Outline

1) Micro-XRF
2) Confocal M-XRF in the laboratory
3) GE-XRS including GE-EPMA
1) Micro-XRF analysis

Micro x-ray beam is created by using polycapillary focusing optic.

X-ray fluorescence emitted in the path of micro x-ray beam is detected.
Polycapillary optics (monolithic type)

- Full lens; Point to point
- Half, semi lens; Point to parallel

Point X-ray source

Focal point

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

Polycapillary X-ray lens (XOS)

Polycapillary full lens - Focal spot size: ≤10 μm, FWHM@17.4keV
  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
Laboratory-made micro-XRF setup

Polycapillary X-ray lens (XOS)

XRF Intensity / cps

<table>
<thead>
<tr>
<th>Scan Distance / ( \mu \text{m} )</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>FWHM</td>
<td>9.64 ( \mu \text{m} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Divergence of the beam

\[
\theta = \tan^{-1} \left( \frac{a}{b} \right) : 84 \text{ mrad}
\]

Sample: Au wire

DXC2018 Workshop: Trace Analysis, K. Tsuji
Ayu is migratory fish between river and sea.

Trace elements that Ayu took accumulate at otolith day by day like tree ring. (a few μm per day)

Since Sr is rich in the sea, Sr distribution gives us the period the Ayu spent in the sea.
2) Confocal M-XRF

Micro-XRF

- Micro x-ray beam
- Energy Dispersive X-ray Detector
- Small region can be analyzed using x-ray focusing optics, such as polycapillary optics.

Confocal micro-XRF

- Polycapillary X-ray half lens for collecting XRF
- Small analyzing volume, 3D limited.
- Reduction of background radiation
- Depth-selective analysis is possible.
2-1) LLD of C-M-XRF 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$_\alpha$ (1.49 keV), and Ti K$_\alpha$ (4.51 keV)
A vacuum confocal XRF was developed at OCU with helpful suggestion from ATI TU-WIEN.
Confocal micro-XRF spectra in air and in vacuum

NIST SRM 621

In vac.

(Mo target)  
In air

(Rh target)  
vacuum

In air

1. Confocal micro-XRF spectra in air and in vacuum
2. NIST SRM 621
3. In vac.
4. (Mo target) In air
5. (Rh target) In vac.
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>
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</table>
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>

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

- $W$: 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),

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2-2) LLD 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

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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

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>
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<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>
2-3) Application of Confocal M-XRF
Analytical modes by Confocal M-XRF

Depth selective elemental mapping

Cross sectional, Depth elemental imaging

D XC2018 Workshop: Trace Analysis, K. Tsuji
X-ray elemental mapping of sardine fry

Depth
0 µm  50 µm  100 µm  150 µm  200 µm  250 µm

Ca
K
Cl
S
Zn

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3D-XRF imaging of sardine fry

DXC2018 Workshop: Trace Analysis, K. Tsuji
Analytical modes by Confocal M-XRF

- Depth selective elemental mapping
- Cross sectional, Depth elemental imaging

- Liquid
- Solid
Confocal Micro-XRF setup and sample

**X-ray tube**
MCBM 50-0.6 B (rtw, Germany)
Mo target, 50 kV, 0.6 mA

**SDD and lens**
Vortex EX-60 (Hitachi high-tech science co.)
Sens. area: 50 mm\(^2\) <130 eV at Mn Ka

*Polycapillary X-ray lens (XOS) : 10 \(\mu\)m*

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating layer</td>
<td>Al Si Ti Sn</td>
</tr>
<tr>
<td>15 (\mu)m</td>
<td></td>
</tr>
<tr>
<td>Chem. conversion</td>
<td>P Mn Ni Zn</td>
</tr>
<tr>
<td>2 ~ 3 (\mu)m</td>
<td></td>
</tr>
<tr>
<td>Plating Zn layer</td>
<td>Al Fe Zn</td>
</tr>
<tr>
<td>10 (\mu)m</td>
<td></td>
</tr>
<tr>
<td>Steel sheet</td>
<td>C Si P Mn Fe</td>
</tr>
</tbody>
</table>

Spatial resolution: 14.5 \(\mu\)m @Au L\(\alpha\)
Sample cell and experimental procedure

Steel sheet was placed in the sample cell.

NaCl solution (3.5 mass%) was filled in the sample cell.
Limit of Detection of metals in solution by Confocal-M-XRF

Standard solutions

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.

