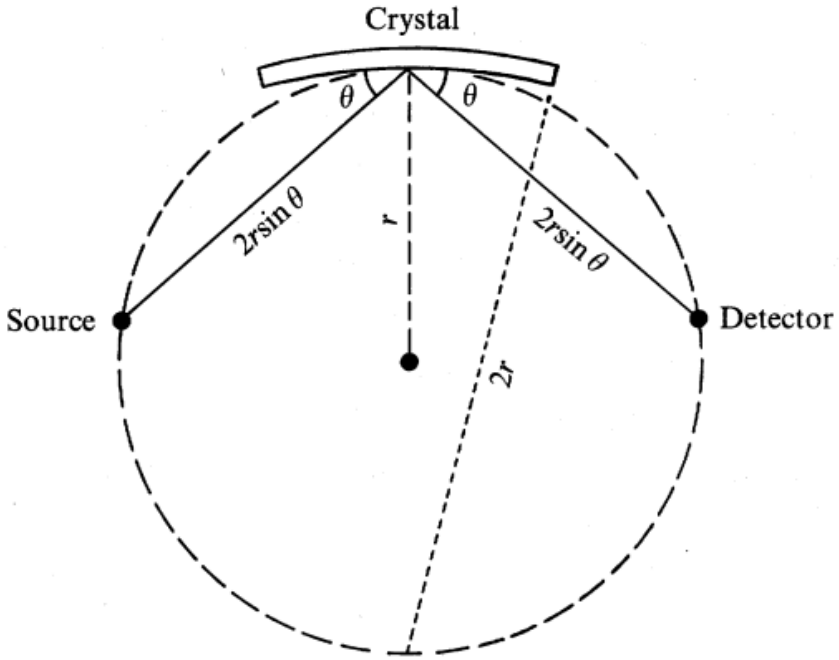
E - the energy of the radiation
F is the frequency of the radiation
c is the speed of light
λ is the wavelength of the radiation
h is Planck's constant



Bragg condition

$$n\lambda = 2d \sin\theta$$

d – the interplanar distance



Variation of λ by variation of θ and d

Crystals for WDS

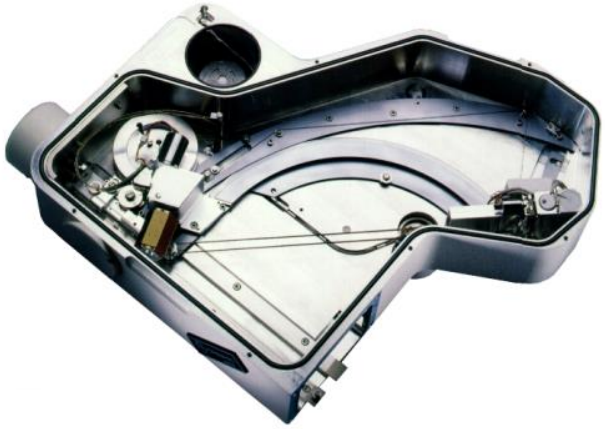
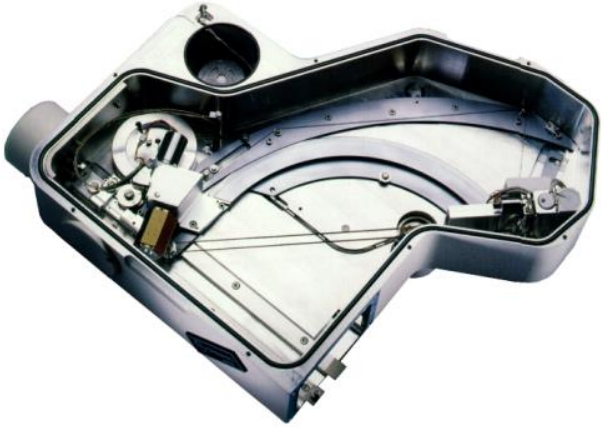
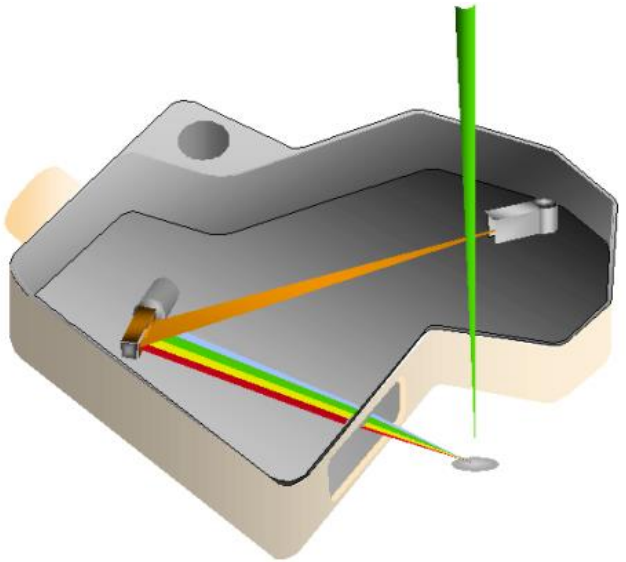


