Micro-XRF and Confocal micro-XRF for Trace Analysis

Osaka City University: Kouichi Tsuji

Outline

1) Micro XRF and confocal M-XRF
2) LOD in vacuum
3) LOD by M-XRF and Confocal M-XRF
4) Secondary effects in confocal M-XRF
1) M-XRF and confocal M-XRF
Micro-XRF

- Small region can be analyzed using x-ray focusing optics, such as polycapillary optics.

Confocal micro-XRF

- Small analyzing volume, 3D limited.
- Reduction of background radiation
- Depth-selective analysis is possible

Polycapillary X-ray half lens for collecting XRF

X-ray scattering XRF, not detected

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Polycapillary optics (monolithic type)

Full lens; Point to point

Half, semi lens; Point to parallel

It is important to use a fine focused x-ray tube.

X-ray total reflection in capillary

Point X-ray source

Focal point

Collimating optic

Polycapillary X-ray lens (XOS)

Polycapillary full lens - Focal spot size: ≤10 μm, FWHM@17.4 keV
Input focal distance: 30.0 mm
Output focal distance: 2.5 mm
Optic enclosure length: 99.5 mm

Polycapillary half lens - Focal spot size: ≤10 μm, at 17.4 keV
Input focal distance: 3.0 mm
Optic enclosure length: 36 mm
Confocal m–XRF analysis of Electric cable

Polymer insulator

Cu wire

Cable coated with polymer insulator
Depth-selective X-ray spectra of electric cable

X-ray beam → Detector

Cu wire

Detector

PVC coating

XRF intensity / count

Energy / keV

Detector

X-ray beam

Depth-selective X-ray spectra of electric cable

Cu wire

CuKα

CuKβ

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2) LOD in vacuum
X-ray transmission in air, He, and vacuum

Calculated X-ray transmission in 3 cm in air, He-gas, and vacuum conditions
Confocal M-XRF in He gas

Experimental setup of confocal micro-XRF instrument with plastic bag including He gas
Confocal-M-XRF spectra in air and He gas

XRF peaks of Al K\textsubscript{\alpha} (1.49 keV), and Ti K\textsubscript{\alpha} (4.51 keV)
Development of a vacuum confocal XRF

Low energy x-rays are seriously absorbed in air. Therefore, XRF analysis in vacuum is effective for detection of low-Z elements.

S. Smolek, B. Pemmer, M. Folser, C. Streli, P. Wobrauschek;

ATI- TU-WIEN confocal micro-XRF spectrometer in vacuum

The extended setup for confocal micro-XRF. Components in the vacuum chamber (a). General setup with the vacuum chamber and outside components (b).

The sample is placed perpendicularly.

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A vacuum confocal XRF was developed at OCU in cooperation with ATI TU-WIEN.
Confocal micro-XRF spectra in air and in vacuum

In vac.

In air

NIST SRM 621

(Mo target)  air
(Rh target)  vacuum
**Standard Reference Material 621**

**Soda-Lime Container Glass**

(In cooperation with the American Society for Testing and Materials)

This Standard Reference Material is for use in checking chemical methods of analysis and for calibrating optical emission and x-ray spectrometric methods of analysis.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Percent by weight</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>71.13</td>
<td>0.03</td>
</tr>
<tr>
<td>Na₂O</td>
<td>12.74</td>
<td>0.05</td>
</tr>
<tr>
<td>CaO</td>
<td>10.71</td>
<td>0.05</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.76</td>
<td>0.04</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.01</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>0.27</td>
<td>0.03</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.13</td>
<td>0.02</td>
</tr>
<tr>
<td>BaO</td>
<td>0.12</td>
<td>0.05</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.040</td>
<td>0.003</td>
</tr>
<tr>
<td>As₂O₃</td>
<td>0.030</td>
<td>0.001</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.014</td>
<td>0.003</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.007</td>
<td>0.001</td>
</tr>
</tbody>
</table>

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## Confocal micro-XRF analysis in air and in vacuum

<table>
<thead>
<tr>
<th>Element</th>
<th>In air [ppm]</th>
<th>In vacuum [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>-</td>
<td>5504</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td>Si</td>
<td>17842</td>
<td>46</td>
</tr>
<tr>
<td>S</td>
<td>254</td>
<td>46</td>
</tr>
<tr>
<td>K</td>
<td>91</td>
<td>36</td>
</tr>
<tr>
<td>Ca</td>
<td>47</td>
<td>28</td>
</tr>
<tr>
<td>Fe</td>
<td>7</td>
<td>19</td>
</tr>
</tbody>
</table>

**LLDs of confocal setups for SRM621 (glass standards) in air and in vacuum**

\[
LLD = 3 \cdot \frac{W}{I_{Net}} \cdot \sqrt{\frac{I_{BG}}{t}}
\]

- \(W\) : concentration (%)
- \(t\) : measuring time (s)
- \(I_{Net}\) : net intensity (cps)
- \(I_{BG}\) : background intensity (cps)

QXAS, developed by The IAEA Seibersdorf Laboratories, was used for analysis.

Shaping time: 3 μs (SRM621),
3) LOD by M-XRF and Confocal M-XRF
Comparison of two setups

Micro-XRF setup

- X-ray tube (Rh target): 50 kV, 0.60 mA (30 W, max. 50 W)
- SDD: Vortex (SII Nano Technology): 50 mm², 128eV @ MnKα
- Polycapillary optics (XOS, spot size: about 10 μm)

Confocal micro-XRF setup

Without the collecting x-ray lens
To evaluate the sensitivity and lower limits of detection (LLDs) of the spectrometers a NIST SRM 621 (Soda-Lime Container Glass) was measured in vacuum.