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Elemental maps in 0-24 hours (after one day)

24 hours / image

Analyzed area: 1680 μm x 600 μm
Step size: 15 μm x 10 μm

NaCl solution
Steel sheet
Scratch

Start
End
Elemental maps in 120-144 hours (after 6 days)

Blister-type corrosion was observed

Fe and Zn were dissolved and enriched inside the blister.
Zn, Fe and Mn under the blister were diffused in the solution, and enriched near the Kapton film. Corrosion process was successfully visualized.
Advantages of C-M-XRF

- A trace analysis of 3D localized region is possible inside of the sample.

- Elemental mapping for solid and liquid samples is possible.
3) Grazing Exit XRS

The surface of the sample should be entirely flat.

We can apply micro beam of x-rays, electrons and charged particles in GE-XRS.

Refraction of X-Rays

GE-XRS is useful for surface sensitive x-ray analysis.

*DXC2018 Workshop: Trace Analysis, K. Tsuji*
Good Combination of GE-XRF with WDS

**LLD for Si in organic materials was reported in ppb level.**


<table>
<thead>
<tr>
<th>Sample</th>
<th>Guide concentration (ppm)</th>
<th>Si content (ppm) ± S.D.</th>
<th>R.S.D. (%)</th>
<th>Detection limit (ppb)</th>
<th>Determination limit (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral water</td>
<td>15</td>
<td>17.2 ± 0.7</td>
<td>4</td>
<td>7.6</td>
<td>25</td>
</tr>
<tr>
<td>Spinach</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lyophilized</td>
<td>15</td>
<td>143 ± 8</td>
<td>6</td>
<td>9.4</td>
<td>31</td>
</tr>
<tr>
<td>Digested</td>
<td>5</td>
<td>4.5 ± 0.1</td>
<td>3</td>
<td>9.6</td>
<td>31</td>
</tr>
<tr>
<td>Serum</td>
<td>1–5</td>
<td>6.6 ± 0.5</td>
<td>8</td>
<td>13.7</td>
<td>46</td>
</tr>
<tr>
<td>Beer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>50</td>
<td>57 ± 5</td>
<td>8</td>
<td>28</td>
<td>96</td>
</tr>
<tr>
<td>Digested</td>
<td>5</td>
<td>5.1 ± 0.6</td>
<td>11</td>
<td>4.2</td>
<td>14</td>
</tr>
<tr>
<td>Urine</td>
<td>1–5</td>
<td>8.7 ± 0.6</td>
<td>7</td>
<td>14</td>
<td>48</td>
</tr>
<tr>
<td>Horsetail extract</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Powder</td>
<td>400</td>
<td>429 ± 2</td>
<td>1</td>
<td>18</td>
<td>62</td>
</tr>
<tr>
<td>Digested</td>
<td>10</td>
<td>23 ± 2</td>
<td>9</td>
<td>3.1</td>
<td>34</td>
</tr>
</tbody>
</table>

*Measuring conditions: analysis time of 500 s, 40 kV and 70 mA.

XRF intensity under total reflection of x-rays

Multi-layer model for calculation

\[ n_{pj} = 1 - \delta_{pj} - i\beta_{pj} \]

\[ \delta_{pj} = N_A (\rho_j / A_j) r e^{\lambda_p^2 (f_0pj + f_{pj}')} / (2\pi) \]

\[ \beta_{pj} = N_A (\rho_j / A_j) r e^{\lambda_p^2 (f''_{pj})} / (2\pi) \]

\[ f_{pj} = f_0pj + f_{pj} + i f''_{pj} \]

\[ r_p = (N_{pj} - N_{pj,j+1}) / (N_{pj} + N_{pj,j+1}) \]

\[ t_{pj} = 2N_{pj} / (N_{pj} + N_{pj,j+1}) \]

\[ N_{pj} = \sqrt{\theta_p^2 - 2\delta_{pj} - 2i\beta_{pj}} \]

Electric filed intensity at depth-\( z \) in layer-\( j \)

\[ E_{pj}(z) = E_{pj}^t \exp(-i2\pi N_{pj} z / \lambda_p) + E_{pj}^r \exp(i2\pi N_{pj} z / \lambda_p) \]

\( \theta_p \) glancing angle

\( N_{pj} \) reflection angle in the layer \( j \)
We can calculate XRF intensity under GE condition in the similar way as TXRF by considering reciprocity theorem.

