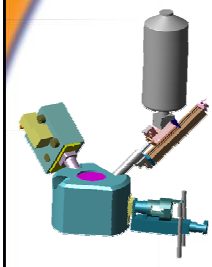
EDS introduction

Qualitative und quantitative Analysis on SEM



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GENESIS Program

Qualitative and quantitative Analysis with Matrix correction ZAF (PhiZAF, PhiRhoZ optional)	Collect SE / BSE-images, Analysis from selected areas and spot analysis	Qualitative and quantitative Element Maps, Linescans, drift correction
Spectrum	**Image**	**Maps/Line**

EDAX Genesis | Spectrum | Image | Maps/Line | Particles | Multi Point

Particles	**Multi Point**
Automated particle analysis Morphology and chemistry (optional)	Automatic measurement of different locations, mapping and linescans (optional)

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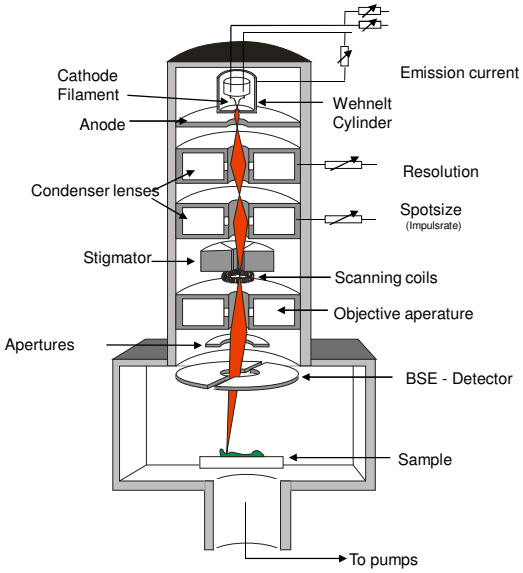
Scanning Electron Microscope (W)



Energy of electrons

$E=U \cdot e$

Beam current = number of electrons

$I = \frac{\Delta Q}{\Delta t}$

3

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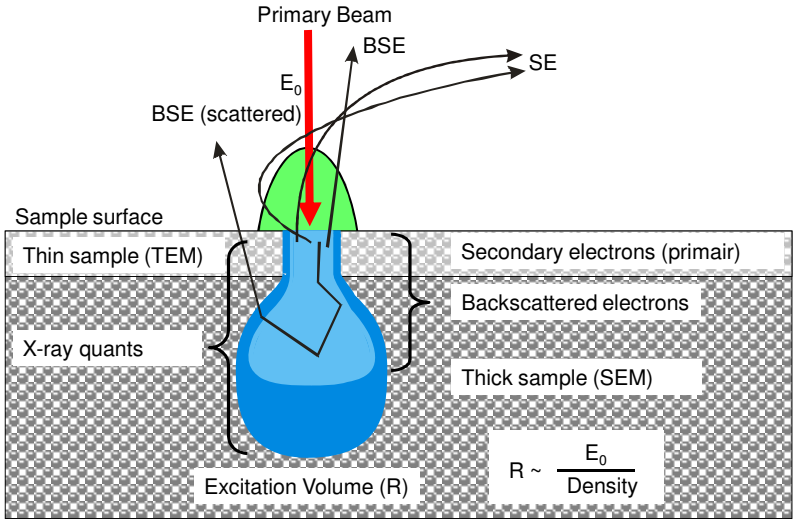
Interaction electrons and sample



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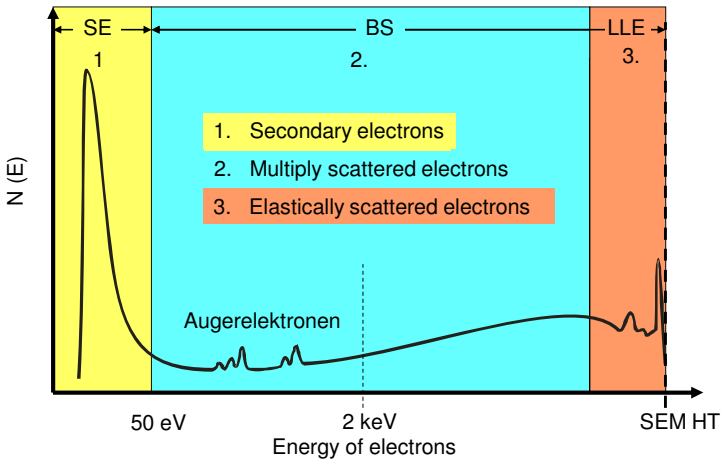
Energy distribution electrons



5

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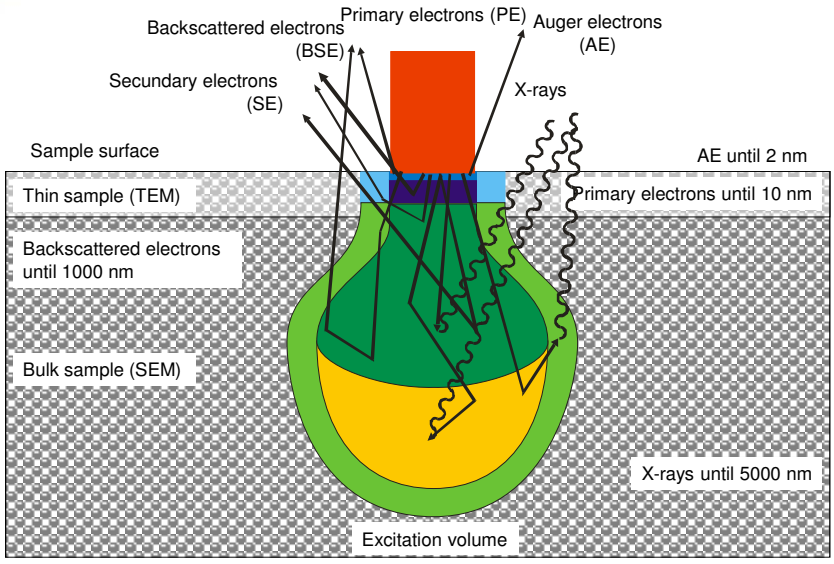
Excitation volume



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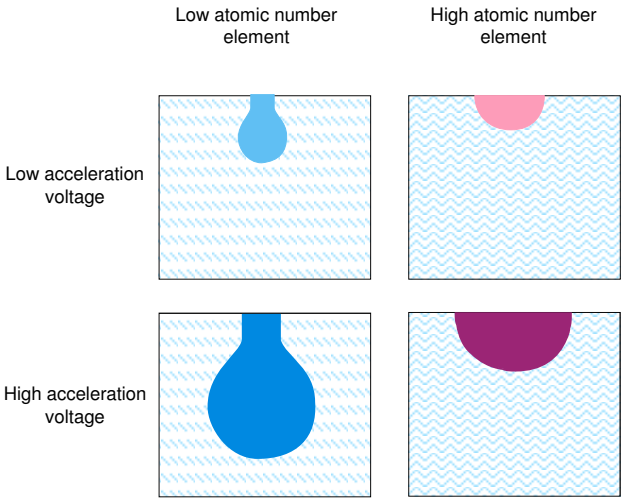
Sample-electron beam interaction



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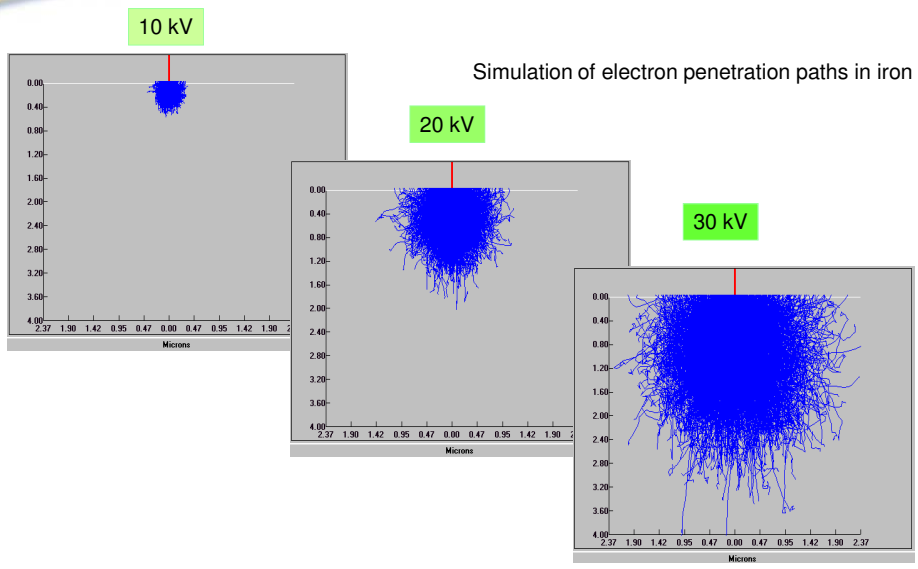
Electron Flight Simulator



Simulation of electron penetration paths in iron

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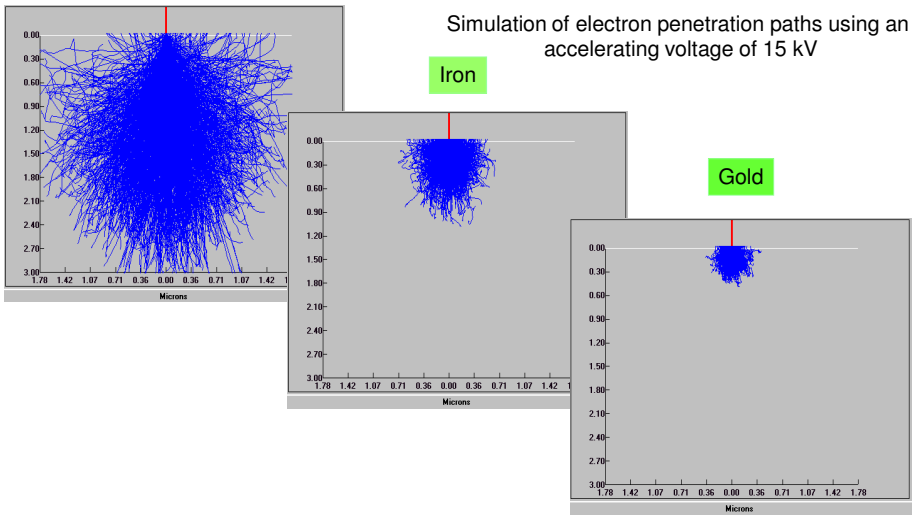
Electron Flight Simulator (continued)

