Electron Microscopy

Advanced Techniques

1. High-Resolution TEM

2. Analytical EM

3. 3D Microscopy, Special Techniques, Trends

Introduction to EDX

Energy Dispersive X-ray Microanalysis (EDS, Energy dispersive Spectroscopy)
summary

- Energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of XRF. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing x-rays that are characteristic of an element’s atomic structure to be identified uniquely from each other.

- To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

Basics of EDX

- a) Generation of X-rays
- b) Detection
  Si(Li) Detector, EDS
- c) Quantification
  EDX in SEM, Interaction volume
  Monte-Carlo-Simulations
  EDX in TEM
- d) Examples
X-ray generation:
Inelastic scattering of electrons at atoms
\[ E_{\text{electron\_in}} > E_{\text{electron\_out}} \]

- Continuum X-ray production (Bremsstrahlung, Synchrotron)
- Characteristic X-ray emission

Core shell ionisation: chemical microanalysis by X-ray, Auger electron and Electron Energy Loss Spectrometries

Designation of x-ray emission lines

1ps
Forbidden transitions in quantum mechanics: conservation of angular momentum

Efficiency of X-ray generation

Relative efficiency of X-ray and Auger emission vs. atomic number for K lines

Ionization cross-section vs. overvoltage $U = E_0/E_{\text{edge}}$
(electron in $\rightarrow$ X-ray out)

Light element atoms return to fundamental state mainly by Auger emission. For that reason, their K-lines are weak. In addition their low energy makes them easily absorbed.

To ionized the incident electron MUST have an energy larger than the core shell level $U > 1$. To be efficient, it should have about twice the edge energy $U > 2$.
Characteristic lines: Moseley's Law

Frequency \( \nu \) of X-rays emitted from K-level vs. atomic number

\[
E = h \nu = c/\nu
\]

\[\nu = 2.4810^5(Z - 1)^2\]

with the Planck constant \( h = 6.626 \times 10^{-34} \) J·s

and 1eV = 1.6 \times 10^{-19} J

EDS range \( \approx 0.3\text{–}20 \) keV

To assess an element all detectable lines MUST be present!!!

Known ambiguities:
Al K\( \alpha \) = Br L\( \alpha \)
S K\( \alpha \) = Mo L\( \alpha \)

EDX spectrum of \((K,Na)NbO_3\)

Characteristic X-ray peaks

Max Energy, 10keV

Continuum, Bremsstrahlung

Electron beam: 10keV

Duane-Hunt limit
b) Detection of X-rays (EDX)

Right: Si(Li) detector
Cooled down to liquid nitrogen temperature

modern silicon drift (SDD) detector:
no LN cooling required
X-Ray energy conversion to electrical charges:
3.8eV / electron-hole pair in average
electronic noise + imperfect charge collection:
130 eV resolution / Mn Ka line

• Detector acts like a diode: at room temperature
  the leak current for 1000V would be too high!
• The FET produces less noise if cooled!
• Li migration at room temperature!
• ->Detector cooling by L-N

Detection limit EDS in SEM

• Acquisition under best conditions
  - Flat surface without contamination
    (no Au coating, use C instead)
  - Sample must be homogenous at the
    place of analysis (interaction
    volume!!)
  - Horizontal orientation of the
    surface
  - High count rate
  - Overvoltage $U = E_0 / E_c > 1.5 - 2$

• For acquisition times of 100sec.:
detection of ~0.5at% for almost all elements
(K,Na)NbO$_3$

Continuum, Bremsstrahlung

Overvoltage, 10keV

Duane-Hunt limit

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Na</th>
<th>K</th>
<th>Nb</th>
<th>O</th>
<th>Total</th>
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<td>8.19</td>
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<td>60.9</td>
<td>100.0</td>
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<td>100.0</td>
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<td>21.1</td>
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<td>20.8</td>
<td>61.1</td>
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</tbody>
</table>

Max. 9.79 10.2 21.1 61.5 1
Min. 7.82 8.66 20.3 60.4 1

(K,Na)NbO$_3$
c) Quantification

- First approach: compare X-ray intensity with a standard (sample with known concentration, same beam current of the electron beam)
- $c_i$: wt concentration of element $i$
- $I_i$: X-ray intensity of char. Line
- $k_i$: concentration ratio

\[ \frac{c_i}{c_{i_{std}}} = \frac{I_i}{I_{i_{std}}} = k_i \]

Yes, but…. Intensity ~ Concentration...?

How many different samples...?
Electron Flight Simulator
**Casino**

- Image of a software interface showing X-rays generated and X-rays detected.

- Diagram with labels: X-rays generated and X-rays detected.
Quantification

Correction matrix

\[
\left[ Z \times A \times F \right] \frac{C_i}{C_i^{\text{std}}} = \frac{I_i}{I_i^{\text{std}}} = k_i
\]

- "Z" describes how the electron beam penetrates in the sample (Z-dependent and density-dependent) and loses energy.
- "A" takes into account the absorption of the X-rays photons along the path to sample surface.
- "F" adds some photons when (secondary) fluorescence occurs.