Table of guaranteed specifications for all crystals

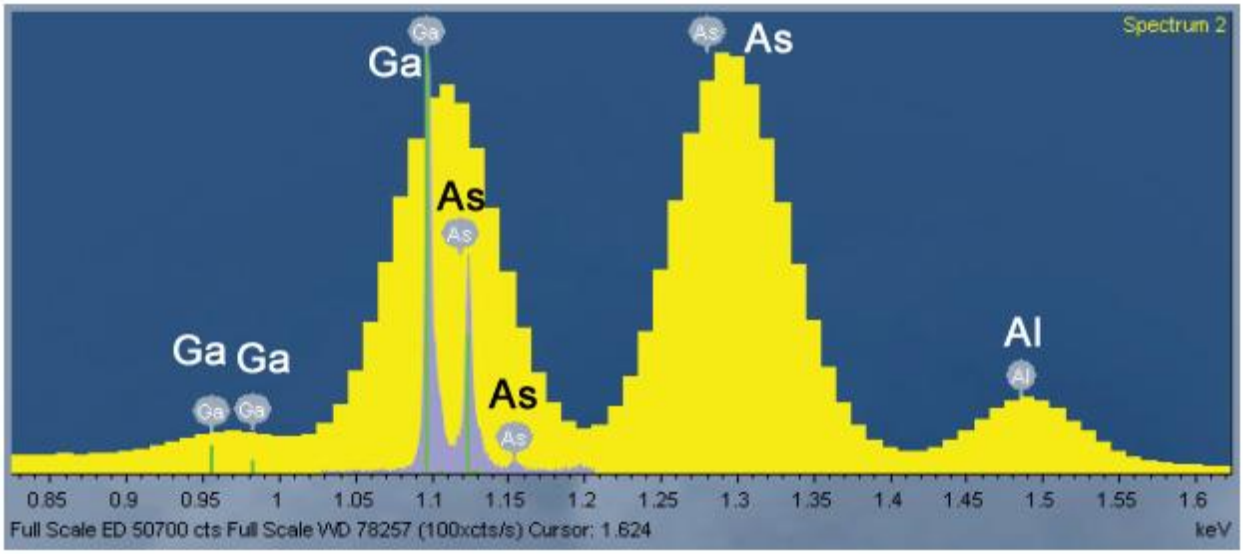
crystal	*spectral line*	*wavelength nm*	*elemental standard*	*kV, detector type*	*resolution eV **	*peak intensity cps/µA*	*p/b*	*sensitivity ppm*
LSM-200	Be Kα	11.4	Be	10, FPC	8	2.4×10^4	40	335
LSM-200	B Kα	6.76	B	10, FPC	15	9.0×10^5	30	63
LSM-80N	B Kα	6.76	B	10, FPC	9	5.7×10^4	60	180
LSM-80N	C Kα	4.47	Vitreous C	10, FPC	14	4.7×10^5	50	68
LSM-80N	N Kα	3.16	BN	10, FPC	16	9.5×10^3	3	1950
LSM-80N	O Kα	2.36	SiO_2	10, FPC	17	1.1×10^5	50	140
LSM-80E	C Kα	4.47	Vitreous C	10, FPC	14	1.3×10^5	57	120
LSM-80E	N Kα	3.16	BN	10, FPC	16	3.4×10^4	13	495
LSM-60	C Kα	4.47	Vitreous C	10, FPC	12	3.2×10^4	70	220
LSM-60	N Kα	3.16	BN	10, FPC	13	5.0×10^3	10	1500
LSM-60	O Kα	2.36	SiO_2	10, FPC	15	1.0×10^5	65	130
TAP	O Kα	2.36	SiO_2	10, FPC	3	5.4×10^3	350	240
TAP	Al Kα	0.834	Al	20, FPC	9	2.7×10^6	800	7
PET	Si Kα	0.7126	Si	20, FPC	2	5.4×10^5	2600	9
PET	Ti Kα	0.2750	Ti	30, FPC/SPC	20	2.7×10^6	500	9
LiF(200)	Fe Kα	0.1937	Fe	30, FPC/SPC	25	1.0×10^6	525	15
LiF(200)	Cu Kα	0.1542	Cu	30, FPC/SPC	40	1.1×10^6	315	18
LiF(220)	Cu Kα	0.1542	Cu	30, FPC/SPC	35	3.0×10^5	400	30
LiF(220)	Ge Kα	0.1255	Ge	30, FPC/SPC	48	3.7×10^5	210	37