Carbon

Iron

Gold

Simulation of electron penetration paths using an accelerating voltage of 15 kV



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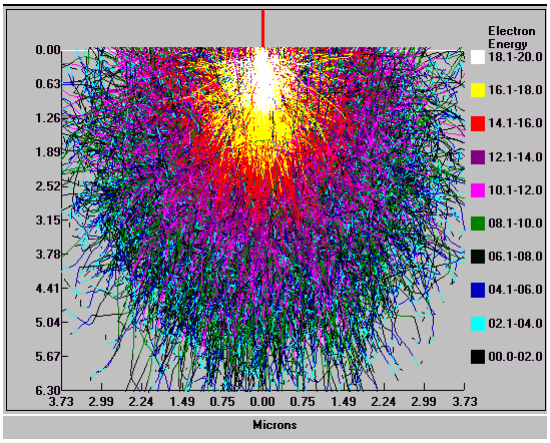
Electron Flight Simulator (continued)

Simulation of electron density
Energy of Electrons as function of SEM voltage used

$CaCO_3$



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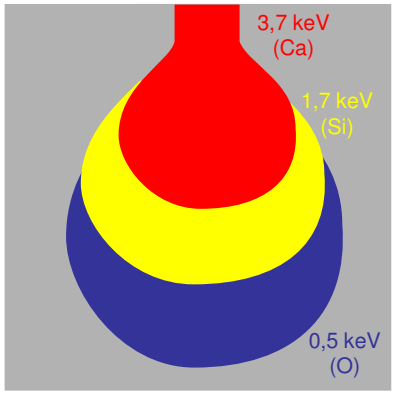
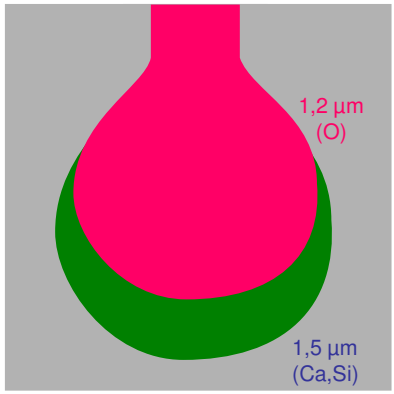
Interaction volume elements

$CaSiO_3$

Energy of electrons



Escape depth of X-rays



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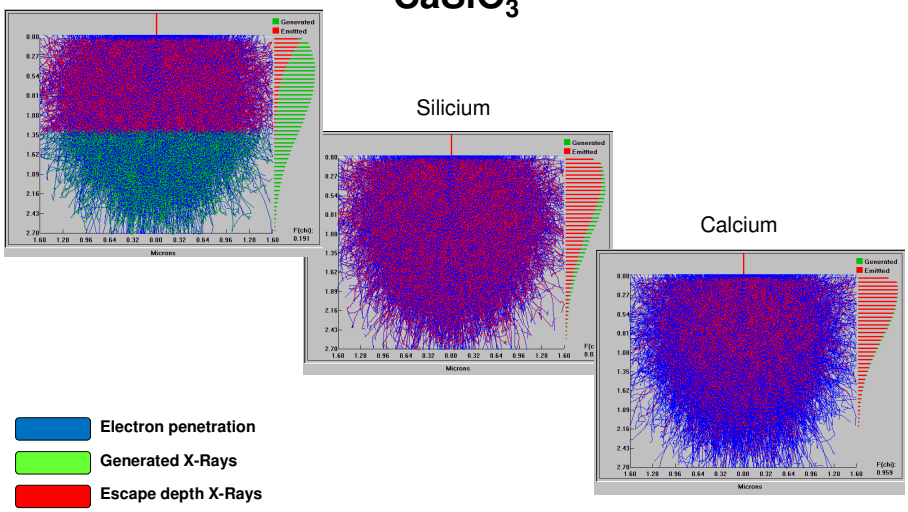
Interaction volume

Oxygen

$CaSiO_3$

Silicium

Calcium



Electron penetration

Generated X-Rays

Escape depth X-Rays

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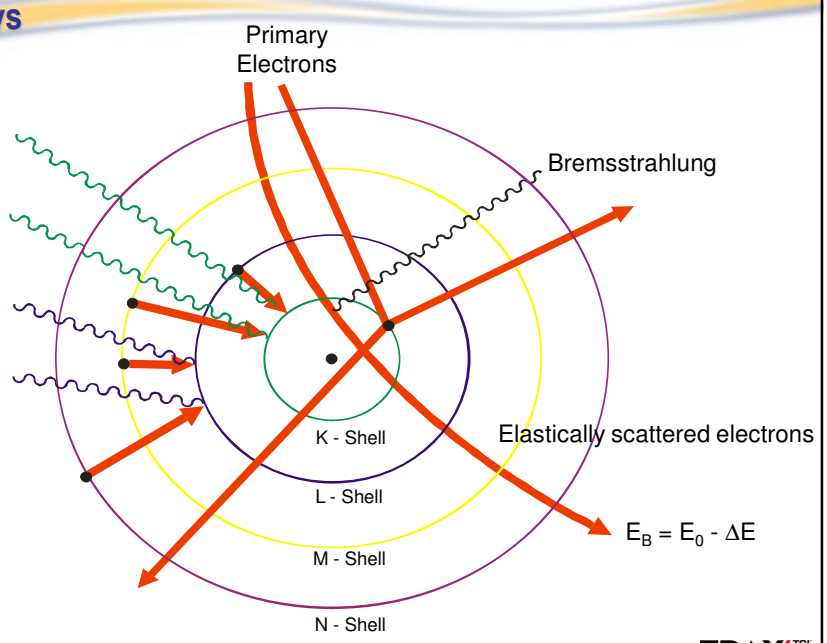
X-rays



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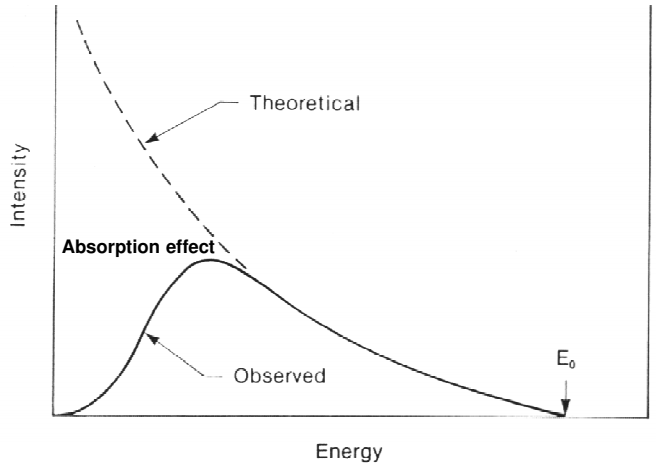
Background in EDS = Bremsstrahlung



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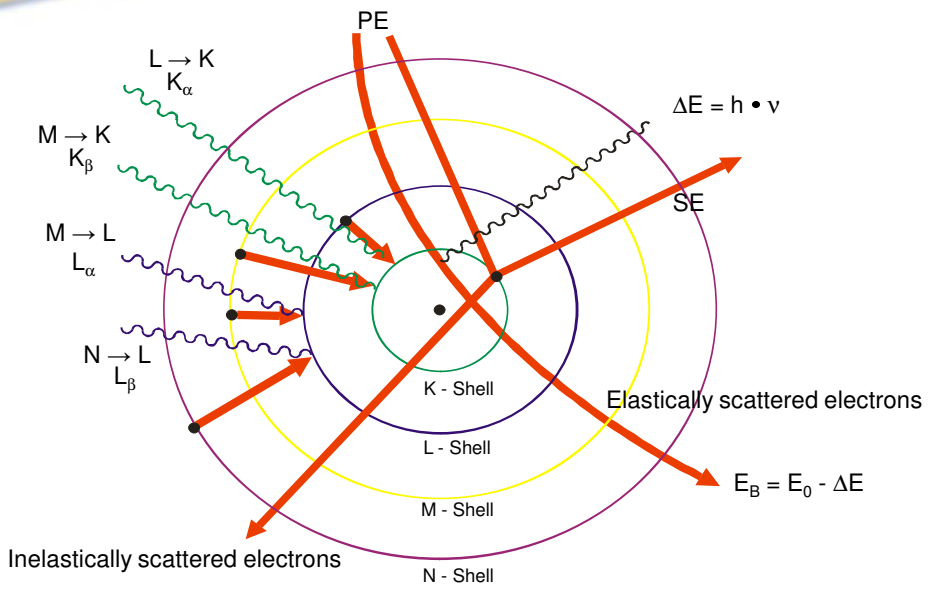
X-rays (continued)



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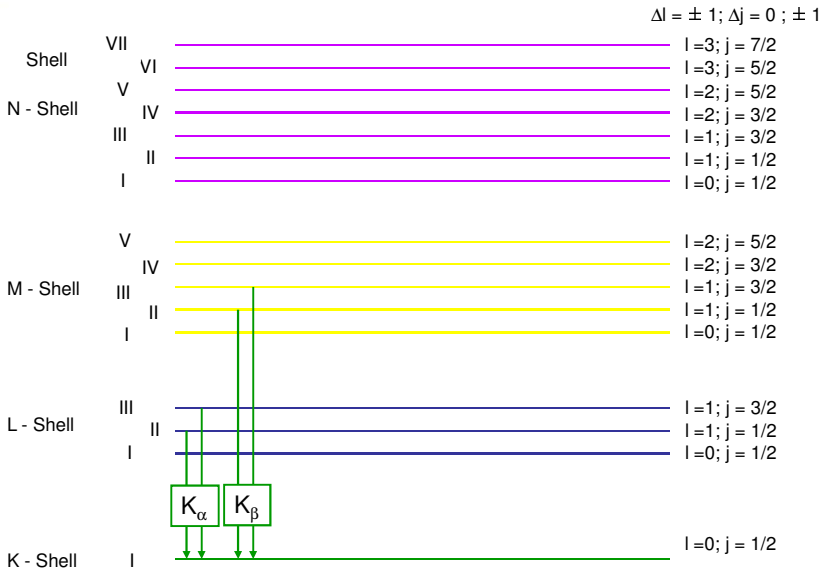
Emission lines



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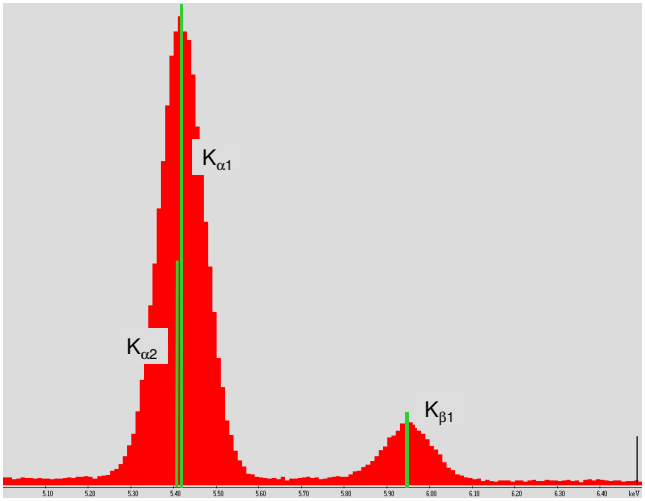
K – Lines



