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CHEM-E5140 Materials Characterization Laboratory

Energy dispersive x-ray spectroscopy (EDS or EDX)
Lecture
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Outline

1. Introduction
2. How do I get the data?
3. What can I analyze with EDS?
4. What kind of samples can be studied?
5. Typical applications

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1. Introduction

- Electron probe microanalysis (EPMA) can be carried out with the scanning electron microscope (SEM) having additional x-ray spectrometers.

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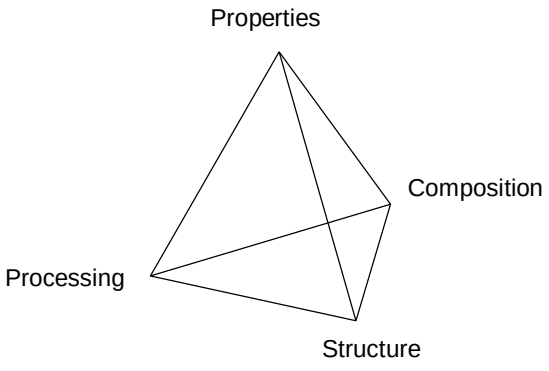
Materials science tetrahedron



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Materials characterization techniques

	Magnification	Resolution	Depth of field	Sample	Other
Basic optical microscope	10-1000x	1-0,2 μm	2-0,2 μm	Flat (polished, etched)	Inexpensive, Reflectivity, FTIR, Raman
Scanning electron microscope	10-200000x	1-100nm	1 mm – 0,1 mm	Usually electrically conductive	**Vacuum,** EDS, WDS, EBSD, CL, EBIC
Transmission electron microscope	>600000x	0,15-0,3 nm	n. 20 nm	Very thin	**Vacuum,** Diffraction, EDS, EELS

Other methods: **XPS (ESCA)**, AES, ...
XRD, XRR,
XRF, **Raman**, AAS, SIMS,PIXE, ...
AFM, STM, μXCT, ...

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2. How do I get the data?

- **Physical basis of the method**
- **How EDS works?**
- **Data acquisition**

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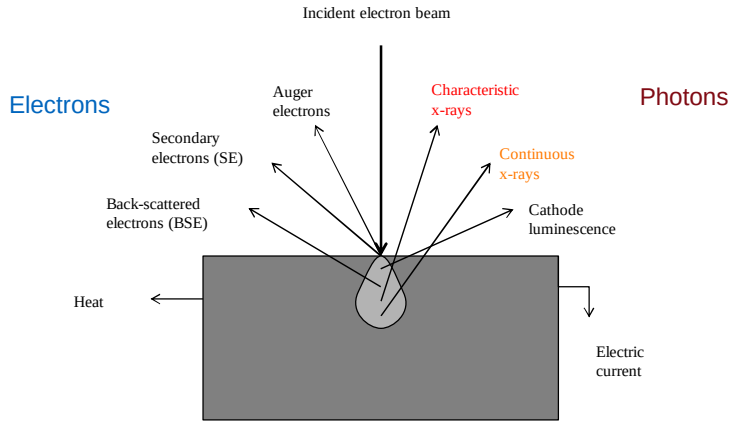
Electron beam specimen interactions



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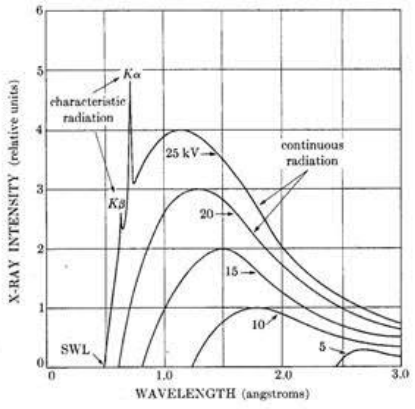
Generation of characteristic x-rays

- When acceleration voltage of primary beam electrons is increased adequately, specific intensity peaks are formed on top of continuous x-ray spectrum at wavelengths (energies) that are ”characteristic” to each element.
- After appearance, these characteristic wavelengths are independent of acceleration voltage.



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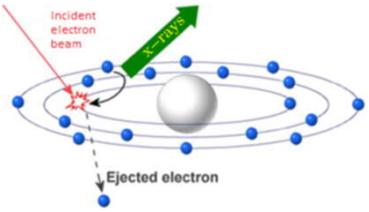
What happens at atomic level

1) Incident electron beam hits the sample

2) An electron is knocked out and a vacancy is produced causing unstable, excited state in atom

3) An electron from a higher energy (outer orbital) falls into the vacancy

4) Excess energy is emitted as a characteristic x-rays



5) The difference between the two shell energies equals the energy of the characteristic x-ray:

$$h\nu = E_f - E_i$$

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Characteristic x-ray nomenclature

- Depending on the shell involved in characteristic x-ray emission:

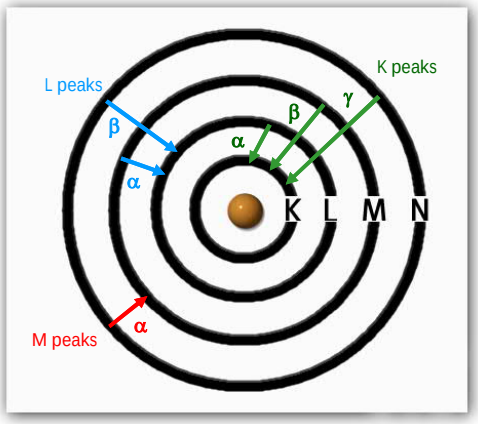
  $h\nu = E_f - E_i$

- we have:

- f = K --> K-series
  i = L -> Kα-lines
  i = M -> Kβ-lines
  i = N -> Kγ-lines

- f = L --> L-series
  i = M -> Lα-lines
  i = N -> Lβ-lines

- f = M --> M-series
  i = N -> Mα-lines



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Quantum mechanics of electron transitions

- Electron transitions that take place as a result of relaxation of excited state have not equal probabilities. Some of the transitions are even quantum mechanically forbidden.
- Calculation of quantum mechanical transition probabilities shows that transitions with:

  - $\Delta l = \pm 1$
  - $\Delta j = 0$ tai ± 1

  are allowed.

- Only with accurate spectrometers fine structures of atomic energy levels are detected in charecteristic x-ray measurements.

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Shells and subshells of atoms

Shell	Subshell number	Quantum numbers				Spectroscopic designation	Maximum electron population
		n	l	j	mj		
K	-	1	0	1/2	±1/2	1s	2
L	1	2	0	1/2	±1/2	2s	2
	2	2	1	1/2	±1/2	2p	2
	3	2	1	1/2	±3/2,±1/2	2p	4
M	1	3	0	1/2	±1/2	3s	2
	2	3	1	1/2	±1/2	3p	2
	3	3	1	3/2	±3/2,±1/2	3p	4
	4	3	2	3/2	±3/2,±1/2	3d	4
	5	3	2	5/2	±5/2,±3/2,±1/2	3d	6
N	1	4	0	½	±1/2	4s	2
	2	4	1	½	±1/2	4p	2
	3	4	1	3/2	±3/2,±1/2	4p	4
	4	4	2	3/2	±3/2,±1/2	4d	4
	5	4	2	5/2	±5/2,±3/2,±1/2	4d	6
	6	4	3	5/2	±5/2,±3/2,±1/2	4f	6
	7	4	3	7/2	±7/2,±5/2,±3/2,±1/2	4f	8

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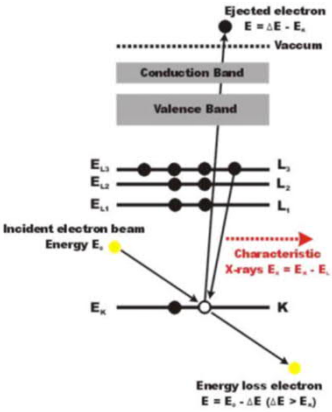
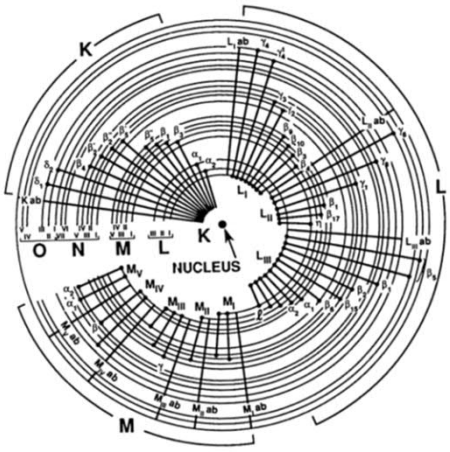
Characteristic x-rays





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Physical basis of x-ray spectroscopy

- Inelastic electron scattering is capable of producing characteristic x-rays, when electron energies exceed the critical energy of exitation.
- **Characteristic x-ray wavelengths are specific to elements**
- The wavelengths obey Moseley's law:

  $\lambda^{-1/2} = C(Z-\sigma)$

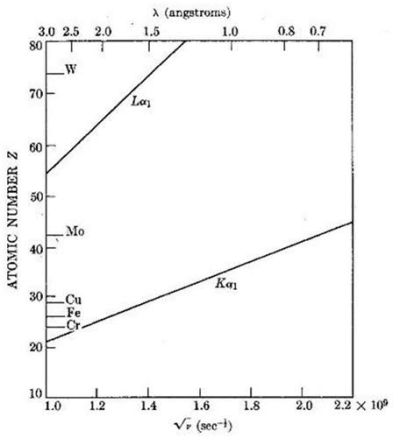
  or

  $E = D(Z-F)^2$

  where Z is the atomic number. C,σ,D and F are electron shell dependent constants and E is energy of the radiation.
- Relation between wavelengths and energy:

  $E = hc/\lambda$

  - wavelength dispersive spectrometry (WDS)
  - energy dispersive spectrometry (EDS)



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Numerical data on characteristic x-ray energies [keV]