- **Difference of analyzing volumes in two setups,**
- **Low transmission efficiency of polycapillary lens, especially in high energy region**
Transmission efficiency of polycapillary optics

Optic parameters:
- Input focal distance: 52 mm
- Output focal distance: 10 mm
- Length: 60 mm
- Collecting angle: 3.3°
- Channel diameter: 10 μm

Figure 3.3.5 Transmission efficiency of a polycapillary optic as a function of the X-ray energy

### LLDs evaluated by the same instrument

<table>
<thead>
<tr>
<th>Element</th>
<th>micro-XRF LLD [ppm]</th>
<th>Confocal micro-XRF LLD [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>6990</td>
<td>5504</td>
</tr>
<tr>
<td>Al</td>
<td>159</td>
<td>80</td>
</tr>
<tr>
<td>Si</td>
<td>98</td>
<td>46</td>
</tr>
<tr>
<td>S</td>
<td>53</td>
<td>46</td>
</tr>
<tr>
<td>K</td>
<td>45</td>
<td>36</td>
</tr>
<tr>
<td>Ca</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>Fe</td>
<td>4</td>
<td>19</td>
</tr>
<tr>
<td>As</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>Zr</td>
<td>24</td>
<td>-</td>
</tr>
<tr>
<td>Ba</td>
<td>74</td>
<td>68</td>
</tr>
</tbody>
</table>
Linear calibration curves were obtained for standard solutions.

<table>
<thead>
<tr>
<th>Surface of solution/ ppm</th>
<th>500 μm depth from the surface/ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>14</td>
</tr>
<tr>
<td>Mn</td>
<td>11</td>
</tr>
<tr>
<td>Fe</td>
<td>11</td>
</tr>
</tbody>
</table>

LOD depended on the depth for evaluation.
Applications of M-XRF and Confocal M-XRF

Point

Line

Mapping

Depth selective imaging

Cross sectional Depth imaging
Sample cell and experimental procedure

Steel sheet was placed in the sample cell.

NaCl solution (3.5 mass%) was filled in the sample cell.

X-ray tube (Mo)

Polycapillaries

SDD

Kapton (Nafion)

3.5% NaCl solution

X-Y-Z stage

Teflon (PTFE) case

Sample cell and experimental procedure

Steel sheet was placed in the sample cell.

NaCl solution (3.5 mass%) was filled in the sample cell.
Sample cell and experimental procedure

**Experimental conditions**

- Area: 1600 μm x 400 μm
- Step size: 50 μm x 10 μm
- Meas. Time: 60 s / pixel
- Total time: 24 h, 5 days

**Sample cell and experimental procedure**

- Acrylic spacer
- 3.5 wt% NaCl solution
- In air
- Under tensile stress
- Zn/Fe sheet
- Scratched

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It was observed that Zn was dissolved from the scratched line into the solution.
It was observed that Zn was dissolved from the scratched line into the solution.
Confocal micro-XRF method was applied for in-situ observation of corrosion process of metals in solution under tensile stress. It was confirmed that Zn was selectively dissolved in NaCl solution for Zn coated Fe sheet.
4) Secondary effects in confocal M-XRF
Secondary excitation in XRF analysis

X-ray Fluorescence

Sample

Primary X-ray

Secondary X-ray fluorescence

: Element A

: Element B

Z : A > B

Atomic number
Secondary excitation in confocal m-XRF setup
Layered sample

- Cu (5 μm)
- Kapton
- Co (25 μm)
- Kapton
- Cu (5 μm)

Si wafer substrate

Cu Kα can excite Co Kα.

Fe K absorption edge Co K absorption edge

Ni K absorption edge

mass absorption coefficient

Energy / keV

Cu foil

Metal foil (Co, Ti, Cr, Stainless steel)

Kapton film (Polyimide film)

Silicon Wafer
Secondary excitation of Co by Cu

Thickness of Kapton film was 0, 7.5, 75, 150 $\mu$m

Without Kapton film

With Kapton film of 7.5 $\mu$m

With Kapton film of 75 $\mu$m

With Kapton film of 150 $\mu$m

Shoulder peak

Additional peak
Secondary excitation process in confocal m-XRF

- Analytical point
- Primary X-ray
- Fluorescent X-ray of Cu
- Fluorescent X-ray of Co

Graph:
- Intensity / counts
- Depth / μm
- Cu
- Co

Analytical volume:
- Cu Foil
- Co Foil
- Kapton

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Simulation of confocal M-XRF intensity

Comparison of Experimental and simulation profiles

![Graphs showing experimental and simulation profiles for Z=-40μm and Z=41.0μm for Cu-Ti and Ti-Cu transitions.](image)

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Wire sample

Cross sectional view

Top view

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Comparison of Experimental and simulation maps

Wire distance \(~156 \mu m\)

Experimental

Simulation

Details: Tuesday Evening, Poster F-45

Calculation of Fluorescent X-ray Intensity for Confocal Micro-XRF Analysis of Inhomogeneous Samples – Part 2

(N. Kawahara)
Summary

• Confocal micro-XRF in vacuum is useful for improving DLs at localized small region.
• This technique is useful for monitoring simple chemical reaction in solution, such as in-situ observation of corrosion process of metals in solution under tensile stress. It was confirmed that Zn was selectively dissolved in NaCl solution for Zn coated Fe sheet.
• We have to pay attention to secondary effects in confocal M-XRF.