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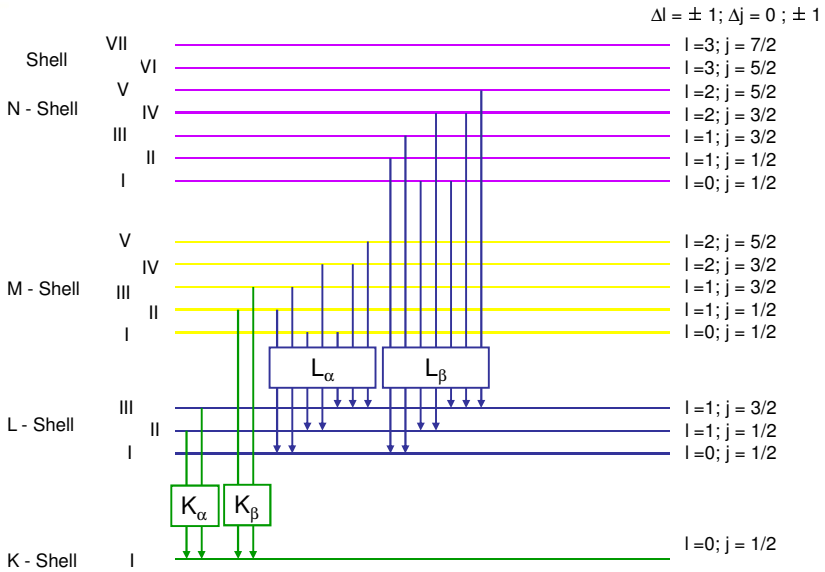
Emission lines (continued)



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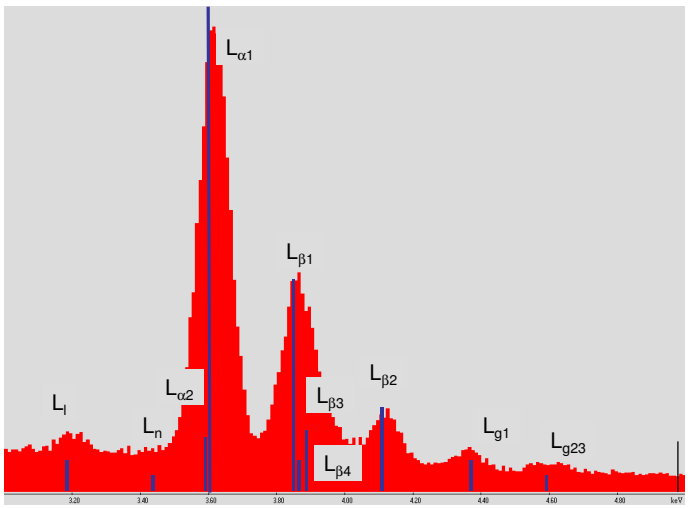
L – Line series



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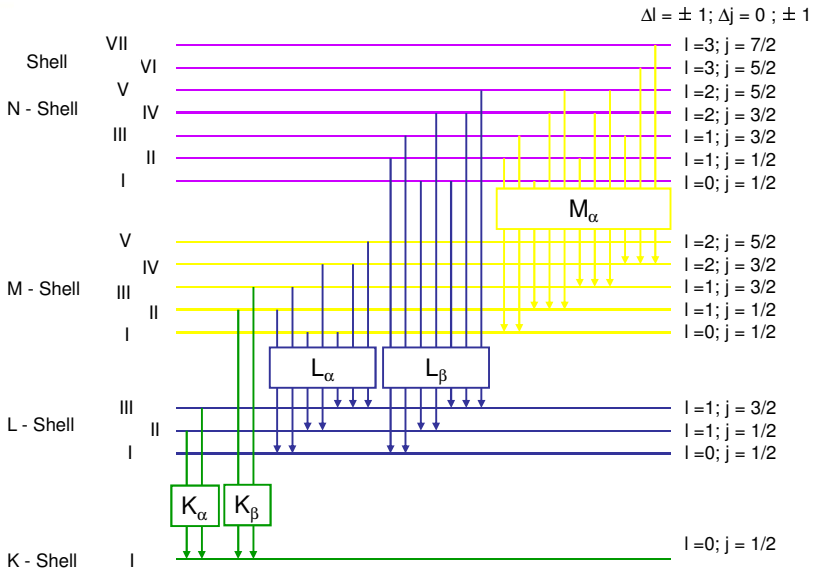
Emissions lines (complete picture)



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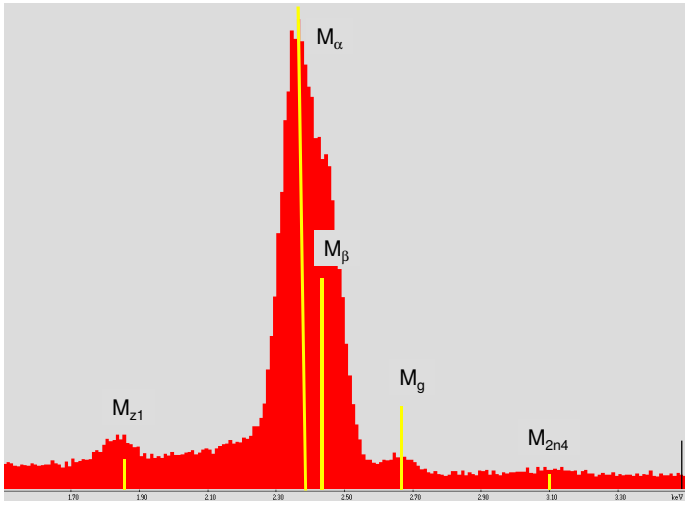
M – Line series



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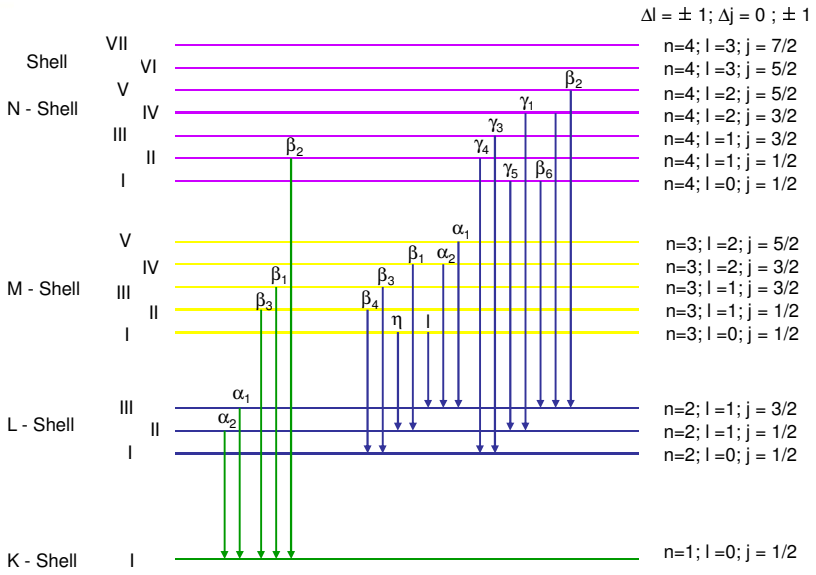
Term schema



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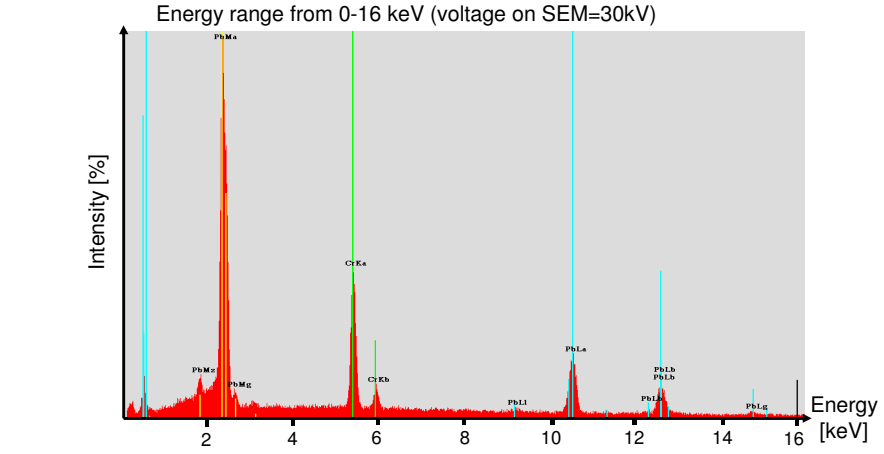
Overview X-ray lines



K - Lines:
Until atomic number 40 (Zr)

L – Lines:
Atomic number (Ga) until 80 (Hg)

M - Lines:
From atomic number > 55 (Ba)

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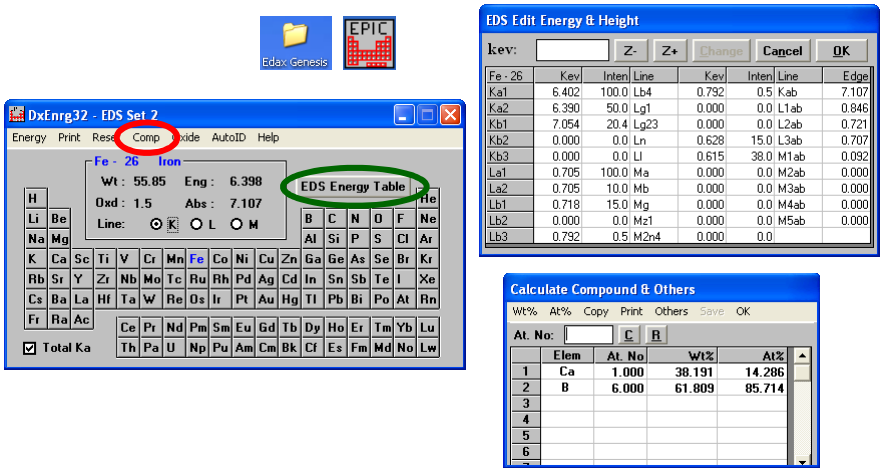
EPIC - Program



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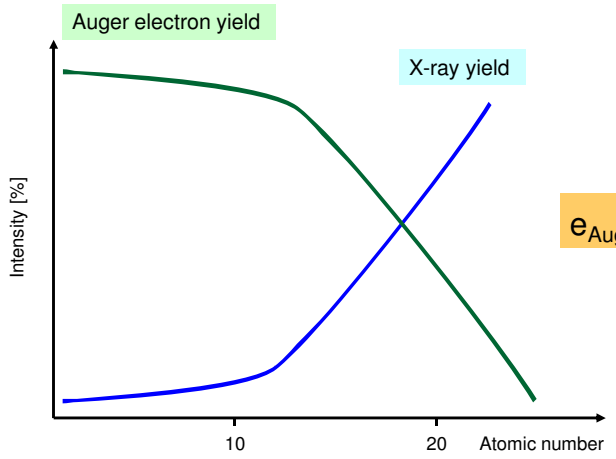
X-ray yields



$e_{Auger} + h\nu = 1$

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Accelerating Voltage

- Overvoltage = Voltage/Peak Energy
- Typically, the accelerating voltage should be 2-3 x the highest energy line and no more than 10 to 20 times the lowest energy line of interest.
- 10 times for Quantitative Analysis
- 20 times for Qualitative Analysis

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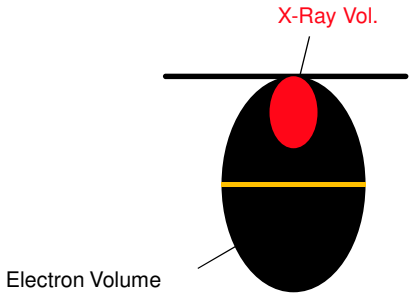
Why should the overvoltage be at least 2 for the highest energy element?

