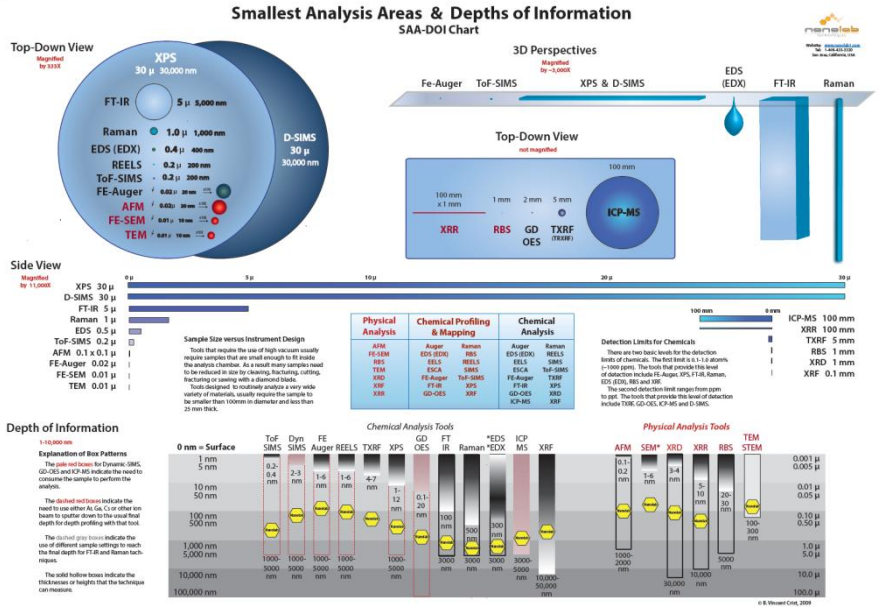
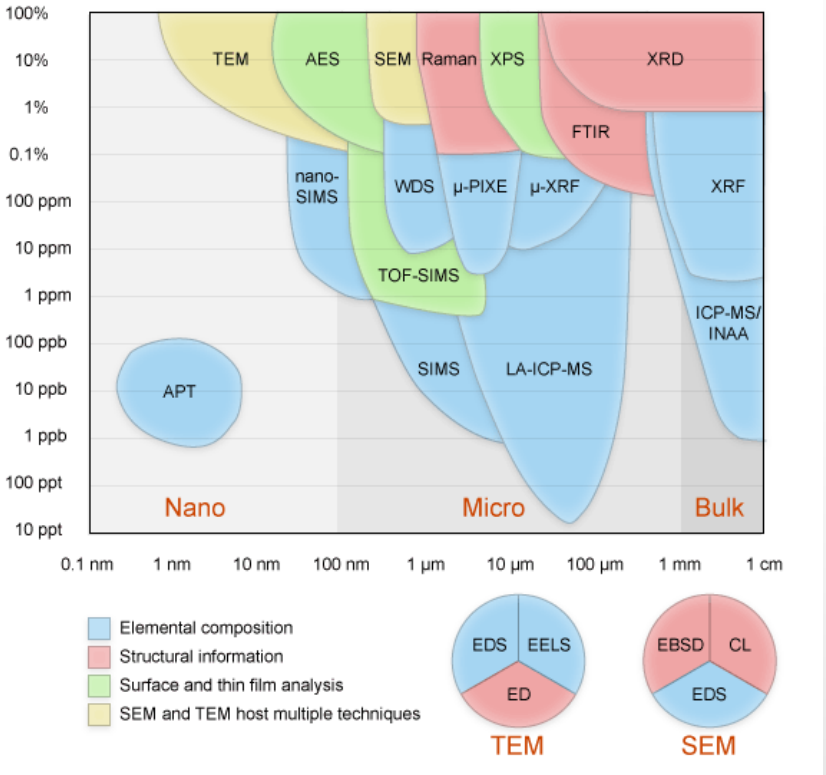
Energy-Dispersive X-ray Microanalysis

An Introduction

Microanalysis



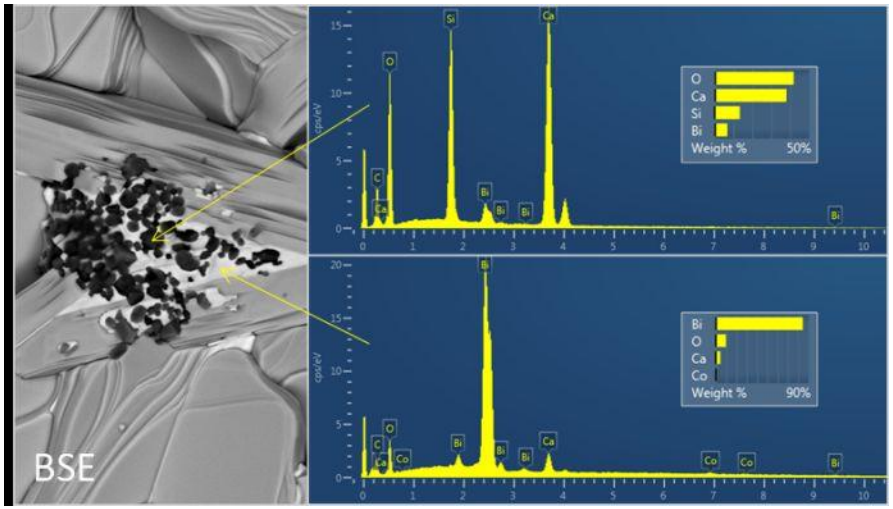
- identification of the chemical elements in measured material (qualitative, quantitative)
- spot size ranges form 100 µm to 100 nm
- in situ measurements

