XRF imaging based on polycapillary optics

Kouichi Tsuji, Shota Aida, Yuki Takimoto

Osaka City University, Osaka, Japan

Overview

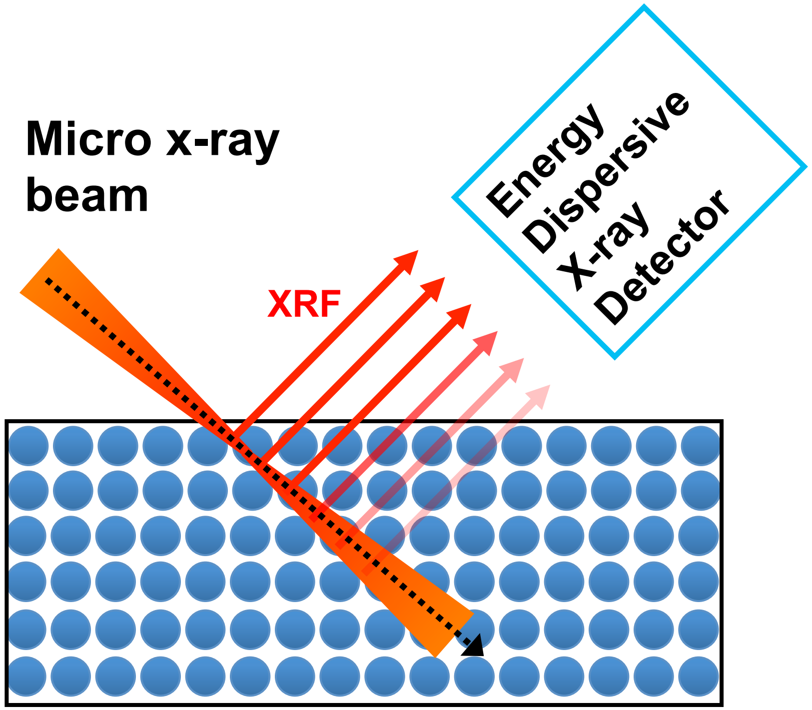
1) Scanning confocal m-XRF imaging
   (focusing polycapillary)

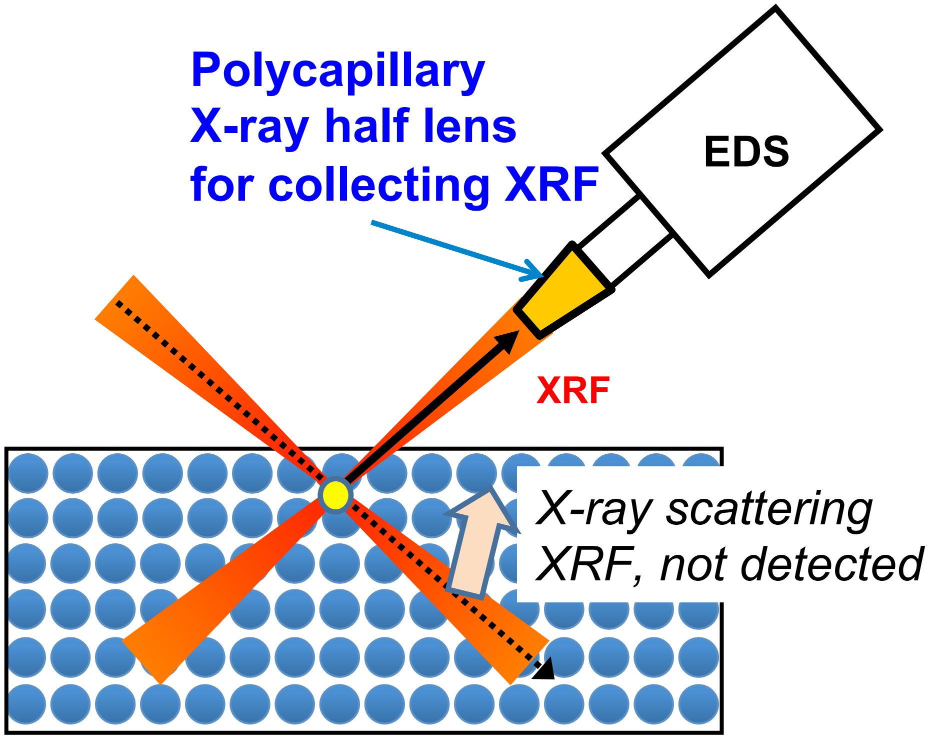
2) WDXRF imaging spectrometer
   (straight polycapillary)

3) FF-EDXRF imaging with CCD camera
   (straight polycapillary)

Conventional micro-XRF

Confocal micro-XRF





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

Polycapillary lens attached to the SSD collects the x-rays emitted from the confocal point.

Nondestructive depth-selective XRF analysis is possible.

Confocal M-XRF setup

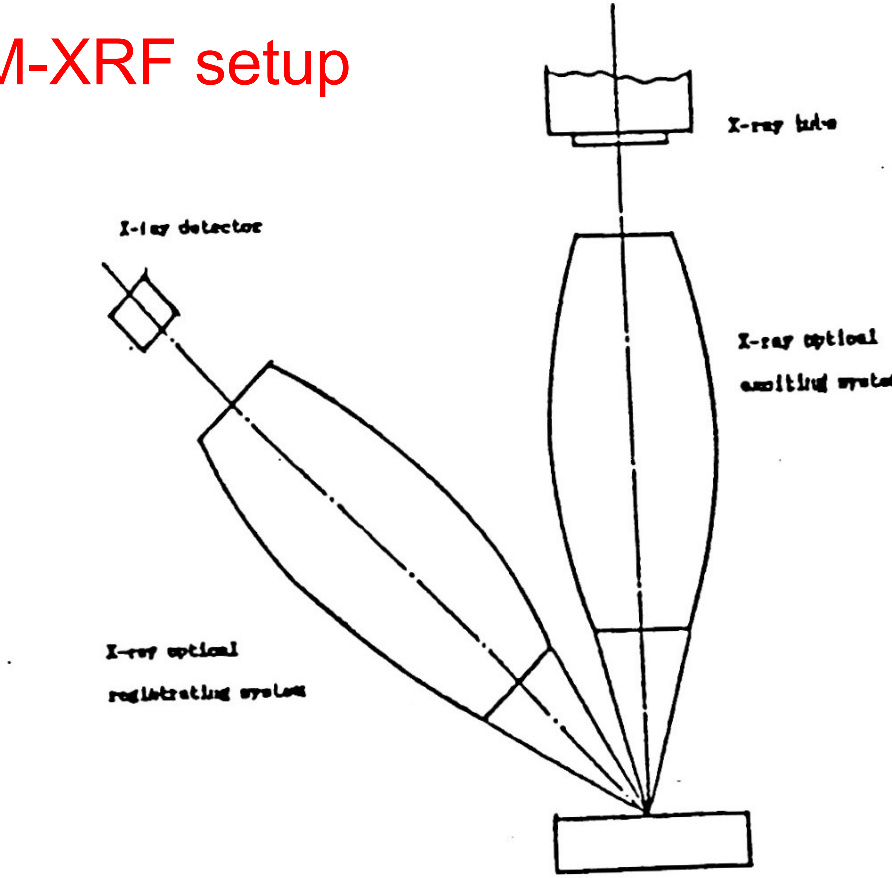
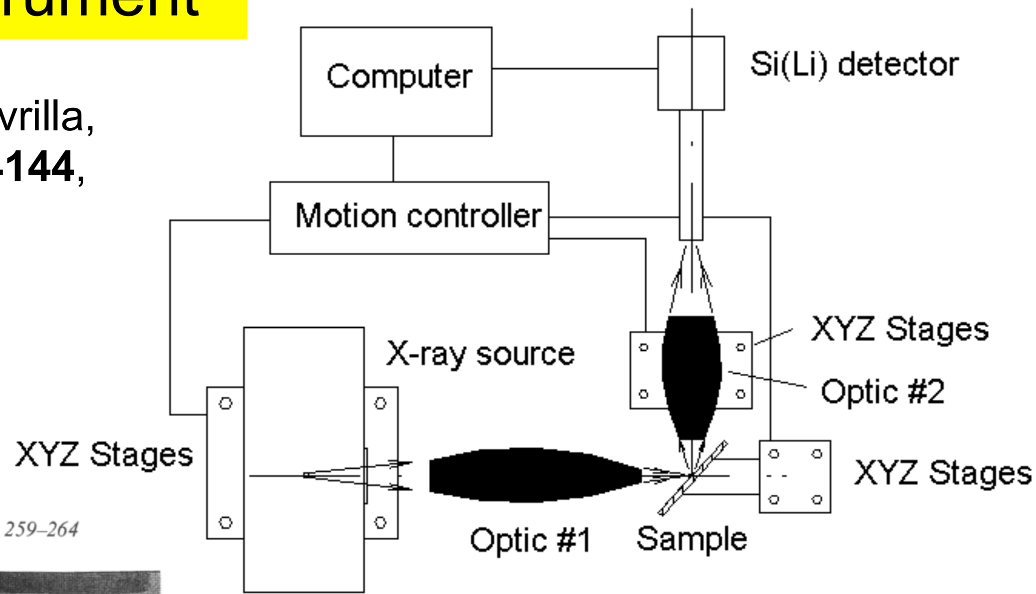


Figure 5. Possible applications of capillary optics for X-ray fluorescence microanalysis. In the lower figure the volume analyzed is defined by the object spot size of one lens and the image spot size of the other. Since the analyzed volume can be interior to as well as on the sample surface, three-dimensional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

W.-M. Gibson, M.A. Kumakhov, *Proceedings of SPIE*, **1736**, 172-189 (1993).

A confocal micro-XRF instrument

X. Ding, N. Gao, G. Havrilla, *Proceedings of SPIE*, **4144**, 174 (2000).



B. Kanngießer et al. / Nucl. Instr. and Meth. in Phys. Res. B 211 (2003) 259–264

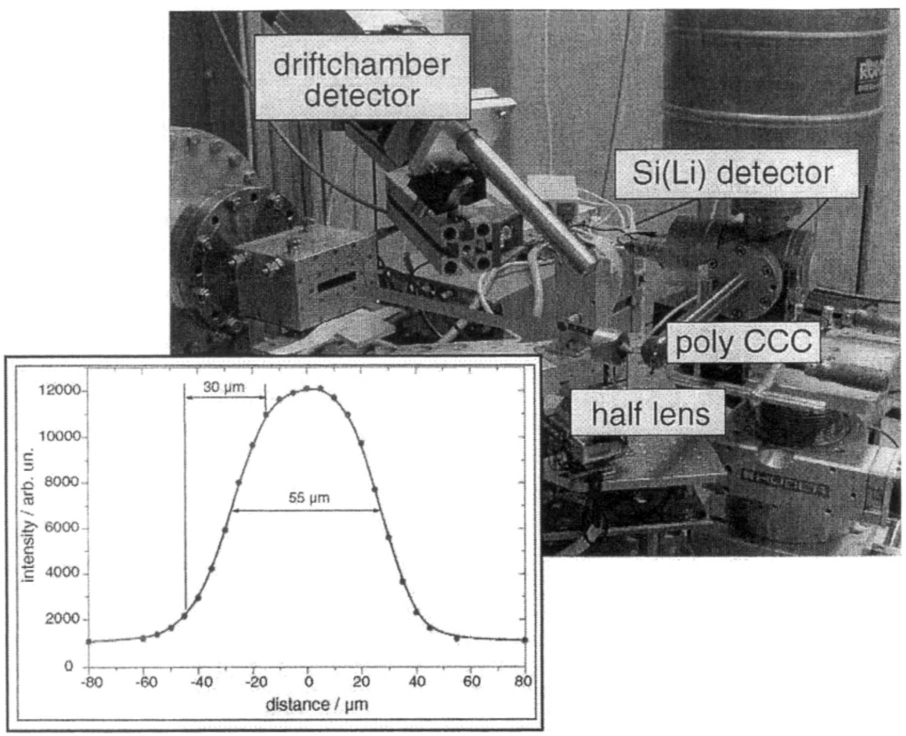


Fig. 2. Photo of the confocal set-up at the BAMline, BESSY II.

B. Kanngieber, W. Malzer, I. Reiche, *Nucl. Instr. and Meth. in Phys. Res. B*, **211**, 259 (2003).

Advantages of confocal m-XRF in the laboratory:

- **Small volume analysis**
- **2D, 3D elemental distribution**
- **Nondestructive depth selective XRF (image)**
- **Inside of the sample (solid, solutions)**
- **Long-time measurement**

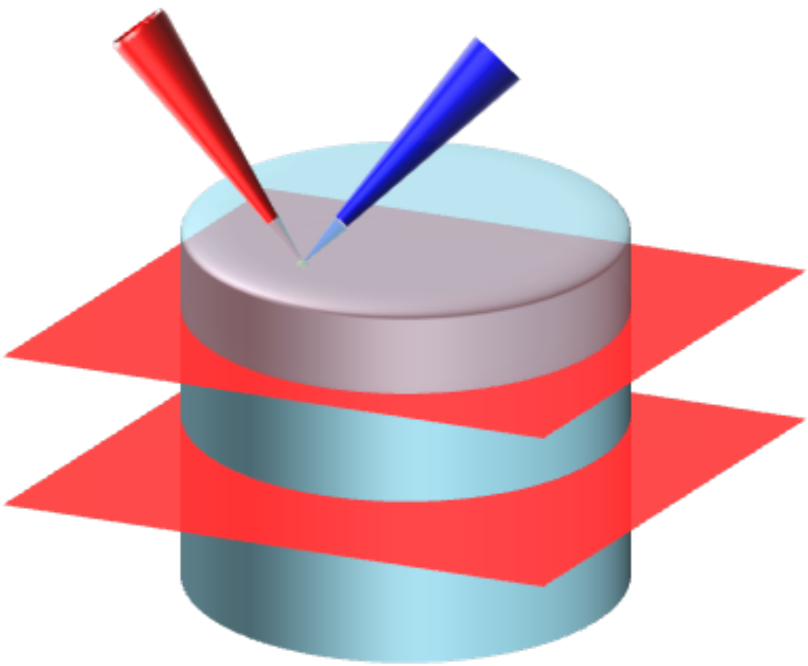
→ ***Monitoring of chemical reactions in the solution by confocal m-XRF***

- K. Tsuji, T. Yonehara, K. Nakano, Application of confocal 3D micro XRF for solid/liquid interface analysis, *Anal. Sci.*, **24** (2008) 99-103.

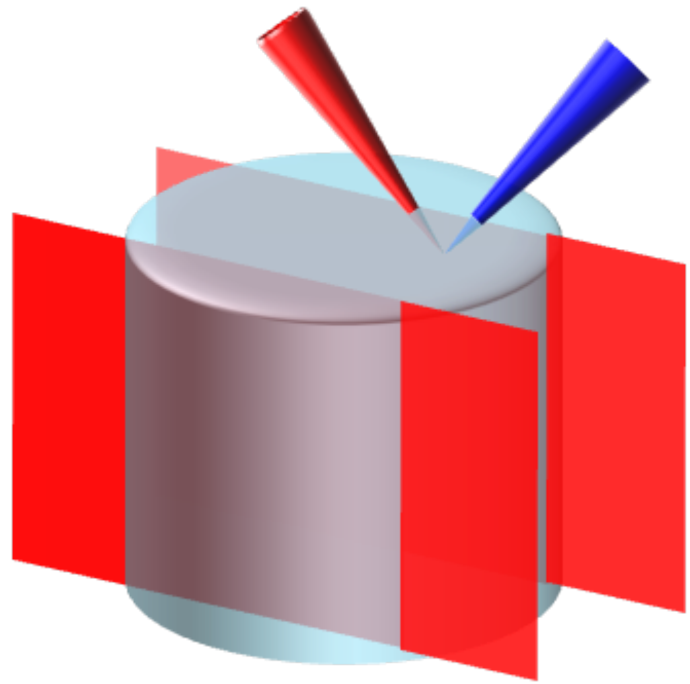
- S. Hirano, K. Akioka, T. Doi, M. Arai, and K. Tsuji, Elemental depth imaging of solutions for monitoring corrosion process of steel sheet by confocal micro-XRF, *X-Ray Spectrom.*, 43 (2014) 216-220. *(monitoring of corrosion process)*

Analytical modes by Confocal M-XRF

Depth selective
elemental mapping

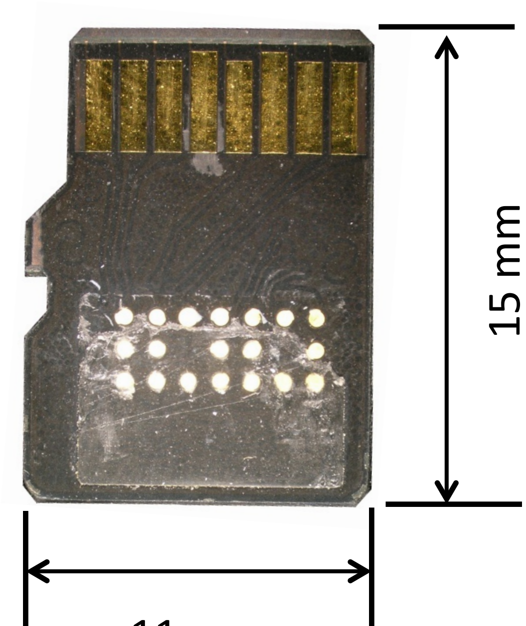


Cross sectional,
Depth elemental imaging



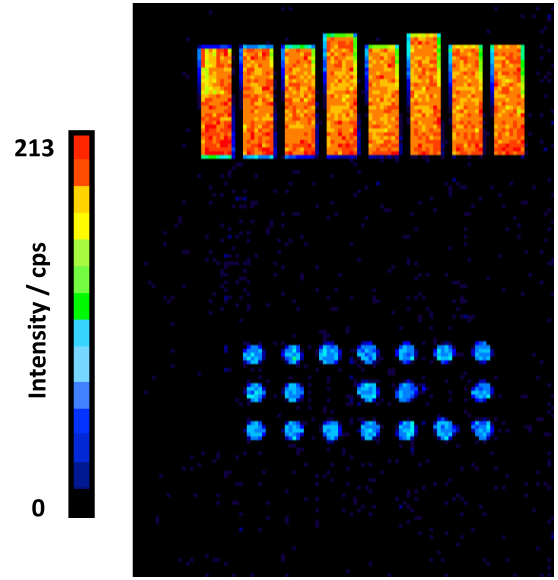
Elemental images obtained by micro-XRF

Micro-SD memory card used for mobile phone



Thickness : 0.8 mm

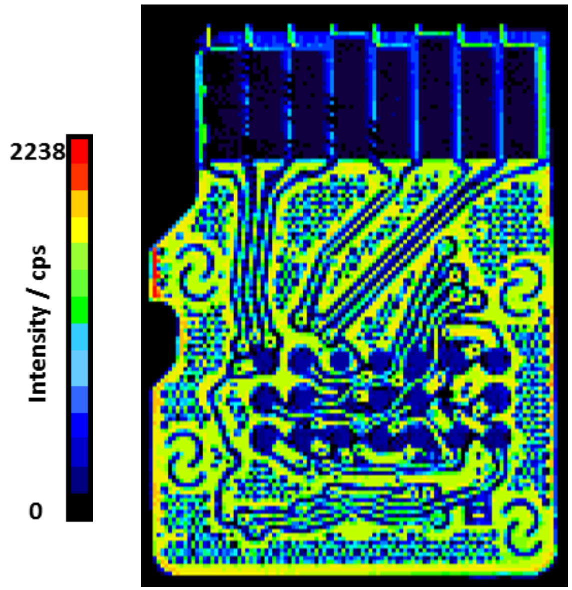
Au La



Contact pad

Red : 200 cps
Blue : 100 cps

Cu Ka



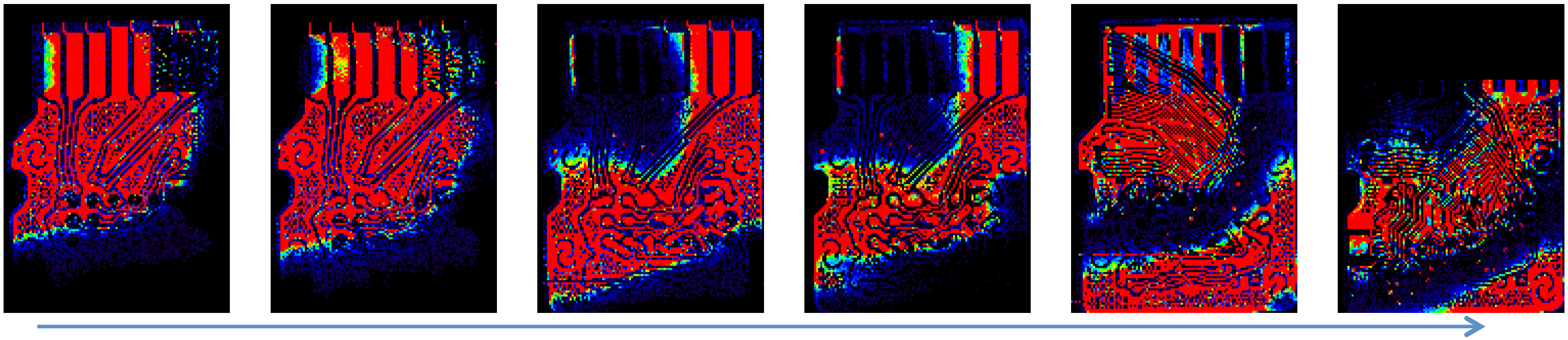
Cu : printed circuit

(Yellow : 1600 cps)

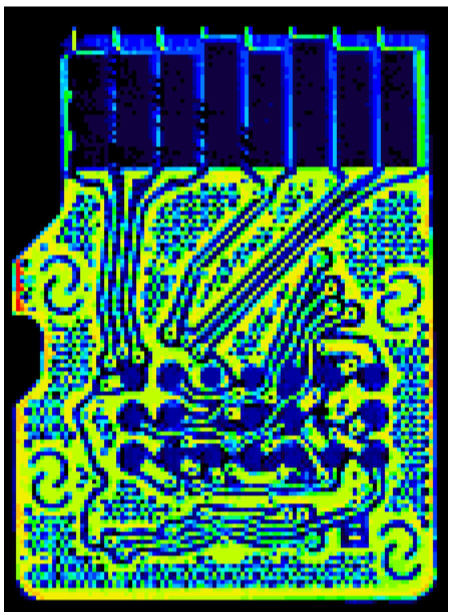
Elemental imaging of the industrial materials is important for defective and quality examination.