Lower overvoltage means a small, poorly excited peak and poor statistical quality in the spectrum



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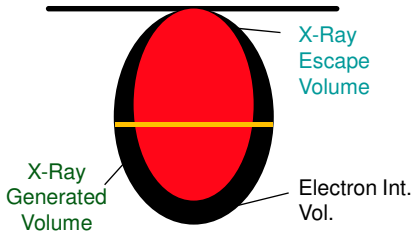
Why should the overvoltage be less than 10 to 20 times the lowest energy element?

High overvoltage means a high absorption condition and a small peak and poor statistics



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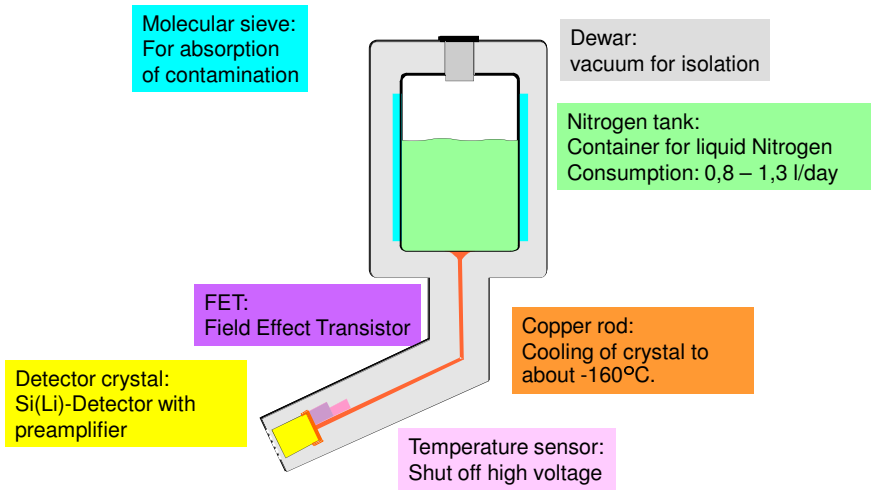
Build-up of EDAX - Detectors



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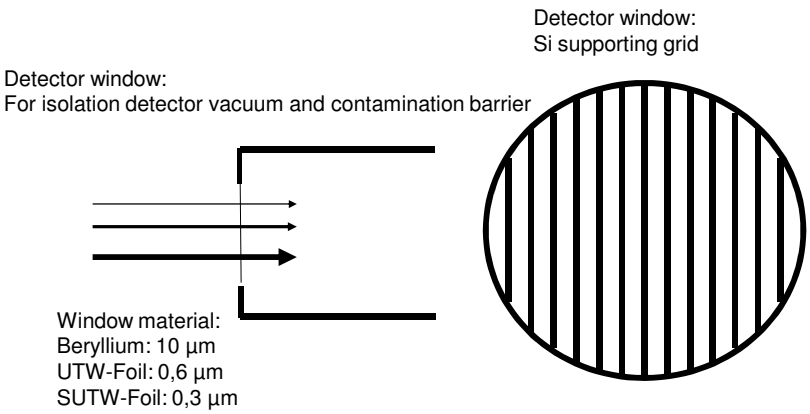
Detector window



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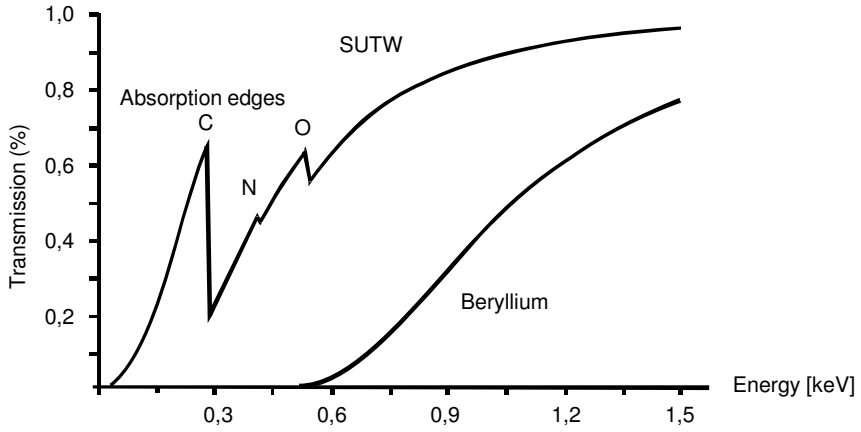
Transmission graphs (continued)



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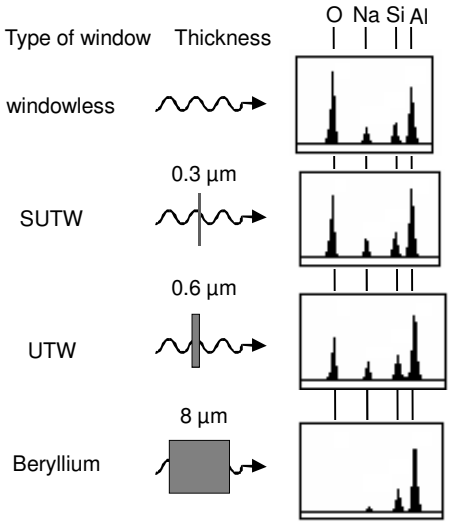
Properties different windows



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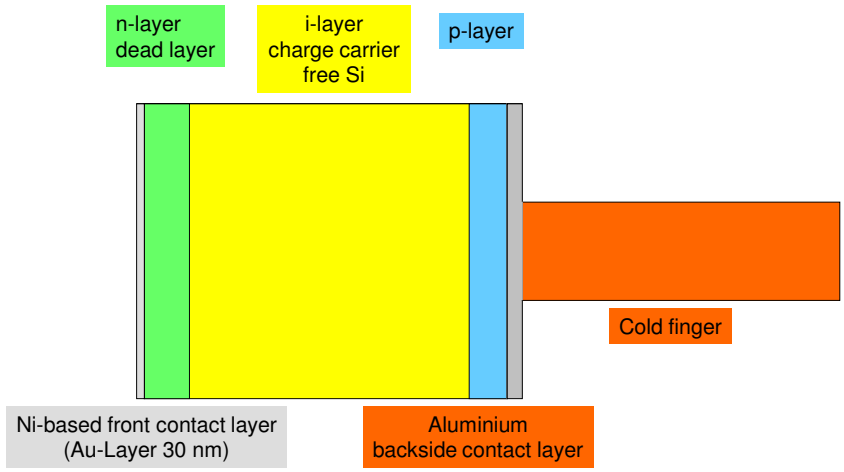
Si(Li) - Detector



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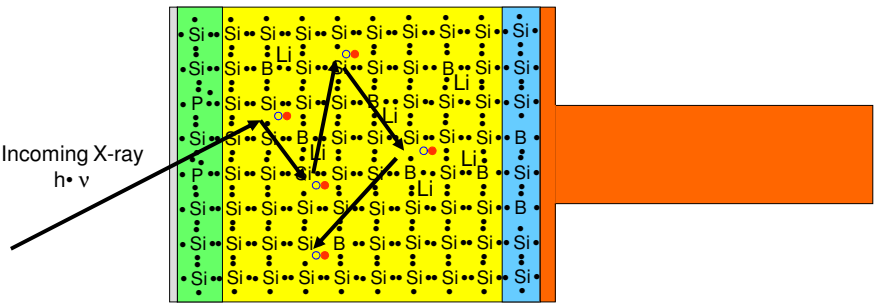
Si(Li) - Function

To create an e-/h+ pair e^- h^+ 3,8 eV

Ni Kα 7477 eV / 3,8 eV = 1968 electron-hole pairs



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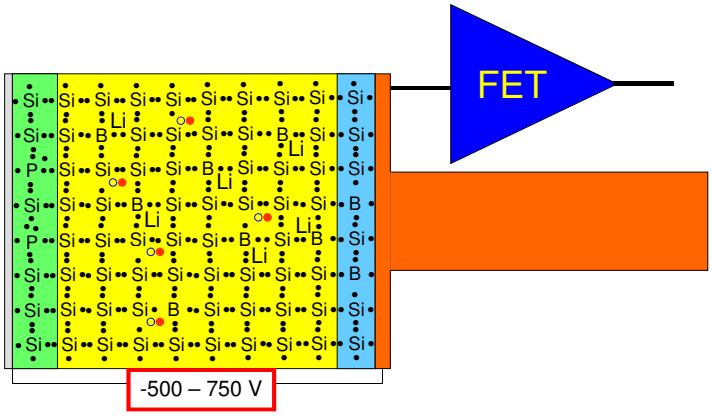
Si(Li) - Funktion



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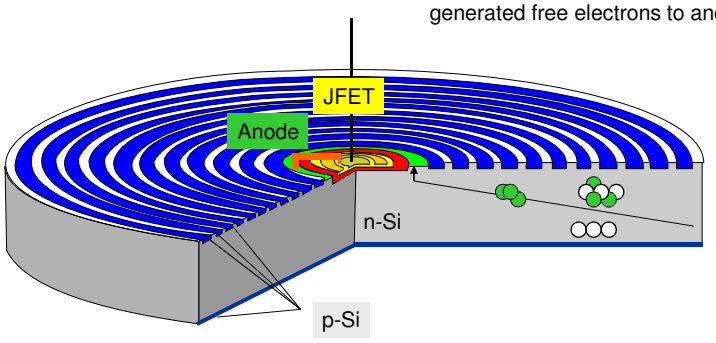
SDD - detector 1