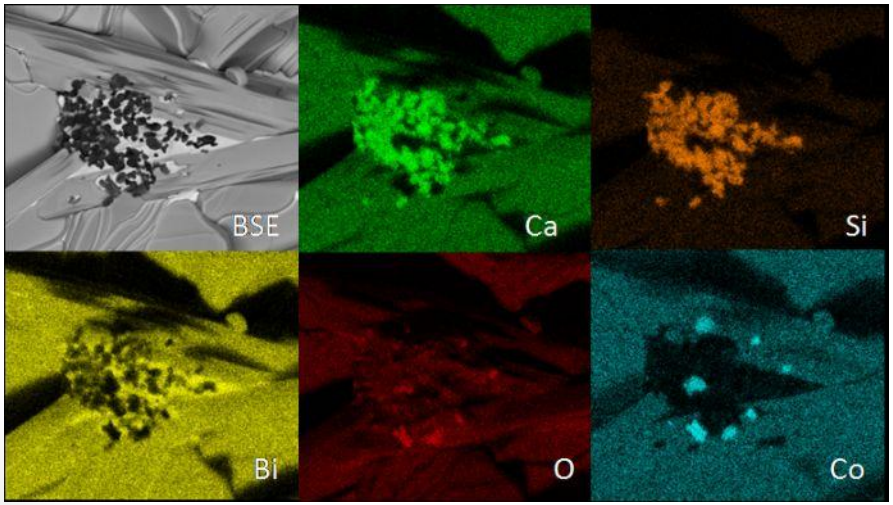


Choosing technique:

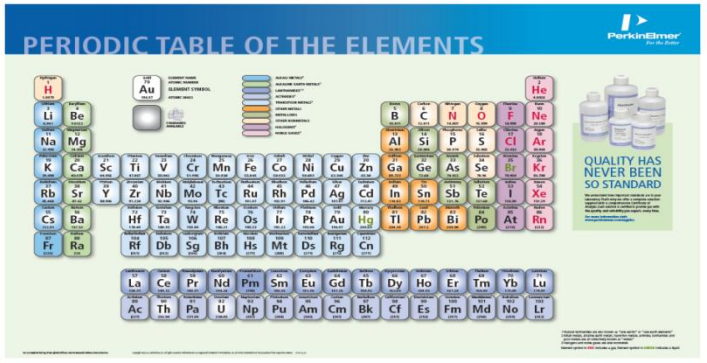
- spatial resolution
- information depth
- detection limit
- qualitative or quantitative? both?
- additional information

Principles of the EDS technique

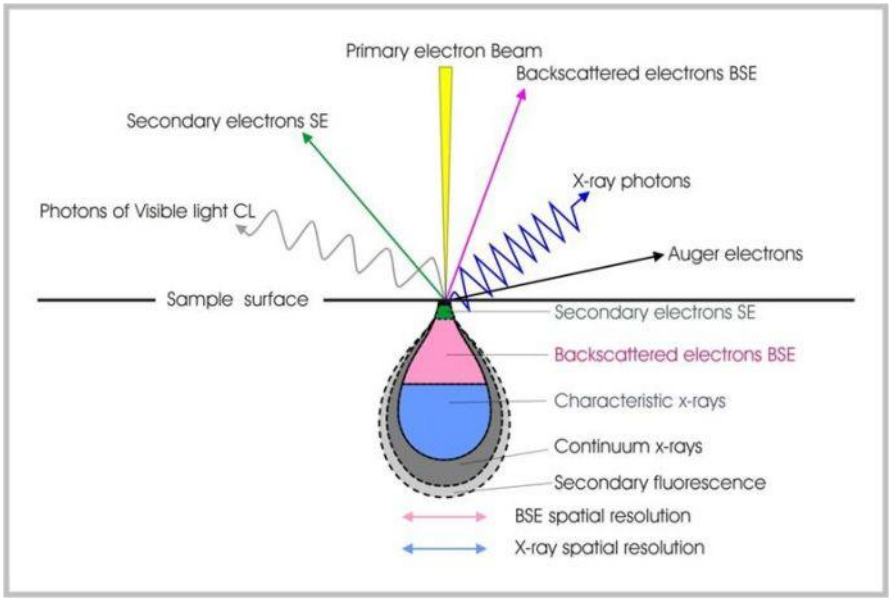




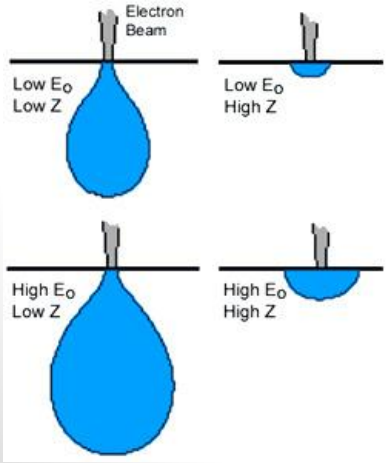
- easy of use, qualitative and quantitative chemical composition
- detection limits – ca. 0.3 wt.%
- wide detection range of elements (Z > 4)
- fast in comparison with other techniques
- non-destructive
- mapping measurements
- energy resolution < 130eV
- spatial and depth resolution – few microns

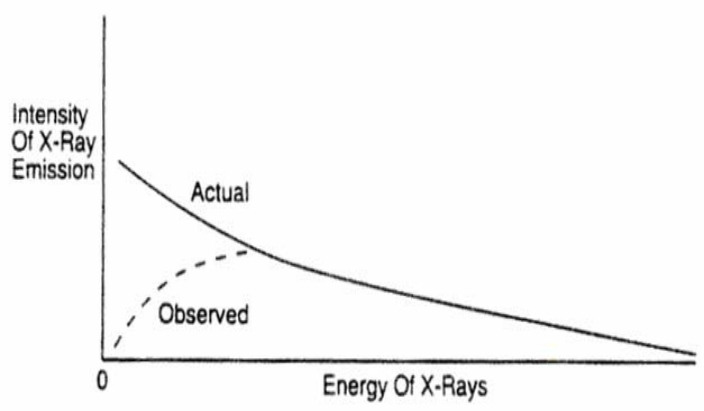


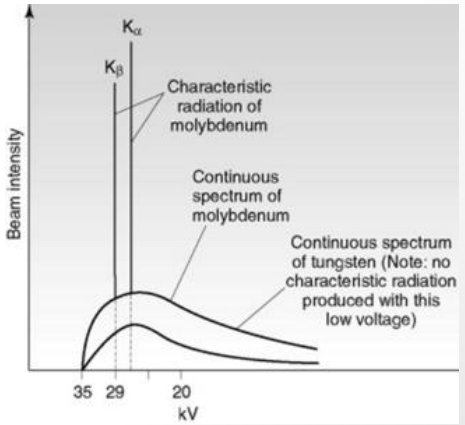
Generation of X-Rays



- electron beam interaction with atoms
- spatial resolution of few microns
- size variation of interaction volume
- Bremsstrahlung and Characteristic X-Rays (Duane-Hunt limit)
- EDS spectrum contain combined X-Ray radiation
- „whale" spectrum

