Advanced Materials Analysis with Micro-XRF for SEM

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Micro-XRF on SEM
Speakers

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Outline

1. What is Micro-XRF for SEM
2. Working principle of Micro-XRF
3. Typical installation
4. Instrument design
5. Why is Micro-XRF for SEM useful? (Comparison between Micro-XRF and EDS)
6. Application examples
7. XRF and combined XRF/EDS quantification
8. The analysis software
9. How to optimize your analytical results (spatial resolution in Micro-XRF)
10. Specifications
11. Advantages
12. Summary
What is Micro-XRF for SEM?

- Contains a microfocus X-ray tube with a target spot size of 50 x 50 µm
- Target material according to analytical requirements: Rh, Mo preferred due to limited overlaps with lines of common elements
- Tube radiation is captured by a polycapillary optics and concentrated on the sample surface down to spot sizes of 35 µm
- Possibility to measure very small samples
- Due to the large dimensions of SEM chambers lenses are typically long → focus to focus distance of about 400 mm
- X-ray detection by a Bruker XFlash® detector → enables good energy resolution and high count rates
Working principle of Micro-XRF for SEM

- X-ray optics (the focused X-ray beam) has to be adjusted to match the location where the e-beam hits the sample (at the respective working distance of the EDS detector)

- Produces a high intensity X-ray spot < 40 µm diameter (area of analysis in the SEM can be made visible using a piece of paper or glass)

- X-ray sample positioning with the SEM stage
  - Allows XRF point measurements
  - Modern SEMs have high-precision motorized stages additionally supporting X-ray element distribution analyses via XRF map and line scan
Working principle of Micro-XRF for SEM
Polycapillary X-ray optics

SEM image of a polycapillary structure. Inner diameter in the range of 2 µm

Images courtesy of IfG GmbH, Berlin
Typical installation

- XTrace can be attached to an inclined SEM port
- Control unit includes HV generator and safety functions
- Fluorescence radiation is measured with an existing (Bruker) EDS detector
- Single user interface for QUANTAX EDS and QUANTAX Micro-XRF
- EDS detector can be installed either on opposite side or next to XTrace
XTrace – instrument design

- Primary filter wheel
- Z – adjustment
- X - Y adjustment
- Warning lamps for HV and X-ray beam
Why is Micro-XRF for SEM useful?
Comparison between XTrace and EDS

1. Technical parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>EDS</th>
<th>XTrace</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spotsize</td>
<td>nm range</td>
<td>35 µm (Mo K)</td>
</tr>
<tr>
<td>Elements</td>
<td>&gt; B (Be)</td>
<td>&gt; Na</td>
</tr>
<tr>
<td>Typical count rate / kcps</td>
<td>2 – 300</td>
<td>3 – 60</td>
</tr>
</tbody>
</table>

2. Sample preparation

Sample preparation for X-ray excitation is simpler because:

- The sample does not have to be electrically conductive
  - No special carbon coating required
- Surface preparation requirements are reduced due to the higher penetration depth for X-rays
Why is Micro-XRF for SEM useful?
Reduced spectral background

3. Analytical parameters

Spectra of a steel sample (CRM 474), measured in a SEM, EDS (blue) and with Micro-XRF (red)

**EDS:** sensitivity limited by high bremsstrahlung background, can “drown” peaks

**Micro-XRF:** photon excitation produces far less background, better sensitivity
Why is Micro-XRF for SEM useful?
Higher heavy element excitation efficiency

3. Analytical parameters

EDS: most sensitive for low energy lines, delivers information on elements that cannot be detected with XRF, e.g. Be, B, C, N

Micro-XRF: higher excitation efficiencies for heavy elements

Spectra of a glass standard (K-963) with more than 10 elements in very low concentrations, EDS (blue) and Micro-XRF (red) – Note the logarithmic scaling of spectra
LOD for Micro-XRF are significantly better for elements with \( Z > 20 \) but depend strongly on analyzed element and **matrix composition**!

- Trace elements in a light matrix: LOD 100 ppm down to even 10 ppm
- Trace elements in a heavier matrix: LOD range 100 ppm to 200 ppm
Why is it useful?  
Comparison between XTrace and EDS

3. Analytical parameters

Advantages of X-ray excitation:

• X-rays penetrate deeper into the sample
• Examination of thicker layers / coatings and of multiple layer structures
• Information depth depends on the sample matrix

Excitation efficiency for electron and photon excitation varies with the atomic number

• Light elements can be better analyzed with EDS
• Mid-range and heavy elements better with XRF

→ Combination of analytical results from electron and X-ray excitation is useful to improve the accuracy of quantification
Get more information from an EDS sample through Micro-XRF analysis!