Depth selective elemental imaging

(micro SD memory card) Cu Kα image

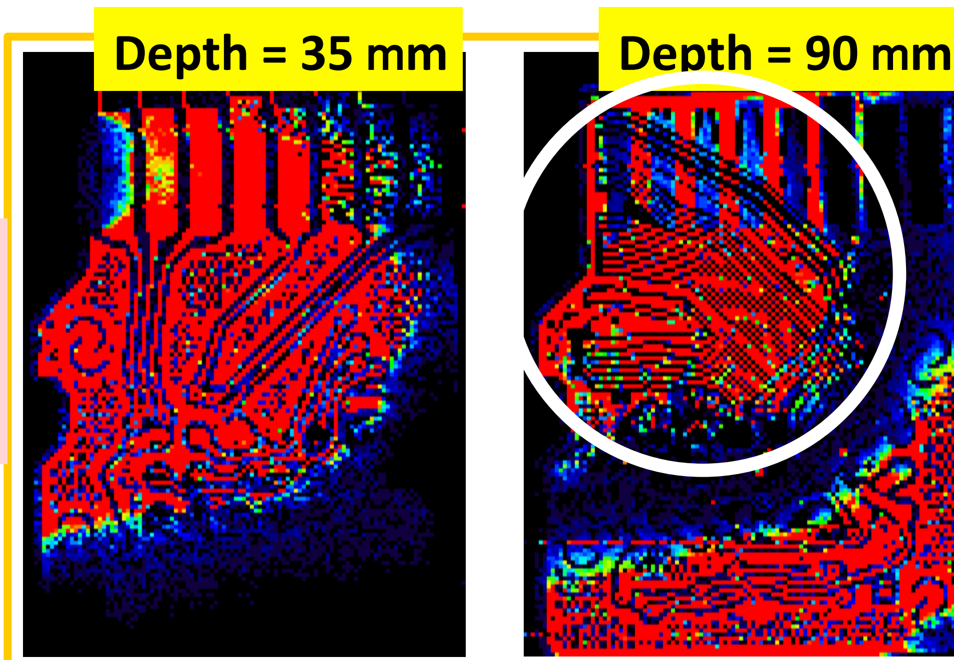


Micro-XRF



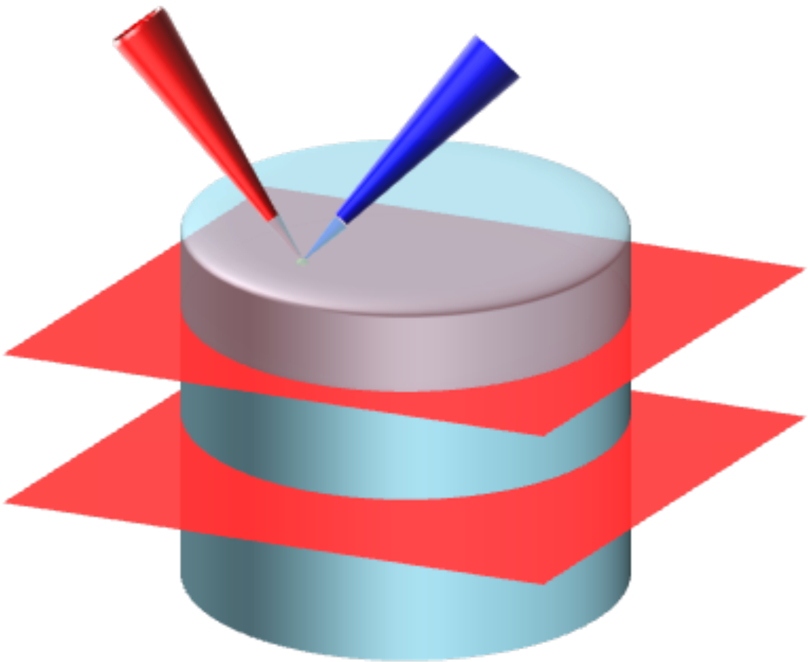
1st printed circuit near surface

3D–XRF

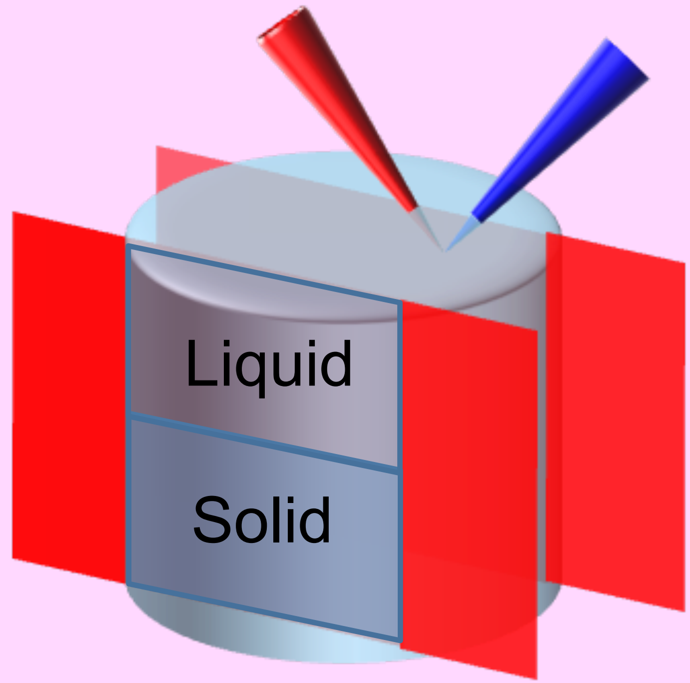


Analytical modes by Confocal M-XRF

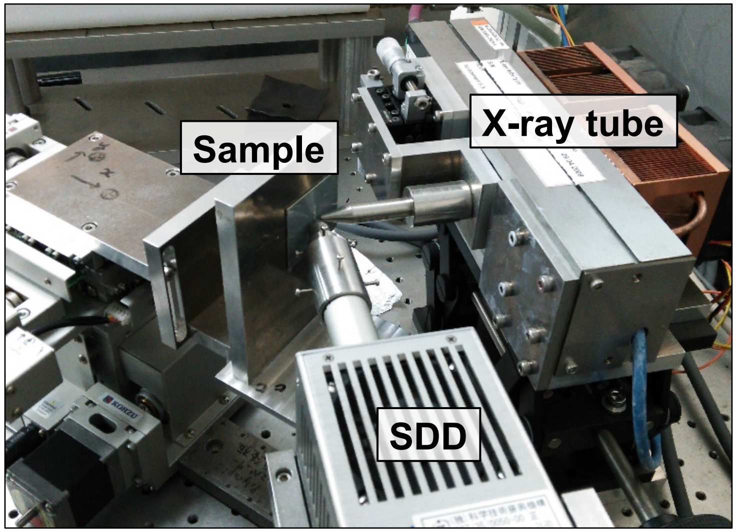
Depth selective
elemental imaging



Cross sectional,
Depth elemental imaging



Confocal Micro-XRF setup and sample



Steel sheet with plating Zn layer

	Thickness	Element
Coating layer	15 mm	Al Si Ti Sn
Chem. conversion	2 ~ 3 mm	P Mn Ni Zn
Plating Zn layer	10 mm	Al Fe Zn
Steel sheet		C Si P Mn Fe

X-ray tube

MCBM 50-0.6 B (rtw, Germany)

Mo target, 50 kV, 0.6 mA

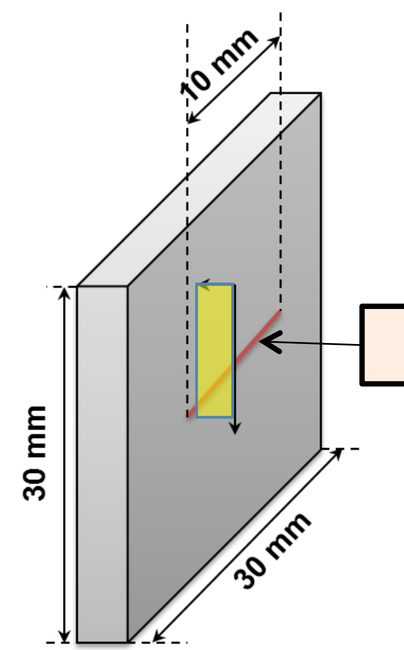
SDD and lens

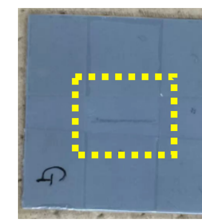
Vortex EX-60 (Hitachi high-tech science co.)

Sens. area: 50 mm^2 <130 eV at Mn Ka

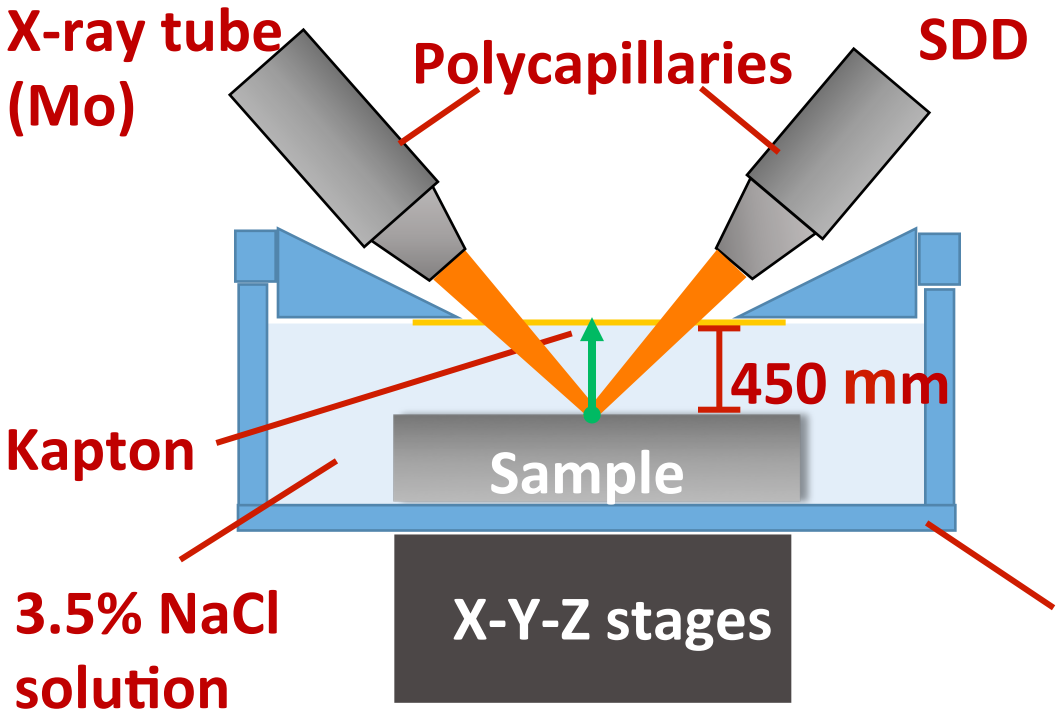
Polycapillary X-ray lens (XOS) :10 mm

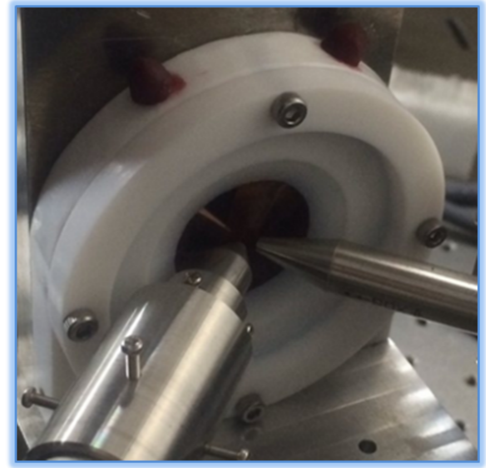
Spatial resolution: 14.5 mm @Au Lα





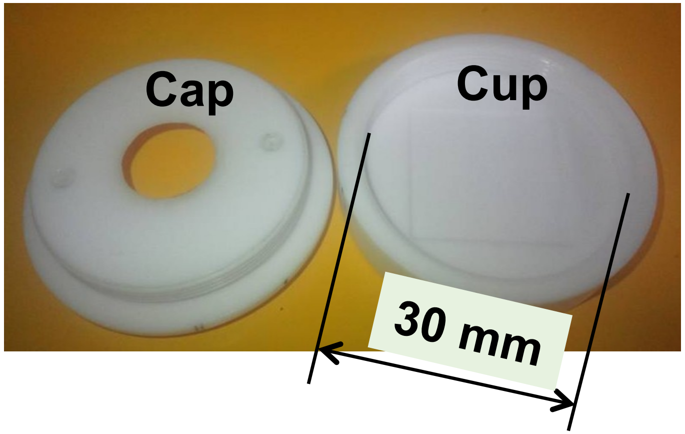
Sample cell and experimental procedure





Steel sheet was placed in the sample cell.

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

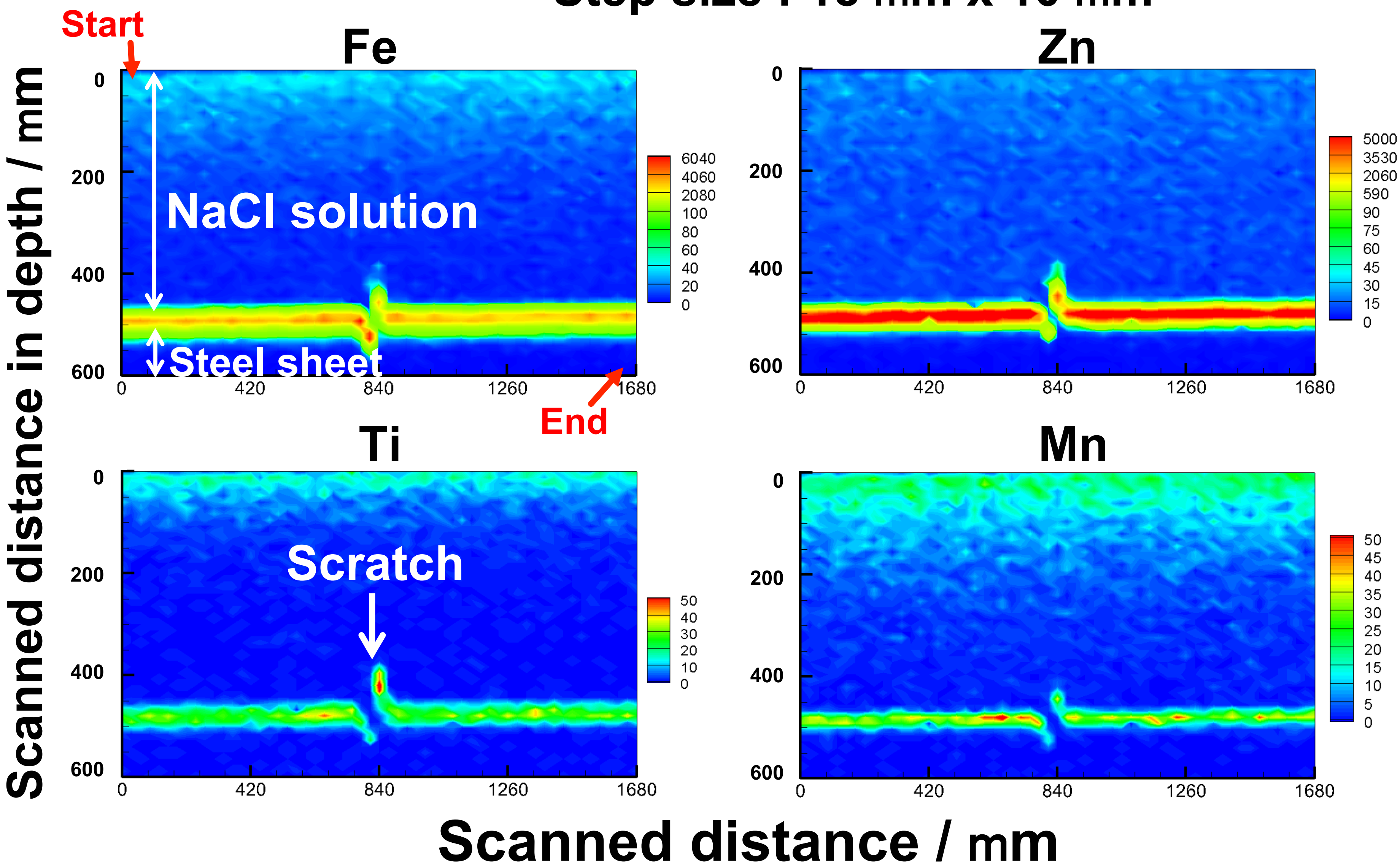


Elemental maps in 0-24 hours (after one day)