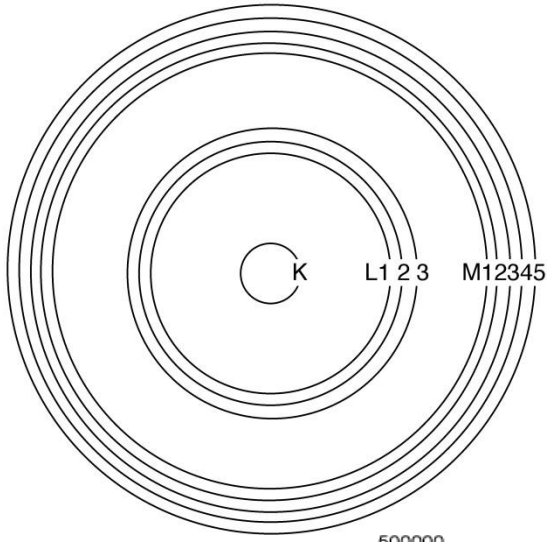






Generation of X-Rays

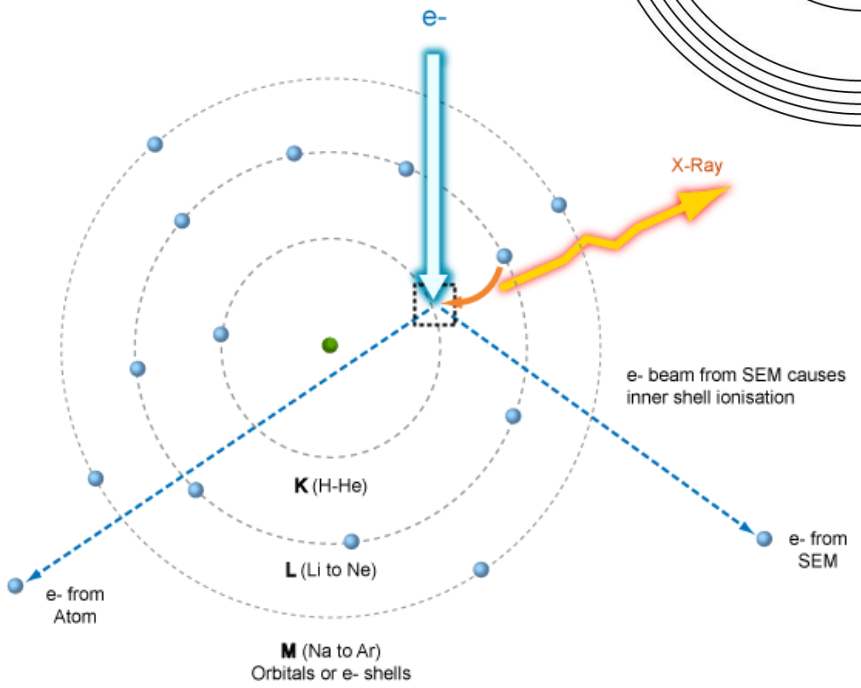
- Bohr model of atom
- inner shells K, L, M
- K shell – highest ionization energy
- two stage process
- each element has specific ionization energy