Z	Element	Kα1	Kα2	Kβ1	Lα1	Lα2	Lβ1	Lβ2	Lγ1
4	Be	0.1085							
S	B	0.1833							
6	C	0.277							
7	N	0.3924							
8	O	0.5249							
9	F	0.6768							
10	Ne	0.8486	0.8486						
11	Na	1.04098	1.04098	1.0711					
12	Mg	1.25360	1.25360	1.3022					
13	Al	1.48670	1.48627	1.55745					
14	Si	1.73998	1.73938	1.83594					
15	P	2.0137	2.0127	2.1391					
16	S	2.30784	2.30664	2.46404					
17	Cl	2.62239	2.62078	2.8156					
18	Ar	2.95770	2.95563	3.1905					
19	K	3.3138	3.3111	3.5896					
20	Ca	3.69168	3.68809	4.0127	0.3413	0.3413	0.3449		
21	Sc	4.0906	4.0861	4.4605	0.3954	0.3954	0.3996		
22	Ti	4.51084	4.50486	4.93181	0.4522	0.4522	0.4584		
23	V	4.95220	4.94464	5.42729	0.5113	0.5113	0.5192		
24	Cr	5.41472	5.405509	5.94671	0.5728	0.5728	0.5828		
25	Mn	5.89875	5.88765	6.49045	0.6374	0.6374	0.6488		
26	Fe	6.40384	6.39084	7.05798	0.7050	0.7050	0.7185		
27	Co	6.93032	6.91530	7.64943	0.7762	0.7762	0.7914		
28	Ni	7.47815	7.46089	8.26466	0.8515	0.8515	0.8688		
29	Cu	8.04778	8.02783	8.90529	0.9297	0.9297	0.9498		
30	Zn	8.63886	8.61578	9.5720	1.0117	1.0117	1.0347		
31	Ga	9.25174	9.22482	10.2642	1.09792	1.09792	1.1248		
32	Ge	9.88642	9.85532	10.9821	1.18800	1.18800	1.2185		
33	As	10.54372	10.50799	11.7262	1.2820	1.2820	1.3170		
34	Se	11.2224	11.1814	12.4959	1.37910	1.37910	1.41923		
35	Br	11.9242	11.8776	13.2914	1.48043	1.48043	1.52590		
36	Kr	12.649	12.598	14.112	1.5860	1.5860	1.6366		
37	Rb	13.3953	13.3358	14.9613	1.69413	1.69256	1.75217		
38	Sr	14.1650	14.0979	15.8357	1.80656	1.80474	1.87172		

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Intensity relations of x-ray lines

- The following common “families of lines” can be used by the microscopist in peak identification:
- Kα : Kβ = 10 : 1
- Lα : Lβ1 : Lβ2 : Lγ = 10 : 7 : 2 : 1
- Mα : Mβ = 10 : 6

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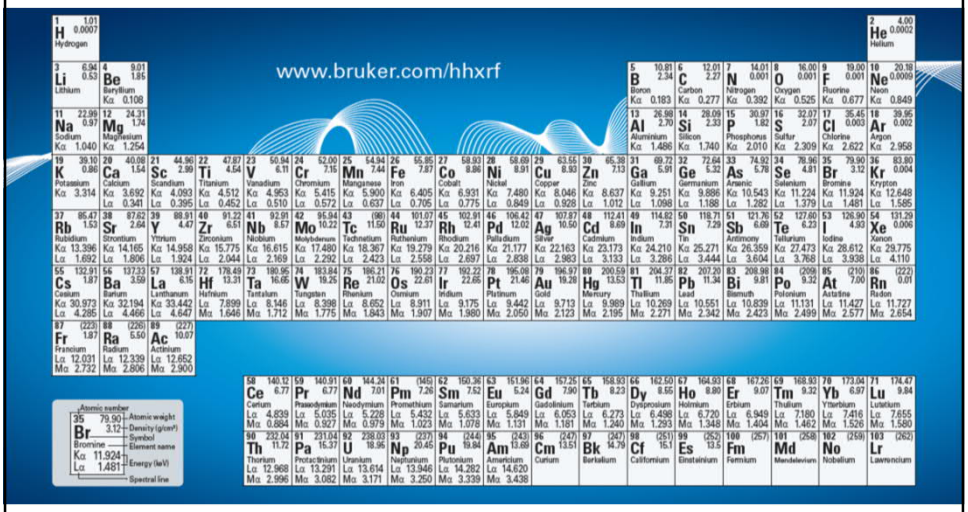
Periodic table of elements and x-ray energies



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How EDS works?

- Starting point of electron probe microanalysis is measurement of x-ray spectrum emitted by the sample. In other words, measurement of x-ray intensity as a fuction of either wavelength or energy
- Historically measurement of wavelength is older and still more precise method
- Measurement of energy is faster, because the whole spectrum is measured simultaneously

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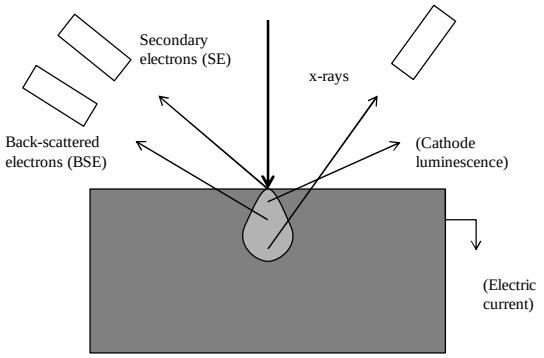
Signal detection



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SEM with x-ray spectrometers

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EDS measurement system

Four primary components of the EDS setup are

- excitation source (electron beam)
- x-ray detector
- pulse processor
- analyzer

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Operation principle of a semiconductor detector

- As an electric component the detector is a reverse biased diode. X-ray photon absorption produces transient current pulse
- X-ray photon absorption generate electron-hole-pairs. Generated total charge is proportional to x-ray photon energy