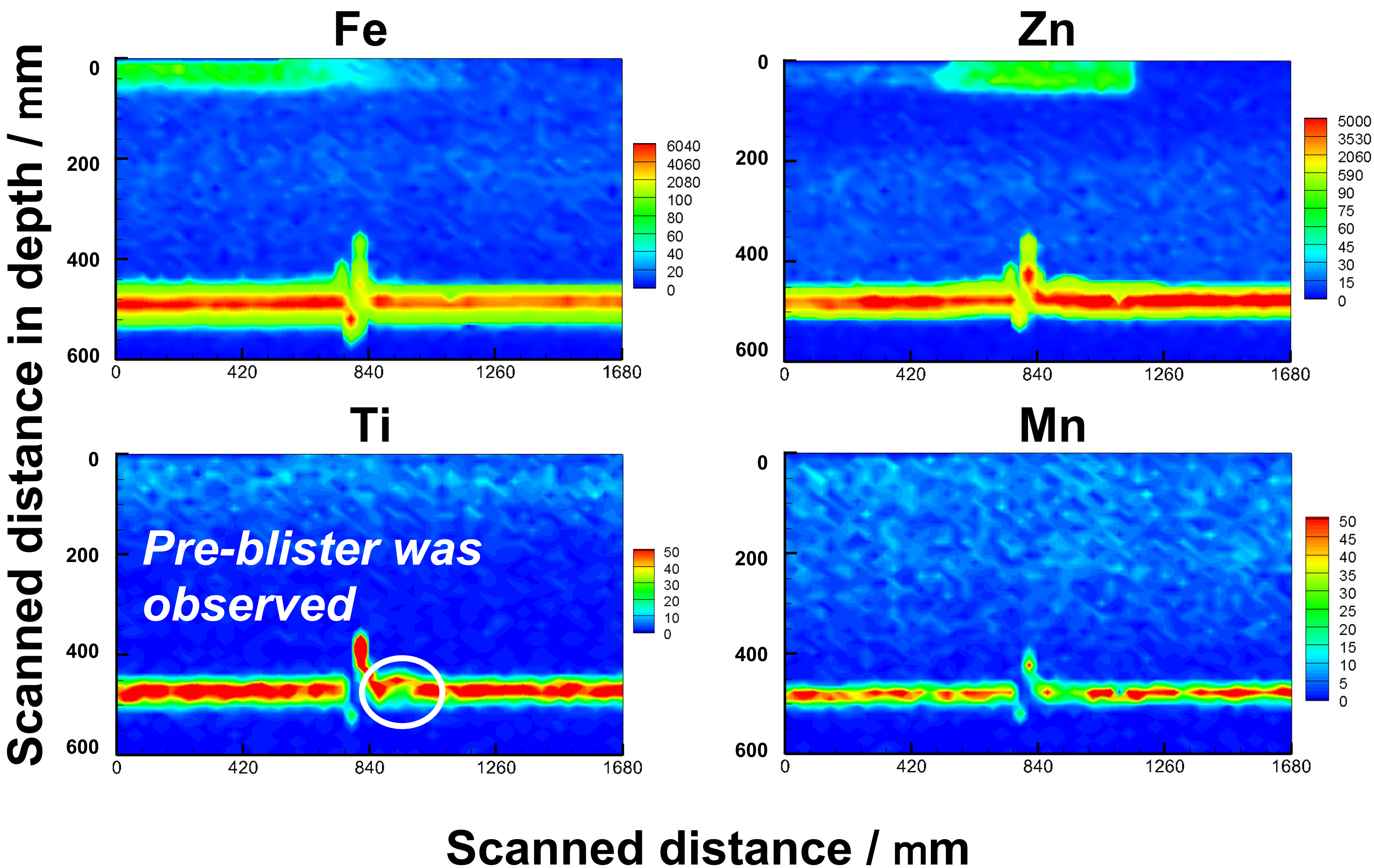
24 hours / image

Analyzed area: 1680 mm x 600 mm

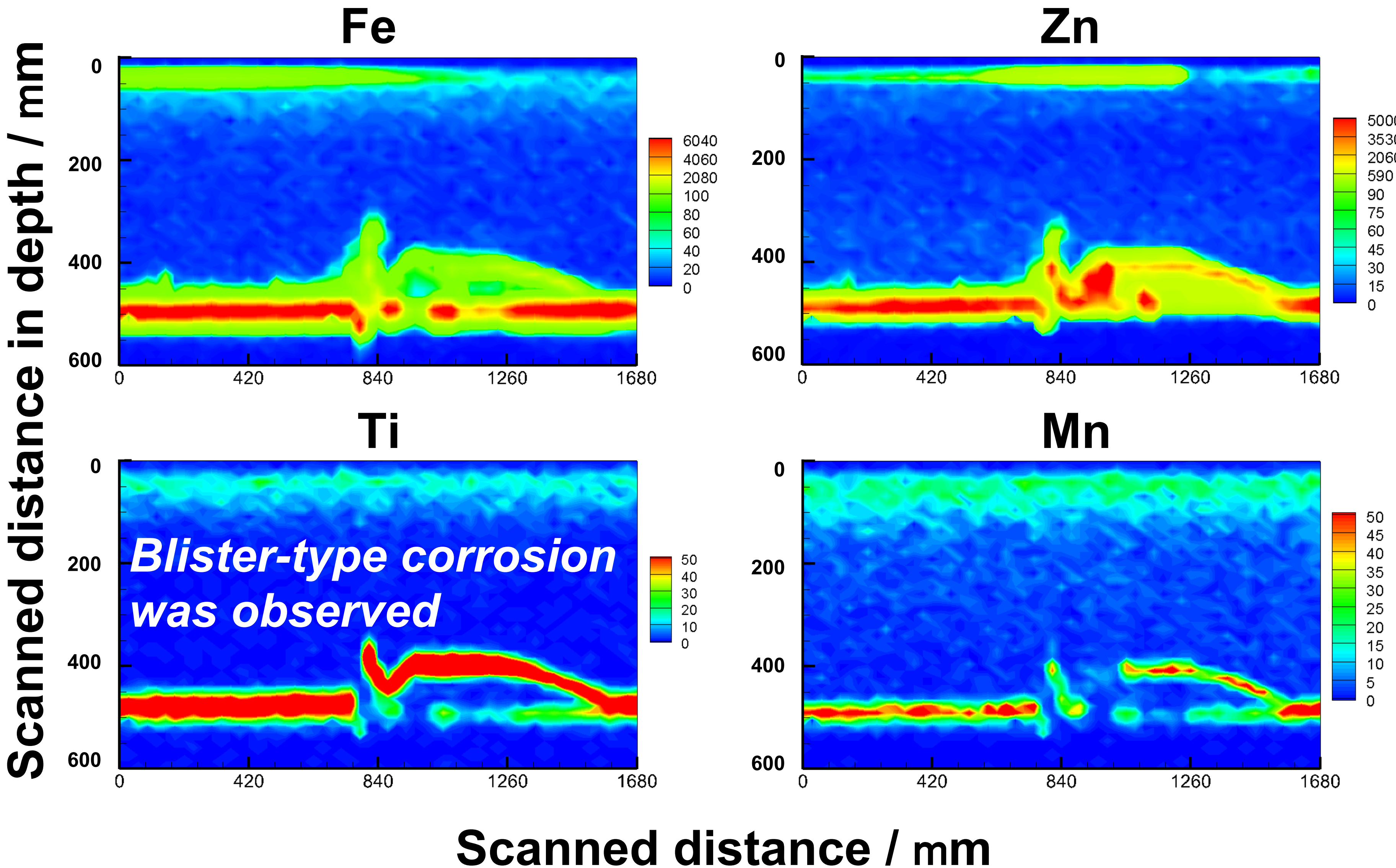
Step size : 15 mm x 10 mm



Elemental maps in 96-120 hours (after 5 days)

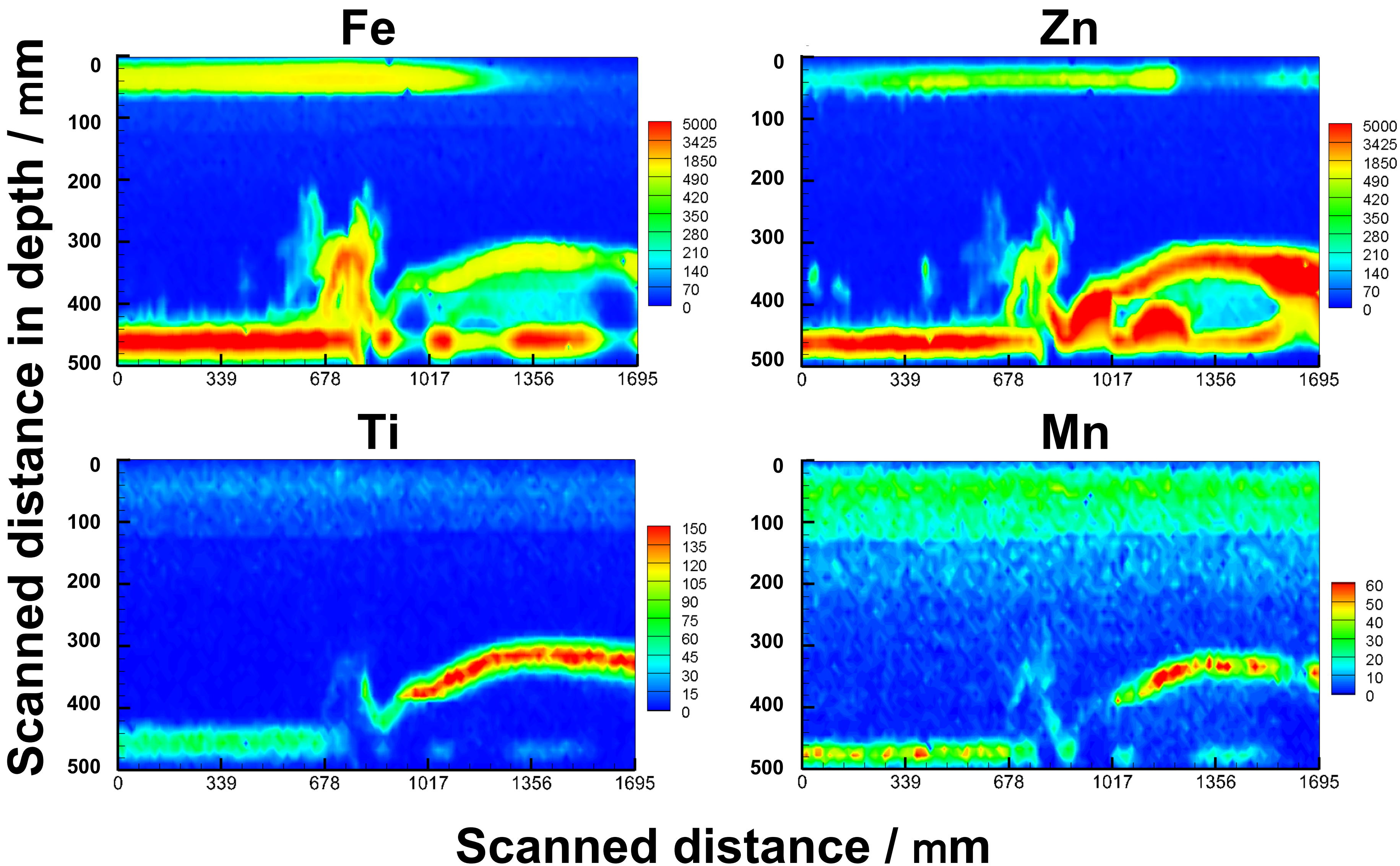


Elemental maps in 120-144 hours (after 6 days)



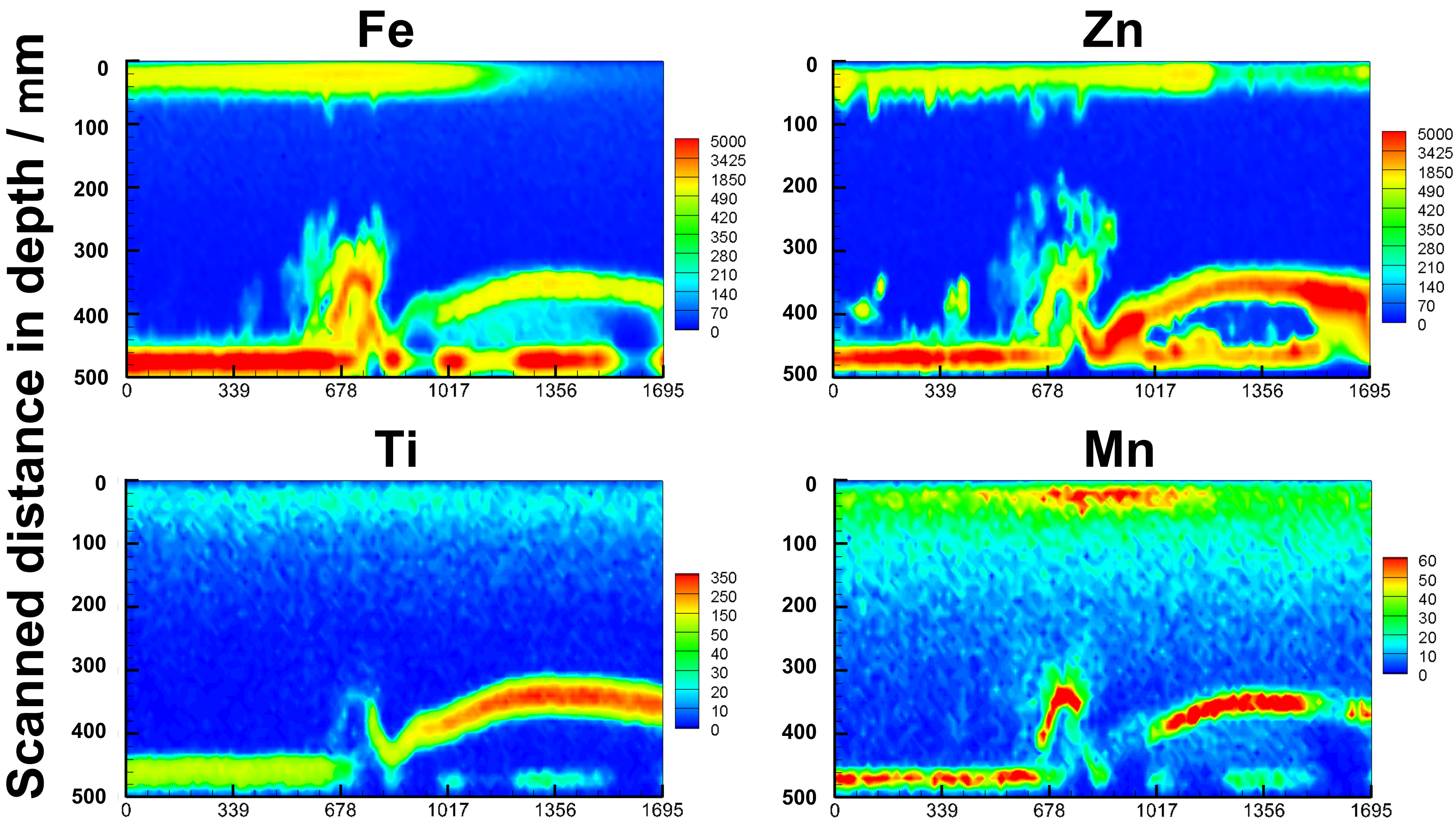
Fe and Zn were dissolved and enriched inside the blister.

Elemental maps in 192-240 hours (after 9-10 days)



Dissolved Fe, Zn, and Mn were diffused into the solution.

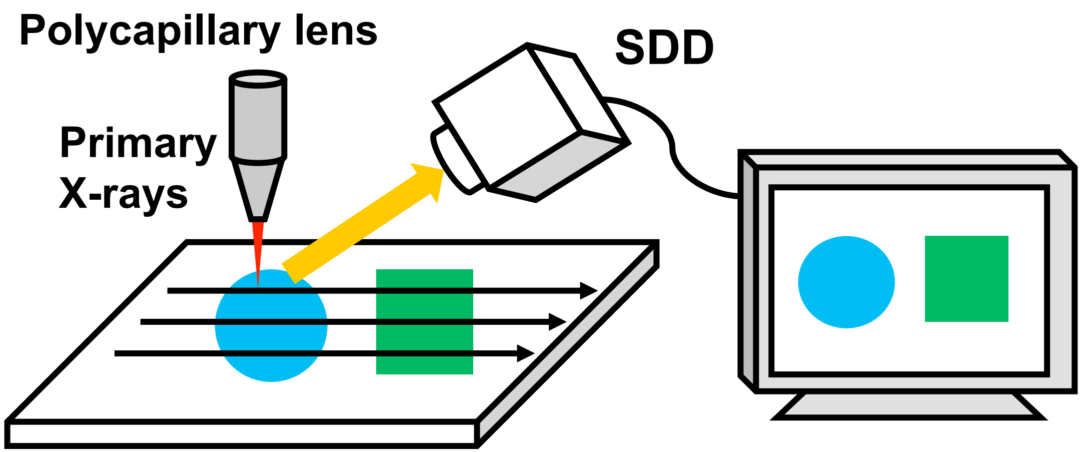
Elemental maps in 240-288 hours (after 11-12 days)



Zn, Fe and Mn under the blister were diffused in the solution, and enriched near the Kapton film. Corrosion process was successfully visualized.

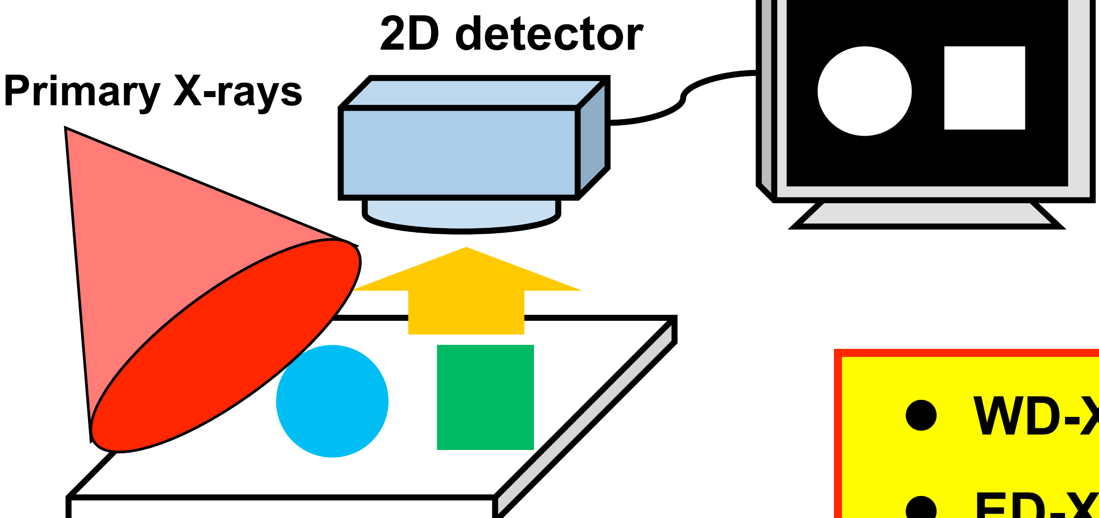
X-ray fluorescence imaging

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.