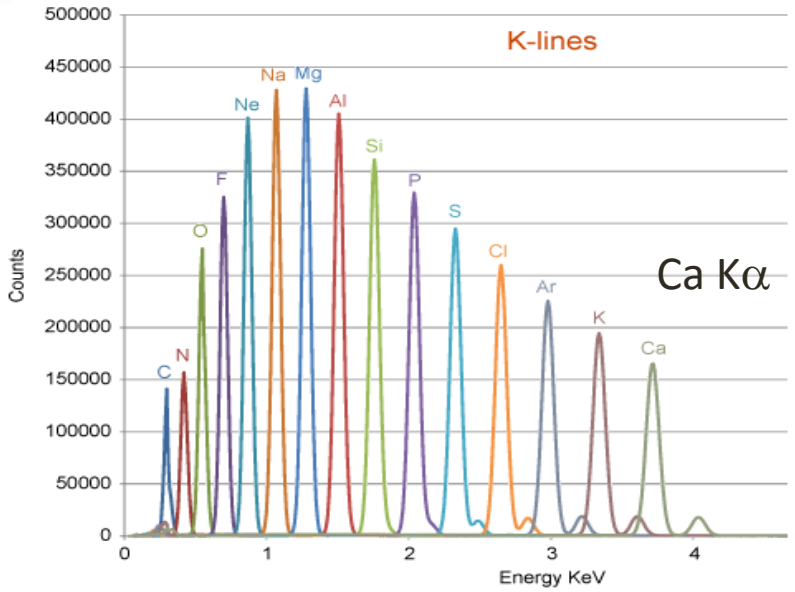


- Siegbahn notation
- EK > EL > EM

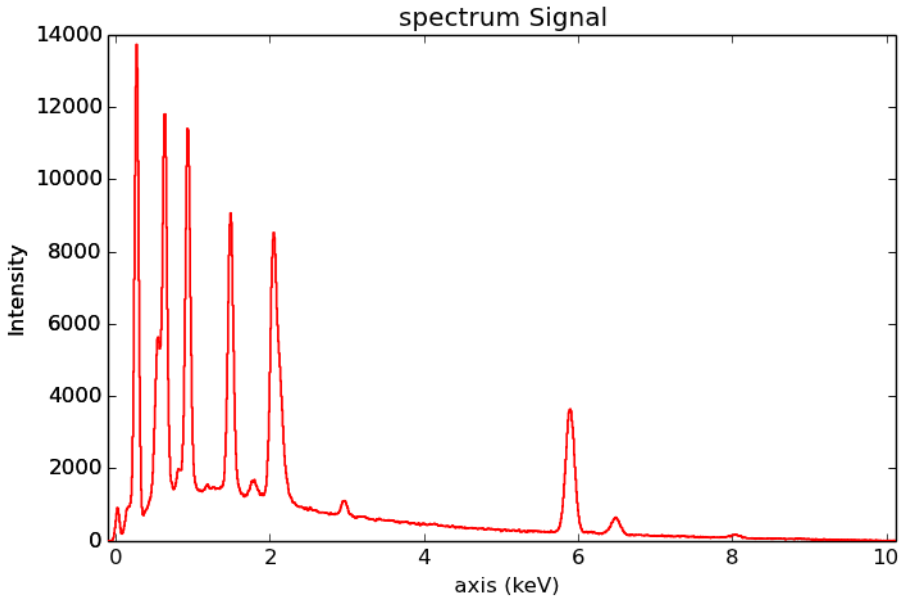
Moseley's law

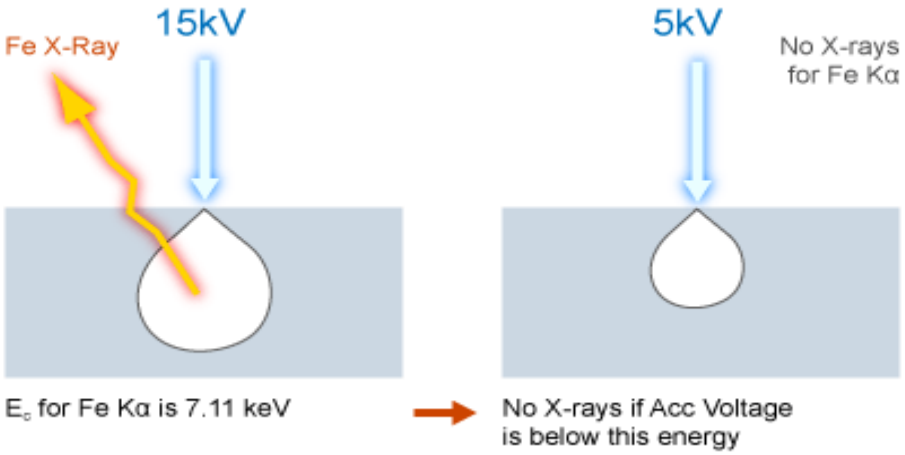
$$E = C_1(Z - C_1)^2$$





Generation of X-Rays





Factors that can influence intensity of the spectrum:

- detector type
- sample type
- concentration
- beam current
- accelerating voltage (5 – 30 keV)

„critical ionization energy"

„overvoltage ratio" $U = \frac{E_o}{E_c}$

optimum value ~ 2.7

at least 2

Detection of X-Rays

- creation of a series of electron-hole pairs
- SSD operating temp. ~ 70°C
- pulse processor removes noises
- longer process time – better resolution
- „dead" time
- analyser divide spectrum into channels

energy dispersive X-ray spectrometer

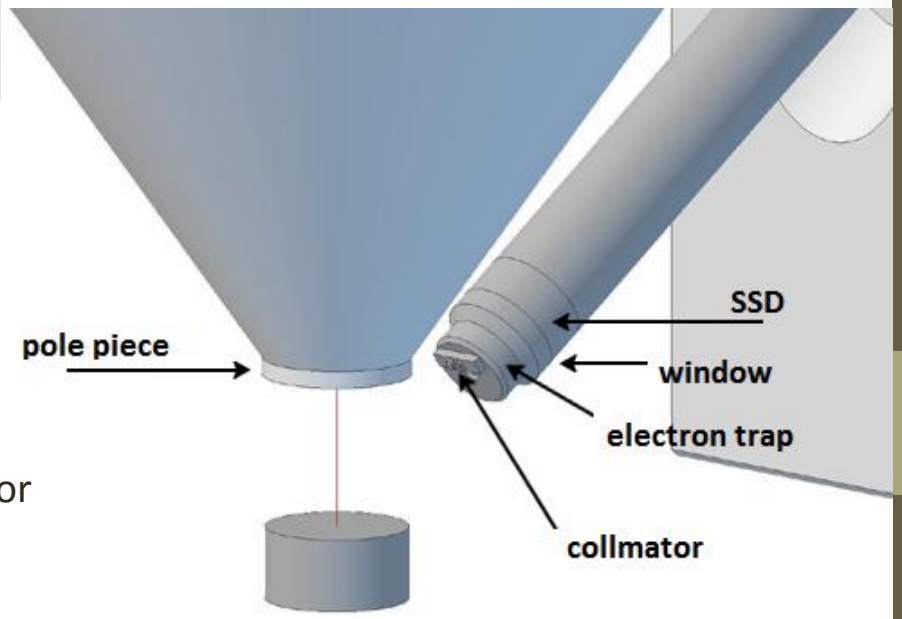
- detector (semiconductor)
- pulse processor
- multi-channel analyser

