1) Fundamentals of capillary optics

2) Instrument of micro-XRF in the laboratory

3) Micro-XRF analysis of biological and industrial samples

4) Confocal micro-XRF (history, instruments)

5) Analytical performance (LLD, spatial resolution)

6) Applications to forensic and solution samples
Introduction

Micro XRF is an important analytical technique as well as TXRF. Micro-XRF enables a trace analysis at small region.

A micro x-ray beam is produced by

- Synchrotron radiation
- Doubly curved crystals (DCC)
- Capillary x-ray focusing optics
Fundamentals of capillary optics

(a) Total reflection on a flat surface

\[ \theta_c : \left( \rho \right)^{1/2} / E \]

(b) Total reflection on an inner wall of bended glass capillary
Single capillary

Fig. 1. Schematic diagram of the calculation model. $\psi$ is the curvature angle of the fiber; $\theta$ is the incidence and reflection angles.


Polycapillary optics (monolithic)

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

Point to point

Point to parallel

Assembly type polycapillary lens

• Combination of fine focus (low-power) x-ray tube and capillary optics
  (Horiba XGT series; single capillary (x-ray guide tube) 10 μm beam size)

• Application of polycapillary optics
  Gain (>1000) compared with single capillary (~100)
  Advanced polycapillary produces 10 μm spot, corresponding to spatial resolution of micro XRF analysis.
Micro XRF instrument

A fine focus x-ray tube

X-ray tube (Mo)

Polycapillary x-ray lens

X-ray detector (SDD)

Sample

X-ray tube (Mo target)
Tube voltage: 50 kV
Tube current: 0.50 mA

X-ray detector: SDD
Energy resolution: 140 eV @ 5.89 keV

Minimum spatial resolution: 10 μm

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A wire scanning method for evaluation of x-ray beam size

X-ray tube, 50 kV—0.5 mA
Step size: 2 μm, Time: 200 s

<table>
<thead>
<tr>
<th></th>
<th>Au Lα</th>
<th>Au Lβ</th>
<th>Au Mα</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FWHM</strong></td>
<td>11.81</td>
<td>11.43</td>
<td>16.15</td>
</tr>
<tr>
<td><strong>Spot size (μm)</strong></td>
<td>10.70</td>
<td>10.28</td>
<td>15.35</td>
</tr>
</tbody>
</table>

Critical angle for total reflection
\[ \theta_c : (\rho \ E)^{1/2} \]
A knife edge scanning method for evaluation of x-ray beam size

Source

X-ray source

PCXL(XOS)

Focal point

24.1 mm

100 mm

2.4 mm

FWHM : 11 μm

Ta Lα (8.15 keV)

Intensity / counts

Scanned distance / μm

Differential curve

Sigmoid curve

Ta knife edge

Scan direction
Micro-XRF analysis of biological and industrial samples
Ayu is “migratory” fish between sea and river.

Glowing day by day, elements that fish took in are accumulated in the otolith.

Concentration of Sr in seawater is about 8 ppm, higher than that in river by a factor of 100.

Therefore, distribution analysis of Sr in otolith will give useful information on migratory environmental history of ayu.

(Finally, we succeeded the discrimination of natural ayu and cultivated ayu.)

T. Nakazawa, et al.  
BUNSEKI KAGAKU, 61 (2012) 637
Elemental maps of otolith

Measurement conditions
50 kV- 0.5 mA
Mapping area: 1600 × 1600 μm
Step size: 20 × 20 μm
Measurement time: 50s/ step

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Micro-XRF analysis of micro-SD card

Micro-SD memory card used for mobile phone

**Thickness:** 0.8 mm

Micro-XRF instrument at OCU

- Polycapillary x-ray lens
- SDD
- Sample holder

**Measurement conditions**
- Mo target: 50 kV- 0.5 mA
- X-ray beam (spot size): 10 μm
- Mapping area: 11 × 15 mm
- Step size: 100 × 100 μm
- SDD: 140 eV @ 5.80 eV
- Measurement time: 10s/ step

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

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Elemental images obtained by micro-XRF

