Confocal Micro-XRF and XRF imaging based on polycapillary optics

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Overview

1) Confocal m-XRF imaging (focusing polycapillary)

2) FF-XRF imaging with x-ray camera (straight polycapillary as angular filter)
1) Confocal M-XRF
Micro-XRF analysis

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

X-ray fluorescence emitted on the path of micro x-ray beam is detected.

Point analysis  Line analysis  Elemental mapping

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Conventional micro-XRF

Confocal micro-XRF

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

Nondestructive depth-selective XRF analysis is possible.

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Idea of confocal M-XRF

Figure 5. Possible applications of capillary optics for X-ray fluorescence microanalysis. In the lower figure the volume analyzed is defined by the object spot size of one lens and the image spot size of the other. Since the analyzed volume can be interior to as well as on the sample surface, three-dimensional analysis is possible.
Confocal micro-XRF instrument


![Diagram of confocal micro-XRF instrument](image-url)
Confocal m-XRF analysis of Electric cable

Polymer insulator

Cu wire

Cable coated with polymer insulator

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Depth-selective X-ray spectra of electric cable

Detector

X-ray beam

Cu wire

Detector

Cu wire

PVC coating

XRF intensity / count

Energy / keV

0

100

200

300

400

0

1

2

3

4

5

6

7

8

9

10

11

12

13

C\text{u}K\alpha, CaK\alpha

PbL\alpha, PbL\beta

TiK\alpha, FeK\alpha, CuK\alpha

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C-M-XRF with vacuum chamber at OCU

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Confocal-XRF setup
Polycapillary X-ray lens

Polycapillary full lens for primary x-ray beam
- 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 for detection of XRF
- Focal spot size: ≤10 µm, at 17.4 keV
  Input focal distance : 3.0 mm; Outer diameter : 10 mm
  Optic enclosure length: 36 mm

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A depth resolution of the confocal micro-XRF spectrometer can be evaluated by a thin layer scanning method.

\[
\text{Depth resolution} = \sqrt{\text{FWHM}^2 - T_{foil}^2}
\]

\(\text{FWHM}\): estimated from XRF intensity profile
\(T_{foil}\): thickness of the thin layer
These samples were prepared using a magnetron sputtering technique at NTT-AT, Japan.

The certified thickness was determined with a stylus-type surface profiler.

<table>
<thead>
<tr>
<th>Element</th>
<th>Energy (K-line)</th>
<th>Certified thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1.487</td>
<td>480 nm</td>
</tr>
<tr>
<td>Ti</td>
<td>4.510</td>
<td>478 nm</td>
</tr>
<tr>
<td>Cr</td>
<td>5.414</td>
<td>498 nm</td>
</tr>
<tr>
<td>Fe</td>
<td>6.403</td>
<td>500 nm</td>
</tr>
<tr>
<td>Ni</td>
<td>7.477</td>
<td>517 nm</td>
</tr>
<tr>
<td>Cu</td>
<td>8.047</td>
<td>483 nm</td>
</tr>
<tr>
<td>Zr</td>
<td>15.774</td>
<td>493 nm</td>
</tr>
<tr>
<td>Mo</td>
<td>17.478</td>
<td>507 nm</td>
</tr>
<tr>
<td>Au</td>
<td>9.711 (L)</td>
<td>501 nm</td>
</tr>
</tbody>
</table>
Depth resolution

Confocal setup in vacuum

Confocal setup in air

Energy / keV

Depth resolution / μm
Confocal micro-XRF spectra in air and in vacuum

NIST SRM 621

In vac.

In air

(Mo target)

(Rh target)

Si
Al
Na
K
Ca
Si
S
Ba, Ti
Fe
As
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>


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

LLDs of confocal setups for SRM621 (glass standards) 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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Secondary effects in confocal M-XRF
Secondary excitation in XRF analysis

X-ray Fluorescence

Sample

: Element A

: Element B

Z : A > B
Secondary excitation in confocal m-XRF setup

1. Primary X-ray
   - Detecting area
   - Analytical point
   - Element A
   - Element B
   - Primary X-ray
   - Fluorescent X-ray of element A
   - Fluorescent X-ray of element B

2. Primary X-ray
   - Detecting area
   - Analytical point
   - No detected
   - Element A
   - Element B
   - Primary X-ray
   - Fluorescent X-ray of element A
   - Fluorescent X-ray of element B

3. Primary X-ray
   - Detecting area
   - Analytical point
   - No detected
   - Element A
   - Element B
   - Primary X-ray
   - Fluorescent X-ray of element A
   - Fluorescent X-ray of element B
Layered sample

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

Si wafer substrate

Fe K absorption edge  Co K absorption edge

Ni K absorption edge

Cu Kα can excite Co Kα.