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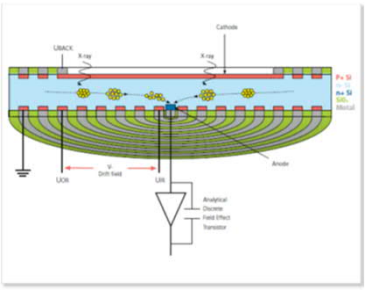
Silicon drift detector (SDD)

- The detector is a semiconductor device that through the process of ionisation converts an x-ray of a particular energy into an electric charge of proportional size.
- SDD devices use a field gradient applied by ring electrodes on its back surface to collect the charge liberated by each x-ray detected, at the anode.
- Anode << cathode ->small capacitance -> high speed
- High speed -> smaal leakige current-> less need for cooling
- Peltier-cooling (-25 °C) is sufficient



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EDS system performance

- EDS measures simultaneously the whole spectrum.
- Although electronics of EDS systems is very fast, processing of a pulse takes certain time (4-100 μs).
- In case of exact energy x-ray photon, measurement process cause statistical variation in measurement result (appr. 145 eV FWHM for a Mn Kα peak).

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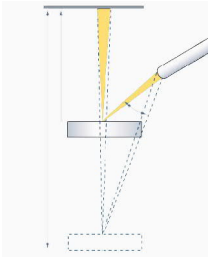
Beam-sample-detector geometry

- Changes in the beam-sample-detector geometry effect measurement results
- If this is not taken into account, systematic errors in intensity measurement arise
- Therefore, specific ”analytical” working distance is defined for each measurement instrument



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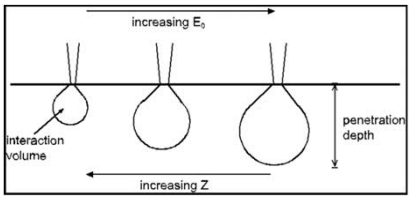
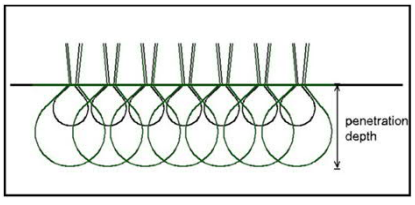
Spatial resolution is dictated by the interaction volume





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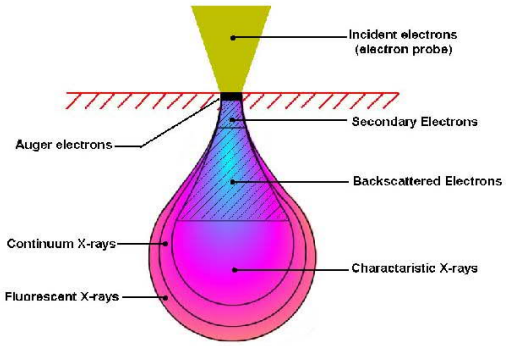
Schematic illustration of interaction volumes for various signals



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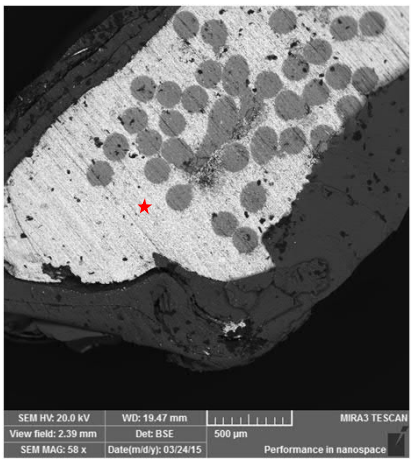
EDS data acquisition



Select:
- Acceleration voltage
- Probe current

Take:
- BSE image

Choose:
- Location to be studied
- Duration of signal acquisition
- Process time for pulse processing

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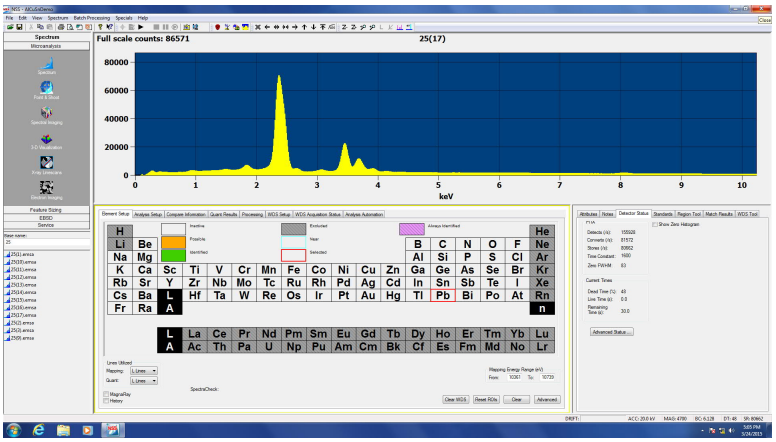
Collection EDS spectrum



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3. What can I analyze with EDS?