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

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

**Au Lα**
- Contact pad
- Red : 200 cps
- Blue : 100 cps

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

DXC2012 Workshop: Trace/TXRF Analysis, K. Tsuji
Comparison of direct elemental analytical techniques of solid materials

<table>
<thead>
<tr>
<th></th>
<th>SEM-EDS (EPMA)</th>
<th>LA-ICP-MS</th>
<th>Micro-XRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental imaging</td>
<td>EDS of characteristic x-rays during scanning electron beam.</td>
<td>After laser ablation, atoms are ionized in ICP, and then, MS.</td>
<td>As the sample is scanned to the x-ray beam, EDS of XRF.</td>
</tr>
<tr>
<td>Spatial resolution</td>
<td>SEM: ~10nm, depending on EB size. EDS: a few μm due to scattering of electrons.</td>
<td>Depending on spot size of laser; min. 5 <del>10 μm Actual analysis: 10</del>20 μm</td>
<td>Spot size of micro beam by polycapillary lens in the laboratory; 10 μm</td>
</tr>
<tr>
<td>Damage</td>
<td>Heating</td>
<td>Ablation</td>
<td>Non-destructive</td>
</tr>
<tr>
<td>Sample requirement</td>
<td>Dried, electric conductivity</td>
<td>Solid materials</td>
<td>Any sample including wet samples</td>
</tr>
<tr>
<td>Environment</td>
<td>In vacuum</td>
<td>In vacuum ~ in air</td>
<td>In vacuum ~ in air</td>
</tr>
<tr>
<td>Trends, advantages</td>
<td>Surface morphology, Down sizing, SEM in low vacuum</td>
<td>Trace analysis by ICP Quantification ?</td>
<td>Improvement of sensitivity and spatial resolution is required.</td>
</tr>
</tbody>
</table>

Others: SIMS, AES, XPS, PIXE, TEM with EDS, LIBS, MALDI-TOF-MS, etc.

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Confocal micro-XRF analysis
Confocal 3D XRF analysis

An x-ray beam, focused by polycapillary lens, irradiates the sample. X-rays from confocal point are collected by a polycapillary half lens.

It is possible to obtain XRF intensity in a spatially small region, leading to nondestructive 3D elemental mapping.
Polycapillary lens attached to the SSD collects the x-rays emitted from the confocal point.

Nondestructive depth-selective XRF analysis is possible.
X-ray spectra of electric cable at different depths

X-ray beam → Detector

Cu wire

PVC coating

XRF intensity / count

Energy / keV

CuKα, CaKα

TiKα, FeKα, CuKα, PbLα, PbLβ

Cu wire

CuKα, CuKβ
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.

A confocal micro-XRF instrument


Fig. 2. Photo of the confocal set-up at the BAMline, BESSY II.
Development of a vacuum confocal XRF

XRF analysis in vacuum is effective for detection of low-Z elements, because absorption of low energy x-rays in air is serious problem.

Previous work for vacuum confocal XRF instruments, from the research group at ATI, TU-WIEN:


CAD design rendering and photograph of the interior of the spectrometer. The polycapillary is mounted on a five-axis adjustable stage; the microscope looks into the chamber through a 8 μm Kapton window, and the sample can be automatically moved in x/y/z.
References of confocal micro-XRF

- Proposal of confocal 3D $\mu$ XRF analysis

- Confocal $\mu$-XRF depth analysis of paint layer

- Depth analysis of Ti, Sr, Zr, Th in diamond

- Vacuum confocal XRF

- Elemental depth imaging of forensic sample
X-ray tube
Target size: 50 μm × 50 μm
Tube voltage: 50 kV,
Tube current: 0.5 mA
25 W, max. 30 W

SDD: X-Flash Detector Type 1201
Sensitive area: 10 mm²,
Energy resolution <150 eV @ 5.9 keV

Polycapillary x-ray lens
Full lens: focal spot size: 40 μm
Half lens: focal spot size: 30 μm
3D-XRF instrument at OCU in 2011

Experimental setup

- X-ray tube (Mo 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 volume (depth resolution): 13.7 μm @ Au Lβ

Polycapillary optics were manufactured by XOS Inc.