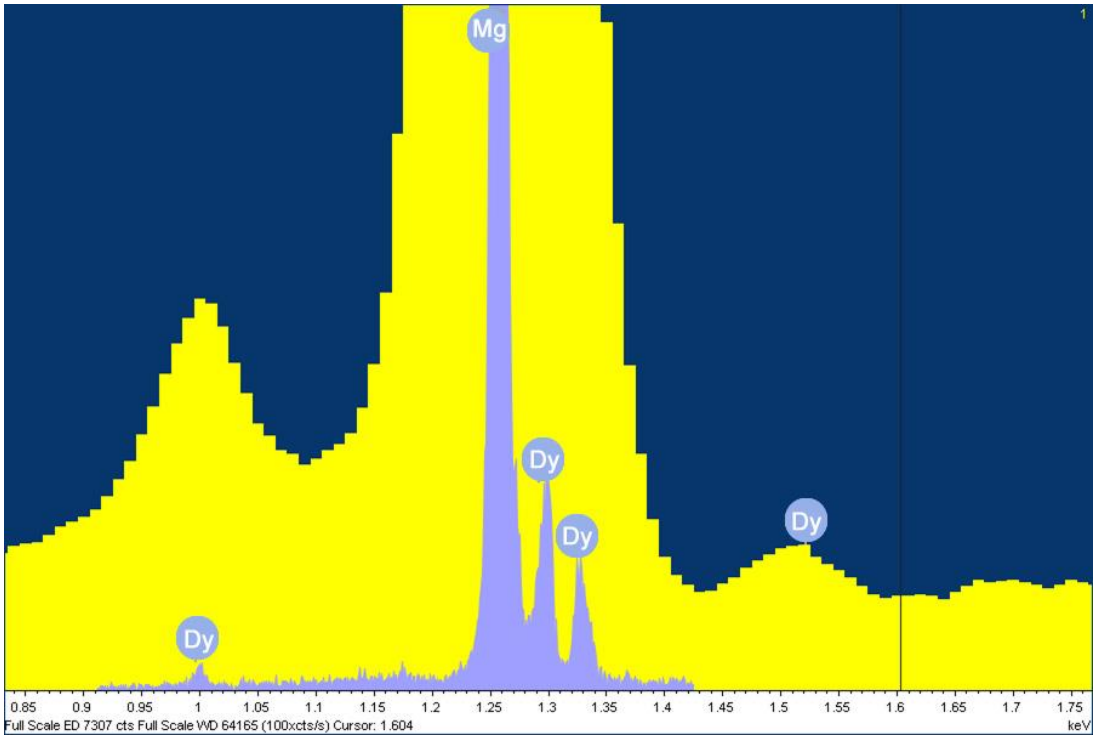
WDS

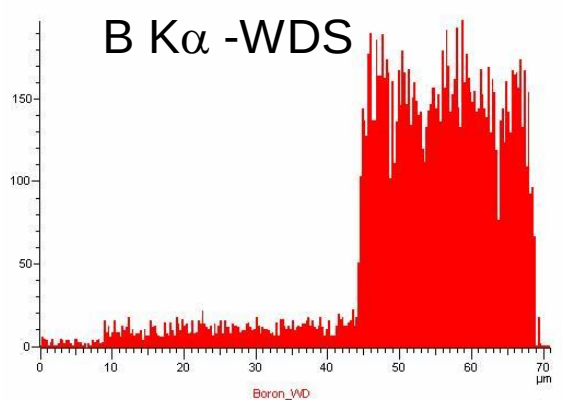


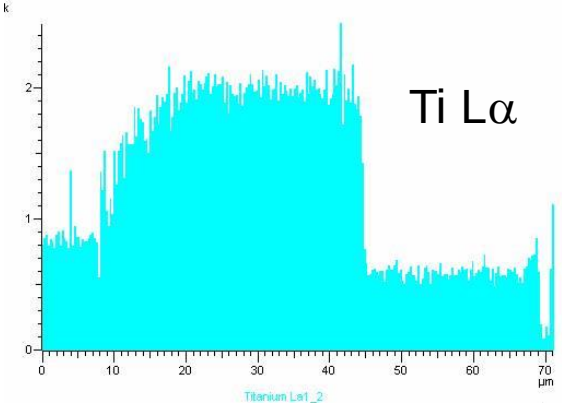


- detects only one energy X-rays in the time
- different signal detection – gas proportional counter
- high energy resolution 2 – 40 eV – peak separation!!
- high count rate capability without compromising energy resolution
- Need of standards for every measured element !!!!!
- time consuming, more complicated
- it has significantly better sensitivity of 100 – 10 ppm

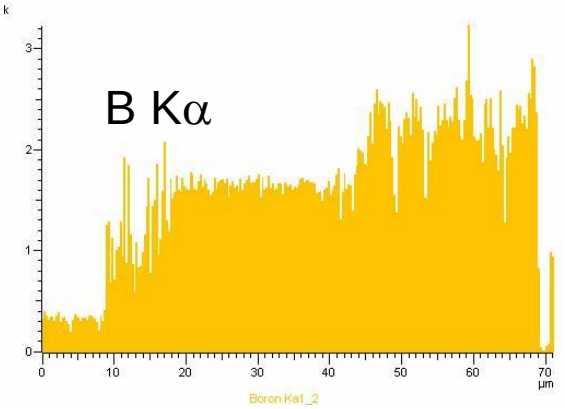

Spectrum 2
Ga
Ga
As
As
As
Ga Ga
As
Al
0.85 0.9 0.95 1 1.05 1.1 1.15 1.2 1.25 1.3 1.35 1.4 1.45 1.5 1.55 1.6
Full Scale ED 50700 cts Full Scale WD 78257 (100xcts/s) Cursor: 1.624
keV

