Macro and micro Full Field X-ray Fluorescence: developments and applications in the Cultural Heritage field

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XRF technique in the cultural heritage field

XRF fulfills several requirements that are considered optimal for the investigation of artworks

- Non-destructive
- Fast and easy to use
- Multi-elemental
- Portable
- Low LoD (~µgr/gr)
- Quantitative

The conventional XRF provides elemental information. Nothing can be argued from the data on their spatial distribution.
Elemental mapping in CH

The non-destructive determination of the elemental distribution in materials under investigation, can be considered crucial for a number of applications in the CH field.

The conventional scanning XRF technique fulfills several requirements that can be considered optimal for the analysis.

Scanning micro and macro XRF allow to obtain two-dimensional maps of elements composing the materials under investigation, with high spatial resolution and high chemical sensitivity.
Scanning XRF: advantages and limits

- **High intensity beam**
- **High spatial resolution**
- **High chemical sensitivity**
- **Long measurement time**
- **Flat geometry**
- **High number of spectra**

**2D scanion step by step or rastering**
Example of scanning micro-XRF

Step: 80 µm & 3 sec.
Matrix 110x100
Total time: 15 hours
Example of scanning macro-XRF

Continuous scanning at 100 um/10msec for 6 h to have the elemental maps of a painting of 50x40 cm dimensions
The experimental set-up defines magnification, spatial-resolution and the field of view.
Magnification

\[ M = \frac{q}{p} \]

Spatial resolution

\[ \sigma^2 \approx \sigma_{\text{geom}}^2 + \sigma_{\text{diff}}^2 = \left[ \frac{(M + 1)D}{M} \right]^2 + \left( \frac{2.44\lambda p}{D} \right)^2 \]

Field of view

\[ \text{FOV} = \frac{2pqD}{s} \]
Field of View (pinhole 100 um)

FOV (cm)

sample-pinhole distance (cm)

Pinhole 75 um spessore
Full Field X-ray Fluorescence with polycapillary optics

Advantages with respect to pinholes: very high efficiency

Limits with respect to pinholes: high cost and no macro-XRF
State of the Art

State of Art

A large area full-field EDXRF imaging system based on a THCOBRA gaseous detector, A. L. M. Silva et al., J. Anal. At. Spectrom., 2015, 30, 343–352

Micropattern Gaseous Detector

Active area of 10x10 cm²

Energy resolution <1.6 keV at 8 keV

Spatial resolution 500 μm

Low cost and very fast

2D - MHSP detector

Telescopic tube

Pinhole

X-ray Tube

Sample

State of Art

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


Macro and Micro Full Field X-ray Fluorescence with an X-ray Pinhole Camera Presenting High Energy and High Spatial Resolution,

F.P. Romano et al., Anal. Chem. 2014, 86, 10892−10899
The Full Field X-ray Pinhole Camera (FF-XPC)

**CCD detector (by ANDOR):**
- 1024x1024 pixels (13µm size and 40 thick)
- $T_{chip}$ = deep cooling down to -100°C (under vacuum)
- Read out speed: 50 kHz, 1 MhZ, 3 Mhz and 5 Mhz
- CCD binning: down to 64x64 pixels (pixel size 208 µm)
- QE: >30% @ 0.5-10 keV (max. 90% @ 4 keV)
- 25 µm Be window (removable)

**PINHOLE collimator:** 50 µm diameter in a W target 75 µm thick. A Pb layer cover both sides of the pinhole for minimizing transmission of high energy X-ray photons

**X-RAY TUBE (by OXFORD):** 50 kV & 2 mA, W anode. A guide of 2.5 cm diameter is used to direct the beam on the samples.
The Full Field X-ray Pinhole Camera (FF-XPC)

X-ray beam

70 mm

152 mm

a) pinhole position in the micro-FF-setup
b) 8 μm thick Kapton window
c) pinhole position in the macro-FF-setup
d) sample position during irradiation
The Full Field X-ray Pinhole Camera
X-ray beam at the sample position
Energy Dispersive X-Ray Fluorescence

The charge generated on a pixel of the CCD by a photon of a given energy is proportional to its energy.

Single-photon measurements allow to minimize the probability of multiple-hit events and to use the CCD as a conventional energy dispersive X-ray detector.

A single-photon image contains a limited number of illuminated pixels.

A multi-image acquisition is necessary to obtain the statistics for the analysis.
Data Processing

The single-photon counting (SPC) frame often present multi-pixel groups that should be corrected.

Processing algorithm: a) identifies these groups in each of the SPC frames. b) searches the presence of a single maximum (single-hit) or of relative maxima in the group (multiple-hits); c) checks if the data, starting from the maxima, follow a monotonic trend and if there is an overlap among the identified distribution.
FOM of data processing

Pure targets Ti at:
38 kV and 1.7 mA
Bin= 2 (512x512)
Readout speed= 1 MHz

Titanium target in the Macro-FF-XRF set-up
Net Count = 188389 (about 160 cps)
Rejected = 6123 (3% of Net count)
Pile-up = 520 (0.27% of Net count) due to a spatial overlap
Live Time = 1000 sec. (50 frames of 20 seconds each)
Total time = 1200 sec. (including readout and processing time)
The pure targets were irradiated at 35 kV & 1 mA. The acquisition was performed in a single photon mode.
Energy Resolution of the CCD detector

FWHM = 133 eV @ 5.9 keV
T = -95°C
Readout speed = 50 kHZ
Bin = 16
Soft X-ray measurement