**We have learnt:**

**EDS:**
- High spatial resolution (nm range),
- Gives topological information
- Sensitivity is limited due to the high spectral background,

**Micro-XRF:**
- Lower spatial resolution (µm range),
- Higher information depth
- Higher sensitivity for heavy trace elements,

→ Combined quantification – EDS for the light elements, XRF for the trace elements

→ XRF point and area analysis, line scans and mapping

→ **Application examples**
Mapping an integrated circuit on a PCB
Comparison XRF and EDS map

Tiled multi-element XRF map
50kV, 600µA
ICR: ~ 8.3 kcps
Map area: 10.3 x 7.7 mm²
Map size: 200 x 150 pixel
Step distance: 51.5 µm

Tiled multi-element EDS map
20kV
ICR: ~ 30 kcps
Map area: 9.6 x 7.2 mm²
Map size: 2048 x 1536 pixels
Mapping an integrated circuit on a PCB
Benefits of high information depth

Map size:
10.3 x 7.7 mm²
Mapping an integrated circuit on a PCB
Benefits of high information depth

Map size: 10.3 x 7.7 mm²
Mapping an integrated circuit on a PCB
Comparison of EDS and XRF sum spectra

Higher interaction depth of XRF provides additional sample information:

- Range between a few microns (heavy matrix) and millimeters (light matrix)
- Au is not detectable in the IC with EDS but with XRF
Maps of a multilayer PCB
Benefits of high information depth

Optical image

Mosaic SE images

Cu distribution with EDS
EDS: 20kV, ICR: ~ 60 kcps

Cu distribution with XRF
XRF: 50kV, 600µA
ICR: ~ 23 kcps
Map area: 10.5 x 0.9 mm²
Map size: 200 x 143 pixel
Step distance: 52.5 µm
Maps of a multilayer PCB
Benefits of high information depth

XRF element distribution

Map size: 10.5 x 0.9 mm²

EDS element distribution
Maps of a multilayer PCB
Analysis option HyperMap

- Spectra storage per pixel
- Internal storage of all element signals
- Offline evaluation with point and area analysis as well as line scans
- Quantification of point and area spectra extracted from the HyperMap database
Maps of a multilayer PCB
Analysis option HyperMap

• Area spectrum and line scan extracted from the HyperMap database
Maps of a multilayer PCB
Comparison of EDS and XRF sum spectrum

Fe as trace element cannot be detected by EDS (LOD), only by XRF

Higher interaction depth provides additional sample information
Analyzing components and circuits on PCB
Comparison of XRF and EDS maps

Tiled multi-element XRF map

- 50kV, 600µA
- Map area: 24 x 18 mm²
- Map size: 200 x 150 pixel
- Step distance: 70 µm

Tiled multi-element EDS map

- 20kV
- Map area: 24 x 18 mm²
Lava from La Palma (Canary Islands)

Trace element detection and distribution

Tiled XRF map

50kV, 600µA
ICR: ~ 14 kcps
Map area: 8.5 x 6.4 mm²
Map size: 210 x 157 pixel
Step distance: 40.5 µm

EDS map

20kV
ICR: ~ 40 kcps
Map area: 2.1 x 1.6 mm²
Map size: 512 x 384 pixel
Lava from La Palma (Canary Islands)
Trace element detection and distribution

Zn and Ni concentrations are below the limit of detection for EDS, but not for XRF!
Lava from La Palma (Canary Islands)
Comparison sum spectrum EDS and XRF

Trace element detection by XRF (Cu, Zn, Ga, Rb, Sr, Y)
Pressed fly ash
Trace element detection

Red: XRF (50kV, 600μA), 300 sec, ICR: 5 kcps
Blue: EDS (15kV), 300 sec, ICR: 14 kcps

XRF improves sensitivity for element lines Z > 11
Analysis of glass
Trace element detection

XRF improves detection of trace elements like: Cr, Ni, Fe, Ga, Ge, Bi, Th
Analysis of copper alloys
Detection of trace elements

- Micro-XRF detects trace elements like Mn and Fe
- Detectability for element lines like Si and Sn will be improved as well

