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 (↔ WDS)

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)
- Inner shell ionization
- Characteristic X-ray emission

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

Designation of x-ray emission lines

Forbidden transitions! quantum mechanics: conservation of angular momentum

Figure 3.37. Comprehensive energy-level diagram showing all electron transitions which give rise to K, L, and M x rays (Woldseth, 1973).
Efficiency of X-ray generation

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

Ionization cross-section vs. overvoltage $U = E_0/E_{edge}$
(electron in -> 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 $U > 2$.

Light elements
Auger Spectroscopy

Heavy elements
EDS

X-ray production vs. atomic number $Z$

X-ray fluorescence yield for K-, L-, and M-shells, as a function of atomic number.
Characteristic lines: Moseley's Law

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

\[
E = h \nu \ \text{and} \ \lambda = c/\nu
\]

\[
\nu = 2.4810^{15}(Z - 1)^2
\]

with the Planck constant \( h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \) and 1 eV = \( 1.6 \times 10^{-19} \text{ J} \)

EDS range ~ 0.3-20 keV

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

known ambiguities:

\( \text{Al K} \alpha = \text{Br} \text{ L} \\lambda \)

\( \text{S K} \alpha = \text{Mo} \text{ L} \\lambda \)

b) Detection of X-rays (EDX)

\[ E = h \nu \ \text{and} \ \lambda = c/\nu \]

\[ E = 1.6 \times 10^{-19} \text{ J} \]

Dewar

LN\(_2\)

FET Preamplifier

Si(Li) Detector

Be Window

Cold finger

signal out
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 and artifacts

Take care when looking for "trace" elements (low concentrations). Don't confuse small peaks with escape peaks!

EDX spectrum of \((\text{K,Na})\text{NbO}_3\)

Electron beam: 10keV
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 $U = E_o / E_c > 1.5$ - 2

For acquisition times of 100sec.: detection of ~0.5 at% for almost all elements

$(K,Na)\text{NbO}_3$

Continuum, Bremsstrahlung

Not ideal!
c) Quantification

First approach: compare X-ray intensity with a standard (sample with known concentration, same beam current of the electron beam)

\[ \frac{c_i}{c_{i\text{std}}} = \frac{I_i}{I_{i\text{std}}} = k_i \]
Intensity ~ Concentration...?

How many different samples...?
Electron Flight Simulator
Monte-Carlo Simulation with CASINO
PRZ Layer K of Element Nb

Non-Absorbed Intensity: 785.94
Absorbed Intensity: 774.06

PRZ Layer LIII of Element Nb

Non-Absorbed Intensity: 4566.37
Absorbed Intensity: 1895.53
40 kV
4 kV

PRZ Layer LIII of Element Nb

- Non-Absorbed Intensity: 38.94
- Absorbed Intensity: 38.40
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-dependant and density dependant) and loose 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

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**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?
   - no
   - Yes!
5. stop
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 $U= E_0 / E_c > 1.5-2$

For acquisition times of 100sec.:
detection of \( \approx 0.5 \text{at\%} \) 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
EDX mapping

Data cube:
In each pixel a spectrum is recorded and stored

Post-acquisition Analysis:
Each spectrum can be analyzed and quantified off-line

Extraction of element maps

Modern EDX Systems

User friendly
Modern electronics (Stability, speed, high count rates)
Drift corrections for long acquisition times (mapping)

Automatic identification (Spectrum synthesis)
“easy” Identification
Elemental mapping: Spectral imaging (data cube), Element selection after acquisition
Data-Export (reporting) Word, Powerpoint, Excel (html, emsa, tif etc.)

EDX has never been as easy
**Nb$_3$Sn multifilament superconducting cables**

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

Prof. R. Flükiger, V. Abächerli, D. Uglietti, B. Seeber
Dept. Condensed Matter Physics (DPMC), University of Geneva
Processing "bronze route"

Cu and Ti are believed to play an important role at the grain boundaries (pinning)

Is the Nb3Sn phase homogenous?

Is it possible to detect Cu and Ti at the grain boundaries?

SEM: reacted filament

SEM BSE images
Qualitative element distribution maps

20 keV
30 min.
Auto ID

Take care with Auto ID etc….

Manual ID
• Acquire first
• Analyze after…

Extraction of element maps

Quantification

~10ms / Spektrum

30min. / 512x384 Datapoints
« Quantify »...?

Improved statistics: 5x5 pixel binning
**Improvement**

- More time
- Less pixel
- Higher current

<table>
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<th>Element</th>
<th>App Conc.</th>
<th>Intensity Corrn</th>
<th>Weight%</th>
<th>Weight% Sigma</th>
<th>Atomic%</th>
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<td>0.7748</td>
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<td>Totals</td>
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<td></td>
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**Limits:**
- gun (FEG)
- Detector speed

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**Limit: detector time constant**

*(process time)*  
*Si(Li)* Detectors

Long time constant: 1-2'000 X-ray/Sec.  
Short time constant: 30-40'000 X-ray/sec.

For fast mapping with high currents:  
SDD (ADD) Detectors  
Detection rates:  
above 100’000 counts/sec

High energy resolution

Fast detector > low energy res  
WDX: even higher energy resolution, but not as easy to use as EDX!
Spatial resolution @ 30kV

Spatial resolution @ 7kV
Overvoltage and penetration depth!

To ionize 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 $U>2$.

- Nb Ka1 16.6 keV
  Nb La1 2.14 keV
- Cu Ka1 8.1 keV
  Cu La1 0.93 keV
- Sn Ka1 25.2 keV
  Sn La1 3.44 keV
- Ta Ka1 8.14 keV
  Ta La1 1.71 keV
- Ti Ka1 4.51 keV
  Ti La1 0.45 keV

Semiconductor materials:

- Cu-K 8.1kV, HT 15kV
  $U = \frac{15}{8.1} = 1.85$
Monte-Carlo Simulations

CASINO (free)
http://www.gel.usherbrooke.ca/casino/What.html

Electron flight simulator (commercial)
http://www.2spi.com/catalog/software/efs31.shtml

DTSA-II (free), NIST
Electron Flight Simulator

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**

$\text{PbMg}_{\frac{1}{3}}\text{Nb}_{\frac{2}{3}}\text{O}_3$ (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>
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<td>Spectrum 9</td>
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<td>7.96</td>
<td>4.11</td>
<td>11.72</td>
<td>56.66</td>
<td>100.00</td>
</tr>
</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)