first detectors – Si(Li) – 1960s

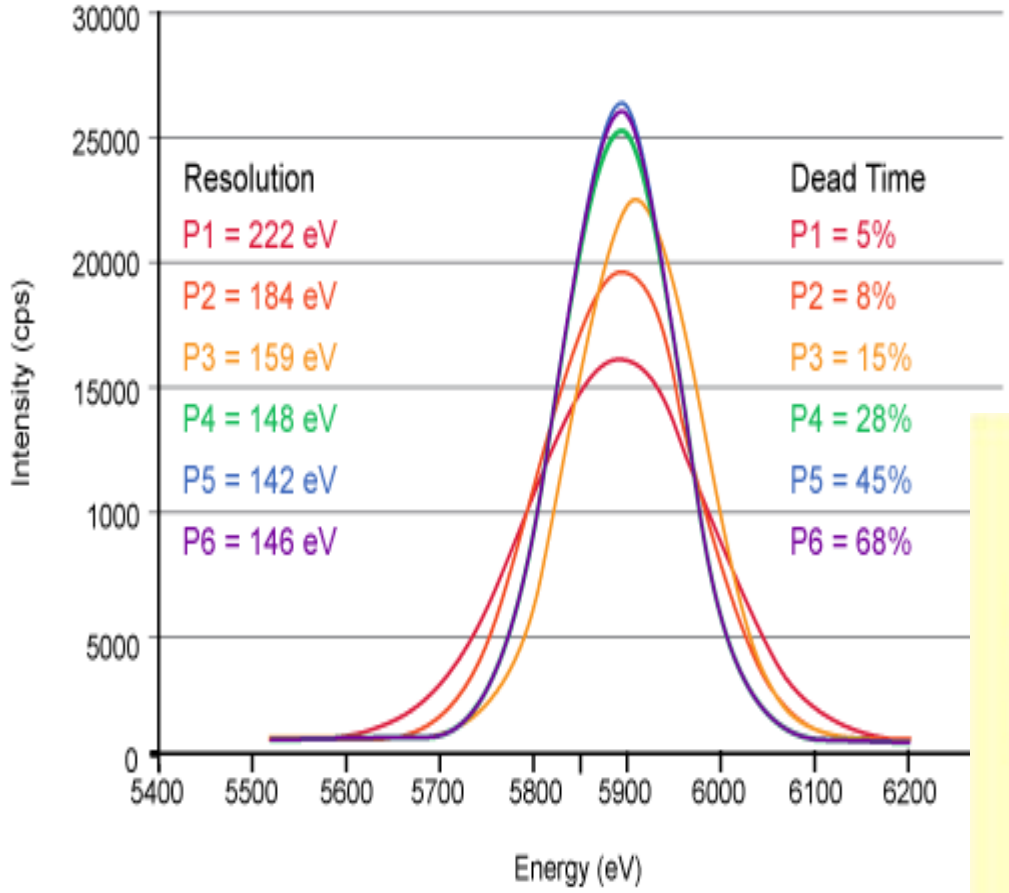
nowadays – SSD

Detector:

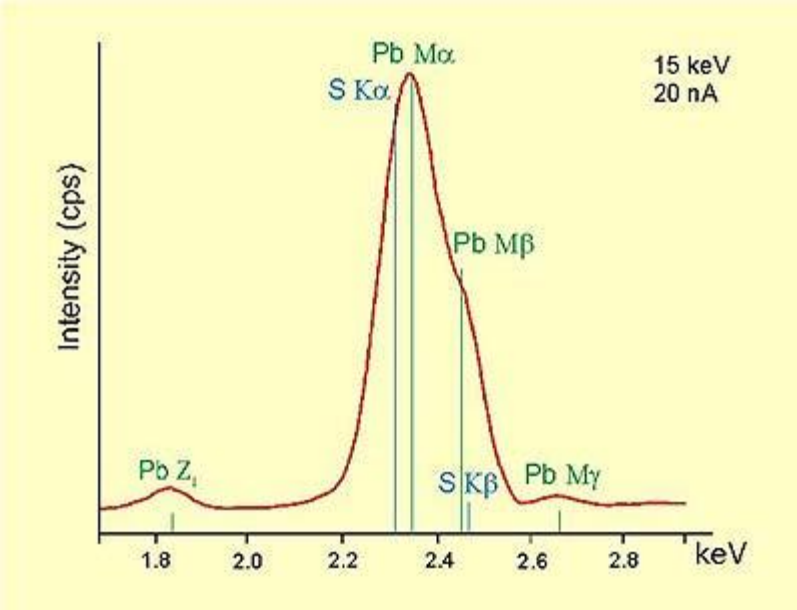
- collimator
- electron trap
- window
- semiconductor
- electronics



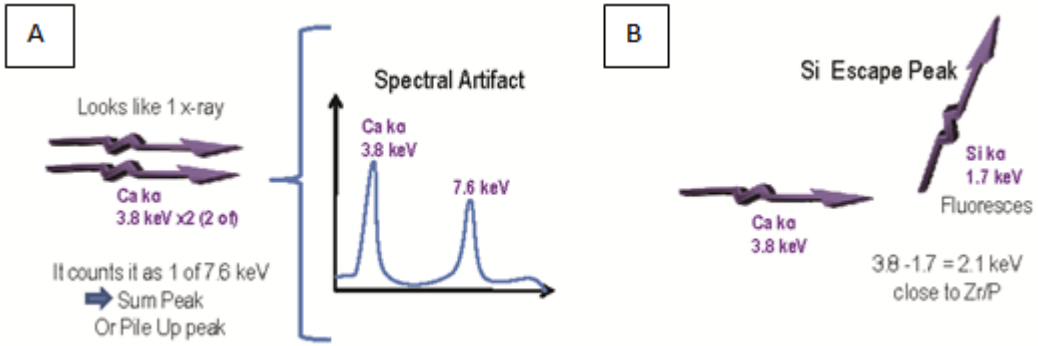
Spectral Resolution



- FWHM describes resolution
- longer process time – better resolution
- Mn Kα standard
- avoiding overlapping peaks