- local composition qualitatively
- local composition quantitatively

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Elemental analysis with EDS

- In a certain sense, interpreting X-ray spectra is simple
- A spectrum from even complex material can be thought of as a scaled sum of spectra from the constituent elements (scaling is non-linear)
- Possible extra peaks are artefacts produced by the measurement system and they can be recognized and removed

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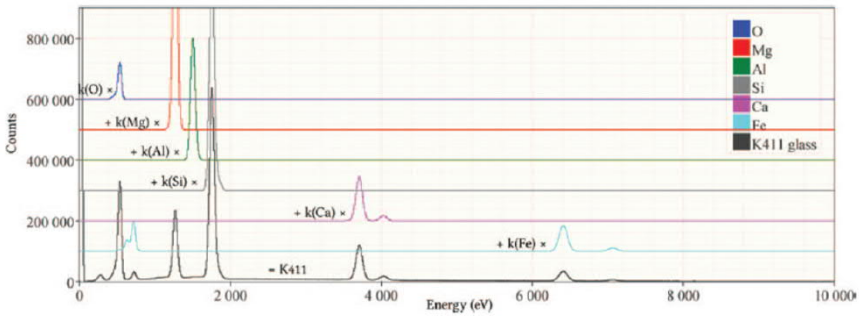
An example showing how the spectrum from a compound can be expressed as the sum of scaled spectra from the constituent elements



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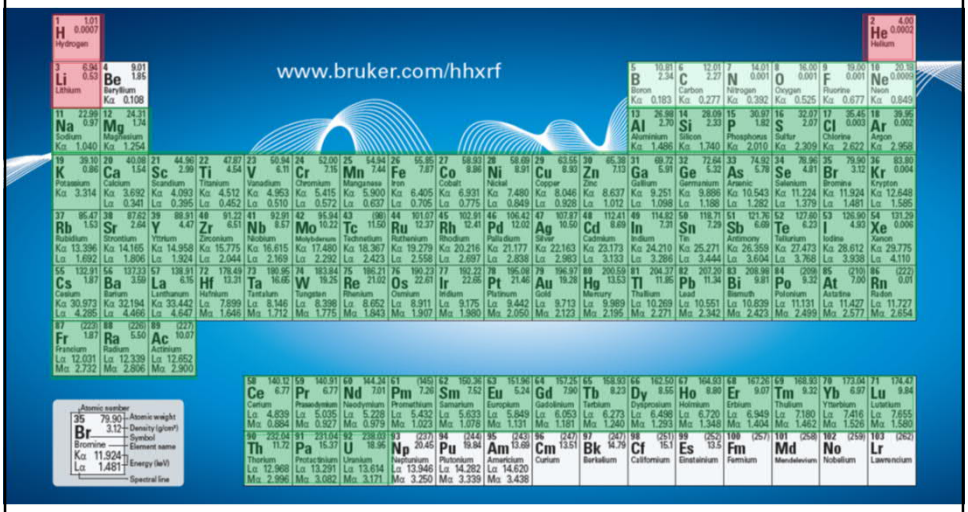
Periodic table of elements and x-ray energies



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Elemental analysis using electron microprobe

- Qualitative analysis
- Quantitative analysis
- Semi-Quantitative analysis

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Modes of data acquisition in microanalysis

- Point analysis
- Line analysis
- Area analysis
- Elemental maps

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Qualitative elemental analysis

- Qualitative elemental analysis involves identification of elements present at studied location of the sample utilizing positions of characteristic x-ray lines emitted from the sample

- Nottice
  - Spectrometer calibration
  - Adequate acceleration voltage (over voltage)
    - > 1,5 * critical energy E_c
  - Spectral artefacts
    - Sum peaks
    - Escape peaks
  - Peak overlaps
    - Peak shape and height
  - K, L, M … peak families and intensity relations
  - Detection limits
    - > 3 * square rooth of background intensity

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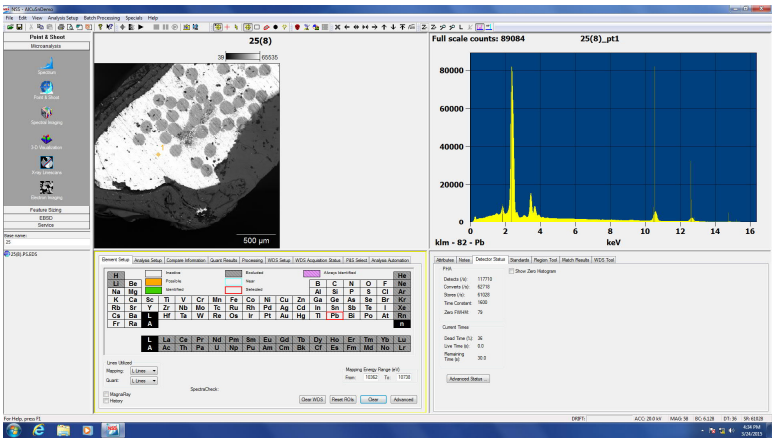
Identification of x-ray lines



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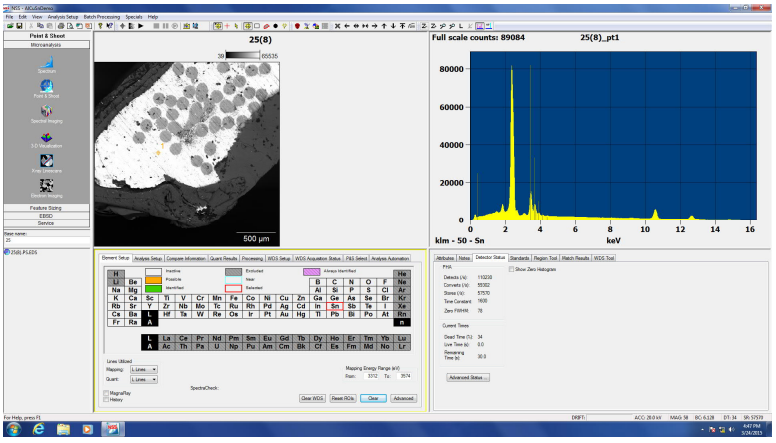
Identification of x-ray lines