In-vacuum 3D-XRF at OCU in 2012

Detector
CCD
X-ray tube
Vacuum Chamber

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XRF Spectra of SRM621 by M-XRF and Confocal-XRF

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.
QXAS, developed by The IAEA Seibersdorf Laboratories, was used for analysis.
A lateral resolution can be evaluated by a wire scanning method.

**Wire scanning method**

- **Metal wires**
  - Au wire (5 μm φ)
  - W wire (10 μm φ)
  - Ni-Cr wire (15 μm φ)
A depth resolution of the confocal micro-XRF spectrometer can be evaluated by a thin layer scanning method.

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

- **FWHM**: estimated from XRF intensity profile
- **\( T_{foil} \)**: thickness of the thin layer

**Newly developed thin metal layers**

| thin film (layer) | Si substrate |

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**DXC2012 Workshop: Trace/TXRF Analysis, K. Tsuji**
These samples were prepared using a magnetron sputtering technique at NTT-AT, Japan.

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

Confocal setup in vacuum

Confocal setup in air
Quantitative confocal 3D-XRF analysis of Plastic CRMs JSAC 0611-0615

Plastic certified reference materials (JSAC 0611 - 0615) containing Cr, Pb, Cd were certified by The Japan Society of Analytical Chemistry.

Certified values of Cr

<table>
<thead>
<tr>
<th>Plastic CRM</th>
<th>Cr (mg/kg)</th>
</tr>
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<tbody>
<tr>
<td>JSAC 0615</td>
<td>212.8</td>
</tr>
<tr>
<td>JSAC 0614</td>
<td>98.6</td>
</tr>
<tr>
<td>JSAC 0613</td>
<td>52.0</td>
</tr>
<tr>
<td>JSAC 0612</td>
<td>25.5</td>
</tr>
<tr>
<td>JSAC 0611</td>
<td>Blank</td>
</tr>
</tbody>
</table>

4.0 mm
Depth Profiles of Cr Kα in Plastic CRMs
JSAC 0611 - 0615

by K. Nakano

Depth profiles of CrKα intensity in plastic certified reference materials JSAC 0612-0615.
The limit of the depth sensitivity for Cr

Depth profiles of CrKα intensity of plastic certified reference materials JSAC 0613 - 0615 (log scale).

Limit of the analyzing depth
Calibration curves of Cr at different depth

Calibration curves of Cr in plastic certified reference materials JSAC 0611 - 0615.
Forensic examination

• Non-destructive analytical methods are required.

• Confocal m-XRF (3D-XRF) enables a nondestructive elemental depth profiling and a depth XRF imaging.

• We have considered that the forensic examination is an important application of confocal m-XRF method.
Paint chips of car

Paint chips (surface coating) of cars after car traffic accidents were measured.

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.
It was confirmed that 3D-XRF is useful for characterization and discrimination of paint chips, which has specific layered structures.

**Depth selective XRF imaging (Cu Kα)**

1st printed circuit near surface

3DXRF gives depth-selective images, which cannot be obtained by micro-XRF.

Micro-SD memory card used for mobile phone

DXC2012 Workshop: Trace/TXRF Analysis, K. Tsuji
Confocal Micro-XRF for monitoring of corrosion process

**Corrosion of low carbon steel occurred in artificial seawater (NaCl 3.5%).**

Spatial resolution of Confocal micro-XRF
- Fe Kα 70 μm
- Cr Kα 100 μm

Confocal micro-XRF setup and sample cell

Sample
- Seawater
- 450 μm
- 20 mm
- 42 mm

X-ray tube
- Detector
- Kapton film
- Analyzing (confocal) point

Steel sample
Monitoring of Fe Kα intensity in the corrosion process

A line scanning of confocal micro-XRF was sequentially performed at the fixed position.

X-ray tube: 50 kV, 0.35 mA
Acquisition time: 50 s
Step size: 10 μm
Scanned distance: 600 μm
Time of a single scan: 1 h

Number of line scans / times correspond to
Corrosion time / hours
Summary

• Capillary focusing optics is useful for micro-XRF in the laboratory.
• Confocal micro-XRF enables nondestructive elemental depth profiles and depth images.
• Applications; biological, industrial, forensic, paints, etc.

Acknowledgement:

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