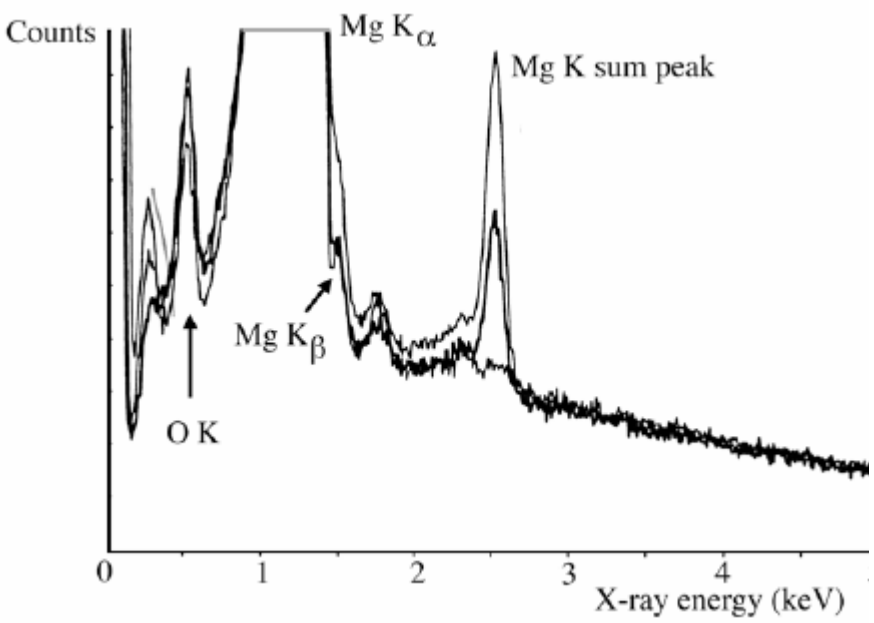


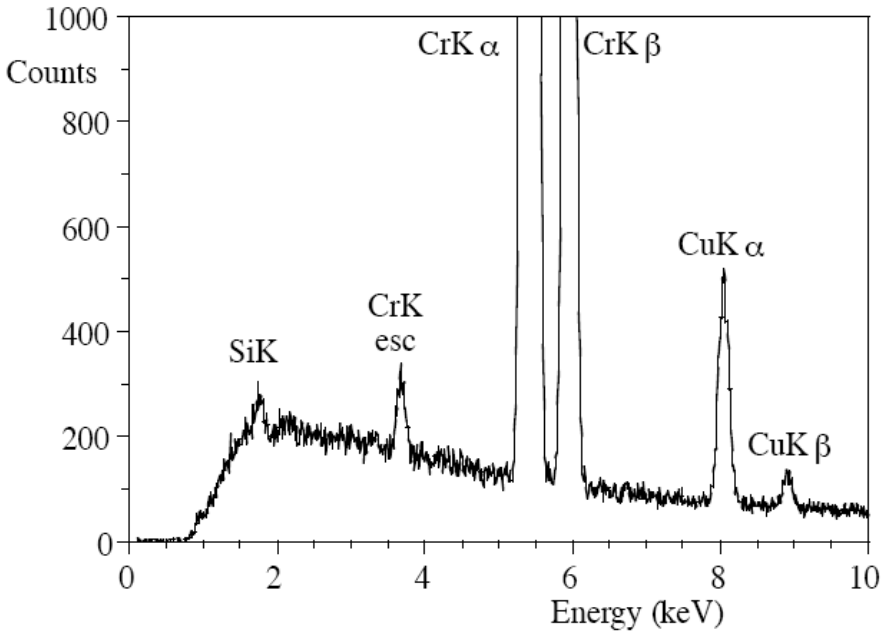
Artifacts



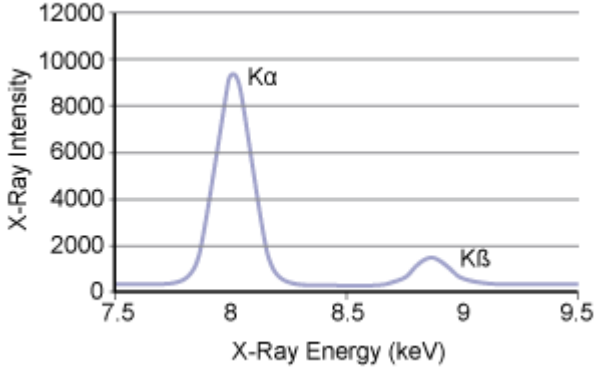
- internal fluorescence peak (Si signal from crystal)
- pile up (sum) peaks
- escape peaks

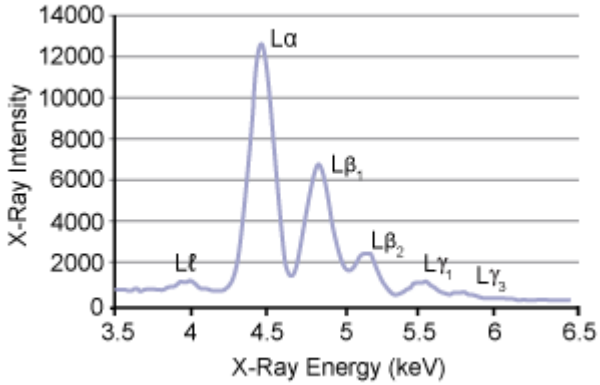
above 60% „dead” time

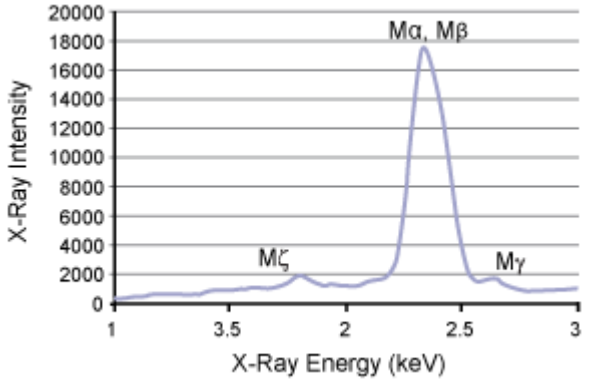




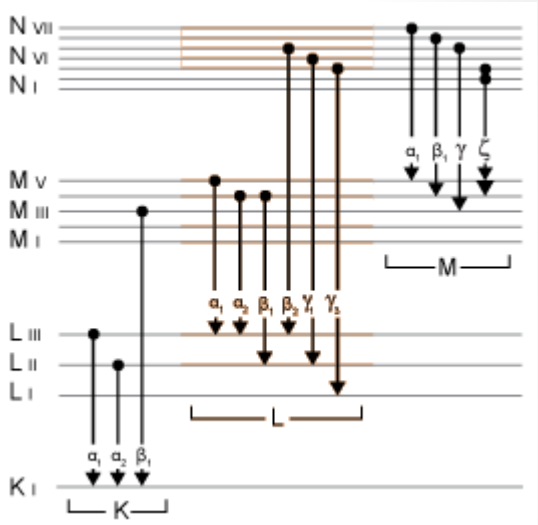
Qualitative Analysis







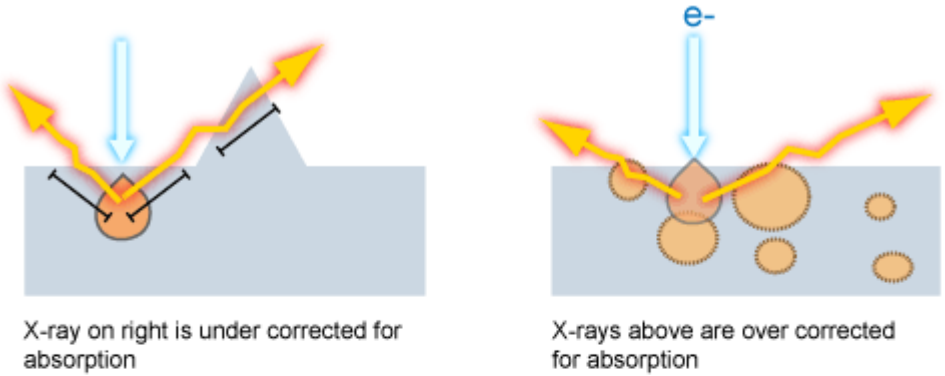
- accelerating voltage
  - optimal – 20 keV
  - enough – 8 keV
- beam current
- instrument geometry
  - WD – 5 mm
- sample preparation
- non-conductive samples
- overlapping peaks