- All rings have different voltage.
- This gradient across rings drives generated free electrons to anode



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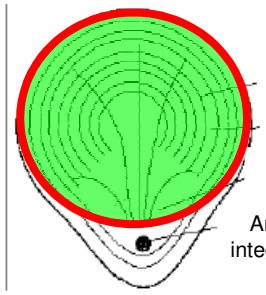
SDD - detector 2



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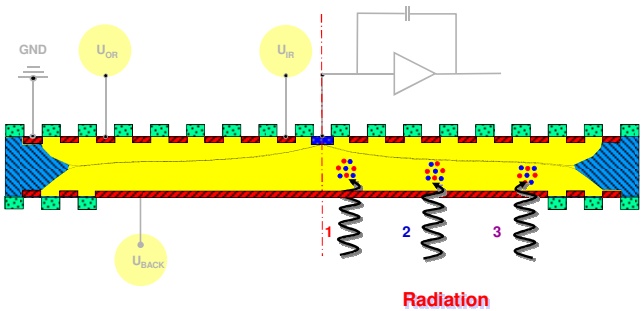
SDD - detector 3

Function of Silicon Drift Detector (3)



Radiation

Absorption of x-rays

J. Kemmer, Andreas Pahlke CET04

KETEK

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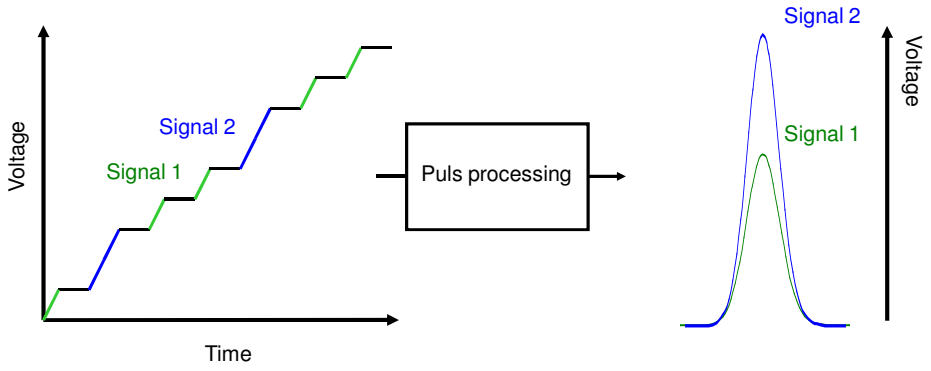
Signal processing



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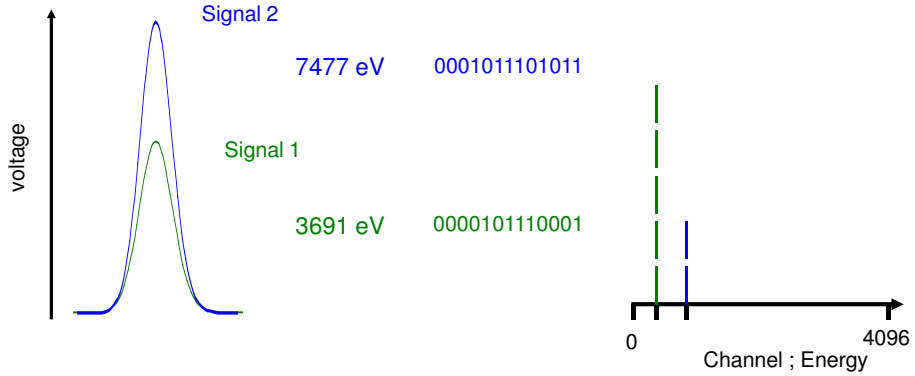
Analog - Digital converters

Voltage | 4096 (2^{12}) channels
5 or 10 eV / channel



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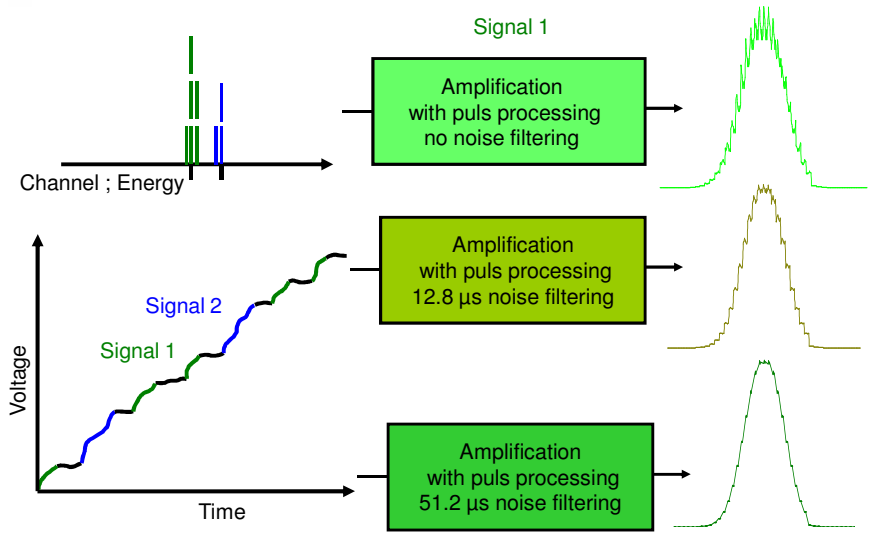
Analog - Digital converters



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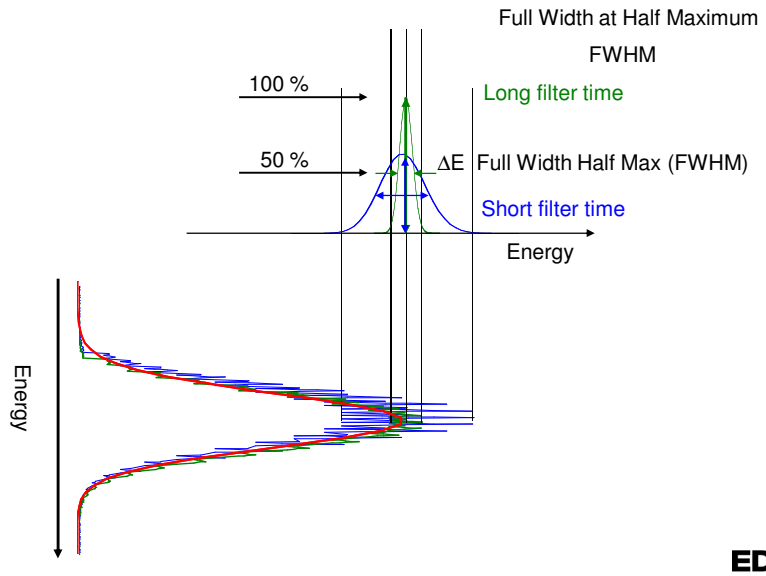
Energy resolution



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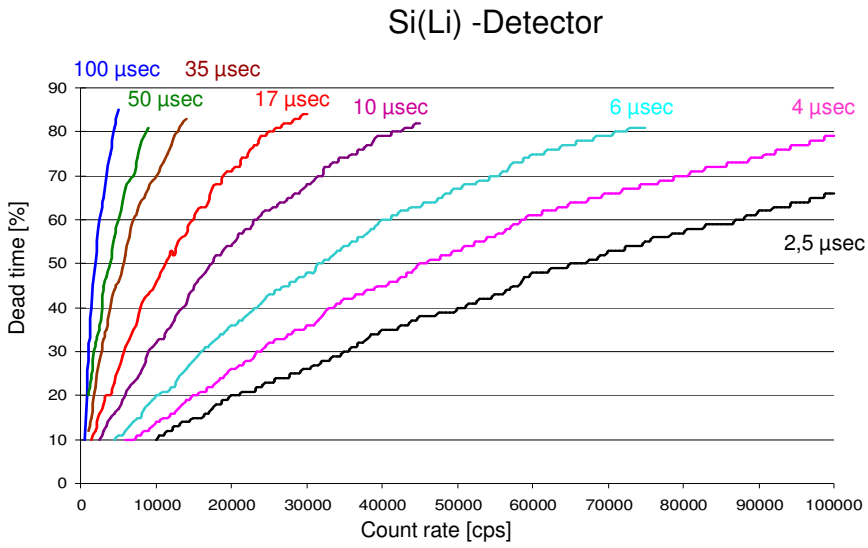
Dead time – Filter times



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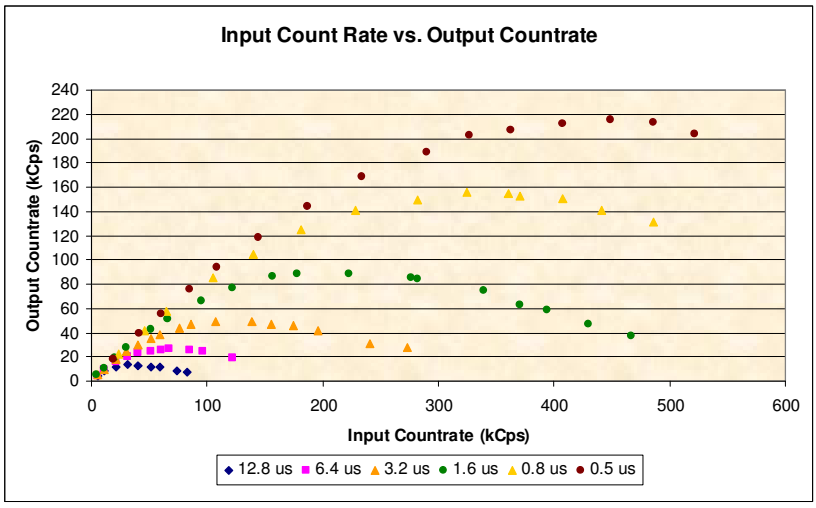
Throughput plot SDD detector



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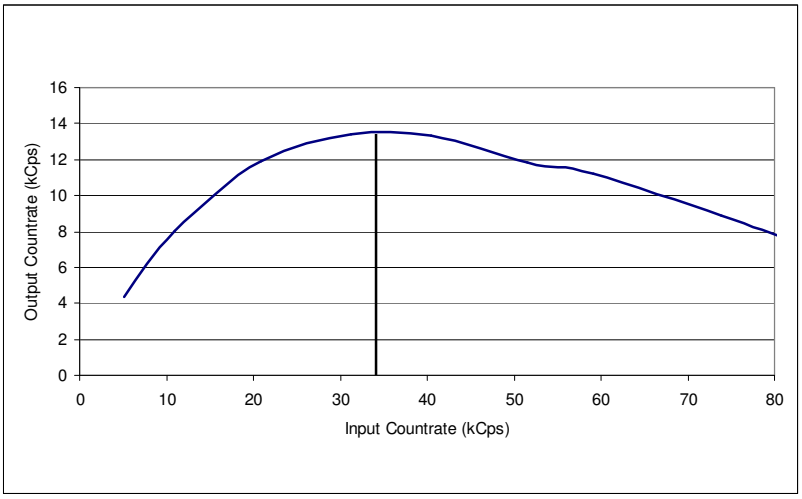
Throughput at 12.8 µs amp time