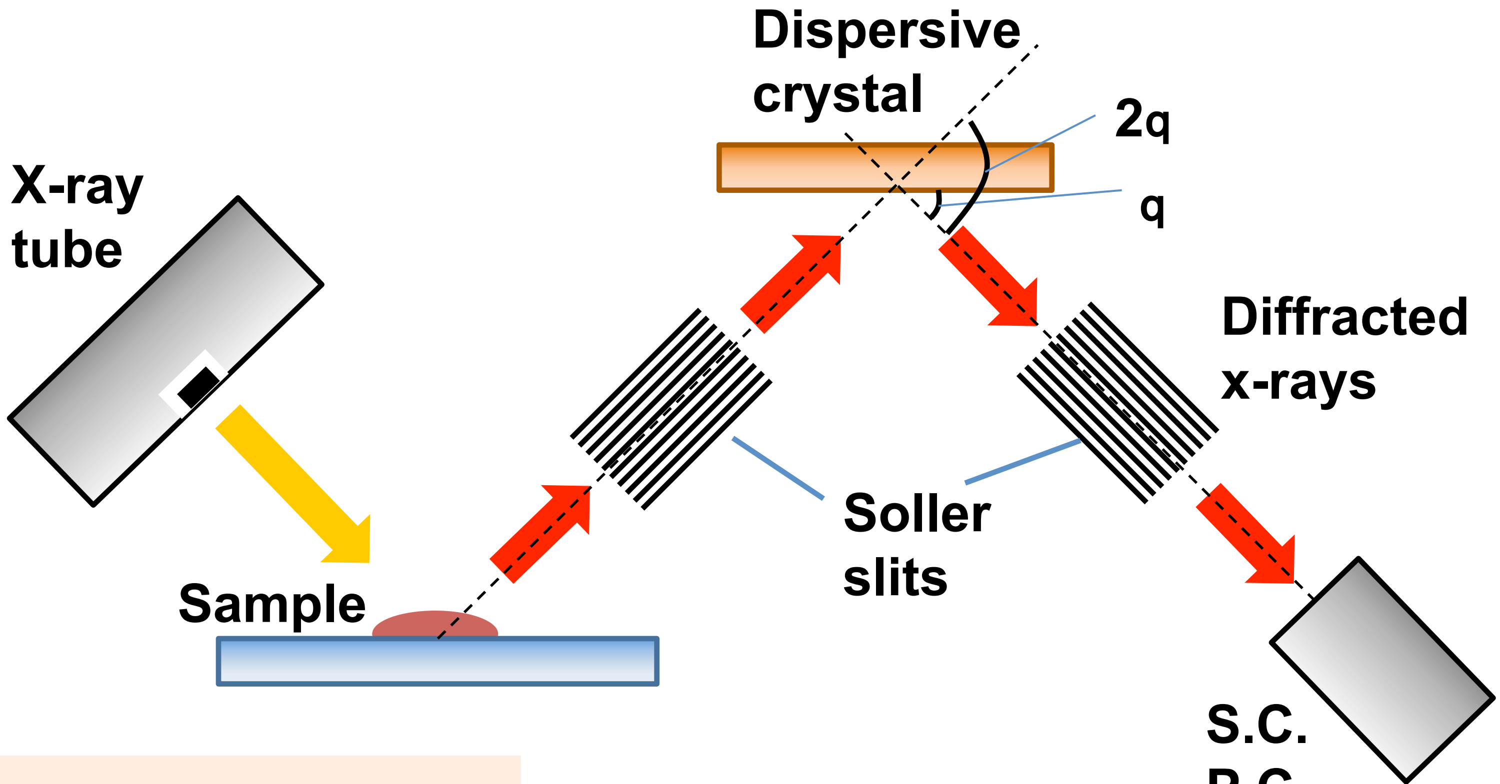
Full Field type XRF imaging



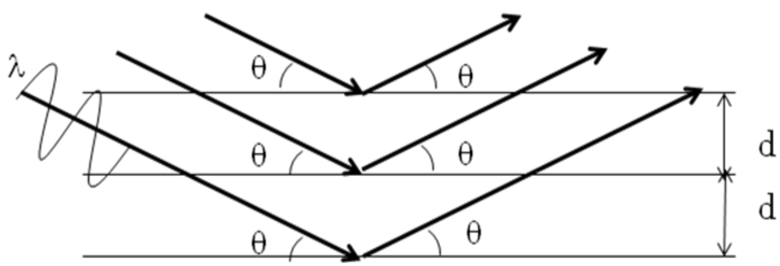
- ◆ X-rays irradiate a large area of a sample.
- ◆ X-ray camera is applied for taking x-ray images (gray scale image).

- **WD-XRF imaging spectrometer**
- **ED-XRF imaging camera**

Conventional WD-XRF

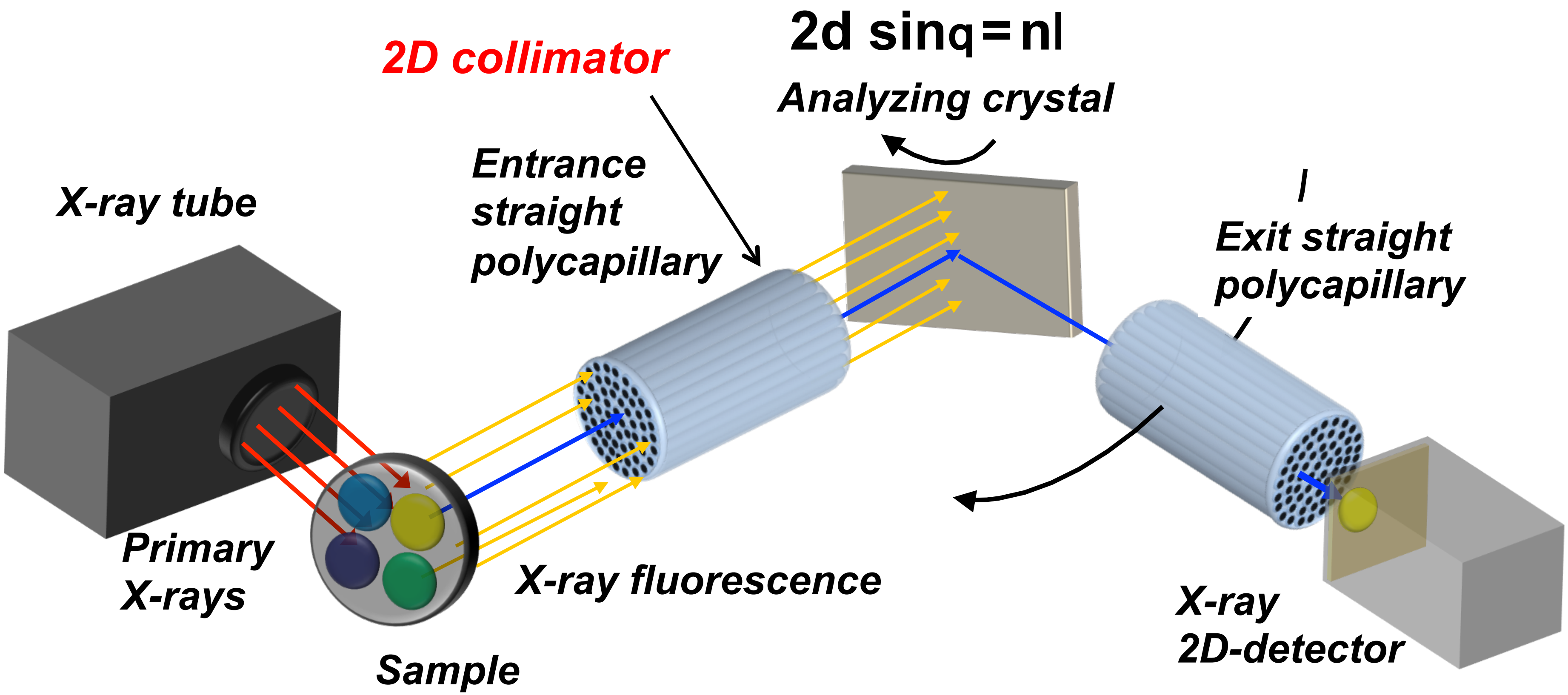


Bragg's law:2d sinq=nl



Soller slits

Concept of WD-XRF imaging spectrometer

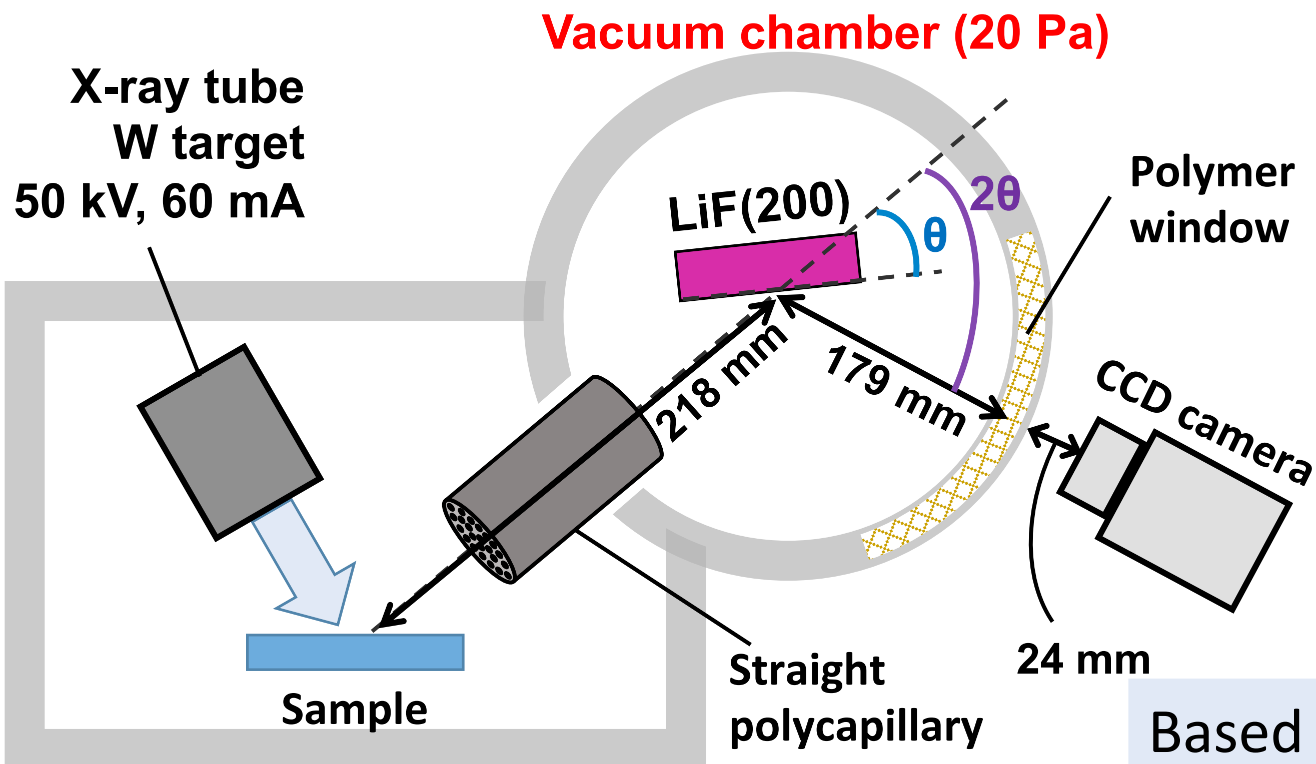


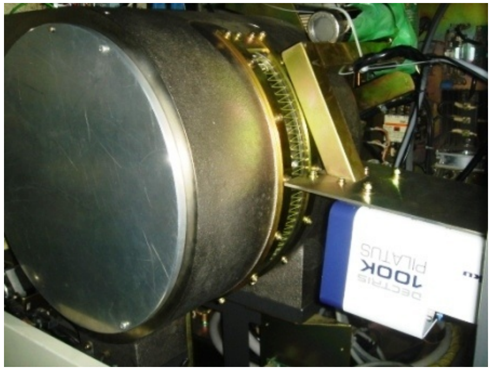
Previous results were reported in the following papers:

K. Tsuji, et al, *Anal. Chem.*, **83** (2011) 6389-6394.

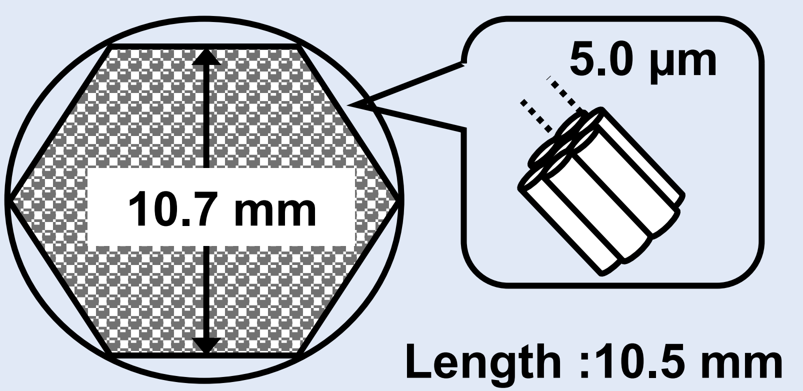
K. Tsuji. et al. *Spectrochim. Acta, Part B*, **83-84** (2015) 43-53.

WD-XRF imaging spectrometer

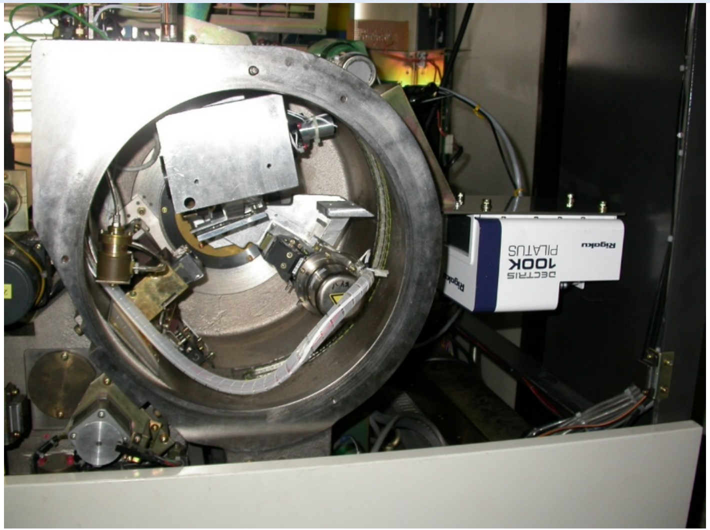




Straight polycapilalry (XOS)