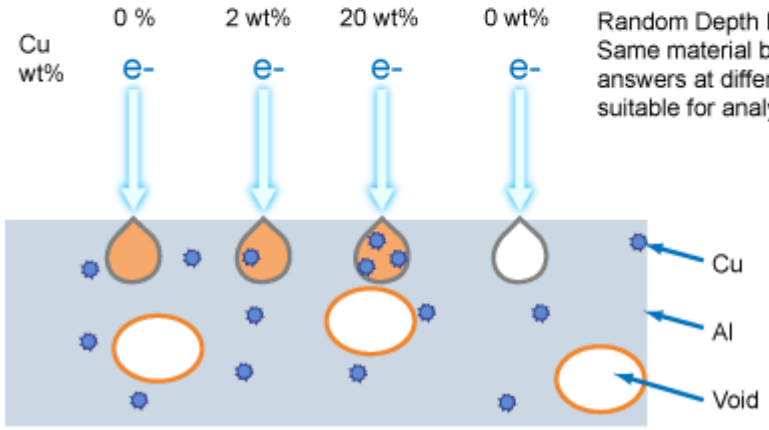
Analysis procedure

1. Identify and label major peaks at 4 keV and above:
   - There are no M family peaks
   - There are at least two resolved peaks for both K and L families so these can be identified along with related minor peaks
   - If there are L family peaks there should be M family peaks at low energy, and these can be identified, e.g. Ta L and M families
   - If there are K family peaks there should be L family peaks at low energy, and these can be identified, e.g. Zn K and L families
2. Any unidentified peaks below 4 keV should be K family peaks, and can be identified.

Quantitative Analysis



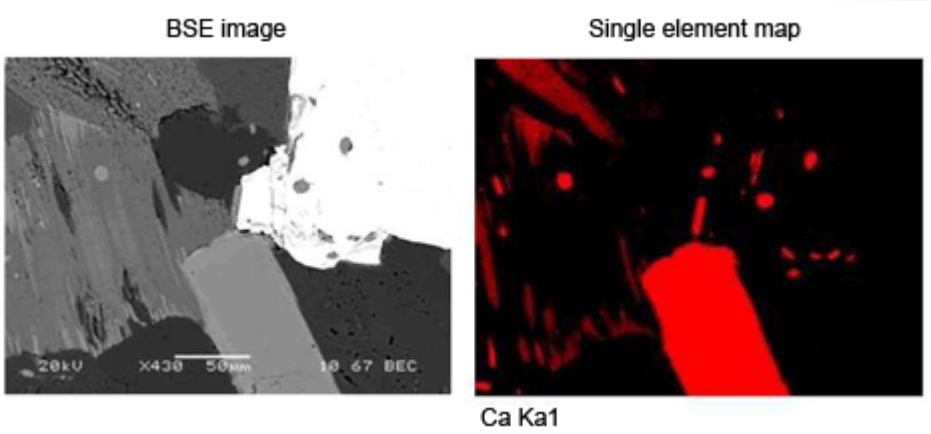
Specimen must be Homogenous over x-ray generation volume for correct answer

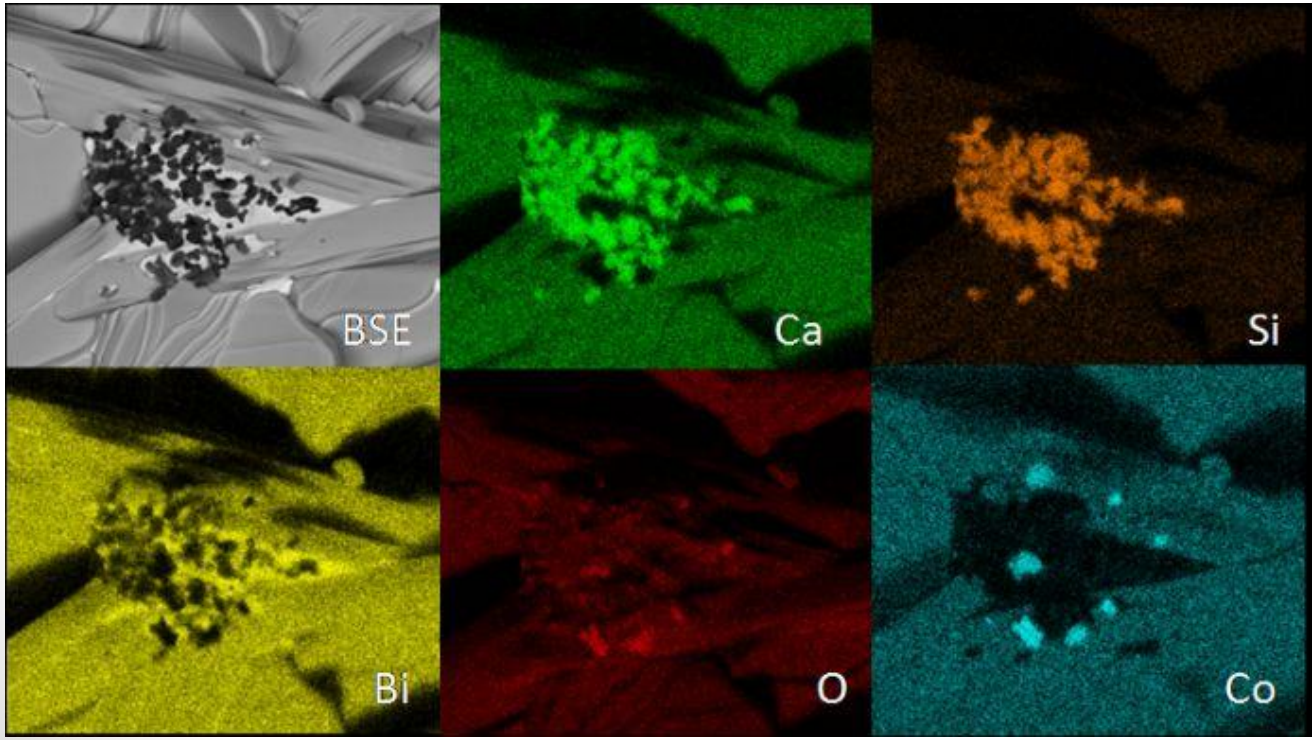


- standardless analysis
- the same operating parameters for qualitative and quantitative analysis
- more „careful" sample preparation (flat, polished samples)
- 2 microns particles for analysis
- carbon coating of non-conductive materials
- poor analysis of light elements (Z<11)
  - strong absorption
  - low number of electrons
- oxygen problem
- ZAF corrections

