

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 <u>http://www.gel.usherbrooke.ca/casino/index.html</u>

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....





EDS spectrum

- qualitative elemental analysis
- quantitative elemental analysis

In stats.	С	0	F	Al	Si	Ca	Ti	Nb
Yes	54.27	0.44		0.19	45.00		0.06	0.04
Yes	53.90	0.78	0.43	0.30	44.50		0.03	0.07
Yes	54.10	1.34	0.54	0.52	43.02		0.27	0.21
Yes	58.54	1.46	1.71	0.26	37.68		0.19	0.16
Yes	53.40	1.53	1.90	0.28	42.24	0.16	0.25	0.25
	58 54	1 53	1 00	0.52	45.00	0.16	0.27	0.25
	53 40	0.44	0.43	0.52	37.68	0.16	0.03	0.25
	In stats. Yes Yes Yes Yes	In stats. C Yes 54.27 Yes 53.90 Yes 54.10 Yes 58.54 Yes 53.40 58.54	In stats. C O Yes 54.27 0.44 Yes 53.90 0.78 Yes 54.10 1.34 Yes 58.54 1.46 Yes 53.40 1.53	In stats.COFYes54.270.44Yes53.900.780.43Yes54.101.340.54Yes58.541.461.71Yes53.401.531.9058.541.531.9053.400.44	In stats.COFA1Yes54.270.440.19Yes53.900.780.430.30Yes54.101.340.540.52Yes58.541.461.710.26Yes53.401.531.900.28Se53.400.440.430.19	In stats. C O F A1 Si Yes 54.27 0.44 0.19 45.00 Yes 53.90 0.78 0.43 0.30 44.50 Yes 54.10 1.34 0.54 0.52 43.02 Yes 58.54 1.46 1.71 0.26 37.68 Yes 53.40 1.53 1.90 0.52 45.00 58.54 1.63 1.90 0.52 45.00 53.40 0.44 0.43 0.19 37.68	In stats. C O F A1 Si Ca Yes 54.27 0.44 0.19 45.00 Yes 53.90 0.78 0.43 0.30 44.50 Yes 54.10 1.34 0.54 0.52 43.02 Yes 58.54 1.46 1.71 0.26 37.68 Yes 53.40 1.53 1.90 0.28 42.24 0.16 58.54 1.53 1.90 0.52 45.00 0.16 53.40 0.44 0.43 0.19 37.68 0.16	In stats. C O F A1 Si Ca Ti Yes 54.27 0.44 0.19 45.00 0.06 Yes 53.90 0.78 0.43 0.30 44.50 0.03 Yes 54.10 1.34 0.54 0.52 43.02 0.27 Yes 58.54 1.46 1.71 0.26 37.68 0.19 Yes 53.40 1.53 1.90 0.22 45.00 0.16 0.27 Yes 58.54 1.53 1.90 0.52 45.00 0.16 0.27 Yes 53.40 0.43 0.19 37.68 0.16 0.25

X-ray elemental mapping



[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.

[EDS Mapping Routines by Thermo Scientific]



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.

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



Interaction versus information volume

Information zones/volumes for different signals



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



Monte-Carlo electron trajectory simulations - CASINO

Silver Ag 20 keV



[INCA Software Help document by Oxford Instruments]







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

Atomic Number (Z)

- 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	$L\alpha = 1, L\beta_1 = 0.7, L\beta_2 = 0.2, L\gamma_1 = 0.08, L\gamma_3 = 0.03, L_1 = 0.04$
М	$M\alpha = 1, M\beta = 0.6, M\zeta = 0.06, M\gamma = 0.05, M_{\rm H}N_{\rm IV} = 0.01$

[Goldstein]

- 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)



Cross section for inner shell ionization Q

$$Q = 6.51 \times 10^{-20} \frac{n_{\rm S} b_{\rm S}}{U E_{\rm c}^2} \log_e(c_{\rm S} U),$$

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



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Overvoltage





Overvoltage

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

 $\begin{array}{l} \mathsf{MgB}_2 \;\; \mathsf{E} = 5 \; \mathsf{keV} \\ \mathsf{U} \; (\mathsf{Mg} \; \mathsf{K}\alpha) \cong 4 \\ \mathsf{U} \; (\mathsf{B} \; \mathsf{K}\alpha) \cong 27 \end{array}$

 $MgB_2 E = 10 \text{ keV}$ U (Mg K α) \cong 8 U (B K α) \cong 55

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



Energy of photons [keV]

Spectrum background

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

$$\Delta E = E_p = h v$$
 $\lambda = h / E_p$



$$I_{cm} \approx i_p \, \overline{Z} \, \frac{E_o - E_V}{E_V}$$

• Spectrum backround – intensity (i_p - current, \overline{Z} - mean atomic number, E_o - incident beam energy, E_V - continuum photon energy)

Effect of spectrum background on linescans

- Line-scans of measured signals at corresponding photon energies
- no background or overlapping maxima correction !!!!
 no quantitative relation between scans of different atoms !!!!