N-Kα (392 eV)
O-Kα (525 eV)

Magnetized Plasma of Air in a ECR Source

Operating without Be window
Micro FF-XRF Imaging at M=6x

Graph showing energy (keV) on the x-axis and counts on the y-axis, with peaks for Ni, Cu, Zn, Fe, Cr, and Pb. Images show distributions of these elements with pixel numbers along the axes.
Full Field X-ray Fluorescence Imaging

- Cu
- Fe
- CuFe
- Zn
- Pb
- Sn

3 cm

512x512 pixels

a) 

Fe

b) 

512x512 pixels

c) 

Cu

d) 

Zn

e) 

Pb

f) 

Sn
Spatial resolution of the FF-XPC
Effects of binning on the spatial resolution in the micro-FF-XRF set-up

Reference pattern:
- Cu target 50 µm thick
- 0.1x 1 mm slits
- 200 µm pitch
Combined macro- and micro- Full Field XRF of painted and glazed pottery

- Combined use of the macro and micro set-up:
  - Small Magnification \(\rightarrow\) Large samples (4x4 cm\(^2\) at \(M=0.35x\)) with a 140 \(\mu\)m spatial resolution (Global Analysis)
  - High Magnification \(\rightarrow\) Small samples (2.5x2.5mm\(^2\) at \(M=6x\)) with high spatial resolution (Local analysis)
Effects of the magnification on the FF-XRF images

2.5x2.5 mm$^2$

micro-FF-XRF

M=6
bin=2

Fe
Manganese-black in different cultures

Manganese-black technique have been used since prehistory and in different geographical area

A precursor Mn-based (Pyrolusite, MnO$_2$) mineral is mixed with Fe-enriched clays

Oxidizing firing up to 950-1100 °C

Two different typology of manganese-black from 450 °C:
MnO$_2$ $\rightarrow$ Mn$_2$O$_3$ (Bixbyite)

from 950°C:
Mn$_2$O$_3$+Fe$_2$O$_3$ $\rightarrow$ MnFe$_2$O$_3$ (Jacobsite)
Manganese black in Bronze Age (2000 B.C.)

FF-XRF

Counts

Fe-Kα + Mn-Kβ

Energy (Kev)

FF-XRF

Mn

Fe
Manganese black in Bronze Age (2000 B.C.)

Conventional $\mu$XRF

![Image of Bronze Age artifact with $\mu$XRF scan results]

- **Fe-Kb**
- **Mn-Ka**

Normalized intensity vs. mm (scan @ 0.2 mm/step)
Manganese black in Nasca pottery (5th cent.)

0.35x magnification
Bin 2 (512x512 pixels)
26 μm pixel → 65 μm with M
5000 serial images in SPC
1 second/frame
1.4 h measurement time
Manganese black in Nasca pottery (5th cent.)

6x magnification
Bin 4 (256×256 pixels)
26 μm pixel size
3000 serial images in 24 h measurement

Fe - red
Mn - green
Fe-Mn - yellow
Glazed pottery (XVI-XVIII Cent.)

FF-XRF

Counts

Energy (keV)

Co

Fe

Sn&Ca

Ni

W

Pb

Pb

Sn

Sn

Ca

PB

Co

Fe

Ca
Glazed pottery (XVI-XVIII Cent.)

μXRF - Linear Scan

Intensity (a.u.)

mm (scan @ 0.2 mm/step)

μXRF - Linear Scan

Normalize Intensity

mm (scan @ 0.2mm/step)
Macro-FF-XRF on small paints
A new micro Full Field XRF set-up with optics and high power tube

X-RAY TUBE: Mo-target, 3KW power, 50 kV & 60 mA

A straight-shaped polycapillary (by IFG) - 21 mm length, 42mm diameter, 20 µm diameter capillaries
Roman coins with a silvered patina

Diocletian introduced the nummus in his monetary reform in 294 A.D.

Nummi were manufactured with a core composed by a quaternary Cu-Ag-Sn-Pb alloy and a thin silvered patina (about 2 µm) in their surface.
The residual patina in the nummi consists of spots of millimeter/sub-millimeter dimensions. It is possible to compare LE-\(\mu\)XRF surface measurements in region with well preserved Ag-patina and without (degraded) patina.
Full Field XRF with pinholes (macro) and optics (micro)

15th–16th century Book of Tides (in coll. with K. Janssens)
Macro Full Field X-ray Fluorescence

Micro Full Field X-ray Fluorescence (1st position)
Depth profiling with a confocal micro XRF set-up

Rh microfocus tube coupled to a polycapillary lens focusing at 26 um (@ the Rh-K) SDD detector, 50 mm2, 133 eV @ 5.9 keV coupled to a polyCCC of 29 um spatial res. @ Fe-K

Analyzed area by the confocal set-up presents a blu pigment in the front side and the gold layer in the obverse side.

Position of the maximum of:
Cu -> 105 um (FWHM 47 um)
Ba -> 110 um (FWHM 66 um)
Ca -> 120 um (FWHM 95 um)
Au -> 275 um (FWHM 47um)
Conclusions

- FF-XRF is a novel and still under development method for mapping materials at the macro and micro scale;

- Different set-up are possible
  - FF-XRF with pinholes are possible;
  - FF-XRF with optics;

- Different detectors:
  - pnCCD
  - MCP gaseous Detectors (other talks in this WS)
  - Conventional X-ray CCDs

- FF-XRF can be used successfully in CH applications (pottery, paints, manuscripts, metals)