Flow chart of quantification

1. Measure the intensities and calculate the concentrations without ZAF corrections.
2. Calculate the ZAF corrections and the density of the sample.
3. Calculate the concentrations with the corrections.
4. Is the difference between the new and the old concentrations smaller than the calculation error?
   - Yes! Stop.
   - No, go back to step 2.
Correction methods:

- ZAF (purely theoretical)
- PROZA Phi-Rho-Z
- PaP (Pouchou and Pichoir)
- XPP (extended Puchou/Pichoir)

- with standards (same HT, current, detector settings)
- Standardless: theoretical calculation of $I_{\text{std}}$
- Standardless optimized: « hidden » standards, user defined peak profiles

Quantitative EDX in SEM

- Acquisition under best conditions
  - Flat surface without contamination, horizontal orientation of the surface (no Au coating, use C instead)
  - Sample must be homogenous at the place of analysis (interaction volume !!)
  - High count rate (but dead time below 30%)
  - Overvoltage $U=V_o/V_c > 1.5-2$
- For acquisition times of 100sec.:
  detection of ~0.5at% possible for almost all elements

- Standardless quantification
  - possible with high accuracy (intensities of references under the given conditions can be calculated for a great range of elements), test with samples of known composition, light elements (like O) are critical...
  - Spatial resolution depends strongly on HT and the density of the sample
Synthesized spectrum

Extraction of element maps

Spectrum imaging
Data cube

EDS in TEM

High spatial resolution!
**EDS in TEM**

- Thin samples -> correction factors weak (A and F can be neglected)
- Very weak beam broadening -> high spatial resolution ~ beam diameter (~nm)

High energy: artifacts!

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**STEM point analysis**

$\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (bulk)

Processing option: Oxygen by stoichiometry (Normalised)

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Mg</th>
<th>Si</th>
<th>Nb</th>
<th>Pb</th>
<th>O</th>
<th>Total</th>
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<tr>
<td>Spectrum 6</td>
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<td>100.00</td>
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<td>Spectrum 7</td>
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</tbody>
</table>

Max. | 30.02 | 13.32 | 13.66 | 23.04 | 60.25 |
Min. | 5.49 | 7.96 | 4.11 | 11.72 | 56.66 |

All results in Atomic Percent
STEM linescan
Pb(Zr,Ti)O₃ (thick film), slight Pb excess

STEM Element Mapping
PMN/PT 90/10 (bulk)
Analytical TEM of multifilament Nb$_3$Sn superconducting wires

Superconducting Nb$_3$Sn cables for high magnetic fields 10-20T:
increase current density, lower cost
Potential Applications:
NMR, Tokamak fusion reactors
Large Hadron Collider (LHC), CERN

Typical cable:
1 x 1.5mm cross-section
121x121 filaments of Nb$_3$Sn
in a bronze (Cu/Sn) matrix

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Processing “bronze route”

“Nano”-engineering: controlled creation of “imperfections” of nm scale (coherence length)

Cu and Ti are believed to play an important role at the grain boundaries: “dirty” grain boundaries = pinning

- Is it possible to detect Cu and Ti at the grain boundaries?
- What is the difference between the grain boundaries depending on where the additives are added to the unreacted material?

SEM: reacted filament (1 out of 14'000)
Typical problems: thinning of heterogeneous specimens: selective thinning

Cross-section, polished mechanically to 30 um, ion milled until perforation

STEM, Dark field: core of filament too thick, preferential etching of bronze matrix

Preparation by Focused Ion Beam
defining and cutting of lamella

“Lift-out”

TEM grid, 3mm diameter
Preparation by Focused Ion Beam
final thinning, “two windows”

“two windows, 5x5 um”

Top view: final thickness of 40-60 nm

Specimen preparation by focused Ion Beam (FIB):
large areas with uniform thickness ideally for EDX Analysis
in the TEM (STEM mode)

SEM (FIB)
thickness: 40-50 nm

Ion milling

STEM-DF

Sample #21

EDS, element maps
**Spot analysis**

**Line profile**

<table>
<thead>
<tr>
<th>Point</th>
<th>Ti % at</th>
<th>Nb % at</th>
<th>Sn % at</th>
<th>Ta % at</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>79.7</td>
<td>17.1</td>
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<td>2</td>
<td>0.4</td>
<td>79.2</td>
<td>17.8</td>
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<td>3</td>
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<td>8</td>
<td>1.2</td>
<td>73.7</td>
<td>22.8</td>
<td>2.1</td>
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<tr>
<td>9</td>
<td>0.9</td>
<td>70.4</td>
<td>26.4</td>
<td>2.1</td>
</tr>
</tbody>
</table>

**Sample #21**

*Grain boundaries? Ti/Cu*

EDX line-scan

Cu and Ti at the grain boundaries: width ~ coherence length (4nm) possible pinning centers!!
grain boundary without Ti

OSIRIS Test
EPFL CIME

1 TECNAI based
   TIA, Compustage (sample holders..)
2 “boxed”
   LN 1 time/week, no viewing screen, motorized apertures
3 X-FEG
4 SUPER-X, EDX
5 STEM HAADF, ADF,BF
 Nb3Sn multifilament cable

128x98 pixels, 128 msec. (1 hour), 1 nA

STEM-DF

EDS, element maps

SEM (FIB) thickness: 40-50 nm

Linescan
128 points, 20 min.

grain boundaries? Ti/Cu
- 400x400 pixels (5umx5um)
- 4msec., (10min.)
- 2.5nA

- 400x400 pixels (500nmx500nm)
- 4msec., (10min.)
- 2.5nA