Metal foil (Co, Ti, Cr, Stainless steel)
Kapton film (Polyimide film)

Cu foil

Silicon Wafer
Secondary excitation of Co by Cu

Thickness of Kapton film was 0, 7.5, 75, 150 μm

Without Kapton film

With Kapton film of 7.5 μm

With Kapton film of 75 μm

With Kapton film of 150 μm

Shoulder peak

Additional peak
Secondary excitation process in confocal m-XRF

Intensities / counts vs. depth (μm):
- ① Cu
- ② Co
- ③ Analytical volume

Diagram:
- Primary X-ray
- Fluorescent X-ray of Cu
- Fluorescent X-ray of Co
- Analytical point
- Detector

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Simulation of confocal M-XRF intensity

Comparison of Experimental and simulation profiles

Analyzing depth: 40 μm in depth

Experimental

Z=-40μm

Cu - Ti

Ti

Cu

Z=41.0μm

Simulation

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Wire sample

Cross sectional view

Top view

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Comparison of Experimental and simulation maps

Wire distance ~156 μm

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Applications of C-M-XRF
Advantages of confocal m-XRF in the laboratory

- Micro analysis of small volume
- Analysis of inside of the sample in solid or solution
- Elemental depth profiling
- Depth XRF imaging (cross sectional)
- Depth-selective XRF imaging
Elemental depth profiling of paint chip of car

Surface coating paint chips of cars after car traffic accidents
(Forensic Science Laboratory, Hyogo Prefecture Police Headquarters, Japan)

Sample No.1: Red paint
Sample No.2: Black paint
Sample No.3: Blue paint

Thickness: 110 µm
Thickness: 170 µm
Thickness: 280 µm

Optical microscope images of cross-sections after angle-polishing.
Automobile paint chip at car traffic accident was analyzed in cooperation with Japanese police forensic laboratory.

Layer structure of paint chip

1st Base
2nd
3rd
4th
6th – 8th

Normalized intensity / a.u.

Surface
Scanned distance (Depth) / μm

0.0
0.2
0.4
0.6
0.8
1.0

1 mm

Cl : automotive topcoat, K : mica, Fe
Cu, Cl : CuPc, K : mica
Ti : TiO₂, Fe : Fe₂O₃, FeTiO₃
Cu, Cl : CuPc, K : mica
Ti : TiO₂, Fe : Fe₂O₃, FeTiO₃
K : mica, Zn : ZnO,
Ti : TiO₂, Fe : Fe₂O₃, FeTiO₃
Zn corrosion inhibitor
Zn, Fe : zinc-coated steel plate

CuPc: Cu-phthalocyanine

Analytical modes by Confocal M-XRF

Depth selective elemental mapping

Cross sectional, Depth elemental imaging
Elemental images obtained by micro-XRF

Elemental imaging of the industrial materials is important for defective and quality examination.

Micro-SD memory card used for mobile phone

Contact pad
Red: 200 cps
Blue: 100 cps

Au Lα

Contact pad
Red: 1300 cps
Green: 800 cps

Ni Kα
**Elemental images obtained by micro-XRF**

50 kV - 0.5 mA  
Mapping area: 11 × 15 mm  
Step size : 100 μm, 10s/step

- **Ti Kα**: hard plastics  
  (Green: 100 cps)

- **Cu Kα**: printed circuit  
  (Yellow: 1600 cps)

- **Br Kα**: epoxy resin  
  (Blue: 60 cps)

---


Depth selective elemental imaging (micro SD memory card) Cu Kα image

1st printed circuit near surface

Depth = 35 µm

Depth = 90 µm

Surface 20 µm 35 µm 50 µm 65 µm 90 µm 120 µm Inside

Micro-XRF

3D-XRF

Advantages of confocal m-XRF

In situ XRF analysis of the inside of the sample in solutions.

Monitoring of chemical reactions in the solution by confocal m-XRF


Analytical modes by Confocal M-XRF

Depth selective elemental imaging

Cross sectional, Depth elemental imaging

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**Confocal Micro-XRF setup and sample**

**Steel sheet with plating Zn layer**

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating layer</td>
<td>15 μm</td>
</tr>
<tr>
<td>Chem. conversion</td>
<td>2 ~ 3 μm</td>
</tr>
<tr>
<td>Plating Zn layer</td>
<td>10 μm</td>
</tr>
<tr>
<td>Steel sheet</td>
<td></td>
</tr>
</tbody>
</table>

- **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 mm² <130 eV at Mn Ka
  - *Polycapillary X-ray lens (XOS):* 10 μm

- **Spatial resolution:** 14.5 μm @Au Lα
Sample cell and experimental procedure

Steel sheet was placed in the sample cell.