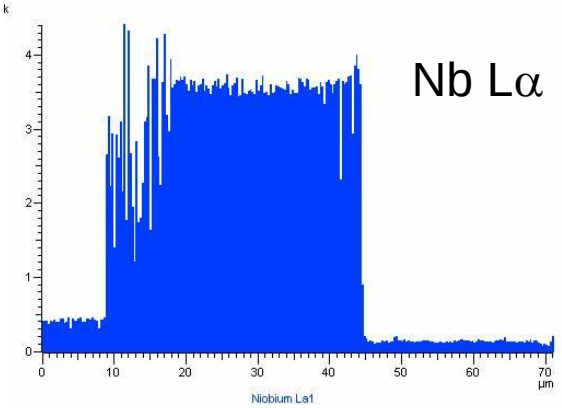

1
Mg
Dy
Dy
Dy
Dy
0.85 0.9 0.95 1 1.05 1.1 1.15 1.2 1.25 1.3 1.35 1.4 1.45 1.5 1.55 1.6 1.65 1.7 1.75
Full Scale ED 7307 cts Full Scale WD 64165 (100xcts/s) Cursor: 1.604
keV

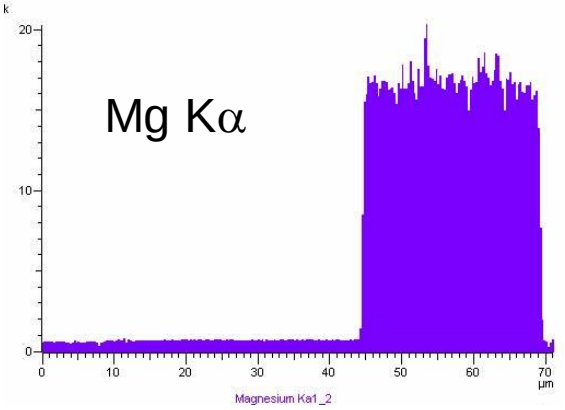

B Kα -WDS
Boron_WD
µm

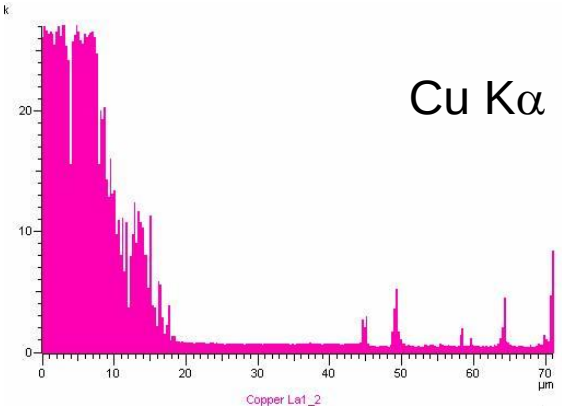

Ti Lα
Titanium La1_2
µm

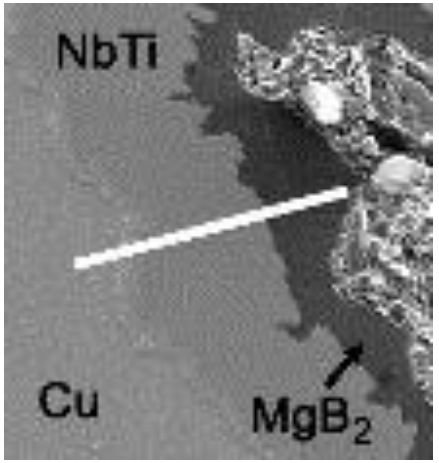
MgB_2/NbTi/Cu

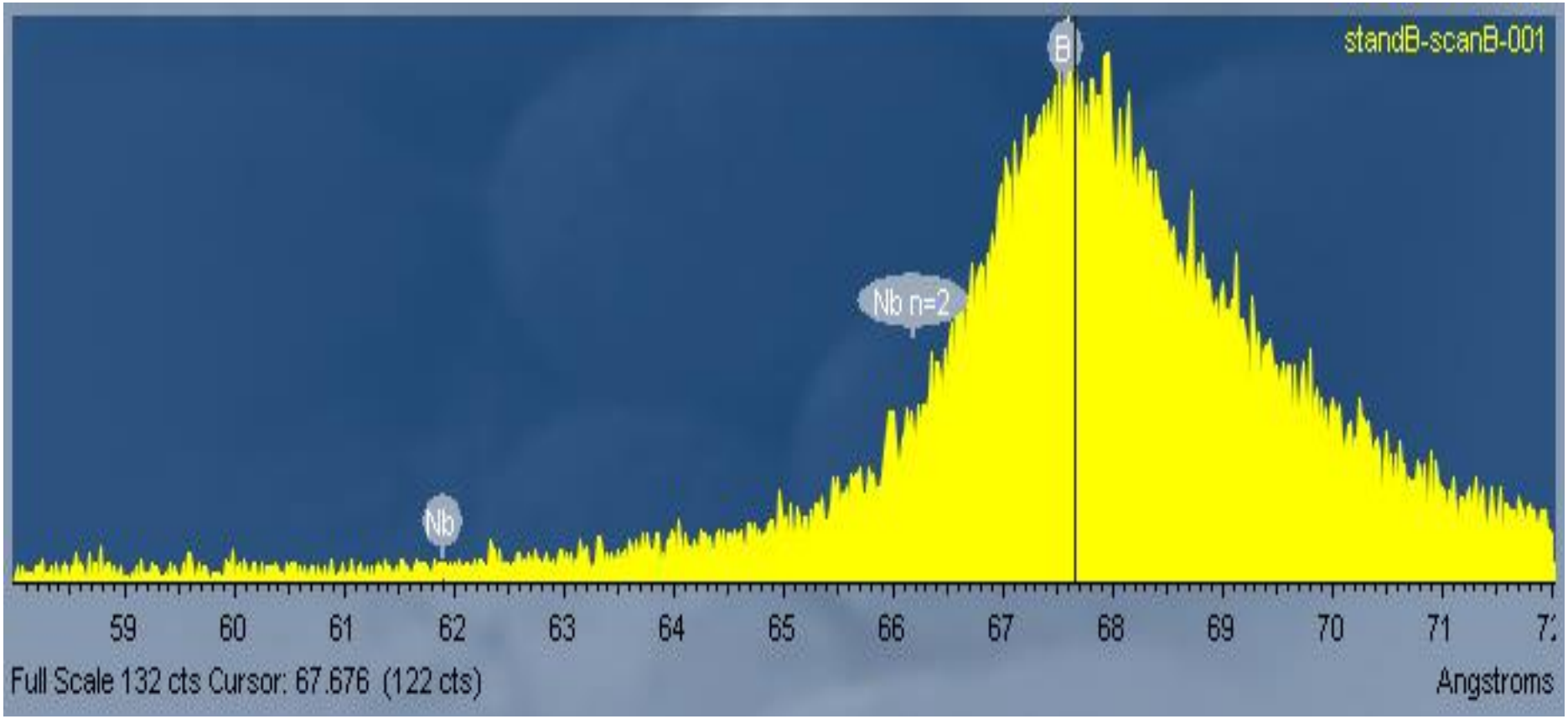

B Kα
Boron Ka1_2
µm


Nb Lα
Niobium La1
µm