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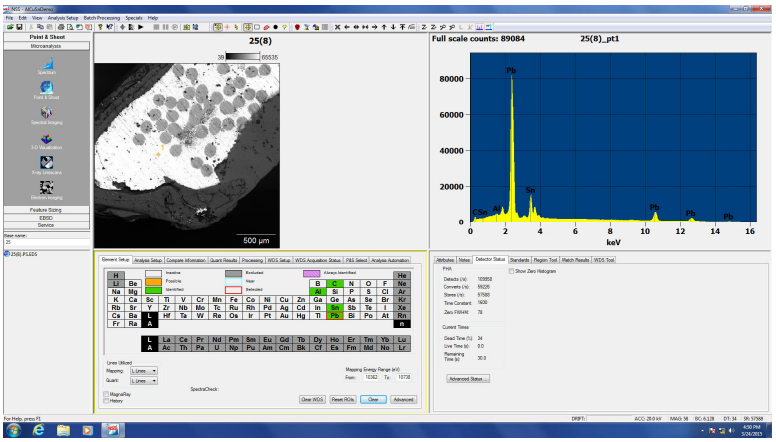
Automatic identification of x-ray lines



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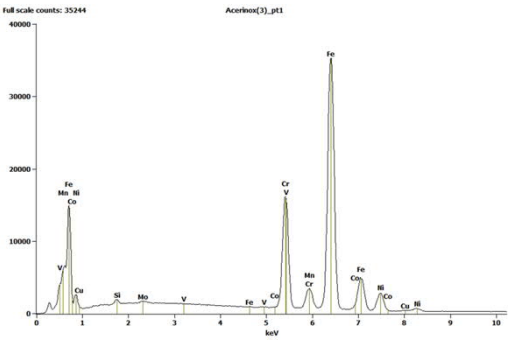
Spectral Resolution Requirements

- Good spectral resolution permits easy isolation, identification, and measurement of peaks
- If peak separation is bigger than ~2x resolution:
  - Peaks are isolated
  - Peak identification is trivial unless the second element is a trace element
  - Software is needed for quantification
- If peak separation is less than ~2x resolution:
  - Peaks overlap in display
  - Peak deconvolution is needed
  - Software is needed for quantification
  - In practice, most spectra require software to analyze peaks, even at highest resolution



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Quantitative elemental analysis

- Quantitative elemental analysis involves measurement of intensities of characteristic x-ray lines emitted from the sample at studied location.
- The analysis is based on assumption that intensities of characteristic x-ray lines are proportional to concentrations of elements in the sample.
- However, proportionality is not linear and intensity correction procedures are needed

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Quantitation of intensity measurements

- Quantitation starts with comparing intensities measured from sample to intensities from known standards. In this way the ratio of the unknown-to-known intensities, *after continuum background is subtracted* and *peak overlaps are counted for*, is established :

$$k_i = (N\text{-}B)_i/(N\text{-}B)_{i0} = I_i/ I_{io},$$

where I_i ja I_{i0} are measured net intensities of peaks measured from the sample and the standard, respectively. N is intensity measured on the sample and B is the corresponding background at the same energy

- Measurements should be performed for all elements that have been identified in qualitative analysis

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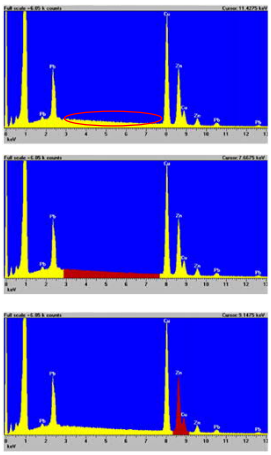
Filtering and deconvolution of raw data

- Quantitative x-ray analysis require peak intensity determination from measured spectrum
- There are two basic questions that are accosiated with this
  - To obtain true peak intensities, background continuum must be subtracted from the raw data. In filtering, effect of noise has to be considered especially in the case of trace elements
  - Because of limited energy resolution peak overlaps occur. This require peak deconvolution.



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The need for matrix corrections

- Matrix corrections deals with effects of compositional differences between the specimen and respective standards to obtain correct concentration values
- Relative intensities are proportional to mass fractions in following manner:

  $C_i/C_{io} = [ZAF]_i * k_i$

  - Z = atomic number correction
  - A = absorption correction
  - F = fluorescence correction
  - C_i = mass fraction of a element
- Z, A, F terms are non-linear correction factors that depend matrix composition and interactions between elements. Several procedures exists for correction calculations.
- Corrections must be applied separately for each element present in the sample

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Matrix effects

- Atomic number effect
  - Atomic number effects backscattering coefficient and the rate of energy loss due to inelastic scattering (stopping power).
- X-ray absorption effect
  - As an x-ray photon travels through the sample, it may be absorbed. Absorption probability depends on mass absorption coefficient radiation, specimen density and x-ray path length. Absorption is exponential.
  - Mass absorption coefficients depend on radiation wavelengths and therefore varies from one x-ray line to another
- X-ray fluorescence effect
  - In heterogenic samples, x-ray photons from atoms with higher atomic number may generate secondary fluorescense x-ray radiation in atoms with lower atomic number