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

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

**Scanned distance in depth / \( \mu m \)**

- **Fe**
  - Start
  - NaCl solution
  - Steel sheet
- **Ti**
  - Scratch
- **Zn**
  - End
- **Mn**

**24 hours / image**

- **Scanned distance in depth / \( \mu m \)**
- **Scanned distance / \( \mu m \)**

**Analyzed area:** 1680 \( \mu m \) x 600 \( \mu m \)

**Step size:** 15 \( \mu m \) x 10 \( \mu m \)**
Elemental maps in 96-120 hours (after 5 days)

Pre-blister was observed
Elemental maps in 120-144 hours (after 6 days)

Fe and Zn were dissolved and enriched inside the blister.

Blister-type corrosion was observed
Dissolved Fe, Zn, and Mn were diffused into the solution.
Zn, Fe and Mn under the blister were diffused in the solution, and enriched near the Kapton film. Corrosion process was successfully visualized.
2) FF-XRF imaging with x-ray camera
**Scanning type XRF imaging**

- Micro x-ray beam is created.
- XRF image is obtained with high spatial resolution.
- Scanning process needs a long acquisition time.

- Polycapillary lens
- SDD

**Full Field type XRF imaging**

- X-rays irradiate a large area of a sample.
- X-ray camera is applied for taking x-ray images (gray scale image).

- Primary X-rays
- 2D detector

**Spectroscopic techniques**

- WD-XRF imaging spectrometer
- ED-XRF imaging camera
Conventional WD-XRF

X-ray tube

Sample

Dispersive crystal

2θ

θ

Soller slits

Diffracted x-rays

S.C. P.C.

Bragg's law: \(2d \sin \theta = n\lambda\)

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Concept of WD-XRF imaging spectrometer

Previous results were reported in the following papers:


WD-XRF imaging spectrometer

Vacuum chamber (20 Pa)

X-ray tube
W target
50 kV, 60 mA

Sample

Straight polycapillary

PLATUS detector was applied

Based on Rigaku RIX-1000

Straight polycapillary (XOS)

LiF(200)

X-ray camera

Polymer window

5.0 µm

10.7 mm

Length: 10.5 mm

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A triangle Ni thin film (50 μm in thickness) was placed on a Cu sheet.

Exposure time for each image: 1 s
Energy resolution

Ni (50 μm)

W target
60 kV, 50 mA
Exposure time: 60 s
In air

Intensity (cps/pixel)

FWHM = 0.545°

77 eV at Ni Kα (7.47 keV)

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Elemental images of 1 Euro coin

W target
50 kV, 60 mA

Exposure time
0.1 s 0.5 s 1 s

Ni $K\alpha$
48.65°

Cu $K\alpha$
45.01°

Zn $K\alpha$
41.78°

K. Tsuji. et al.
SAB, 83-84

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A new X-ray pinhole camera for energy dispersive X-ray fluorescence imaging with high-energy and high-spatial resolution

F.P. Romano \textsuperscript{a,b,\textdagger}, C. Altana \textsuperscript{b,c}, L. Cosentino \textsuperscript{b}, L. Celona \textsuperscript{b}, S. Gammino \textsuperscript{b}, D. Mascali \textsuperscript{b}, L. Pappalardo \textsuperscript{a,b}, F. Rizzo \textsuperscript{b,c}

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\item \textsuperscript{c} Dipartimento di Fisica e Astronomia, Università di Catania, Via S. Sofia 64, 95123 Catania, Italy
\end{itemize}

Photon counting

Fig. 2. Energy response of the CCD detector. CCD counts indicate the raw and digitized data generated by the analog to digital converter of the CCD.

Fig. 3. The fluorescence spectrum of Fe measured using the X-ray pinhole camera. The energy resolution is 157 eV at Fe–K\textalpha line.

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To perform a single photon counting, an x-ray shutter was used. A straight polycapillary gives 1:1 image for the sample to the CCD.