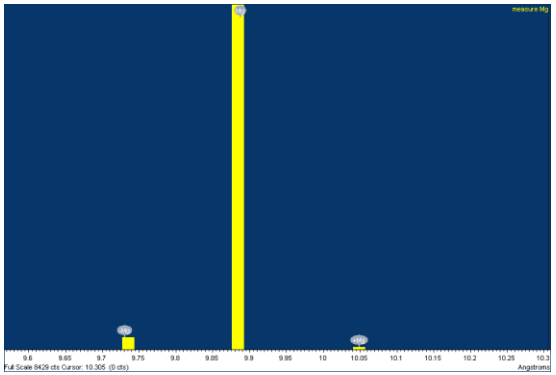

Mg Kα
Magnesium Ka1_2
µm

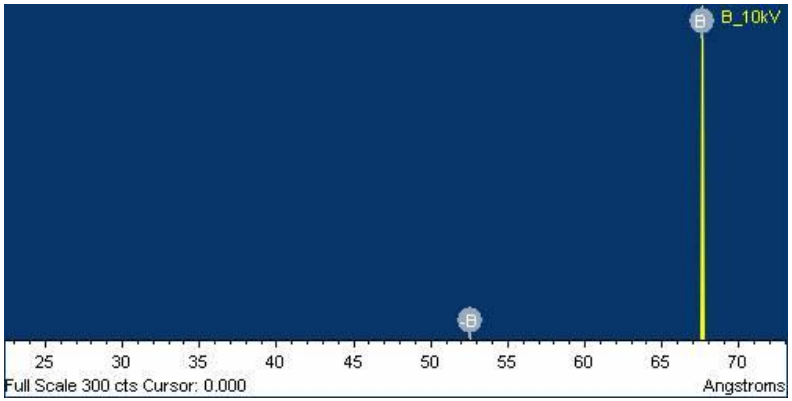

Cu Kα
Copper La1_2
µm

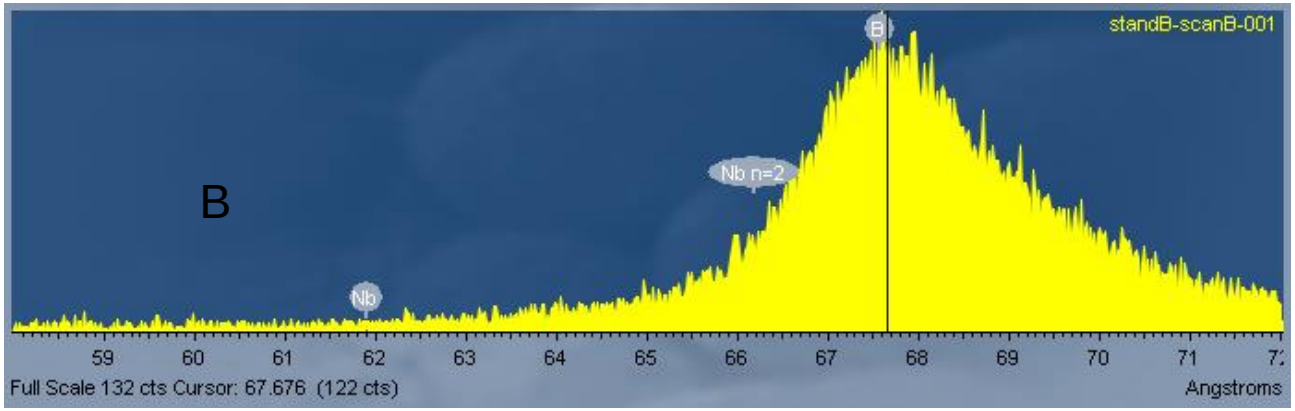

NbTi
Cu
MgB2

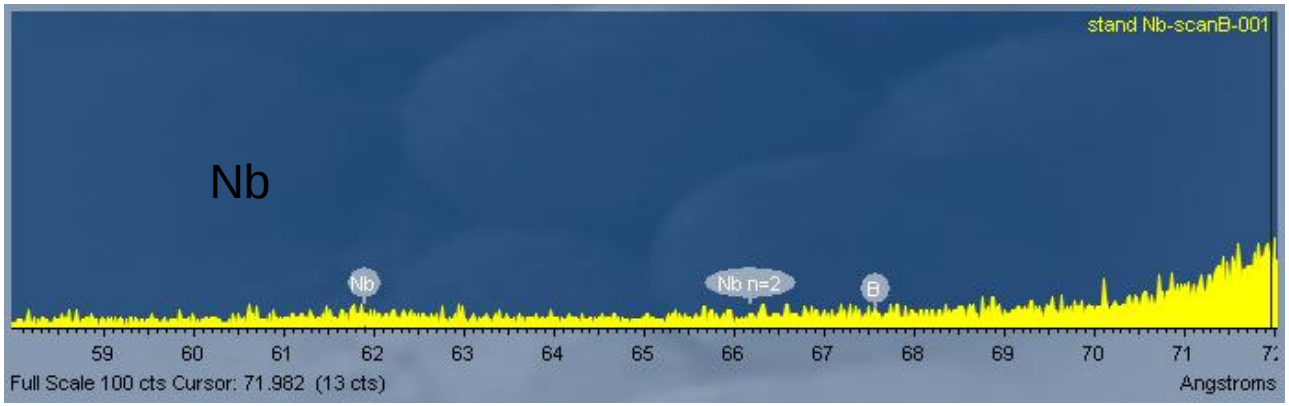


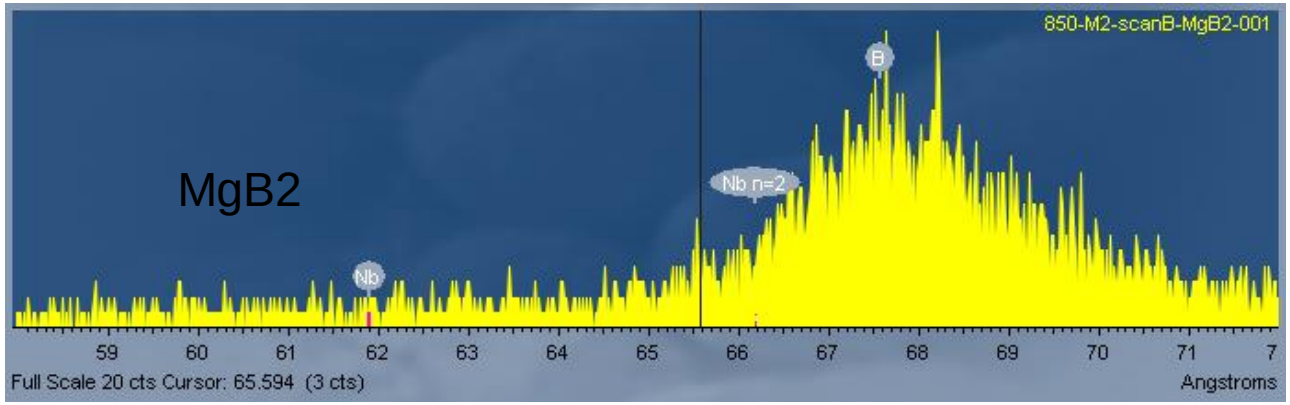
Line table editor






standB-scanB-001
B
Nb n=2
Nb
59 60 61 62 63 64 65 66 67 68 69 70 71
Full Scale 132 cts Cursor: 67.676 (122 cts)
Angstroms


stand Nb-scanB-001
Nb
Nb n=2
B
59 60 61 62 63 64 65 66 67 68 69 70 71
Full Scale 100 cts Cursor: 71.982 (13 cts)
Angstroms


850-M2-scanB-MgB2-001
MgB2
B
Nb n=2
Nb
59 60 61 62 63 64 65 66 67 68 69 70 71
Full Scale 20 cts Cursor: 65.594 (3 cts)
Angstroms

EDS X WDS

EDS

- Complete spectrum of energies is acquired – and stored - simultaneously
- Complete spectra are stored – appropriate for later re-calculation or an element searching without measurement
- Low energy resolution – some combination of elements are difficult to recognize (Mo-S, Nb-B, ...)
- Data collection quick and analysis relatively simple – ideal for qualitative and rapid quantitative analysis
- Sensitivity – several tenths of wt% - several 1000 ppm

WDS

- High energy resolution
- Ability to deal with higher count rates
- Sensitivity – typically of one to two order of magnitude lower concentration (100 – 10 ppm) – appropriate for trace analysis
- More complicated to set up, measure and more tedious to obtain results
- More expensive

Thank you for your attention

Any questions?