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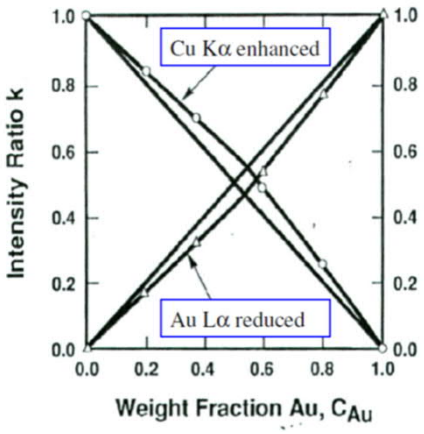
Matrix effects in binary Cu-Au alloy



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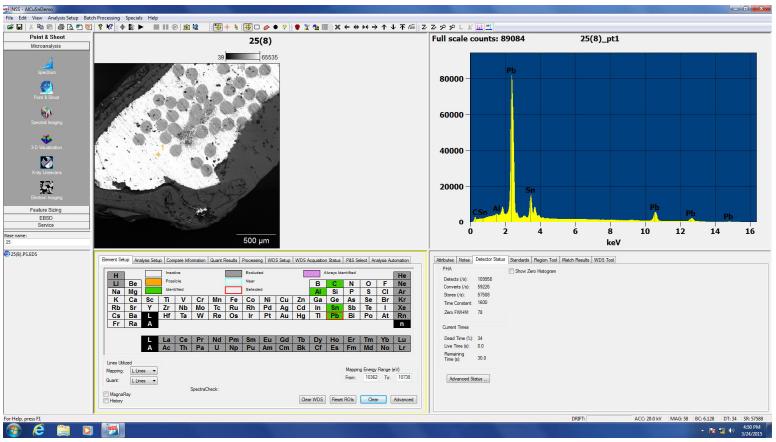
Qualitative results



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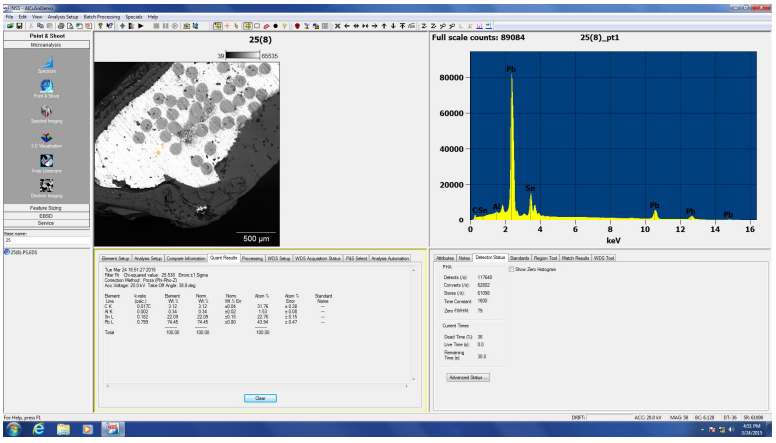
Quantitative results



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Classification of concentration into categories

- Major elements: more than 10 wt%
- Minor elements: 1-10 wt%
- Trace elements: les than 1 wt%

- Light elements Z<11 (Na)

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Semi-quantitative elemental analysis

- Applies theoretically calculated or ”factory measured” standards stored in computer memory.
- Good for examination of ratios element is sample.
- Fast to apply
- Doesn’t warn about missing elements

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Modes of data acquisition in microanalysis

- Point analysis
- Line analysis
- Area analysis
- Elemental maps

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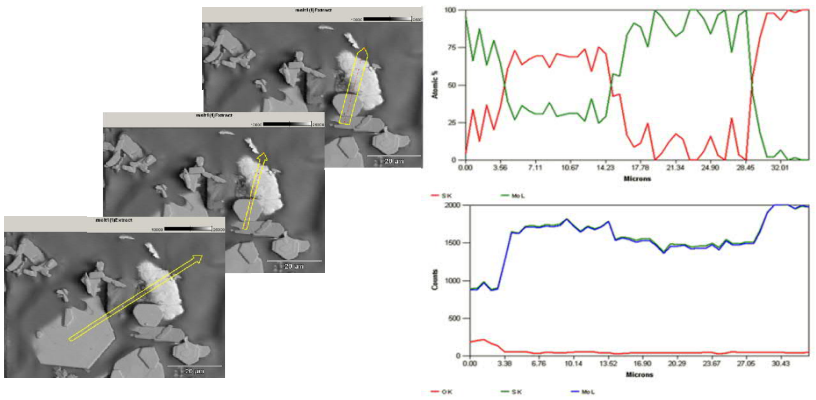
Line analysis