- Backside illumination type
- Pixels: 1024 pixel x 1024 pixel (512 x 512), (256 x 256)
- Pixel size: 13 µm x 13 µm
- Area: 13.3 mm x 13.3 mm
- Cooling: -90 °C
Straight polycapillary as angular filter

< Straight polycapillary (XOS) >

<table>
<thead>
<tr>
<th>Specification</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optic dimension (flat to flat)</td>
<td>20 mm</td>
</tr>
<tr>
<td>Channel diameter</td>
<td>12 µm</td>
</tr>
<tr>
<td>Enclosure Diameter</td>
<td>25 mm</td>
</tr>
<tr>
<td>Optic length</td>
<td>13 mm</td>
</tr>
<tr>
<td>Open area</td>
<td>65%</td>
</tr>
</tbody>
</table>

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Energy resolution

- Mo tube: 30 kV, 2 mA
- Pure metals: Ag, Au, Co, Cu, Fe, Ni, Ti, Zn
- Exposure time: 1s / frame
- Total frames: 100 frames
- 256 pixel x 256 pixel

XRF spectrum of pure Fe metal

Energy resolution / eV

$y = 6.4288x + 107.43$

$R^2 = 0.9627$

142 eV @ Fe K$\alpha$

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Spatial resolution

- Mo tube: 30 kV, 2 mA
- Pure metals: Co, Cu, Fe, Ni, Ti, Zn foils (50 µm in thickness), and Pb (1 mm)
- Exposure time: 1 s / frame
- Total frames: 900 frames
- Effective pixels: 256 pixel x 256 pixel, 512 pixel x 512 pixel

<table>
<thead>
<tr>
<th>Element</th>
<th>FWHM (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>256 x 256 (Bin = 4)</td>
</tr>
<tr>
<td>Co Kα</td>
<td>337</td>
</tr>
<tr>
<td>Cu Kα</td>
<td>241</td>
</tr>
<tr>
<td>Fe Kα</td>
<td>352</td>
</tr>
<tr>
<td>Ni Kα</td>
<td>297</td>
</tr>
<tr>
<td>Pb Lα</td>
<td>150</td>
</tr>
<tr>
<td>Ti Kα</td>
<td>521</td>
</tr>
<tr>
<td>Zn Kα</td>
<td>241</td>
</tr>
</tbody>
</table>
FF-ED-XRF imaging of electronic circuit card

- Mo tube: 30 kV, 10 mA
- Exposure time: 0.05 s
- Total frames: 9000 frames
- 256 pixel x 256 pixel

Total exposure time: 7.5 min.
**FF-ED-XRF imaging of electronic circuit card**

- Mo tube: 30kV, 10 mA
- Exposure time: 0.05 s
- Total frames: 9000 frames
- 256 pixel x 256 pixel

*Simultaneous elemental images were obtained.*

*Total exposure time: 7.5 min.*
# Comparison of XRF imaging techniques

<table>
<thead>
<tr>
<th>Scanning type</th>
<th>SEM-EDS</th>
<th>(C)-M-XRF</th>
<th>WDXRF</th>
<th>ED-camera</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Source</strong></td>
<td>Electrons</td>
<td>X-ray tube</td>
<td>X-ray tube</td>
<td>X-ray tube</td>
</tr>
<tr>
<td><strong>scanning</strong></td>
<td>Electron beam scanning</td>
<td>Sample scanning</td>
<td>Without scan (but angle scan)</td>
<td>Without scan</td>
</tr>
<tr>
<td><strong>Spatial resolution</strong></td>
<td>1 µm</td>
<td>10 µm</td>
<td>~ 300 µm</td>
<td>&lt; 50 µm</td>
</tr>
<tr>
<td><strong>Energy resolution</strong></td>
<td>~ 140 eV</td>
<td>~ 140 eV</td>
<td>&lt; 70 eV (~ 40 eV)</td>
<td>~ 140 eV</td>
</tr>
<tr>
<td><strong>Advantage</strong></td>
<td>High spatial resolution</td>
<td>3D analysis by C-M-XRF</td>
<td>Short exposure time (~ 1 s) High energy-reso.</td>
<td>Simultaneous multi-elemental imaging</td>
</tr>
<tr>
<td><strong>Drawback</strong></td>
<td>Vacuum Damages Electrical conductivity</td>
<td>Long acquisition time for large sample</td>
<td>Large equipment Ange scan</td>
<td>Photon counting for weak x-rays Long acquisition time</td>
</tr>
</tbody>
</table>

"DXC2018 Workshop: Micro XRF, K. Tsuji"
Summary

• Scanning-confocal M-XRF was applied for elemental depth profiling, depth-selective XRF imaging, also monitoring the corrosion process of the steel sheet in the solution.

• FF-WD-XRF imaging was introduced. The advantage of this technique is a fast imaging less than 1 s with good energy resolution.

• FF-ED-XRF imaging with CCD camera was introduced. Elemental distribution on the surface was imaged through straight polycapillary (angular filter) by single photon counting analysis.