The reciprocity theorem in optics is described as “a point source at \( P_0 \) will produce at \( P \) the same effect as that of a point source of equal intensity placed at \( P \) will produce at \( P_0 \”).
XRF intensity under glancing incidence and grazing exit conditions

\[
I_{fj} \propto \int_0^{d_j} \left[ E_{pj}^t \exp\left(-i2\pi N_{pj} z / \lambda_p \right) \\
+ E_{pj}^r \exp\left(i2\pi N_{pj} z / \lambda_p \right) \right] \\
\times \left[ E_{fj}^t \exp\left(-i2\pi N_{fj} z / \lambda_f \right) \\
+ E_{fj}^r \exp\left(i2\pi N_{fj} z / \lambda_f \right) \right] \left| ^2 \right. dz
\]

Glancing incidence process

Grazing exit process

◆ GI-XRF intensity is calculated with a grazing angle of 90°
◆ GE-XRF intensity is calculated with a normal incidence.

Calculation procedure is based on the theory shown in the following paper:

Calculation procedure is based on the theory shown in the following paper:
Free software for calculation of angle-dependent XRF intensity

http://www.a-chem.eng.osaka-cu.ac.jp/tsujilab/

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Calculations of GE-XRF & GI-XRF Intensity

- Single Layer GE-XRF
- Single Layer GI-XRF
- Double Layer GE-XRF
- Double Layer GI-XRF
- Implants with Gaussian profile GE-XRF
- Implants with Gaussian profile GI-XRF

You can use links above to calculate fluorescent intensity as a function of the grazing exit or glancing incident angle.

Related papers (please refer the following papers when you use the results obtained by this program)

Element at top layer

Layer thickness (nm)

Substrate

Layer Material: Ti
Layer Atomic Number: 22
Layer Atomic Weight: 47.867 g/mol
Layer Density: 4.54 g/cm³
Layer Thickness: 10.0 nm

Substrate Material: Si
Substrate Atomic Number: 14
Substrate Atomic Weight: 28.086 g/mol
Substrate Density: 2.33 g/cm³

Fluorescent X-Ray wavelength: 2.750 Å
Atomic Scattering Factor for Layer material: real -2.28 and imaginary 0.5560
Atomic Scattering Factor for Substrate material: real 0.41 and imaginary 0.9596

Primary X-Ray wavelength: 0.711 Å
Atomic Scattering Factor for Layer material: real 0.29 and imaginary 0.4352
Atomic Scattering Factor for Substrate material: real 0.08 and imaginary 0.0706
Primary X-Ray beam incident angle: 1.0 rad
Layer Material: 
Substrate Material: 
Layer Thickness: 1900 nm

Calculated Fluorescent Intensity Profile of with wavelength of 540 Å

DATA FILE
Enhancement of XRF Intensity for Thin Layers under GE

Rh tube (40 kV, 70 mA), <10 Pa, WDS (LiF200), GE-XRF (0.1 mrad step)

Carbon: 25 nm
Nickel: 1 nm
Carbon: 25 nm
Platinum: 1000 nm

Si wafer

Ni layer: 1 nm
Carbon: 49 nm

Ni layer: 1 nm
Carbon: 50 nm

Ni layer: 1 nm
Carbon: 51 nm

Fig. 6. Experimental angle dependence of Ni Kα for the Ni layer (1 nm) sandwiched with carbon layers of 49 nm (a), 50 nm (b) and 51 nm (c) in thickness. These curves were measured at a slit width of 10 μm, a counting time of 100 s at each emission angle changed with a step angle of 0.01 mrad.
Elemental X-ray images obtained by grazing-exit electron probe microanalysis (GE-EPMA)

Kouichi Tsuji,*†a,b Rik Nullens,a Kazuaki Wagatsuma,b and René E. Van Grieken,a

Fig. 1 A simple illustration of the interaction volume of electron beams for a single particle on a flat sample carrier. The regions observed by conventional EPMA (a) and GE-EPMA (b) are shaded (◼). In conventional EPMA, X-rays from both the particle and the sample carrier are detected. In contrast, only the X-rays emitted from the particle are measured by GE-EPMA.
Experimental Setup of GE-EPMA

EPMA (JEOL: JXA 8621) Sample stage

Conventional EPMA

(a) \[
\text{EDX} \quad \text{X-rays}
\]

GE-EPMA

(b) \[
\text{electron beams} \quad \text{EDX}
\]

Sample stage

stepping motor

sample
X-Ray Spectra in GE-EPMA (EDS)

Exit angle: ~0°

Exit angle: 45°

A single particle analysis is possible.