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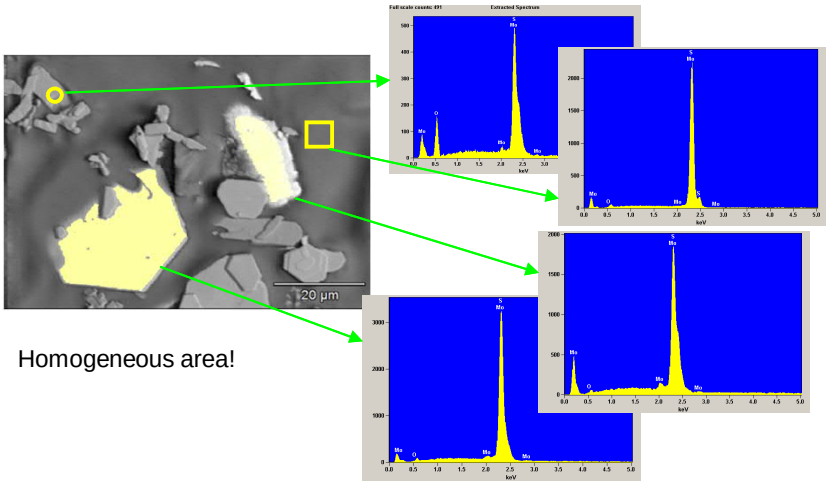
Area analysis



- Homogeneous area!

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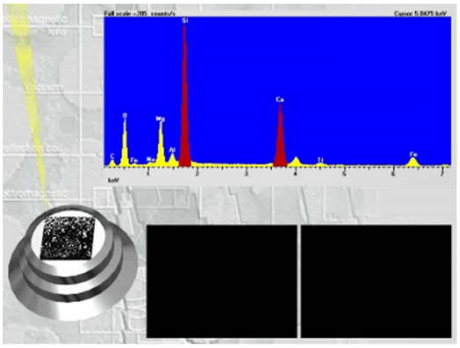
Measurement of elemental maps



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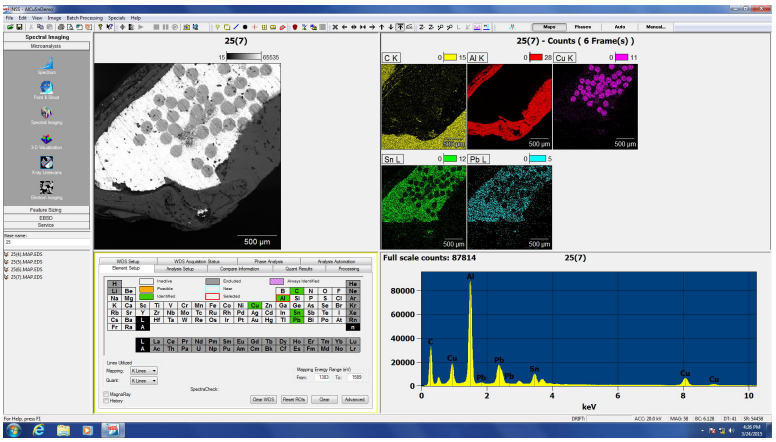
Elemental maps



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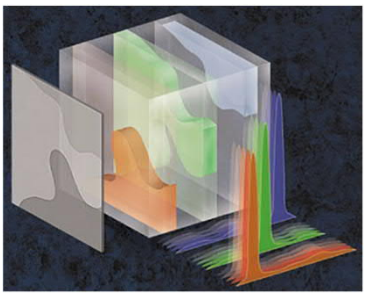
Spectral imaging

- In spectral imaging, spectral information is collected at every pixel of an image.
- Results 3-D data cube:
  - X, Y, Spectrum
- Data can be processed later with off-line computer:
  - Spectrums
  - Linescans
  - Maps
- Creates new possibilities!



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4. What kind of samples can be studied?

- Basic requirements for suitable samples
- Sample preparation

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Basic requirements for suitable samples

- Flat polished specimen are needed for quantitative analysis
- Specimen need to be homogeneous over the extend of electron and x-ray interaction volumes
- Specimen need to be stable under electron beam

- Topographic samples can be analysed qualitatively
- Coatings for electric conductivity

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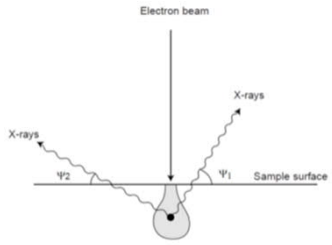
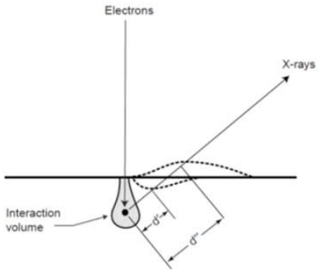
Geometrical effects





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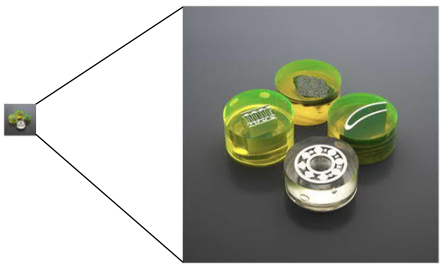
Materialographic sample preparation



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5. Typical applications

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Typical applications of EPMA in materials science and engineering

- Identification and quantification of **local elemental composition** of features down to micrometer sizes
- Analysis of compositional gradients at cross-sectional samples of coatings and interfaces
- Elemental mapping of heterogeneous specimens
- Phase identification together with supporting measurements (previous knowledge, EBSD, XRD)

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Overview of instrument capabilities

- High magnification
- Large depth of field

- Chemical information in micrometer scale (BSE, EDS, WDS)
- Crystallographic information (EBSD)

More than just a microscope

- Special techniques (EBIC, CL, voltage contrast)
- In-situ experiments (temperature, strain, etc.)

More than just composition and structure

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Thank you for your attention

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