Based on Rigaku RIX-1000



Elemental images of 1 Euro coin

W target
50 kV , 60 mA

K. Tsuji. et al.
***SAB*, 83-84**
(2015) 43.

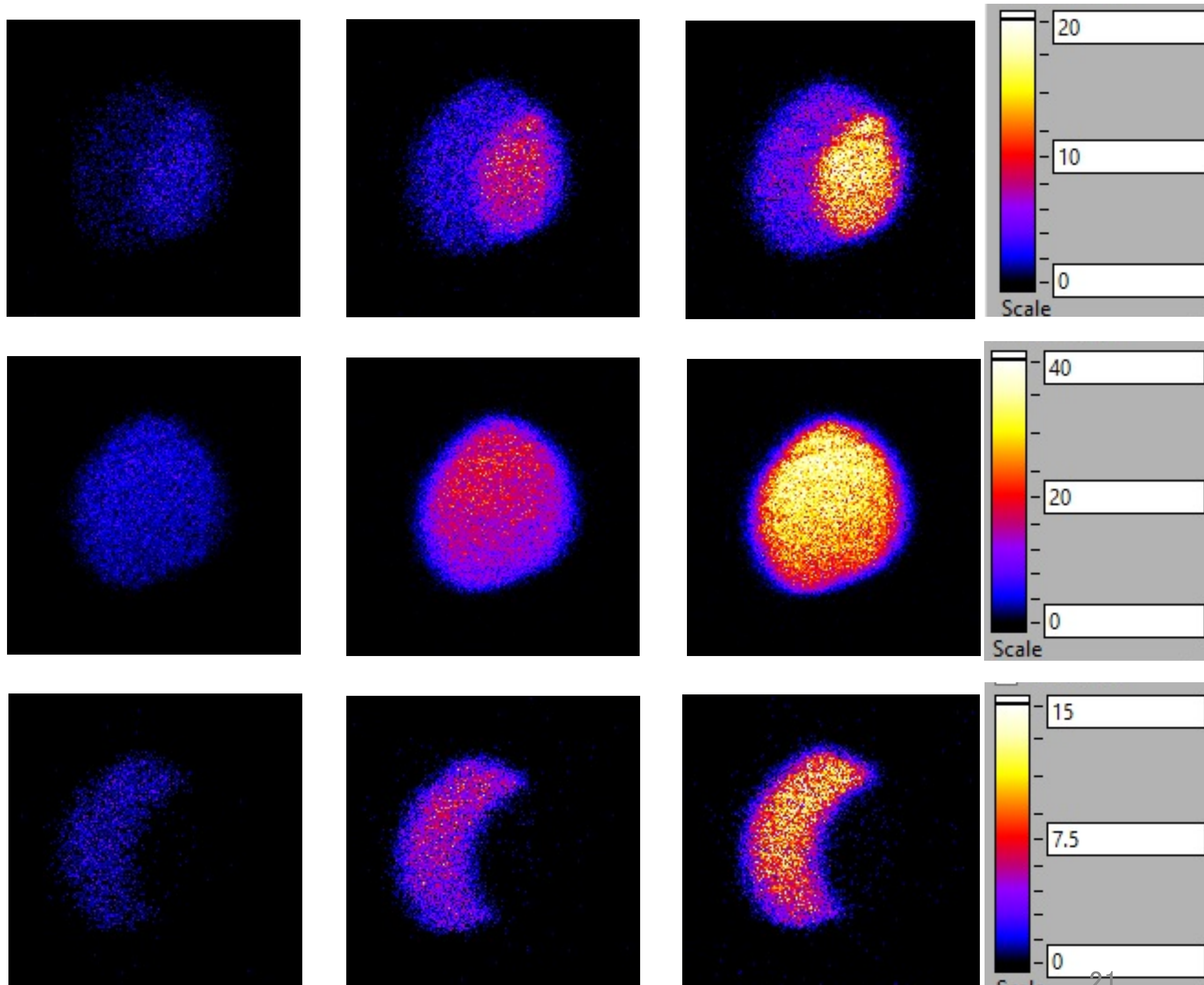
Exposure time

0.1 s   0.5 s   1 s

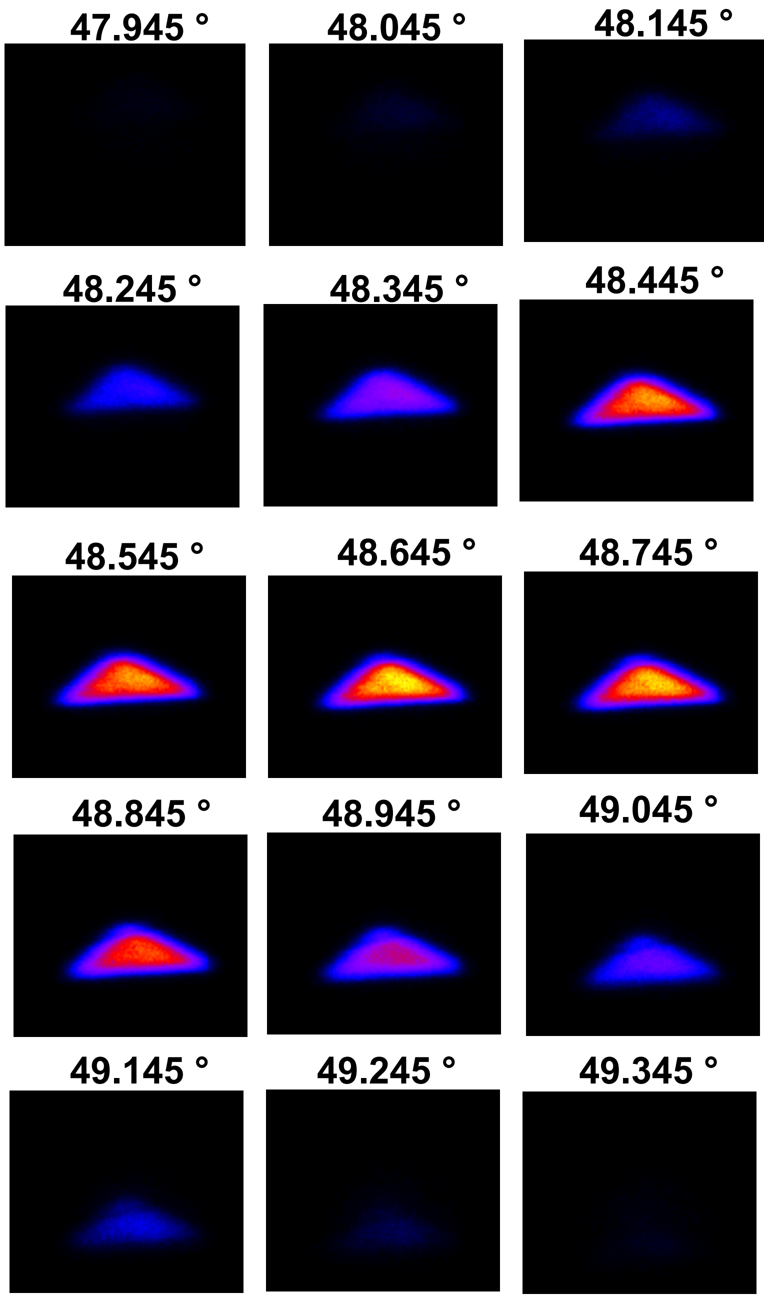
Ni Ka **48.65°**

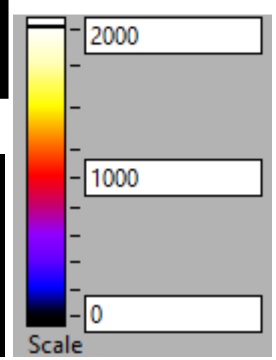
Cu Ka **45.01°**

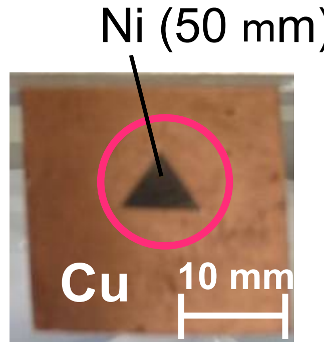
Zn Ka **41.78°**



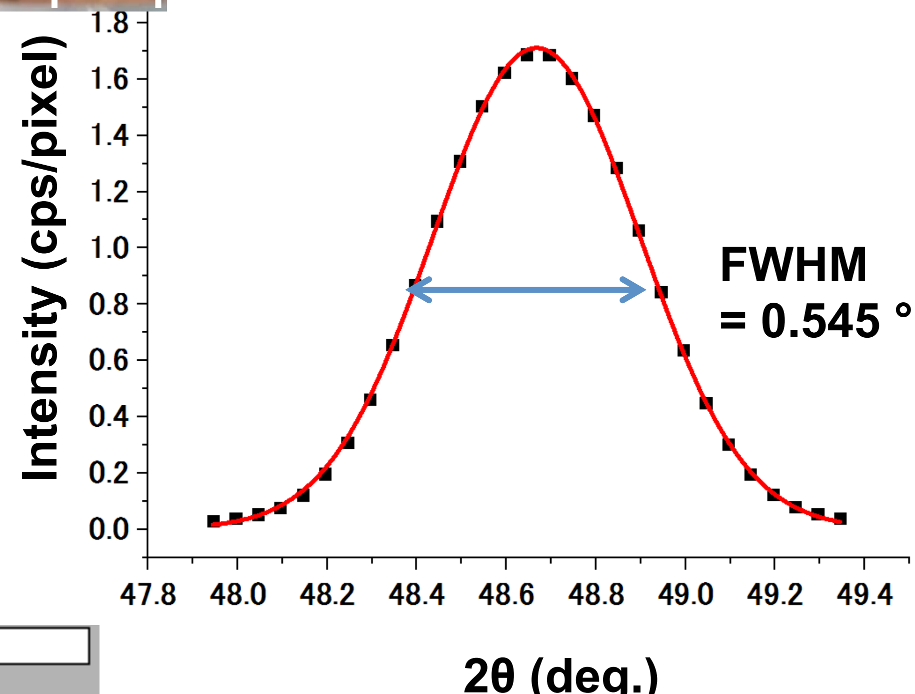
Energy resolution





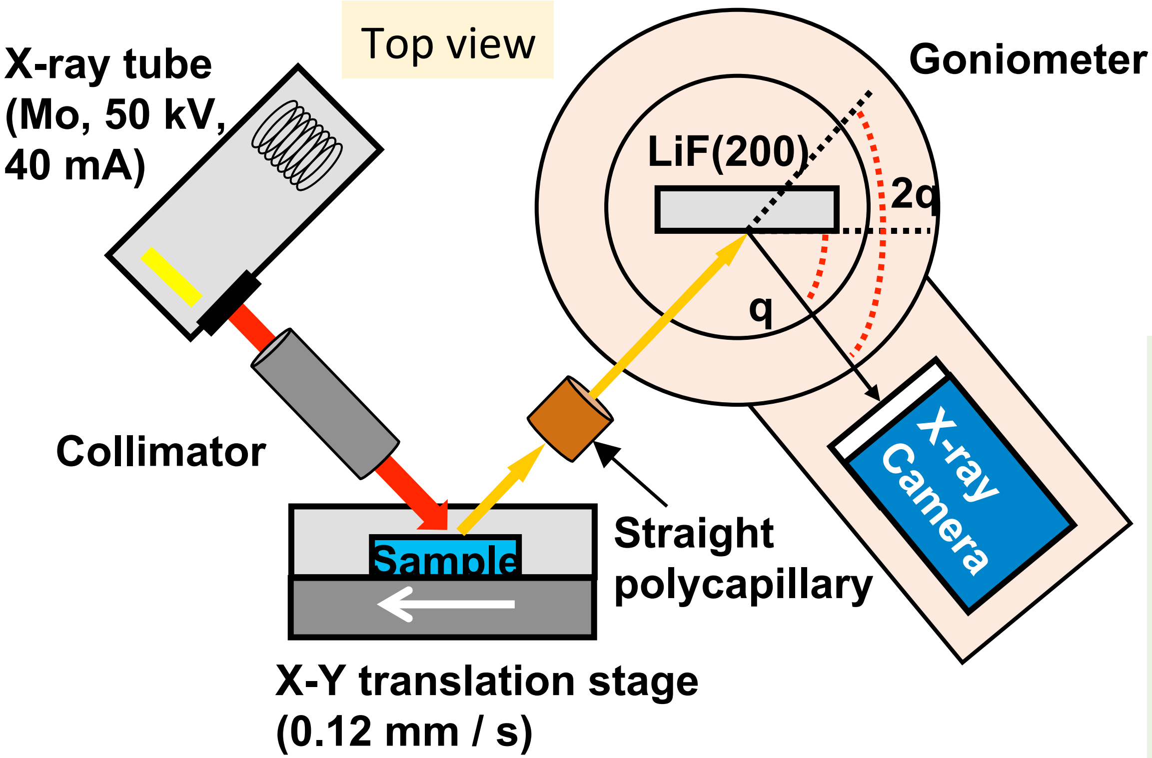


W target
60 kV , 50 mA
Exposure time : 60 s
In air



77 eV at Ni Ka (7.47 keV)

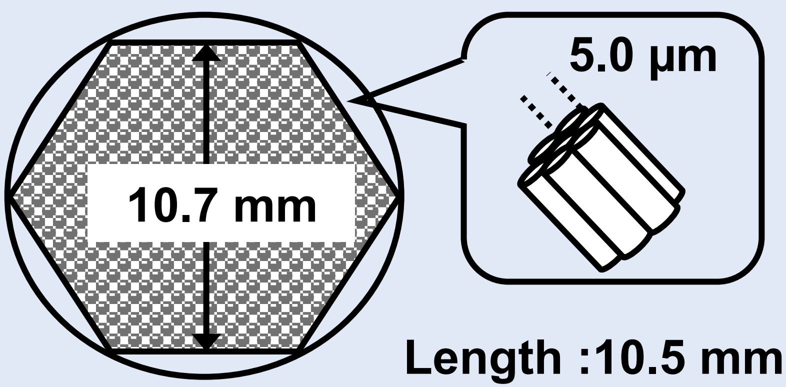
WD-XRF imaging spectrometer



HiPix-3000(Rigaku)

- 2D Hybrid Pixel Array Detector
- Sensitive area : 77.5 x 38.5 mm
- Pixel size : 100 x 100 mm
- Pixels : 775 x 385 pixels
- Dimensions : 147(W) x 93(H) x 180(D) mm

Straight polycapilalry（XOS）



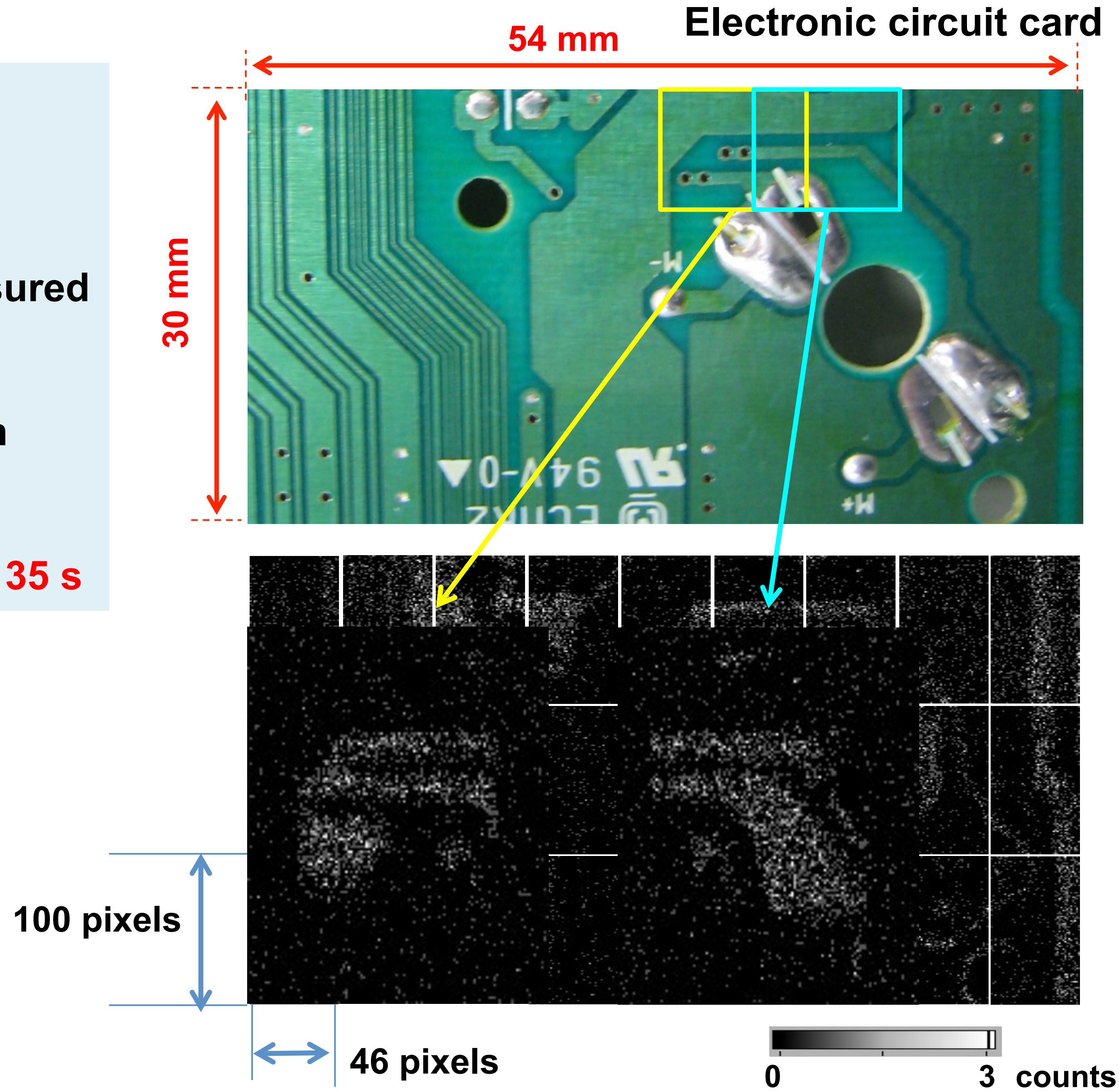
WDXRF imaging of Br in electronic circuit card

Mo target
50 kV , 40 mA
in air

The sample was measured in 27 segments.

Exposure time at each segment: 5 s

Total exposure time: 135 s



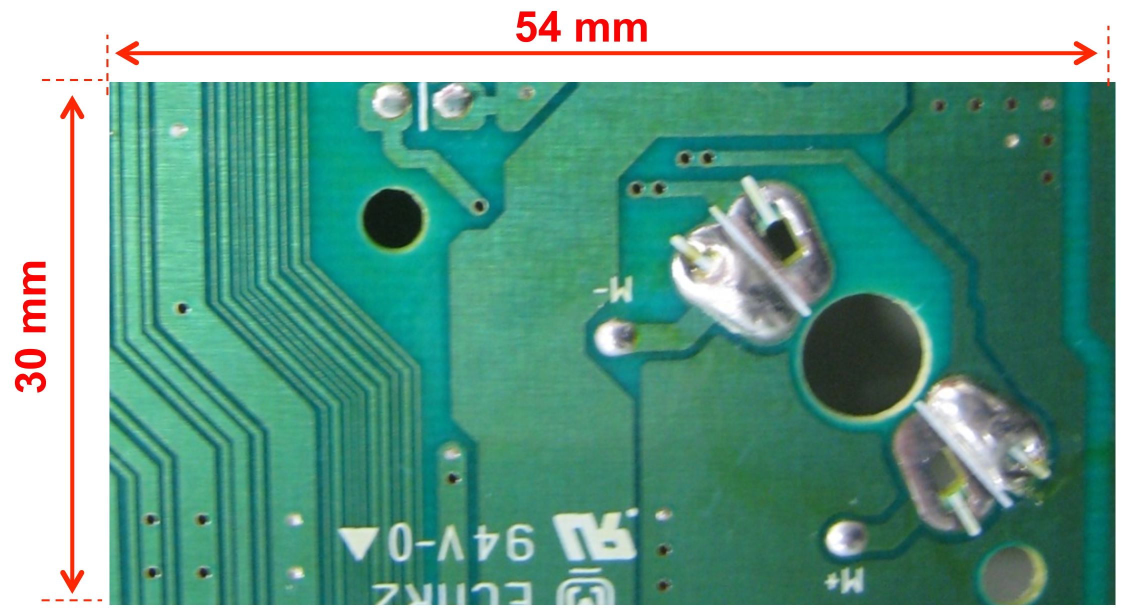
WDXRF imaging of Cu in electronic circuit card

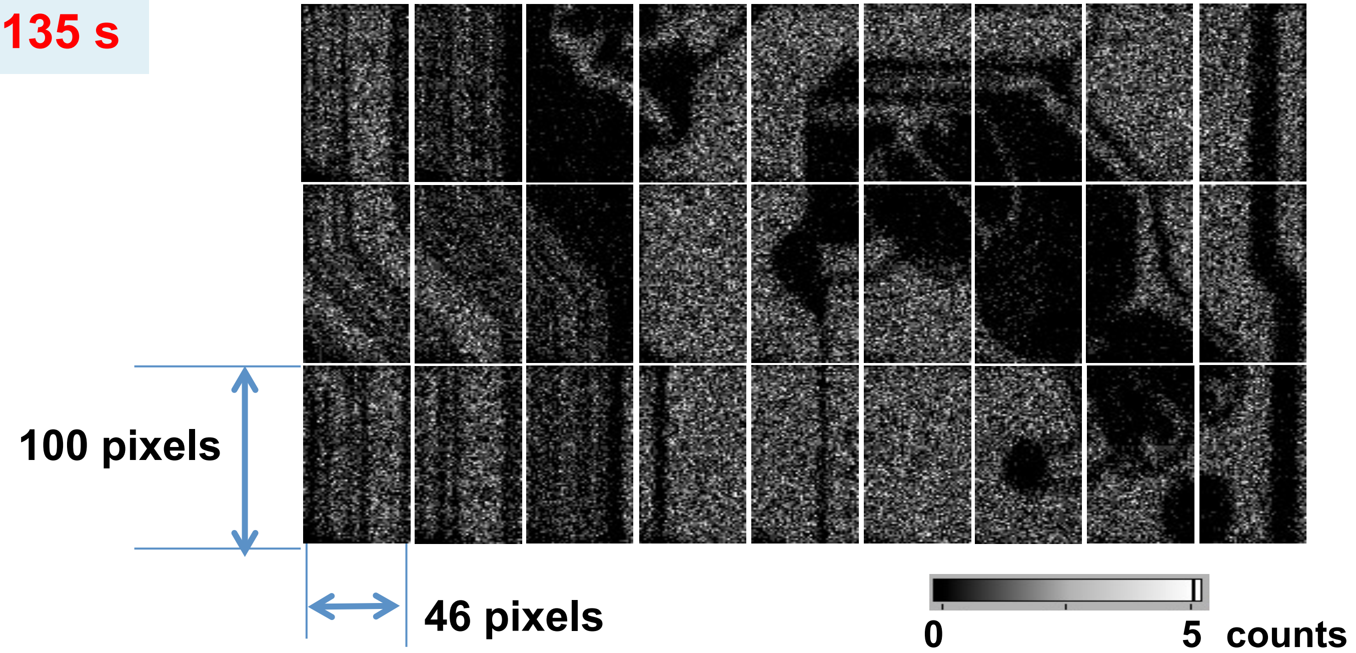
Mo target
50 kV , 40 mA
in air

The sample was measured in **27 segments**.

Exposure time at each segment: **5 s**

Total exposure time: **135 s**



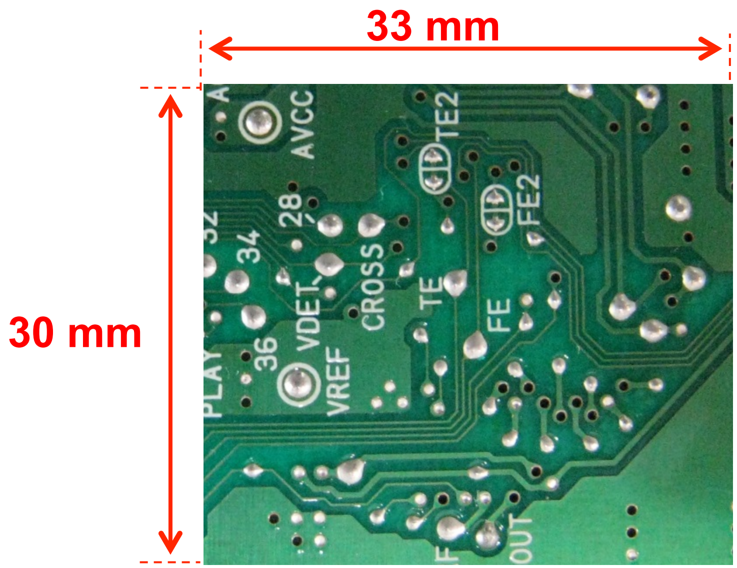


WDXRF imaging of Cu, Pb, and Br

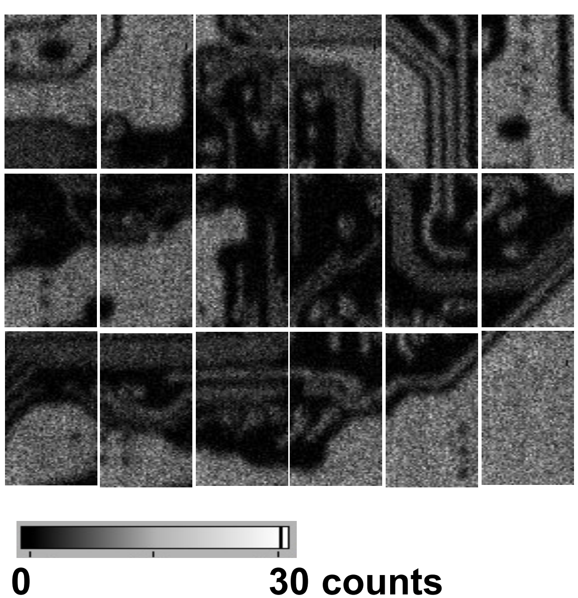
The sample was measured in 18 segments.