X-ray absorbtion

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

$$I = I_0 \exp\left[-\left(\frac{\mu}{\rho}\right)^{x\text{-ray}}(\rho t)\right]$$
$$\left(\frac{\mu}{\rho}\right) = KZ^4 \left(\frac{1}{E}\right)^3 \qquad \text{density thickness}$$

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 "machine" really do?

- A. An e-beam 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 operator verifies them *qualitative analysis*
- C. software subtracts the spectrum background and calculate peak areas I_i
- D. It calculates k-factor $k = \frac{I_i}{I_{(i)}}$ for each found element
- E. By iterative process it re-calculates composition considering different physically based corrections and normalizes the composition to 100%

C-D – quantitative analysis

A. Spectrum acquirement



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 characer 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)

Spectral artifacts resulting from detection process

- "Escape" peaks with energy E_x-1.74 keV during absorption of photon energy a secondary photon can escpe from the detector + decreasing of E_x peak
- Si internal fluorescence peak – due to excitation of Si of detector (~ 0.2 wt %)
- Si (and Au) absorption edges – due to low energy X-ray absorption in protecting window and detector upper layers



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-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"



 $Ga_2O_3(140 \text{ nm})$ on AI_2O_3 substrate

C. Quantitative analysis

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



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

D. Quantitative analysis

• **k** - factors $\mathbf{k} = {^{I}i}/_{I(i)} = {^{C}i}/_{C(i)}$ approximation to quantitative analysis

Castaing's first

 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 O K CuL MgK Total	1.64 0.60 97.40 0.37 100.00	7.91 2.17 89.04 0.88 100.00	0.0110 0.0065 0.9619 0.0035	1.3756 1.3494 0.9891 1.2489	0.4867 0.8084 0.9985 0.7526	1.0001 1.0016 1.0000 1.0000		
Element	Net Int	e. Bk	gd Inte.	Inte. Err	or	P/B		
C K O K CuL MgK	2.78 1.98 163.02 0.70		0.09 0.20 0.15 0.06	2.93 3.68 0.37 6.18	3 1 112 1	82.63 0.07 20.45 .0.72		



- The same physical concept based on characteristic Xray detection
- the measured X-rays are selected by diffraction on buildin crystals to measure 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	wavelength	elemental	kV,	resolution	peak	p/b	sensitivity
	line	nm	standard	detector type	eV *	intensity		ррт
						cps/µA		
LSM-200	Be Kα	11.4	Be	10, FPC	8	2.4 x 10⁴	40	335
LSM-200	Β Κα	6.76	В	10, FPC	15	9.0 x 10⁵	30	63
LSM-80N	Β Κα	6.76	В	10, FPC	9	5.7 x 10⁴	60	180
LSM-80N	Ο Κα	4.47	Vitreous C	10, FPC	14	4.7 x 10⁵	50	68
LSM-80N	Ν Κα	3.16	BN	10, FPC	16	9.5 x 10 ³	3	1950
LSM-80N	Ο Κα	2.36	SiO ₂	10, FPC	17	1.1 x 10⁵	50	140
LSM-80E	Ο Κα	4.47	Vitreous C	10, FPC	14	1.3 x 10⁵	57	120
LSM-80E	Ν Κα	3.16	BN	10, FPC	16	3.4 x 10⁴	13	495
LSM-60	Ο Κα	4.47	Vitreous C	10, FPC	12	3.2 x 10 ⁴	70	220
LSM-60	Ν Κα	3.16	BN	10, FPC	13	5.0 x 10 ³	10	1500
LSM-60	Ο Κα	2.36	SiO ₂	10, FPC	15	1.0 x 10⁵	65	130
ТАР	Ο Κα	2.36	SiO ₂	10, FPC	3	5.4 x 10 ³	350	240
TAP	ΑΙ Κα	0.834	A	20, FPC	9	2.7 x 10 ⁶	800	7
PET	Si Kα	0.7126	Si	20, FPC	2	5.4 x 10⁵	2600	9
PET	Τί Κα	0.2750	Ti	30, FPC/SPC	20	2.7 x 10 ⁶	500	9
LiF(200)	Fe Kα	0.1937	Fe	30, FPC/SPC	25	1.0 x 10 ⁶	525	15
LiF(200)	Cu Kα	0.1542	Cu	30, FPC/SPC	40	1.1 x 10 ⁶	315	18
LiF(220)	Cu Kα	0.1542	Cu	30, FPC/SPC	35	3.0 x 10⁵	400	30
LiF(220)	Ge Kα	0.1255	Ge	30, FPC/SPC	48	3.7 x 10⁵	210	37



- detects only one energy X-rays in the time
- different signal detection gas proportional counter
- high energy resolution 2 40 eV
- high count rate capability without compromising energy resolution
- Need of standards !!!!!
- time consuming, more complicated







MgB₂/NbTi/Cu





Line table editor



9.8 9.65 9.7 9.75 9.8 9.65 9.9 9.95 10 10.05 10.1 10.15 10.2 10.25 10 Full Scale 9429 dts Curson: 10.305 (0 cts) Angetron









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