Cu alloy sample

Red: XRF (50kV, 600µA), 120 sec, ICR: 64 kcps
Blue: EDS (20kV), 120 sec, ICR: 8 kcps
Combined quantification of EDS and XRF spectra

How does it work?
• The software performs the combined quantification automatically
• Elements Z<=12 will be quantified with EDS as well as element lines Z>12 if >5 wt%, minor and trace elements below 5 wt% will be quantified with XRF

When is it useful?
• For samples with a wide range in compositions including light and heavy elements and /or trace elements (e.g. glass, metals in polymers)
  ➔ Complete characterization of the sample
  ➔ Improved quantification results

Requirements
• The sample has to be homogenous – lateral and in depth
• No layer system
• No surface contamination
Results through combined quantification
NIST 620 certified glass standard

<table>
<thead>
<tr>
<th>Element</th>
<th>Certificate</th>
<th>EDS / wt% Norm.</th>
<th>XRF / wt% Norm.</th>
<th>EDS+XRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>46.82</td>
<td>45.71</td>
<td>45.58</td>
<td>46.03</td>
</tr>
<tr>
<td>Na</td>
<td>10.68</td>
<td>10.54</td>
<td>10.32</td>
<td>10.61</td>
</tr>
<tr>
<td>Mg</td>
<td>2.22</td>
<td>2.32</td>
<td>2.27</td>
<td>2.33</td>
</tr>
<tr>
<td>Al</td>
<td>0.95</td>
<td>1.34</td>
<td>0.89</td>
<td>0.89</td>
</tr>
<tr>
<td>Si</td>
<td>33.70</td>
<td>33.94</td>
<td>34.99</td>
<td>34.18</td>
</tr>
<tr>
<td>S</td>
<td>0.11</td>
<td>0.16</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>K</td>
<td>0.34</td>
<td>0.37</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>Ca</td>
<td>5.08</td>
<td>5.30</td>
<td>5.34</td>
<td>5.34</td>
</tr>
<tr>
<td>Ti</td>
<td>0.01</td>
<td>&lt;LoD</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>0.03</td>
<td>0.28</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>As</td>
<td>0.04</td>
<td>0.04</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Sr</td>
<td>-</td>
<td>0.00</td>
<td>0.04</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Red: XRF (50 kV, 600 µA), 100 sec
Blue: EDS (15 kV), 100 sec

- Glasses are materials with a wide variety of constituents (light and heavy elements)
- Glasses contain trace elements
- Complete sample information through combined quantification
Results through combined quantification
Metals in polymers

- Metal additives are used to tailor polymer properties for the desired application – these trace elements are detectable by XRF
- Complete sample information

<table>
<thead>
<tr>
<th>Element</th>
<th>Certificate</th>
<th>EDS* / wt% Norm.</th>
<th>XRF wt% Norm.</th>
<th>EDS+XRF*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>N/A</td>
<td>78.76</td>
<td>--</td>
<td>78.99</td>
</tr>
<tr>
<td>N</td>
<td>N/A</td>
<td>13.85</td>
<td>--</td>
<td>13.96</td>
</tr>
<tr>
<td>O</td>
<td>N/A</td>
<td>6.86</td>
<td>--</td>
<td>6.90</td>
</tr>
<tr>
<td>Cr</td>
<td>0.1483</td>
<td>0.4</td>
<td>64.8</td>
<td>0.12</td>
</tr>
<tr>
<td>Br</td>
<td>0.0006</td>
<td>&lt;LoD</td>
<td>&lt;LoD</td>
<td>&lt;LoD</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0026</td>
<td>&lt;LoD</td>
<td>&lt;LoD</td>
<td>&lt;LoD</td>
</tr>
<tr>
<td>Hg</td>
<td>0.0396</td>
<td>&lt;LoD</td>
<td>29.12</td>
<td>0.02</td>
</tr>
<tr>
<td>Pb</td>
<td>0.0060</td>
<td>&lt;LoD</td>
<td>6.05</td>
<td>0.004</td>
</tr>
</tbody>
</table>

* Neglecting hydrogen content
Results of XRF quantification
Copper alloy

- Copper alloys contain heavy elements and some of them in traces
- XRF quantification shows good results. It is not necessary to perform a combined quantification.