Exposure time at each segment: 60 s

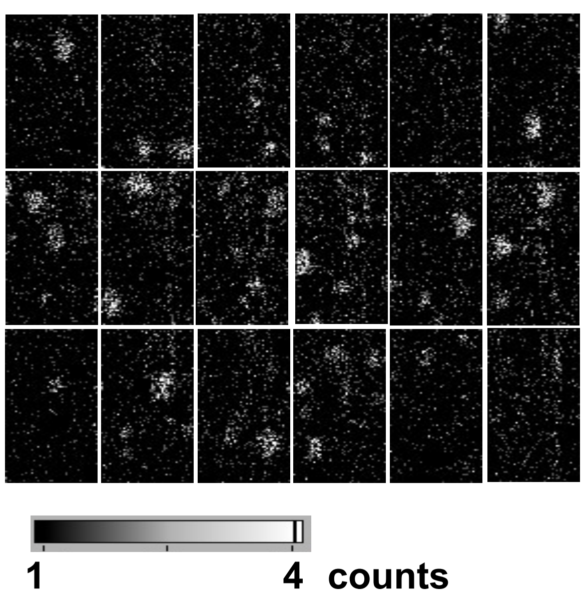
Total exposure time:
1080 s (x 3)



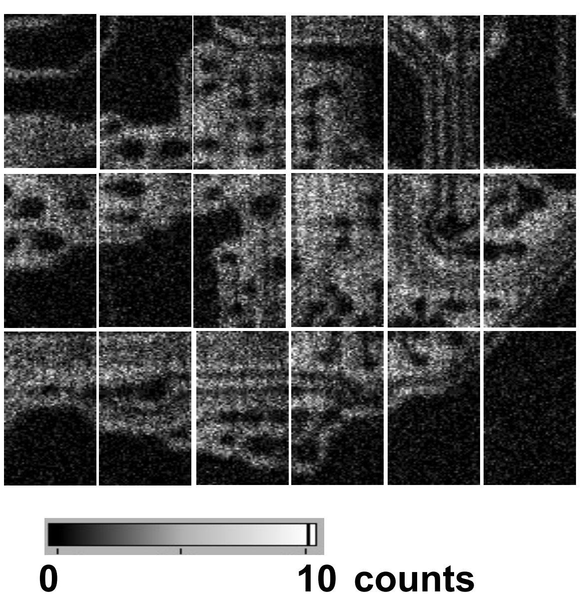
Cu Ka



Pb La

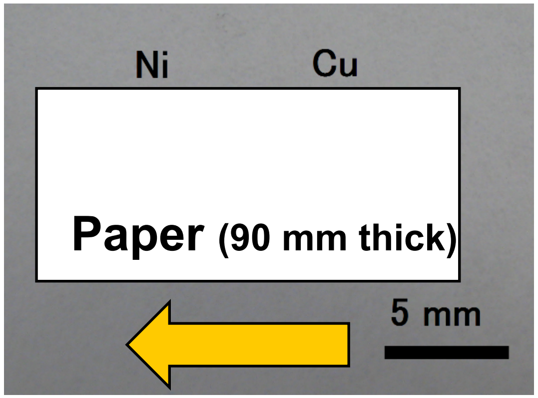


Br Ka



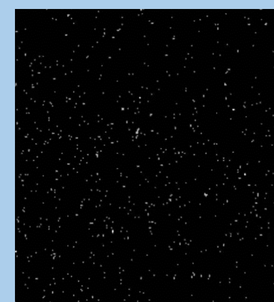
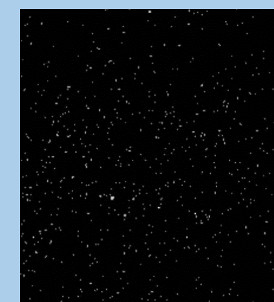
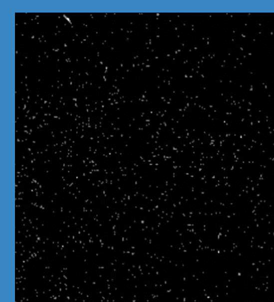
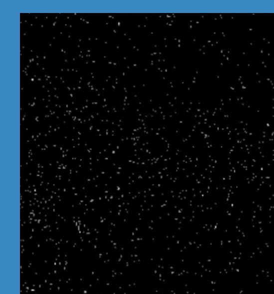
XRF observation of moving objects

Thin metal films (Ni, Cu in 10 mm thickness) were covered with a paper. Then, they were measured as they were moved.



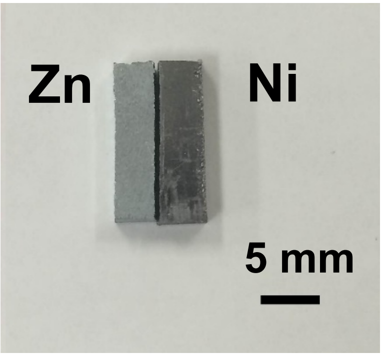
Moving direction with 0.12 mm/s.

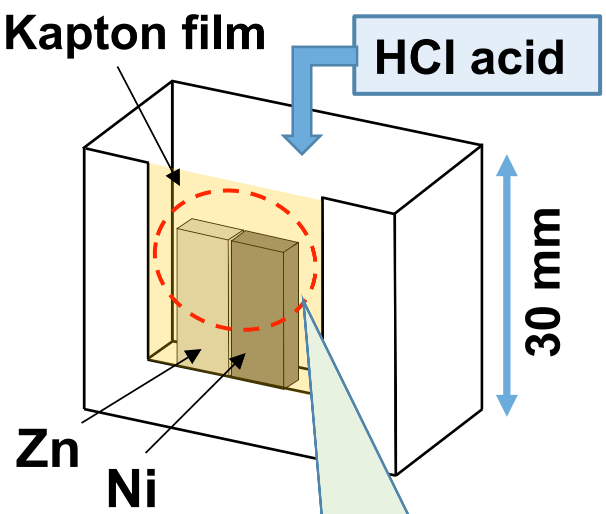
- **Exposure time: 3 s and 5 s per frame**
- **Total exposure time: 225 s**

Exposure time & frame	Ni Ka (q: 24.3°)	Cu Ka (q: 22.5°)
3 s 75 frames		
5 s 45 frames		

Element-selective imaging of moving objects

XRF observation of dissolution process



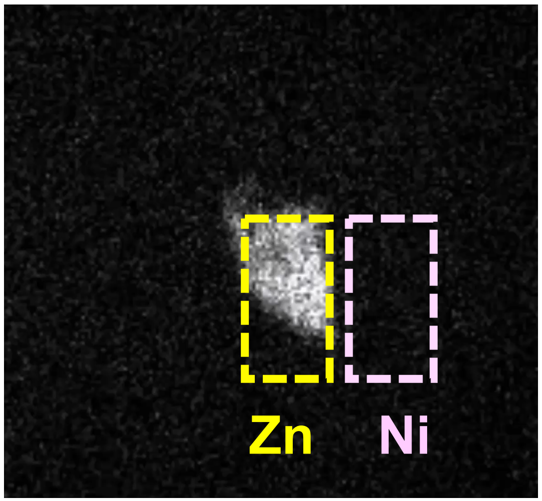


Analyzing area: about **10 mm in diameter**

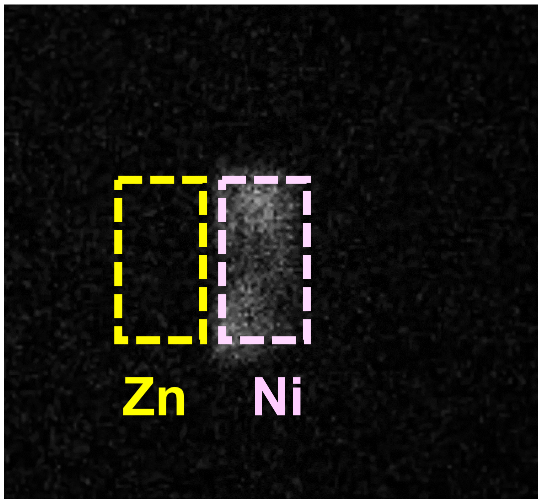
Exposure time: 60 s / frame

Total frames: 150 frames (150 min.)

Zn Ka

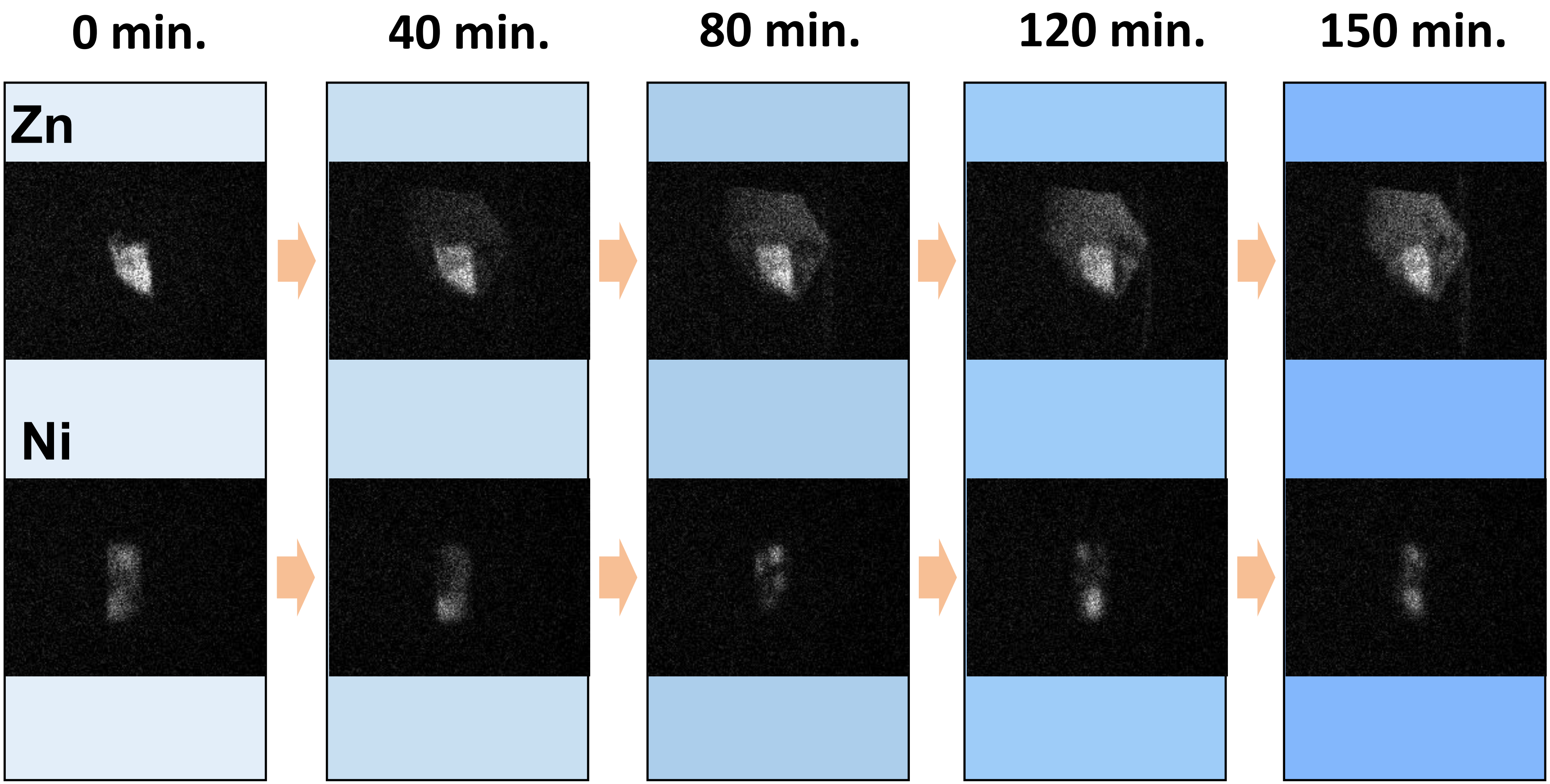


Ni Ka



- Zn was dissolved and diffused in the HCl solution.
- Ni was not dissolved so much.
- Emission of H_2 bubble affected XRF observation.

XRF observation of dissolution process



- Zn was dissolved and diffused in the HCl solution.
- Dissolution speed of Ni was slow.

FF-ED-XRF imaging spectrometer

F. P. Romano, et al., *Spectrochimica Acta Part B*, **86** (2013) 60–65.

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

F.P. Romano [a,b,*], C. Altana [b,c], L. Cosentino [b], L. Celona [b], S. Gammino [b], D. Mascali [b], L. Pappalardo [a,b], F. Rizzo [b,c]

[a] *IBAM, CNR, Via Biblioteca 4, 95124 Catania, Italy*
[b] *INFN-LNS, Via S. Sofia 62, 95123 Catania, Italy*
[c] *Dipartimento di Fisica e Astronomia, Università di Catania, Via S. Sofia 64, 95123 Catania, Italy*

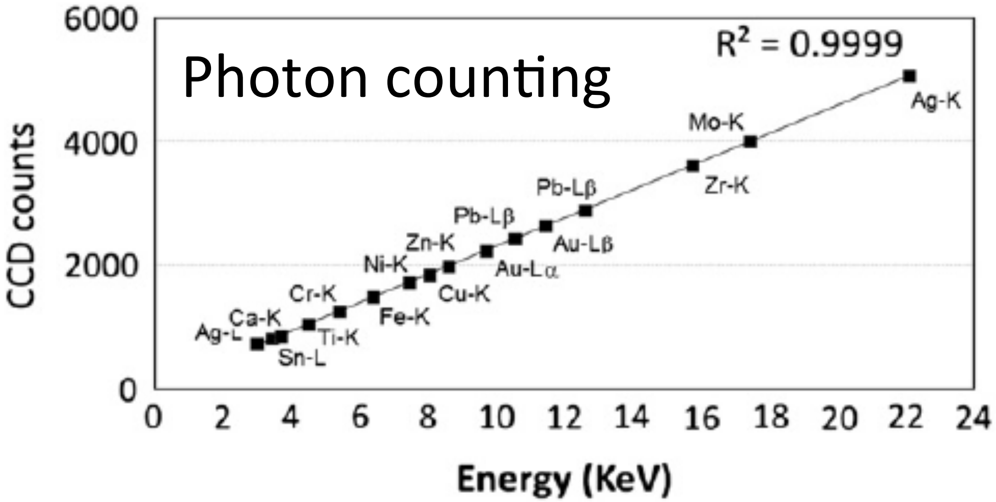


Fig. 2. Energy response of the CCD detector. CCD counts indicate the raw and digitized data generated by the analog to digital converter of the CCD.

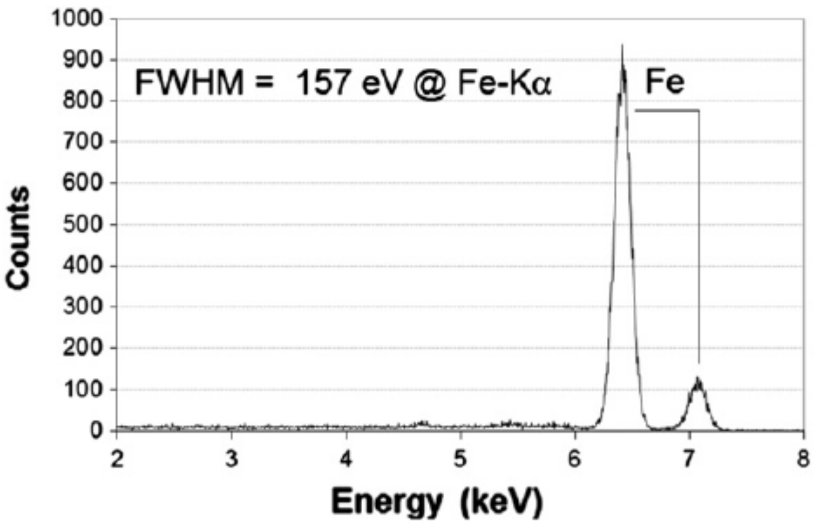
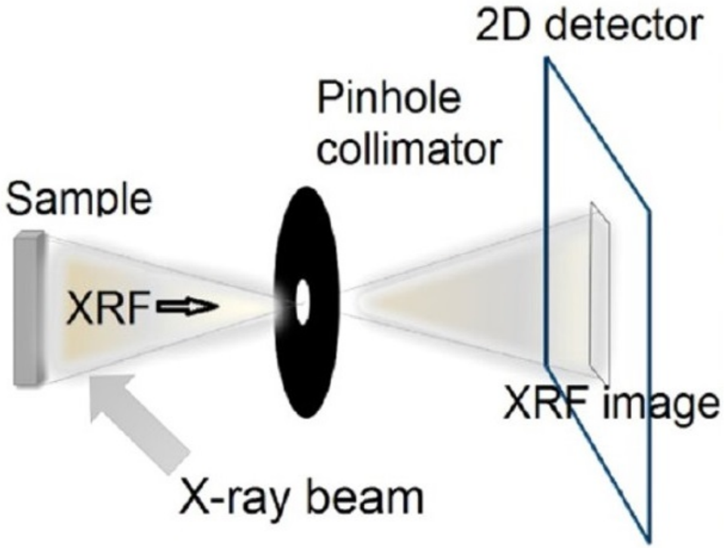


Fig. 3. The fluorescence spectrum of Fe measured using the X-ray pinhole camera. The energy resolution is 157 eV at Fe–Kα line.

FF-ED-XRF imaging spectrometer

F. P. Romano, et al., *Anal. Chem.*, **86** (2014) 10892.



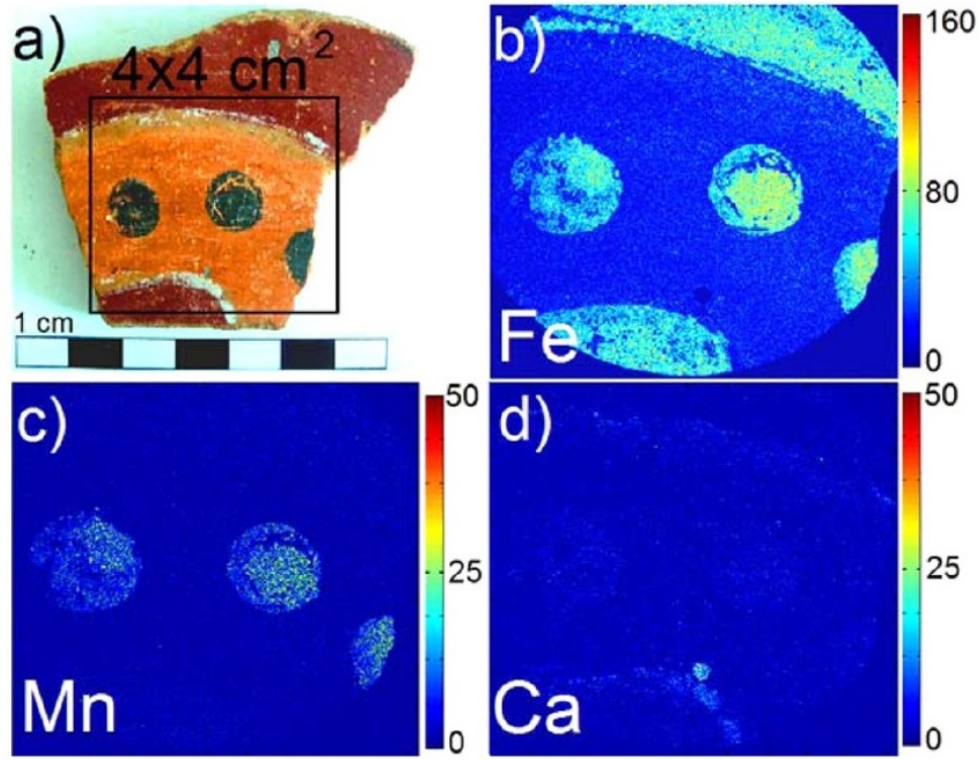
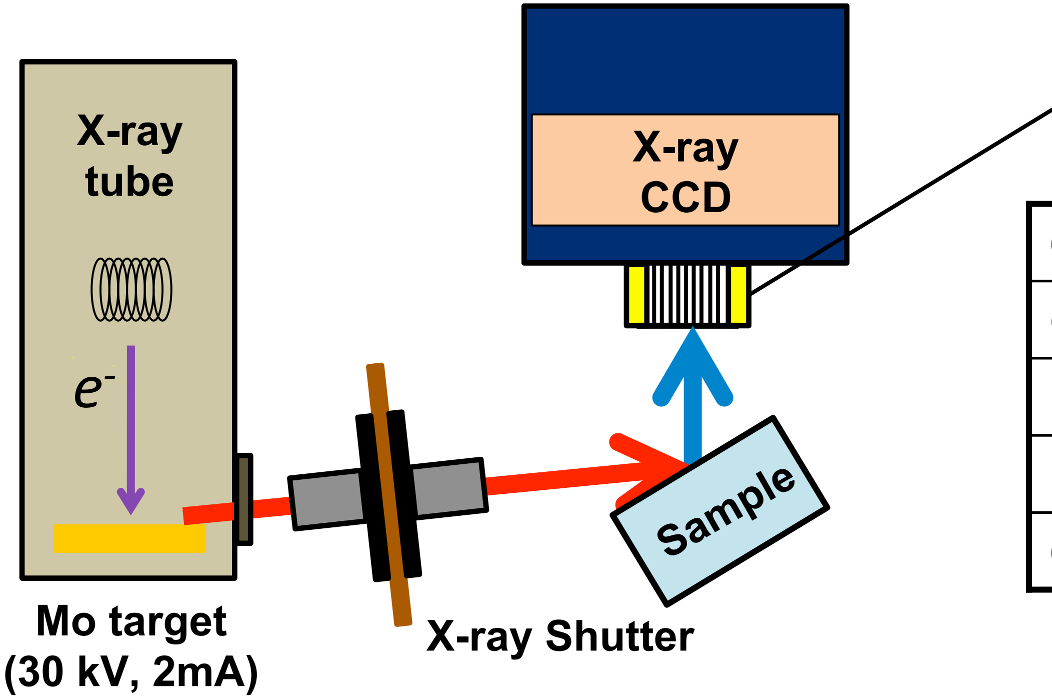


Figure 9. A Nasca pottery investigated in the macro-FF-XRF setup.