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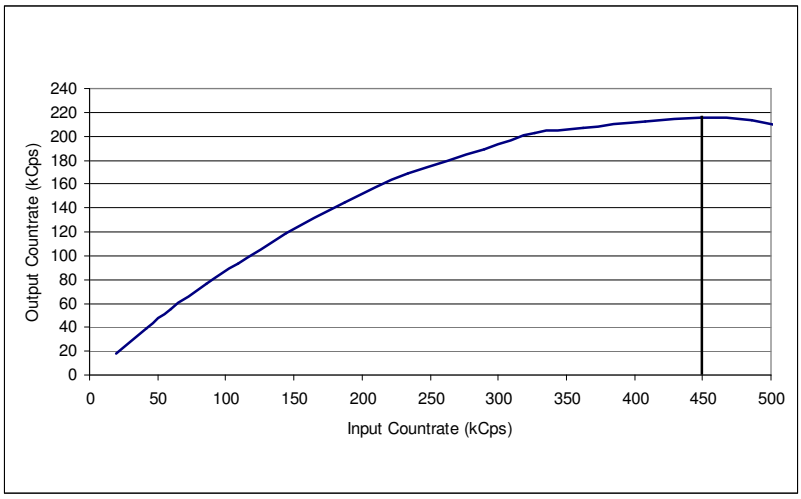
Throughput at 0,5 µsec amp time



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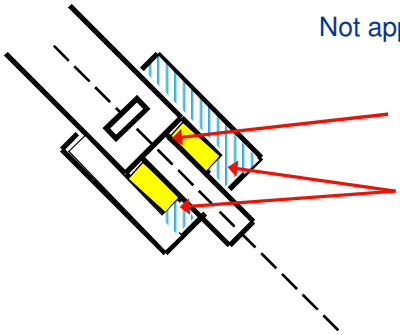
Collimators



Not applicable for in-lens SEMs

SUTW or UTW Window

Magnets to deflect BSE

If BSE reach the detector they will produce background anomalies --a hump in the background at high energies.

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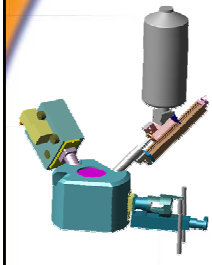
Spectral artefacts



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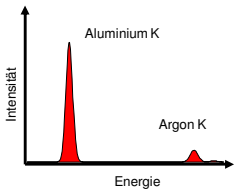
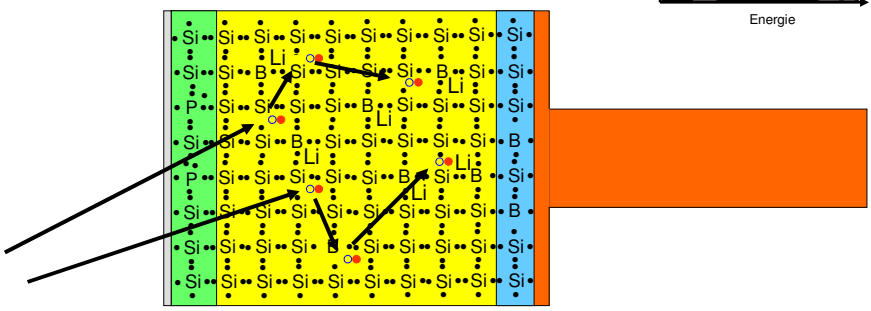
SUM peaks

X-ray 1 from Aluminium	1,486 eV
X-ray 2 from Aluminium	1,486 eV
X-ray from Argon	2,992 eV





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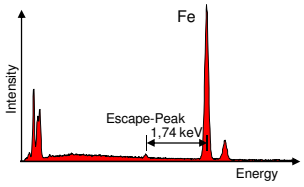
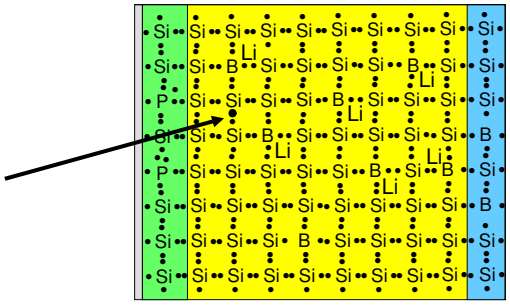
Escape Peaks

X-ray from Iron	6,40 keV
X-ray from Silicium	- 1,74 keV
X-ray from Lanthanum	4,66 keV





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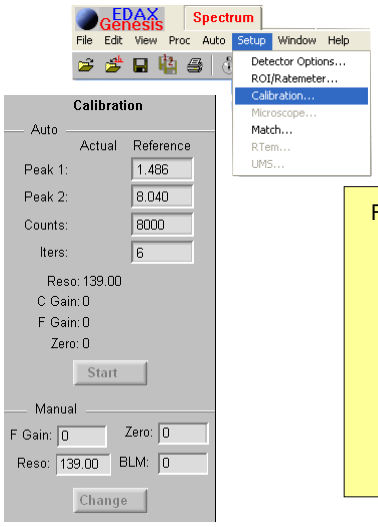
System Calibration



Sample: Al / Cu
Magnification at least 100x
Acceleration voltage : 25-30 kV
Peak heights AlKa and CuKa about the same
Working Distance: for EDS analysis

Filter time (µs)	Count rate [cps]
1,6	8000
3,2	8000
6,4	8000
12,8	8000
25,6	6000
51,2	4000
102,4	2000

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Calibration data

Values of calibration done within Genesis stored in c:\windows\calibrat.csv

Date | Filter time | Calibration value | eV/ch | Iterations | Position Cu peak | Dead time | Temp

Date	Time	Tim Con	Reso	C Gain	F Gain	Zero	CPS	EvCh	FS	Itera	Peak1	Peak2	LSecs	Dead Tim	Det Input	EDI2 Temp
23.4.07	18:18	100	128.3	924	3	-158	963	10	8000	1	1.485	8.040	352.3	32	1	32.91
23.4.07	18:30	50	129.1	918	0	-64	2108	10	8001	2	1.486	8.040	167.5	34	1	32.91
23.4.07	18:41	35	128.7	946	-116	-99	4244	10	8001	2	1.486	8.039	87.80	46	1	32.97
23.4.07	18:50	17	135.4	949	-117	-95	7911	10	8002	2	1.486	8.039	53.00	43	1	33.09
23.4.07	19:00	10	140.8	959	-120	-102	7857	10	8008	2	1.486	8.039	57.40	29	1	33.11
23.4.07	19:10	6	151.3	950	7	-66	7801	10	8001	6	1.486	8.040	63.10	19	1	33.05
23.4.07	19:20	4	157.8	960	5	-117	8035	10	8013	6	1.486	8.041	57.40	29	1	33.07

Time | Resolution | Count rate | Counts | Pos Al peak | Live time | Detector

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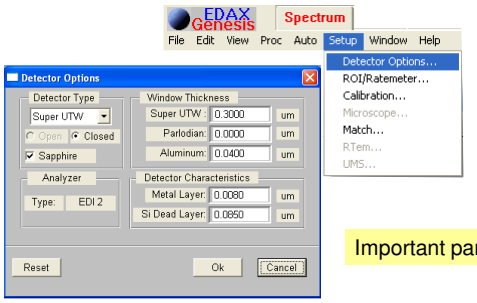
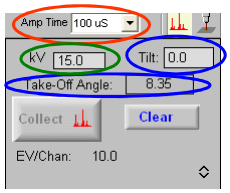
EDAM - Parameters





Important parameters for quantitative analysis

„Amp Time“ (Filter time) determines energy resolution

„Acc. Voltage“ Energy from electrons

„Tilt angle“ has influence on absorption

„Take-Off Angle“ is calculated by software

„Detector type“ is fixed parameter

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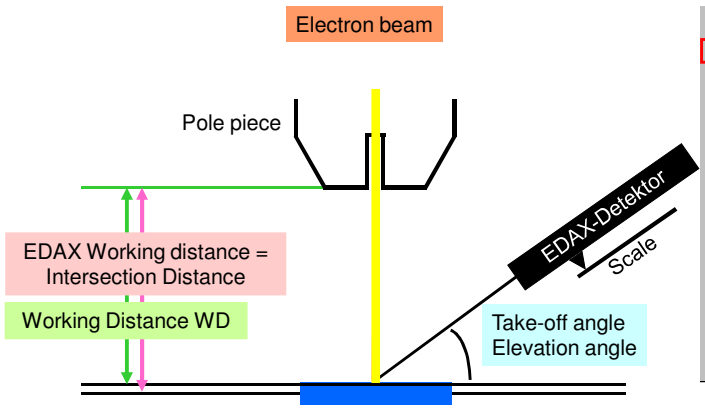
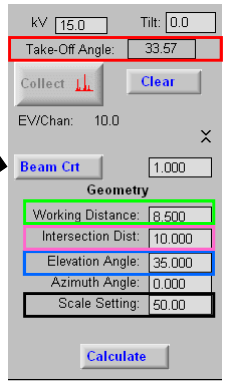
Microscope parameters





ID= where electron beam contacts the line through the middle of the EDS detector

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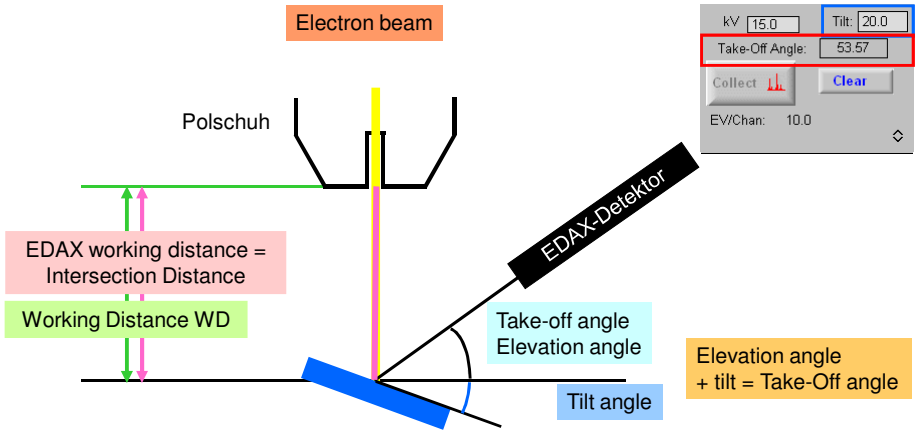
Microscope parameters