Element	Wt %	At %	K-Ratio	Z	A	F
C K	87.90	94.56	0.6749	1.0136	0.7575	1.0000
O K	5.37	4.34	0.0101	0.9946	0.1889	1.0000
AuM	0.87	0.06	0.0070	0.6411	1.2516	1.0003
S K	0.34	0.14	0.0031	0.9313	0.9960	1.0065
ClK	1.00	0.36	0.0090	0.8914	1.0082	1.0086
PdL	4.53	0.55	0.0371	0.7396	1.1064	1.0000
Total	100.00	100.00				

Mapping


BSE image
Single element map
20kV X430 50µm 10 67 BEC
Ca Ka1


BSE
Ca
Si
Bi
O
Co

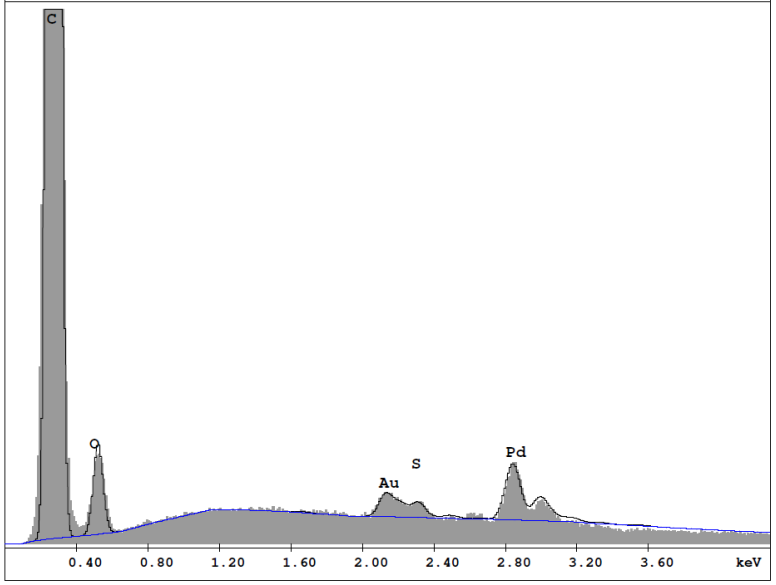
Practical Examples

c:\edax32\genesis\genspc.spc

Label:Chlorite (Nrm.%= 38.86, 20.96, 34.83, 1.14, 3.84, 0.28)

kV:15.0 Tilt:0.0 Take-off:36.2 Det Type:SDD Apollo X Res:133 Amp.T:12.80

FS : 7663 Lsec : 71 24-Feb-2016 10:50:12



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

Element	Wt %	At %	K-Ratio	Z	A	F
C K	87.83	94.57	0.7410	1.0141	0.8320	1.0000
O K	5.76	4.65	0.0109	0.9950	0.1909	1.0000
AuM	1.78	0.12	0.0143	0.6416	1.2490	1.0001
S K	0.35	0.14	0.0032	0.9319	0.9881	1.0044
PdL	4.29	0.52	0.0351	0.7400	1.1046	1.0000
Total	100.00	100.00				

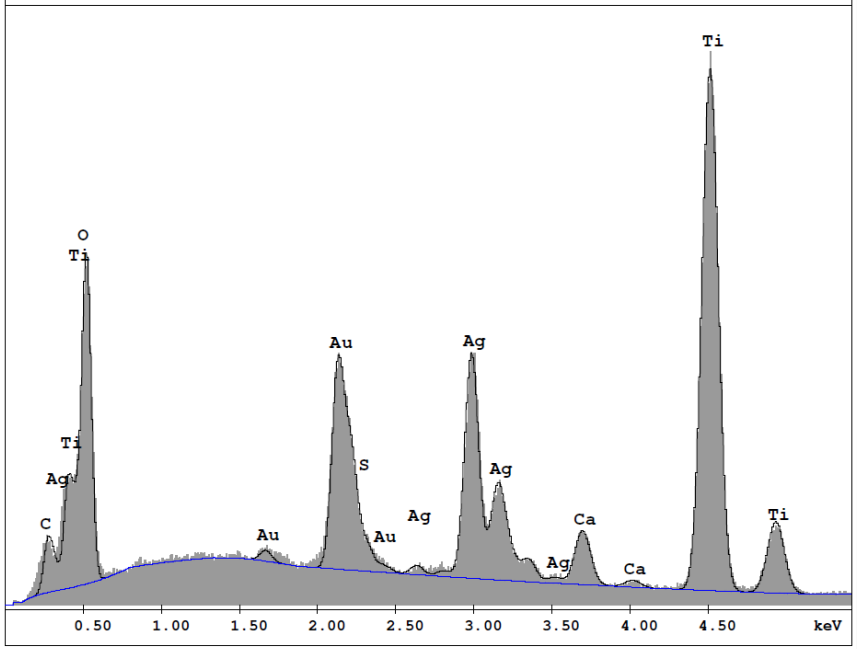
Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	5208.56	7.91	0.16	658.18
O K	106.96	15.66	1.30	6.83
AuM	41.02	54.78	3.55	0.75
S K	23.91	53.33	5.67	0.45
PdL	97.41	53.23	1.74	1.83

C:\MPC Photo\m_holdynski\20150325\TiO2_10V_01Au_01Ag_biel.spc

Label:Chlorite (Nrm.%= 38.86, 20.96, 34.83, 1.14, 3.84, 0.28)

kV:15.0 Tilt:0.0 Take-off:34.4 Det Type:SDD Apollo XL Res:136 Amp.T:12.8

FS : 6468 Lsec : 65 25-Mar-2015 15:31:00



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

Element	Wt %	At %	K-Ratio	Z	A	F
C K	1.86	5.65	0.0072	1.1857	0.3264	1.0004
O K	23.89	54.48	0.0414	1.1624	0.1490	1.0000
AuM	16.19	3.00	0.1327	0.7653	1.0700	1.0006
S K	0.72	0.82	0.0063	1.1052	0.7797	1.0096
AgL	18.87	6.39	0.1616	0.8774	0.9638	1.0122
CaK	2.37	2.15	0.0229	1.0796	0.8770	1.0228
TiK	36.10	27.50	0.3287	0.9875	0.9216	1.0003
Total	100.00	100.00				