<table>
<thead>
<tr>
<th>Element</th>
<th>Certificate</th>
<th>XRF / wt% Norm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.001</td>
<td>&lt;LoD</td>
</tr>
<tr>
<td>Cu</td>
<td>82.05</td>
<td>81.72</td>
</tr>
<tr>
<td>Zn</td>
<td>17.92</td>
<td>18.28</td>
</tr>
</tbody>
</table>
Micro- XRF for SEM applications

Versatility in element analysis

- Geology
- Minerals and mining
- Glass and ceramics (glass chips, paint chips)
- Metals and alloys (Ni, Zi, Co, Ti alloys, stainless steel, brass, bronze)
- Metals in polymers
- Archeology and archeometry (ceramics, pigments, ink)
- Semiconductors
- Printed circuit boards and electronic components
- Fly ash (combustion residue)
ESPRIT 2.0 analytical software suite
Integrated user interface

- All devices integrated under one user interface
- Use EDS and XRF alone or simultaneously
- In case of EDS measurement X-ray beam shutter is closed (HV on)
- In case of single XRF measurement e-beam is blanked
Parameters influencing spatial resolution
Chromium Siemens Star

Determined by intensity per pixel, spot size, step size

Tilting the specimen towards the X-ray source improves X-ray spot resolution:
## XTrace – Technical Specifications

<table>
<thead>
<tr>
<th>Sample types</th>
<th>Solid, particles</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Excitation</strong></td>
<td>high brilliance X-ray tube with polycapillary optics</td>
</tr>
<tr>
<td><strong>Target material</strong></td>
<td>Rh, Mo (other target materials on request)</td>
</tr>
<tr>
<td><strong>X-ray tube parameters</strong></td>
<td>50 kV, 600 µA (maximum 30 W, depending on X-ray tube)</td>
</tr>
<tr>
<td><strong>Spot size</strong></td>
<td>Equal or less than 40 µm for Mo K</td>
</tr>
<tr>
<td><strong>Detection</strong></td>
<td>XFlash® silicon drift detector (30 mm² recommended)</td>
</tr>
<tr>
<td></td>
<td>energy res. &lt; 123 eV</td>
</tr>
<tr>
<td><strong>Count rate</strong></td>
<td>Approx. 60 kcps for pure Mn, Fe or Cu (with 30 mm² SDD)</td>
</tr>
<tr>
<td><strong>Element distribution analysis</strong></td>
<td>HyperMap capability, Line scan, objects like rectangles, ellipses and polygons</td>
</tr>
<tr>
<td><strong>Result presentation</strong></td>
<td>Quantification results, statistical evaluation, element distribution</td>
</tr>
<tr>
<td><strong>Power requirements</strong></td>
<td>110–240 V (1P), 50/60 Hz</td>
</tr>
<tr>
<td><strong>Dimensions</strong></td>
<td>W x D x H: 300 x 250 x 140 mm, 11 kg</td>
</tr>
<tr>
<td><strong>Safety</strong></td>
<td>Radiation safety using to two independently working electronic vacuum switches → X-ray shutter cannot be opened if specimen chamber is vented</td>
</tr>
</tbody>
</table>

16 October 2013
Advantages

• XTrace does not interfere with the normal operation of the SEM
• XRF analytical results comparable to benchtop XRF spectrometers
• 2 types of analysis in SEM (electron + photon excitation)
• One integrated user interface for EDS + Micro-XRF
• Including XRF line scan, mapping, object analysis
• Micro-XRF can be used for inhomogeneous samples and
• Combined quantification only for homogeneous samples
• Use of the existing SEM stage for XRF element distribution measurements and
• Existing (Bruker) EDS detector for spectra acquisition
Summary

• XTrace is attached to an inclined SEM port
• XTrace excitation radiation can be concentrated to spot sizes down to 35 µm
• The use of polycapillary optics ensure high count rates of up to 60 kcps for pure elements like Fe or Cu
• Bruker SDD offers stable energy resolution of 123 eV for this count rate (XFlash® 6 | 30 ultimate version)
• Advantage of Micro-XRF is the high sensitivity for trace elements
• Examination of thicker layers and of multiple layer structures
• Micro-XRF LOD range between 10 – 200 ppm (varies with the atomic number and depends on the sample matrix)
Summary

- XTrace allows XRF distribution analysis both as line scan and map. Spatial resolution is determined by spot size but also by step size and measured intensity.
- Data collection as HyperMap offers the possibility of comprehensive data evaluation after measurement.
- XTrace can be used for a wide range of different examinations – basic research, failure analysis or quality control for different types of materials.
Thank you for your attention!

If you have further questions please do not hesitate to contact our speakers:

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Innovation with Integrity