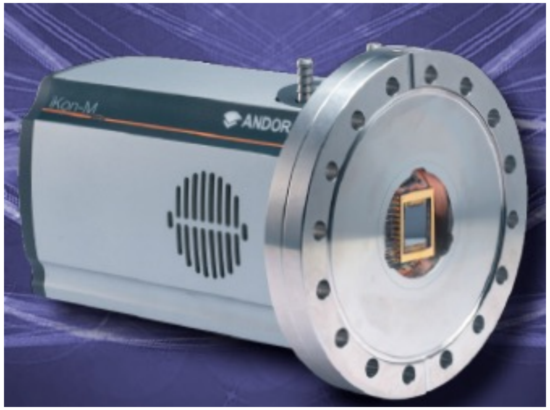
Bin=2, readout speed = 1MHz,
Spatial reso. = 170 mm, Energy reso. = 180 eV
Measurement time = 5000 s

FF-ED-XRF imaging spectrometer at OCU



< Straight polycapillary by XOS >

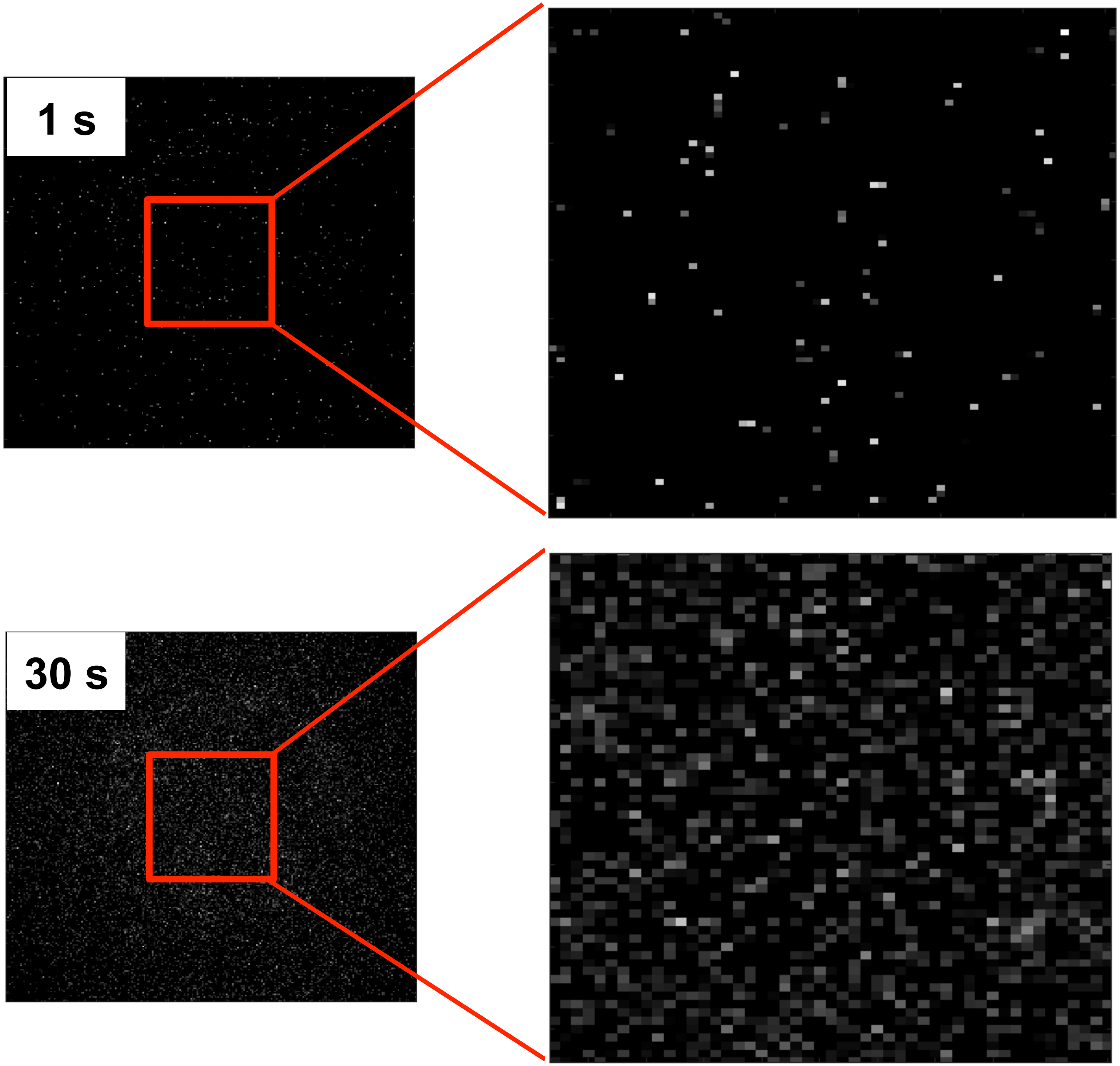
Outer diameter	11 mm
Channel diameter	6.5 mm
Enclosure diameter	18 mm
Enclosure length	10 mm
Open area	60 %



Andor iKon-M

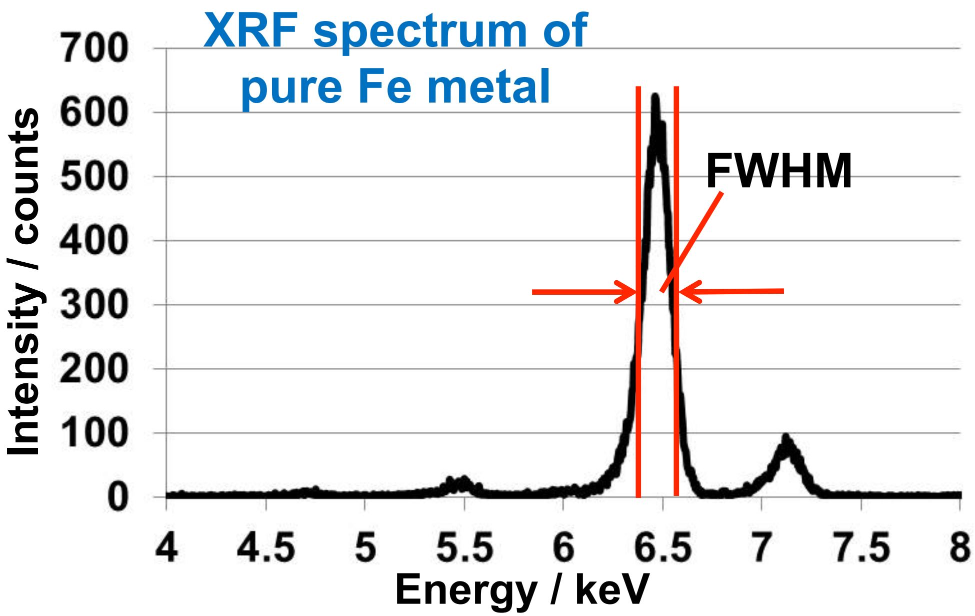
- Backside illumination type
- Pixels : 1024 pixel x 1024 pixel
  (512 x 512), (256 x 256)
- Pixel size : 13 mm x 13 mm
- Area : 13.3 mm x 13.3 mm
- Cooling : - 90 ℃

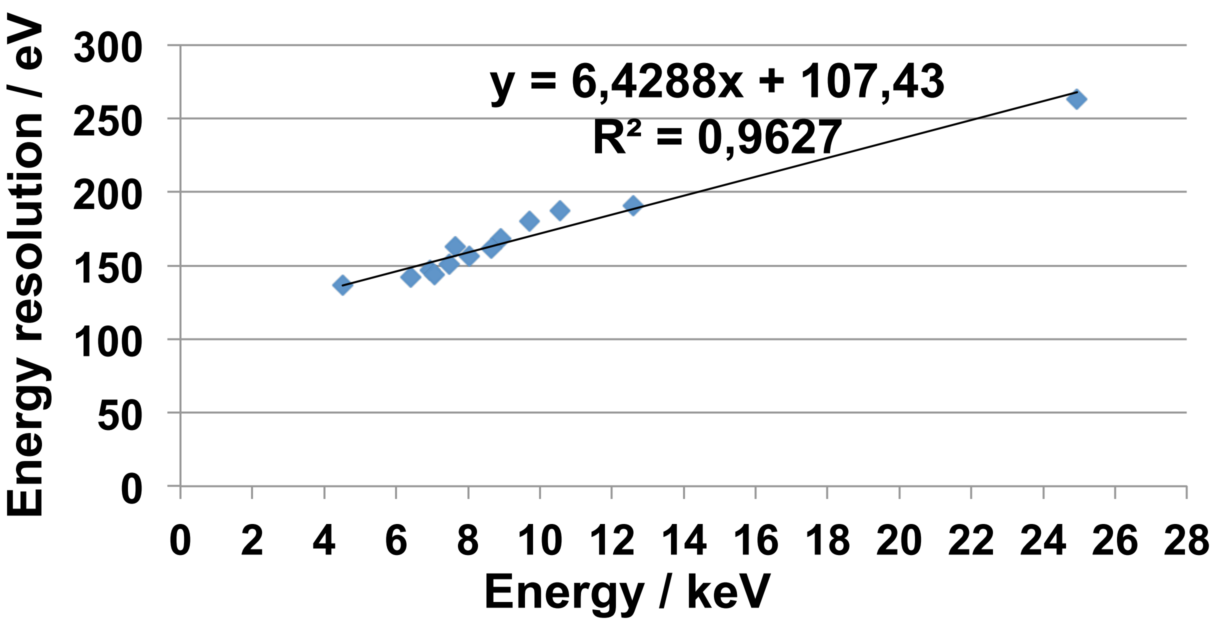
Photon counting



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

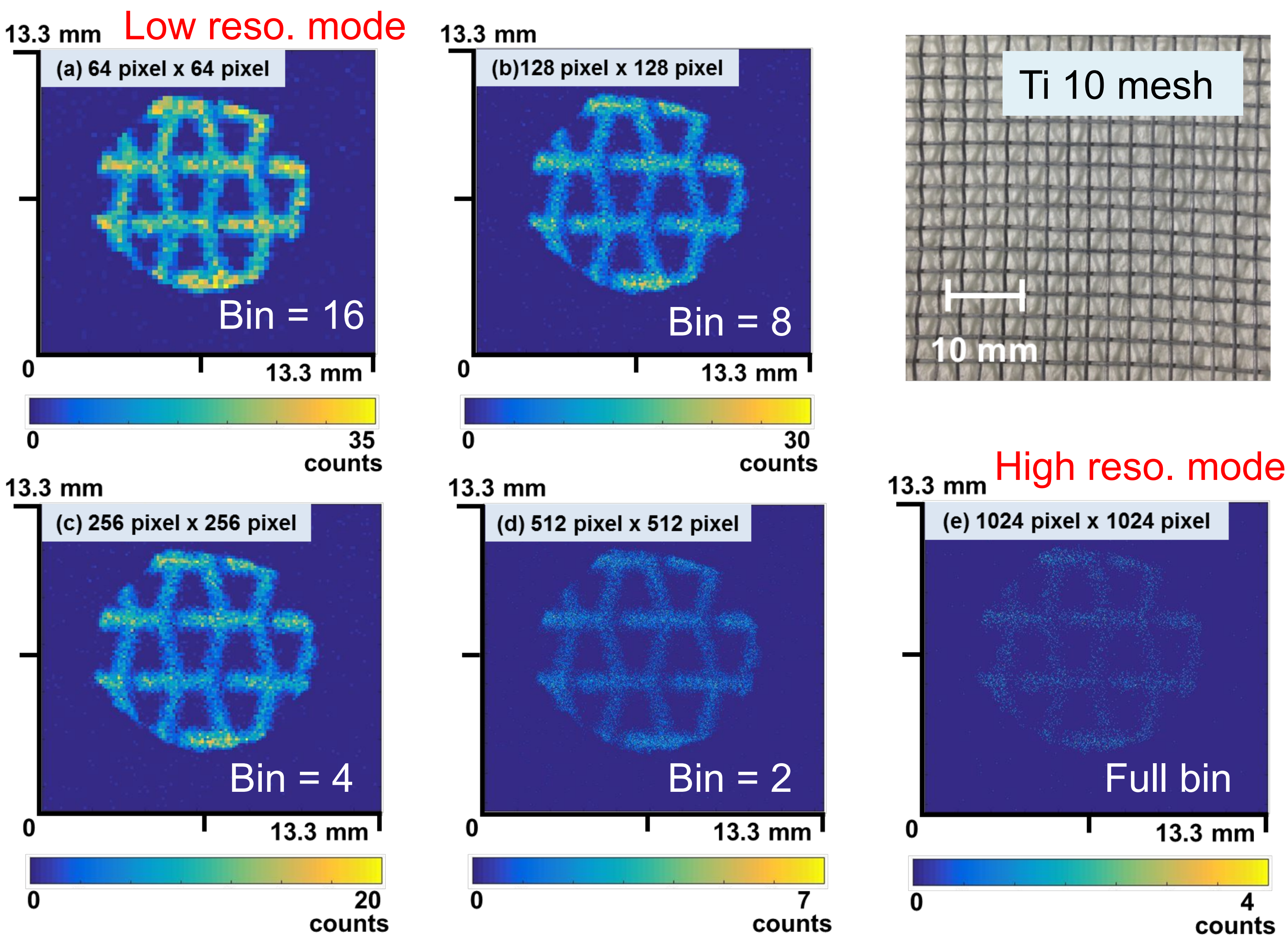




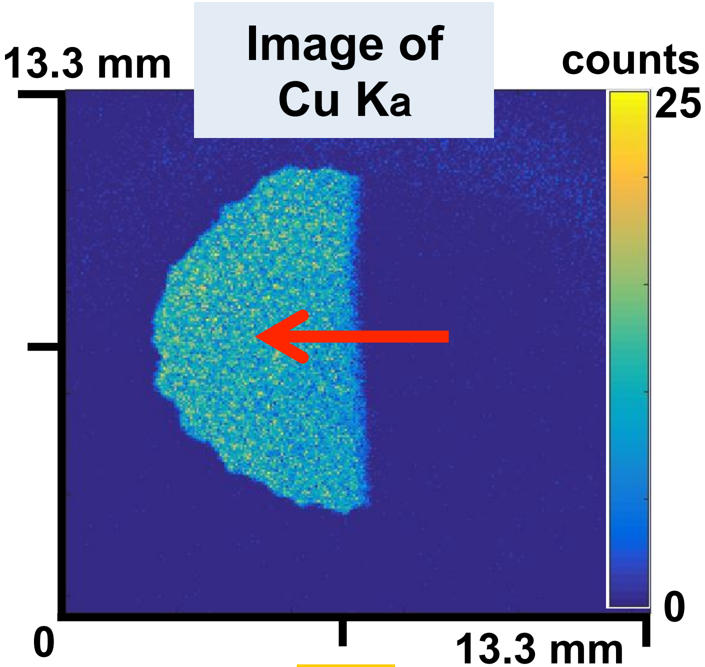
142 eV @ Fe Ka

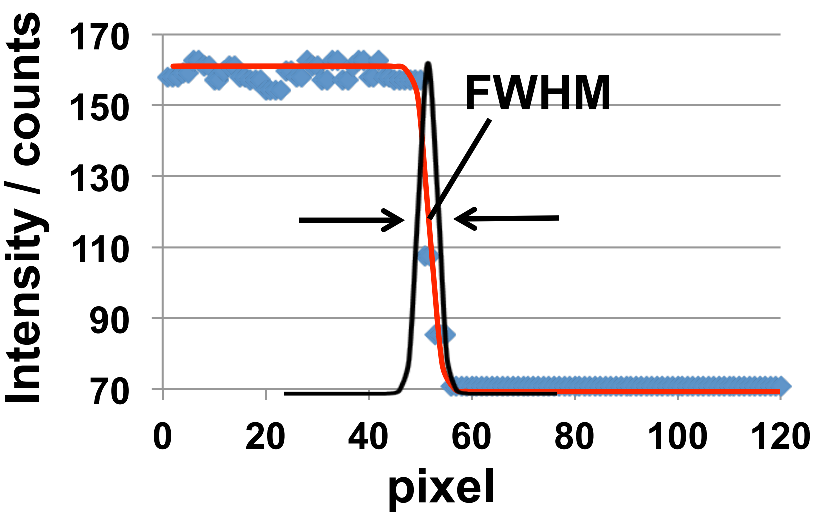
Spatial resolution

2 s / frame, 600 frames (1200 s), Mo: 30 kV, 2 mA, with difference effective pixels



Spatial resolution

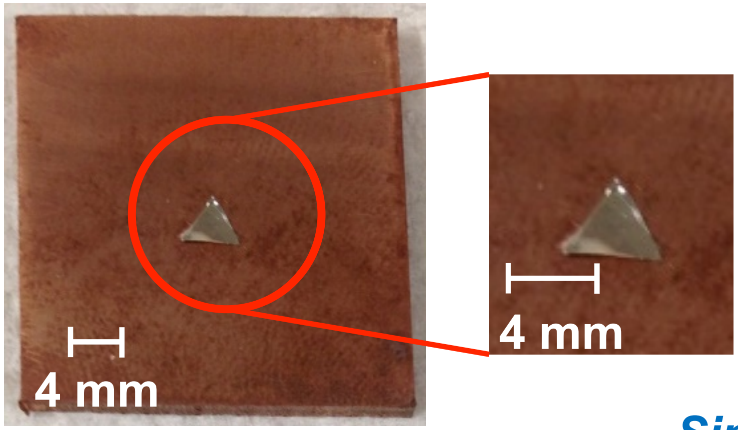




- Mo tube : 30 kV, 2 mA
- Pure metals: Co, Cu, Fe, Ni, Ti, Zn foils (50 mm in thickness), and Pb (1 mm)
- Exposure time : 1 s / frame
- Total frames: 900 frames
- Effective pixels : 256 pixel x 256 pixel
512 pixel x 512 pixel

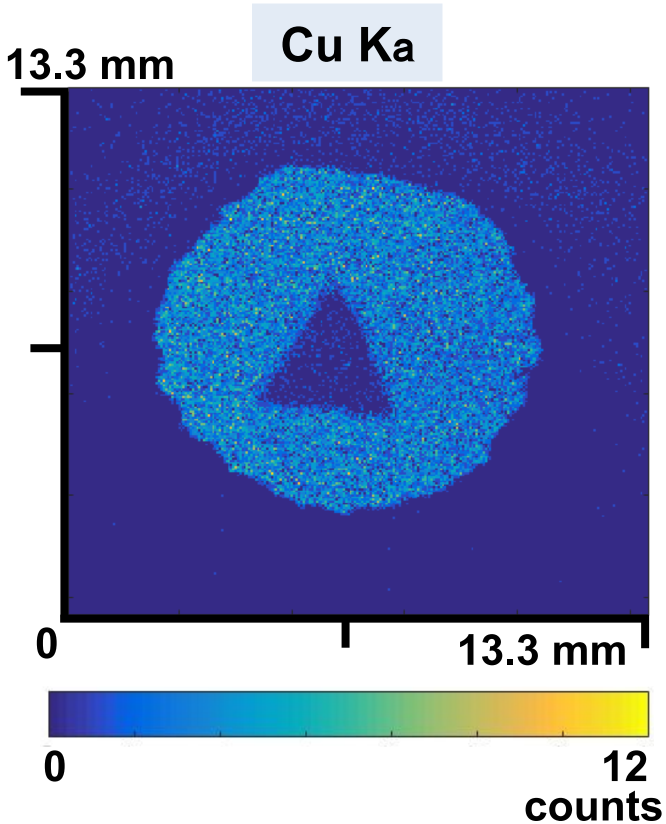
Element	FWHM (mm)	
	256 x 256 (Bin = 4)	512 x 512 (Bin = 2)
Co Ka	337	51
Cu Ka	241	33
Fe Ka	352	52
Ni Ka	297	41
Pb La	150	16
Ti Ka	521	73
Zn Ka	241	30