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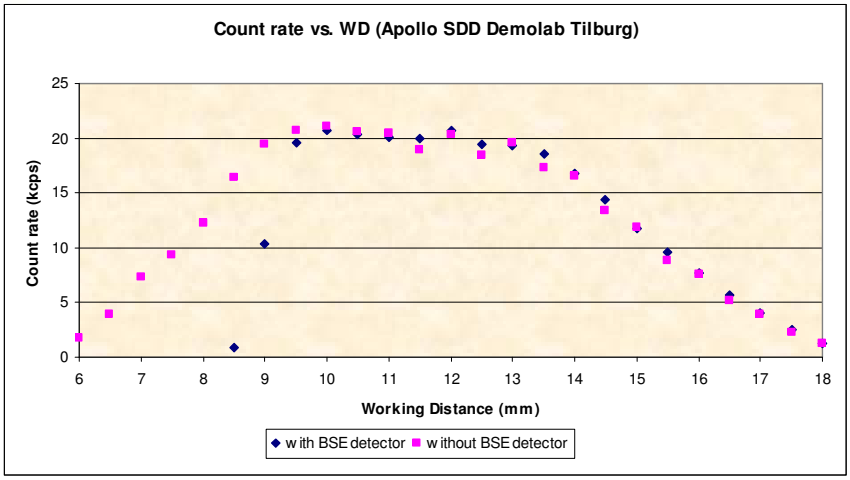
Microscope parameters



Every SEM with an EDS detector has an ideal working distance for EDS analysis. EDS, however, could be performed at other working distances (see plot above)

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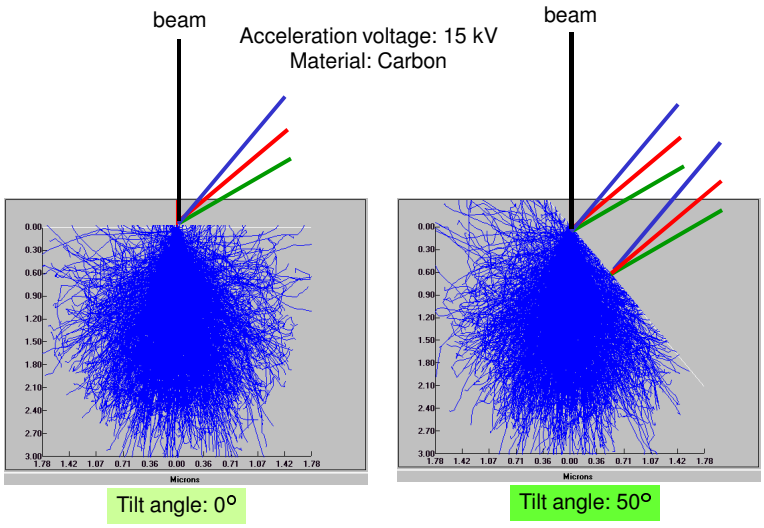
Tilted sample



Tilt angle: 0°

Tilt angle: 50°

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Influence of take-off angle

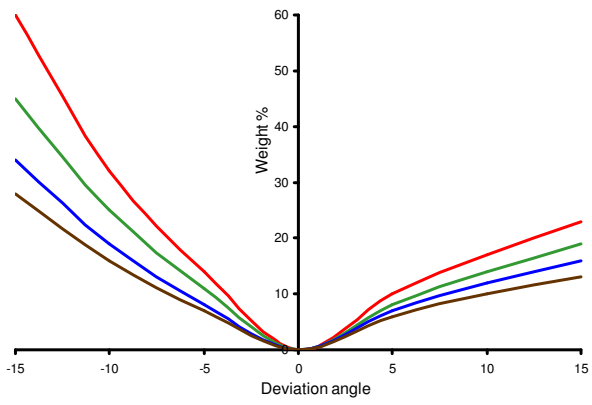
Determination of Al concentration in a Cu / Al alloy
Depending on take-off angle (TOA)

TOA 30°

TOA 35°

TOA 40°

TOA 45°



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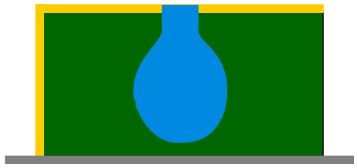
Requirements for best quantitative results

smooth surface

homogeneous probe

flat surface

no charging



samples with grains

samples with topography

Multilayer samples

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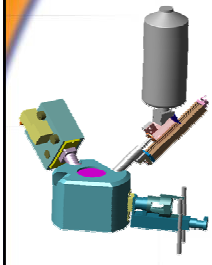
Quantification



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advanced microanalysis solutions
AMETEK

Quantitative analysis

- How to interpret a spectrum
- The K-ratio
- ZAF corrections
- Assumptions/requirements for ZAF and microanalysis
- Analysis with standards and standardless analysis
- What happens when we don't satisfy the ZAF assumptions

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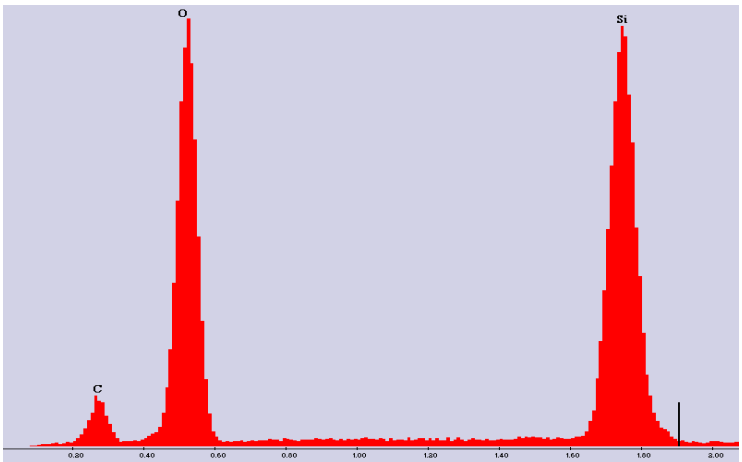
Can we estimate weight % from a spectrum?

- The short answer is no!
- The peak heights will vary with the beam voltage.
- kV used was 10 kV.



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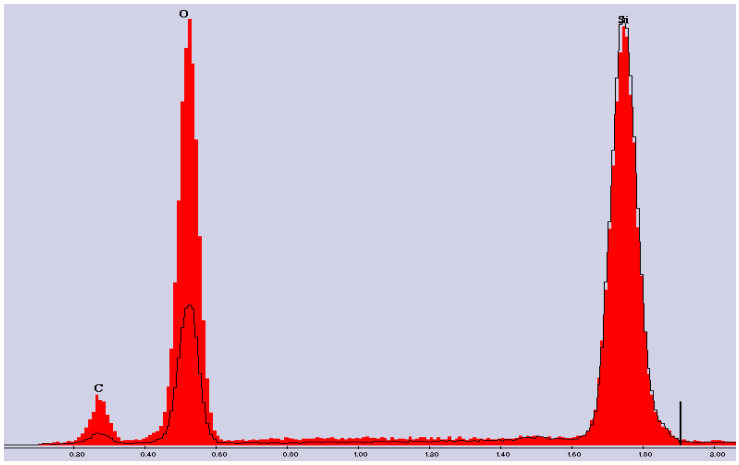
Can we estimate weight % from a spectrum?

- The lined spectrum was collected at 20 kV.
- The sample is SiO2 and it has been carbon coated.



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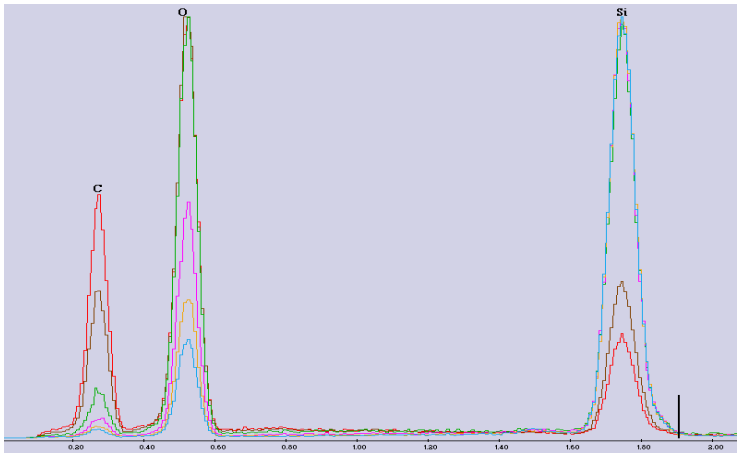
EDAX TSL

Can we estimate weight % from a spectrum?

- 6 spectra of SiO2 collected at 4 kV (red), 5 kV, 10 kV, 15 kV, 20 kV and 25 kV (cyan).



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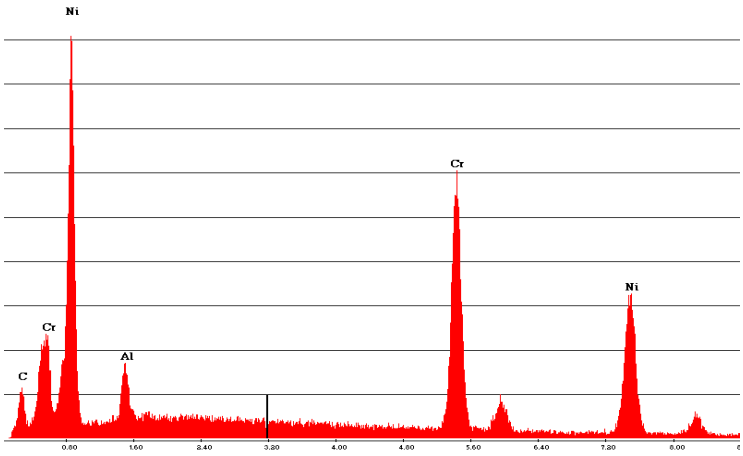
Can we estimate weight % from a spectrum?

- This spectrum was collected at 15 kV.
- It is Al (3%), Cr (38.5%), and Ni (58.5%).