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GE-EPMA of inclusion in Stainless steel

Inclusions (about 0.2 μm)

Extracted inclusions on carbon film

Tohru Awane, et al.,
“Grazing Exit Electron Probe Microanalysis of Submicrometer Inclusions in Metallic Materials”,
A single inclusion analysis by GE-EPMA

- Exit angle: 30°
- GE-EPMA of a single inclusion

**Information**

- Inclusion + steel
- Steel
- Single inclusion
- Extracted inclusion

Energy (eV)
Quantitative GE-EPMA of inclusion on the steel

<table>
<thead>
<tr>
<th>inclusion no.</th>
<th>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>SiO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>SO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>MnO</th>
<th>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.2</td>
<td>37.4</td>
<td>4.2</td>
<td>14.1</td>
<td>40.3</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>2.2</td>
<td>35.4</td>
<td>2.9</td>
<td>15.2</td>
<td>40.0</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>39.6</td>
<td>3.1</td>
<td>17.0</td>
<td>38.3</td>
<td>nd</td>
</tr>
<tr>
<td>4</td>
<td>3.2</td>
<td>41.9</td>
<td>2.2</td>
<td>15.0</td>
<td>37.6</td>
<td>nd</td>
</tr>
<tr>
<td>5</td>
<td>3.1</td>
<td>39.2</td>
<td>3.5</td>
<td>14.9</td>
<td>30.1</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>2.2</td>
<td>40.5</td>
<td>3.2</td>
<td>13.2</td>
<td>41.0</td>
<td>nd</td>
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<tr>
<td>7</td>
<td>1.6</td>
<td>41.0</td>
<td>3.6</td>
<td>16.7</td>
<td>37.2</td>
<td>nd</td>
</tr>
<tr>
<td>8</td>
<td>2.6</td>
<td>37.4</td>
<td>1.3</td>
<td>15.7</td>
<td>43.1</td>
<td>nd</td>
</tr>
<tr>
<td>9</td>
<td>2.4</td>
<td>39.0</td>
<td>3.9</td>
<td>16.0</td>
<td>31.9</td>
<td>7</td>
</tr>
<tr>
<td>av</td>
<td>2.4</td>
<td>39.0</td>
<td>3.1</td>
<td>15.3</td>
<td>37.7</td>
<td>(2.4)</td>
</tr>
<tr>
<td>SD</td>
<td>0.5</td>
<td>2.0</td>
<td>0.9</td>
<td>1.2</td>
<td>4.2</td>
<td>_</td>
</tr>
</tbody>
</table>

**(A) GE-EPMA**

Quantification was possible without influence of steel. No- sample preparation.

<table>
<thead>
<tr>
<th>inclusion no.</th>
<th>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>SiO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>SO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>MnO</th>
<th>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
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<td>41.7</td>
<td>3.2</td>
<td>16.1</td>
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<td>(0.3)</td>
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<td>1.9</td>
<td>2.5</td>
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**(B) Extracted Inclusions**

Conventional EPMA of extracted inclusion

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Calculation of GE-EPMA Intensities

Monte Carlo simulation for Si wafer by CASINO program.

Depth distribution of Si Kα X-rays. (e⁻: 20 keV, 100,000)

Calculation of Electron-Induced X-ray Intensities at Grazing Exit Angles

\[ I \propto \int_{0}^{d} I_e (Z) |E_j (Z)|^2 \, dz \]

To improve spatial resolution in EPMA analysis

Volume of x-ray production was evaluated by Monte Carlo simulation (Casino program).


Comparison of the theoretical lateral resolutions (nm) obtained with conventional vs. GE-EPMA (beam diam. = 50 nm)

<table>
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</table>
GE-EPMA of Ni Films on Si wafer

Calculation of Electron-Induced X-ray Intensities under Grazing Exit Conditions
Kouichi Tsuji, Kouhei Tetsuoka, Filip Delalieux, Shigeo Sato

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Advantages of GE-XRS

- Micro beam such as x-ray micro beam, electron beam and charged particle beam can be applied for surface trace analysis of localized region.

- A single particle analysis is possible by GE-EPMA.
Summary

• Confocal micro-XRF in vacuum is useful for improving DLs at localized small region.

• C-M-XRF was applied for monitoring of corrosion process of steel sheet in NaCl solution.

• Grazing Exit XRS is useful for surface sensitive x-ray trace analysis. Micro beams such as x-rays, electrons and charged particles can be applied for primary beam. In this case, localized surface analysis was possible.