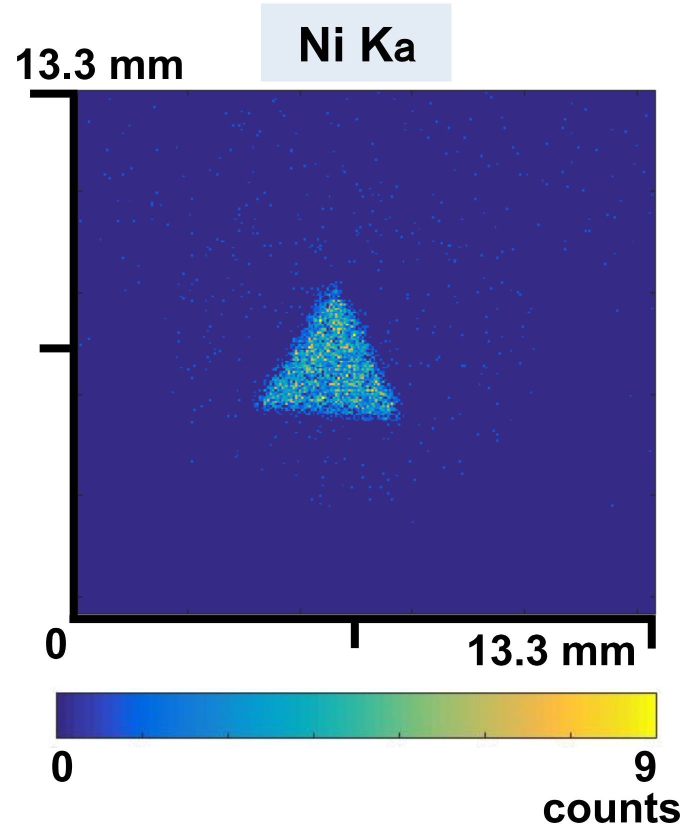
FF-ED-XRF imaging of Cu and Ni



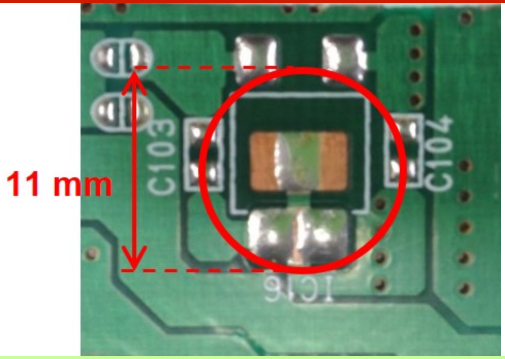
- Mo tube: 20 kV, 2 mA
- Cu-Ni sample : Ni film (50 mm) on Cu
- Exposure time: 1 s / frame
- Total frames: 600 frames (= 600 s)
- Effective pixels: 256 pixel x 256 pixel

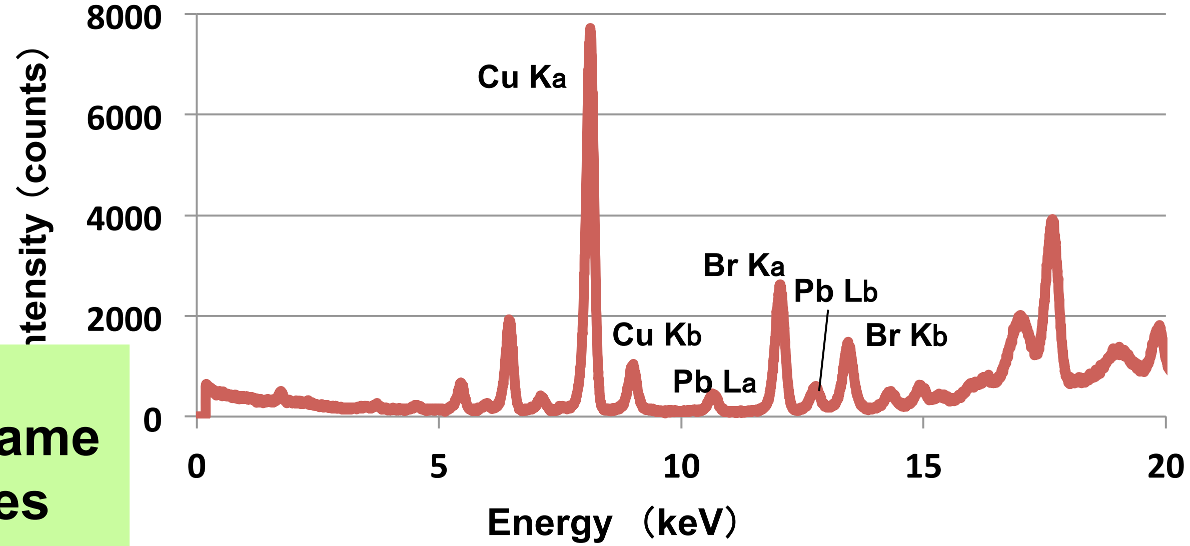
Simultaneous elemental imaging was possible.



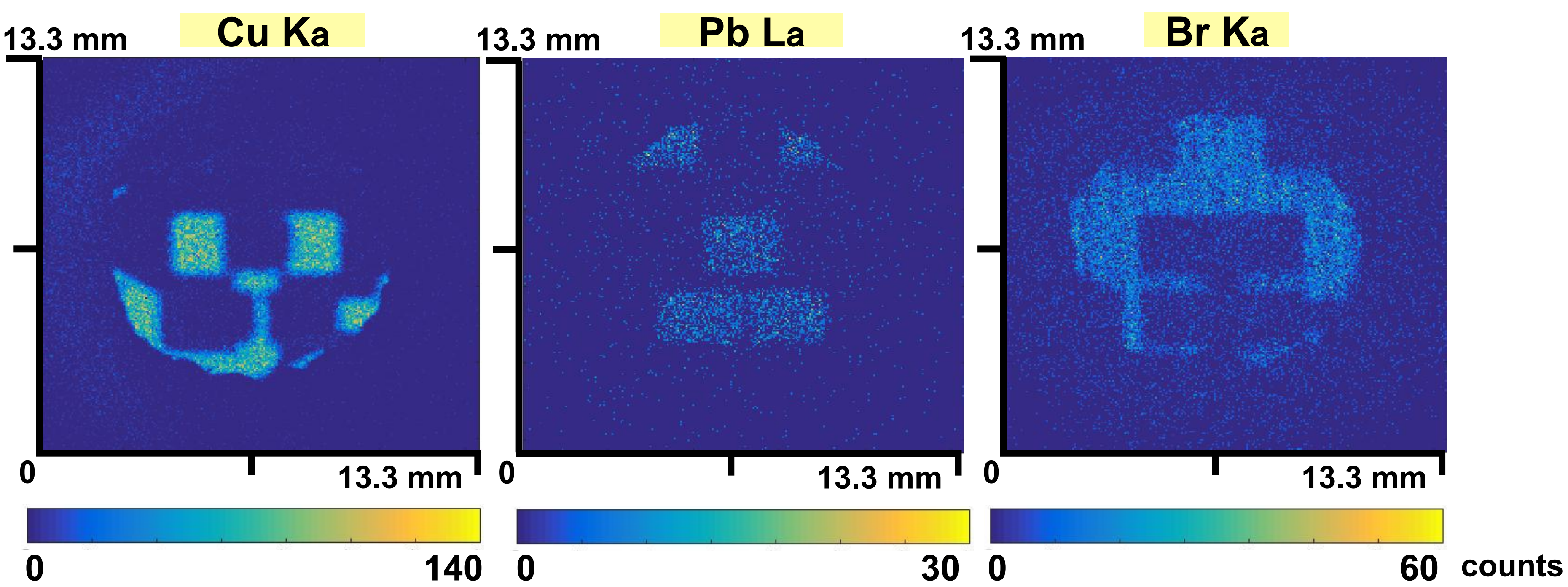


FF-ED-XRF imaging of electronic circuit card

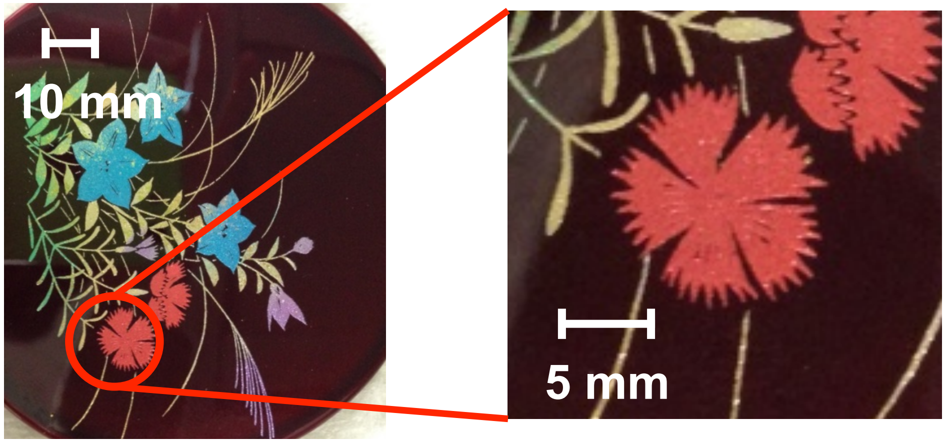




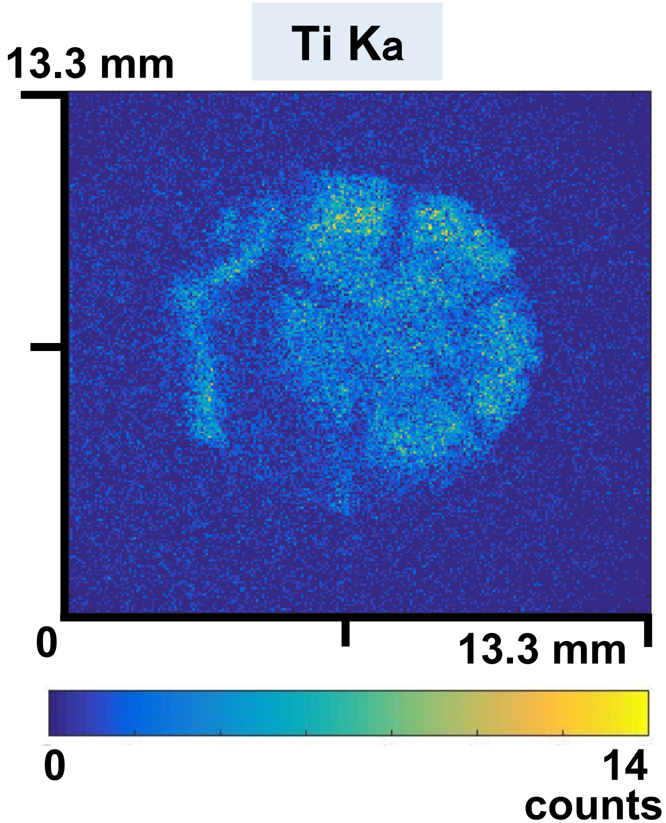
- Mo tube: 30kV, 10 mA
- Exposure time: 0.5 s / frame
- Total frames: 3600 frames
- 256 pixel x 256 pixel

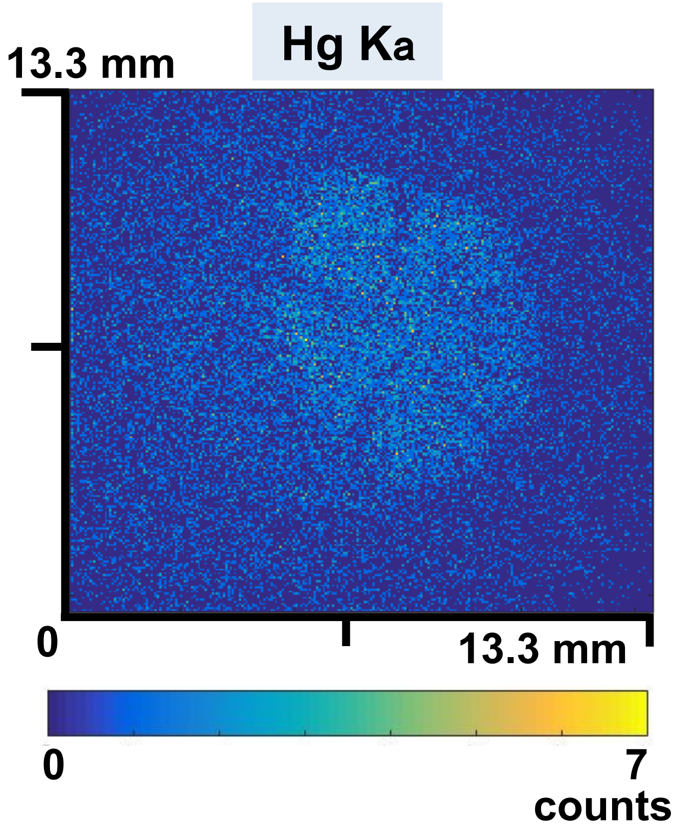


FF-ED-XRF imaging of lacquer art craft

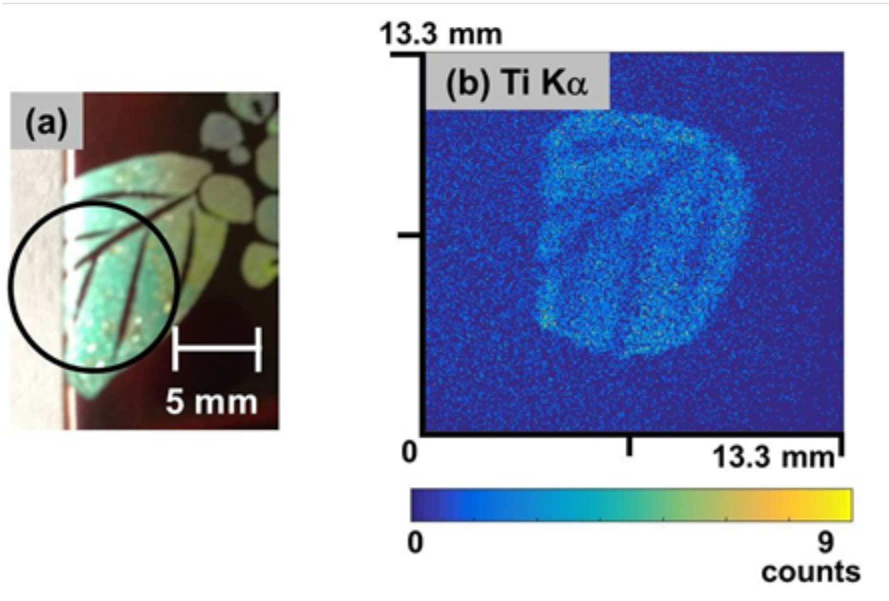


- Mo: 30kV, 10 mA
- Exposure time: 0.1 s / frame
- Total frames: 9000 frames (15 min.)
- 256 pixel x 256 pixel

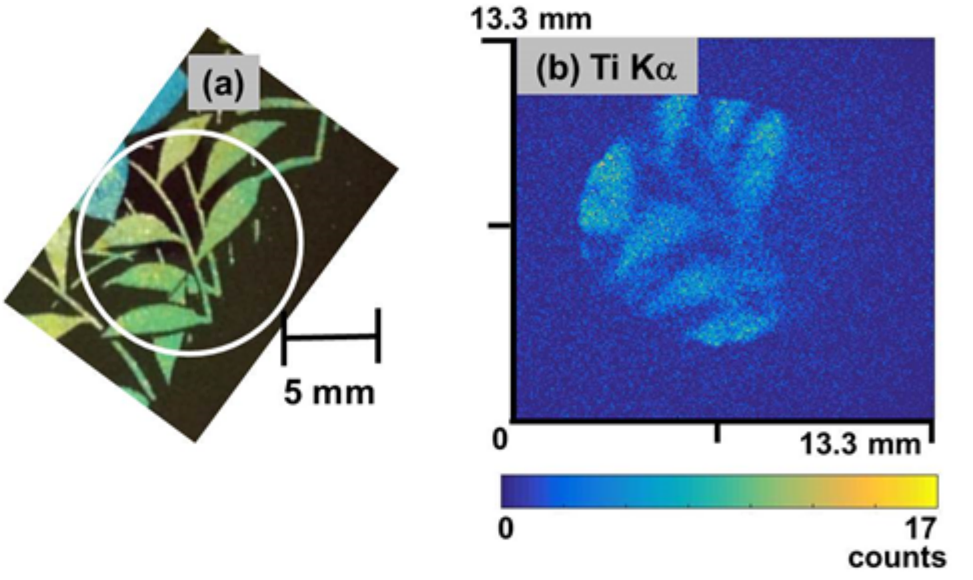


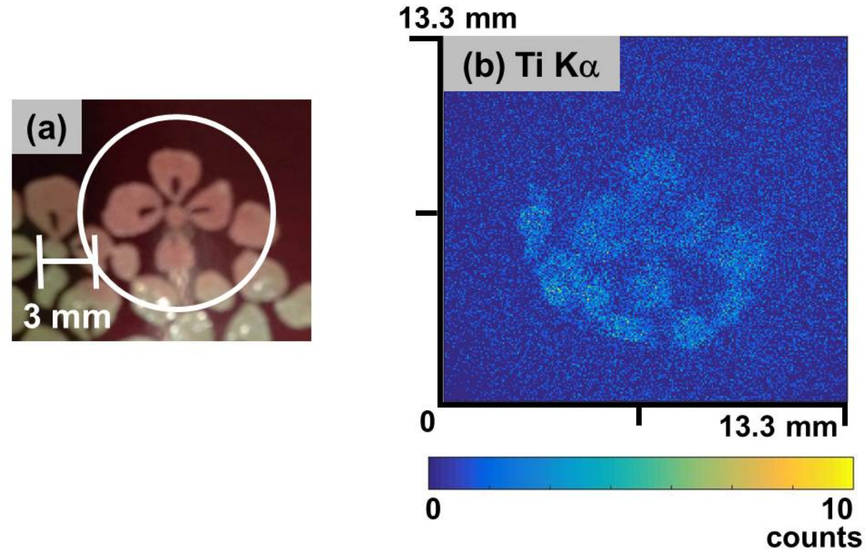


FF-ED-XRF imaging of lacquer art craft



- Mo: 30kV, 10 mA
- Exposure time: 0.1 s / frame
- Total frames: 9000 frames (15 min.)
- 256 pixel x 256 pixel





Comparison of XRF imaging techniques

	Scanning type		**FF (projection) type**	
	SEM-EDS	**(C)-M-XRF**	**WDXRF**	**ED-camera**
Source	Electrons	X-ray tube	X-ray tube	X-ray tube
scanning	Electron beam scanning	Sample scanning	Without scan (but angle scan)	Without scan
Spatial resolution	1 mm	10 mm	~ 300 mm	< 50 mm
Energy resolution	~ 140 eV	~ 140 eV	< 70 eV (~ 40 eV)	~ 150 eV
Advantage	High spatial resolution	3D analysis in C-M-XRF	Short exposure time (~ 1 s) High energy-reso.	Simultaneous multi-elemental imaging
Drawback	Vacuum Damages Electrical conductivity	Long acquisition time for large sample	Large equipment Ange scan	Photon counting for weak x-rays Long acquisition time

Summary

- Scanning-confocal M-XRF was applied for observing the corrosion process of the steel sheet in the solution.
- WD-XRF imaging spectrometer was developed. It was applied for elemental imaging of moving objects and dissolution process of metals.
- FF-ED-XRF imaging with CCD camera was developed. Analytical performance and its applications were shown.

Acknowledgements

We appreciate Rigaku for cooperation of WDXRF imaging experiment.

We also appreciate for kind suggestions from Dr. Romano for FF-XRF imaging camera.