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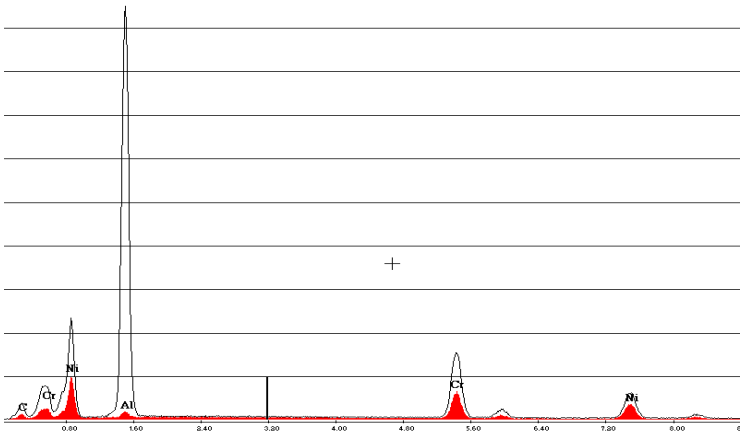
Can we estimate weight % from a spectrum?

- The best 1st approximation to quant analysis is to compare peak inten-sities to the intensity of the pure elements collected under identical conditions.
- Red spectrum: unknown sample
- Black spectrum: intensities for pure elements at identical conditions



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Basics of quantitative analysis

- The best 1st approximation to quant analysis is to compare peak intensities to the intensity of the pure elements collected under identical conditions.

$$k\text{-ratio} = \frac{Intensity\ Element\ Sample}{Intensity\ Pure\ Element}$$

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Basics of quantitative analysis

- To correct the k-ratios, we need to calculate Z, A, and F.
- The problem that we have is that we can not calculate Z, A, and F unless we know the composition of the sample.
- We get around this problem by doing an iterative calculation.
  - The first iteration might assume that the k-ratio is correct.
  - Each new weight % is used to calculate new ZAF values.
  - We keep doing this until the last iteration produces no change.

$$Weight\ \% = \frac{k\text{-ratio} \times 100\ \%}{Z \cdot A \cdot F}$$

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Analysis with or without standards

- The simple formula for quant is the same regardless of whether standards are used or not.
- When standards are used the "intensity pure element" is actually measured.
- In the standardless mode the intensity of the pure element is calculated from a formula.

$$k\text{-ratio} = \frac{\text{Intensity Element Sample}}{\text{Intensity Pure Element}}$$

$$\text{Weight \%} = \frac{k\text{-ratio}}{Z \cdot A \cdot F} \times 100\ \%$$

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Basics of quantitative analysis

- The K-ratios are close to being correct for the Cr and Ni but is only ½ of the correct value for Al.

Elem	Wt %	At %	K-Ratio	Z	A	F
AlK	3.21	6.44	0.0149	1.0896	0.4267	1.0003
CrK	36.80	38.29	0.3774	0.9866	0.9910	1.0489
NiK	59.99	55.27	0.5891	1.0014	0.9806	1.0000
Total	100.00	100.00				

Element	Net Inte.	Backgrd Inte.	Error	P/B
AlK	17.11	7.96	3.36	2.15
CrK	110.58	5.18	0.99	21.35
NiK	71.59	2.76	1.23	25.94

- ZAF corrections are used to compensate for errors in the k-ratio and correct for differences in the X-Ray yield for the pure element as compared to our sample.
  - Z is a BSE correction.
  - A is the absorption correction.
  - F is a fluorescence correction.

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Assumptions and their ramifications

- ZAF corrections are required to make the K-ratio more accurate
- ZAF corrections make assumptions about our sample :
  - the sample is homogeneous
  - the sample is perfectly smooth
  - the sample is infinitely thick to the electron beam
- When we satisfy these assumptions, the quant results should be reasonably accurate, but….

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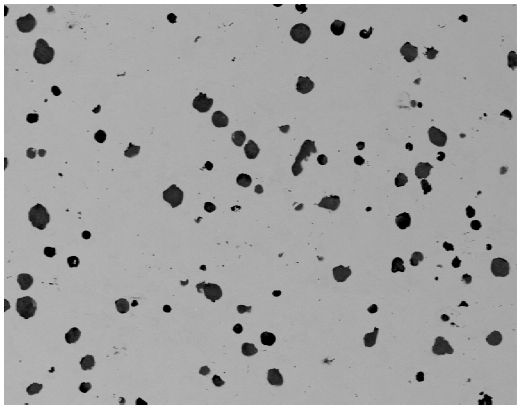
When we don't satisfy the assumptions → the heterogeneous sample

- Sample is ductile iron as seen in BSE mode.
- The dark areas are graphite (C) and the brighter matrix is Fe.
- The C-rich area is 6.3% by area of the sample



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When we don't satisfy the assumptions → the heterogeneous sample

- A multi-phase sample (e.g. carbon inclusions in a steel) produces a spectrum with C and Fe peaks
- C X-Rays are heavily absorbed in Fe and a strong absorption correction (/0.2) is calculated
- But, the C x rays escape from carbon where there is very little absorption
- Thus, a correction is made for an effect that has not happened and the C wt % is much too high (about 12 weight %).

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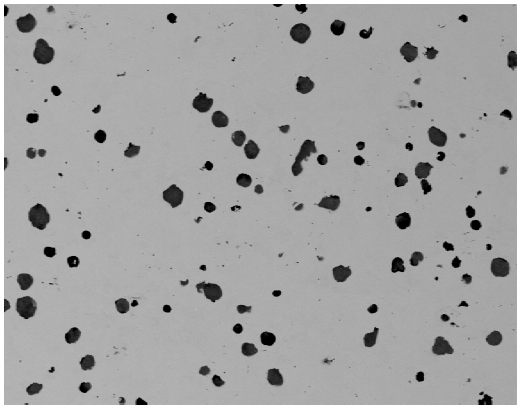
When we don't satisfy the assumptions → the heterogeneous sample

- The calculation of the area fractions by the densities of the two phases produces an estimate of about 2% C and 98% Fe.
- The K-ratio of the C is actually about 2.5%.



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Standardless Quantification

$$WT\% = Z \cdot A \cdot F \cdot \frac{I^{meas}}{I^{STD}} \qquad k = \frac{I^{meas}}{I^{STD}}$$

I^{meas}	measured intensity
I^{STD}	pure element intensity
Z	atomic number correction
A	absorption correction
F	fluoresence correction

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Standardless Quantification –complete formula

$$I^{CalcSTD} = n\frac{\Omega}{4\pi}\varepsilon_d\omega\rho f_x\frac{N^0}{A}R\int_0^{E_c}\frac{Q_i(E,E_c)}{dE/d(\rho z)}dE$$

$I^{CalcSTD}$	calculated intensity
n	number of electrons (beam current)
$\frac{\Omega}{4\pi}$	solid angle
ε_d	detector efficiency
ω	fluorescence yield
ρ	excitation probability
$\int_{E_0}^{E_j}\frac{Q_i(E,E_c)}{dE/d(\rho z)}dE$	excitation volume
$f_x\frac{N^0}{A}R$	absorption correction

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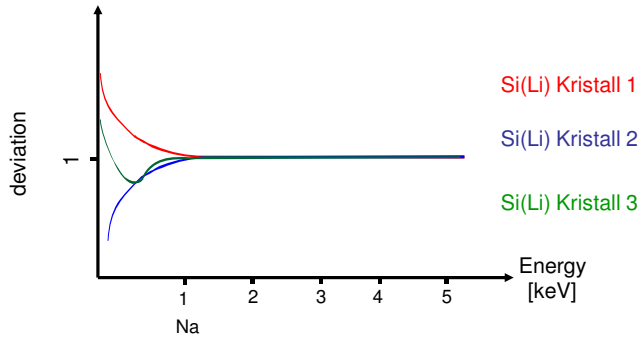
Standardless Quantification



$$WT\% = Z \cdot A \cdot F \cdot \frac{I^{meas}}{SEC \cdot I^{Calc\,STD}}$$

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Standardless quantification – independent on kV

Accelerating voltage [kV]		10	15	20	25	composition
A - Factor		0,7478	0,5733	0,4341	0,3363	
Gew%	Si K	3,14	3,24	3,25	3,23	3,22
	Fe K	96,86	96,76	96,65	96,77	96,78

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ZAF matrix correction

Steel sample at 25 kV

Element	k - ratio	Z	A	F	wt%
Cr K	0,1927	0,995	0,986	1,203	16,33
Mn K	0,0099	0,979	0,996	1,010	1,010
Fe K	0,7176	0,999	0,957	1,012	74,08
Ni K	0,0735	1,018	0,893	1,000	8,61

Without ZAF correction Chromium too high: 19,27 wt%

with ZAF correction EDAX - ZAF - Factor= 1,18 $\frac{0,1927}{1,18} \cdot 100 = 16,33$

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Matrix correction

Example of steel sample, run at different kV
showing standardless quantification is independent on kV

kV : 25.00 Tilt : 0.00 Take-off : 35.00 Tc : 40
Detector Type : SUTW Resolution : 144.00 Lsec : 100

EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	K-Ratio	Z	A	F
SiK	0.54	0.0020	1.1074	0.3348	1.0018
CrK	18.67	0.2157	0.9949	0.9842	1.1798
MnK	0.89	0.0087	0.9784	0.9940	1.0089
FeK	71.60	0.6878	0.9985	0.9512	1.0114
NiK	8.31	0.0710	1.0175	0.8398	1.0000
Total	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
SiK	6.16	12.64	7.04	0.49
CrK	316.52	15.24	0.58	20.77
MnK	11.40	13.41	4.37	0.85
FeK	797.74	12.49	0.36	63.87
NiK	62.87	9.30	1.35	6.76

kV : 15.00 Tilt : 0.00 Take-off : 35.00 Tc : 40
Detector Type : SUTW Resolution : 144.00 Lsec : 100

EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	K-Ratio	Z	A	F
SiK	0.59	0.0039	1.1440	0.5716	1.0009
CrK	18.57	0.2099	0.9979	0.9940	1.1394
MnK	1.12	0.0111	0.9796	0.9978	1.0065
FeK	71.09	0.7031	0.9978	0.9826	1.0087
NiK	8.62	0.0823	1.0126	0.9432	1.0000
Total	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
SiK	15.99	30.87	4.28	0.52
CrK	247.46	19.75	0.66	12.53
MnK	10.83	16.72	4.85	0.65
FeK	561.78	14.96	0.43	37.55
NiK	41.10	10.16	1.74	4.05

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Times for image collection

Matrix	Inte.F/reads	10 Stripes	1 Stripe	1 Stripe, Matrix 2048x1600	
[Pixel]		time [s]	time [s]	Int.F.	time [s]
8192x6400	128	1140	1125	1	25
4096x3200	128	300	278	16	34
2048x1600	128	80	70	32	39
1024x800	128	30	18	64	49
512x400	128	6,0	5	128	70
256x200	128	2,3	1,5	256	112
128x100	128	1,4	1,0	512	210
64x50	128	1,1	0,5	999	365

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