XRF imaging of historical paintings on the macro-scale: Capabilities and limitations

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Trieste, 14.07.15
Outline

> Scientific investigation of historical paintings
> XRF and XRF imaging
> XRF imaging of historical paintings
  ▪ Experiments at synchrotron sources
  ▪ Mobile instruments with X-ray tubes
  ▪ Comparison
> Limitations of MA-XRF
> Other Groups
> Conclusions
Scientific investigation of historical paintings

- Investigate the creation process (*pentimenti*)
  - Contribute to discussions of authenticity and painting technique
- Visualize later restorations and degradation processes
  - Support the conservation of artworks
- Visualize overpainted works
  - Fill gaps in the oeuvre of an artist
- Identify materials
  - Contribute to discussions of authenticity and painting technique

It is of highest importance that as much of the painting’s original structure is preserved, so that all investigations must be nondestructive and sampling limited as far as possible.
Local, microscopic investigations of samples provide a minimal destructive, detailed insight.

Macroscopic investigations provide an overview and allow to estimate how representative a sample is.
• **XRR: X-ray Radiography**
  - No elemental contrast
  - Often dominated by the lead white distribution
  - Can contain strong contributions from the support
Scientific investigation

- **XRR: X-ray Radiography**

“Saul and David”, Rembrandt and/or studio, Oil on canvas, ca. 130x165 cm, Mauritshuis Museum, Den Haag, NL

Elemental contrast would allow to distinct between paint layers containing pigments of different elemental composition.

For a long time no method allowing to obtain elemental distribution images was available for the investigation of historical paintings.

Only Neutron-Activation Autoradiography (NAAR) allowed since the 1960s for the acquisition of images with elemental contrast, but required high logistical effort.

In 2007 scanning macro-XRF was for the first time successfully used to image an hidden painting.
First successful visualization of a historical overpainted work by scanning macro-XRF (MA-XRF).

*Patch of Grass*
Vincent van Gogh, 1887
oil on canvas, 30 cm × 40 cm
Kröller-Müller Museum, Otterlo, The Netherlands

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Introduction: XRF

Primary radiation

Vacancy

K L M N
Introduction: XRF
Introduction: XRF

L-Lines

K-Lines

α β α β γ

K L M N
Introduction: XRF

The energy of a fluorescence line is dependent on the atomic number (Z) and line specific constants (Moseley’s law):

\[ E(Z) = c_1 (Z - c_2)^2 \]
# Introduction: XRF

- Best detectable by K-lines
- Best detectable by L-Lines
Introduction: XRF imaging

Stacks or 3D data cubes of spectra
Introduction: XRF imaging

Fe elemental distribution image

![Fe elemental distribution image](image)

**Fe-K**

![Energy vs. Counts graph with Fe-K peak highlighted](image)

**Fe-K**

![Energy vs. Counts graph with Fe-K peak highlighted](image)

**Fe-K**
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_Patch of Grass_  
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XRF imaging of historical paintings: SR

Synchrotron:

Bending magnet:

Images: www.wikipedia.org
Synchrotron sources
- High intensity
- Monochromatic
- (Coherent radiation)
- (Polarized radiation)
- Stationary
- Limited availability
Why the investigation of historical paintings started at synchrotron sources:

- Intense primary radiation (not essential, as historical paintings feature several 100 µm thick layers of heavy metal salts)

- Monochromatic radiation (not essential, as it mainly simplifies data evaluation but is not necessary)

- Availability of large motor stages and knowledge of instrument development and experimental control software (essential)

- In all scanners the scanning speed was not as much limited by the statistics of the data acquired, but the synchronization of motorized stages and detector(s).
XRF imaging of historical paintings: SR

"Pauline im weissen Kleid"
Attributed to Philipp Otto Runge
~1805
Private collection
Matthias Alfeld

XRF imaging of historical paintings: SR

Beamline L, HASYLab@DESY Hamburg, Germany
35 keV Energy
4 Si-Drift-Detectors
Collimated beam:
0.5x0.3 mm
Ca. 50*25 cm²
3.5 days
XRF imaging of historical paintings: SR

Fe: Earth pigments
XRF imaging of historical paintings: SR

Pb-L: Lead white
Matthias Alfeld

XRF imaging of historical paintings on the macro-scale: Capabilities and limitations

Co: Cobalt blue
Hg-L: Vermilion
XRF imaging of historical paintings: SR

Sb: Naples Yellow
Reconstruction (hair)
reconstruction (hair)  

radiograph

Drawing by Philipp Otto Runge (ca. 1805)

The applications for scanning macro-XRF with synchrotron sources is limited by several factors:

- Beamtimes are not easily available and are of limited duration
- The painting has to be transported and moved through the beam
- The size of the painting is limited

The dimensions of the painting are 40 cm x 30 cm.
“Supper at Emmaus”, Caravaggio
Primary beam
SDD
slit system
Beamline L, HASYLab@DESY Hamburg, Germany
35 keV Energy
4 Si-Drift-Detectors
Collimated beam: 0.5x0.3 mm
Ca. 50*25 cm²
3.5 days
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XRF imaging of historical paintings: mobile instruments

X-ray tube sources
- Easily available
- Transportable
- Polychromatic
- Limited intensity

Image X-ray tube: www.wikipedia.org
XRF imaging of historical paintings: mobile instruments

Name: Instrument D (University of Antwerp)
Source: 10 W Rh X-ray tube
Optic: 0.5 or 0.8 mm Pb pinhole
Detectors: 4 SDDs
Range: 60 x 60 cm²
Speed: 10 pixel/s

DESY results
0.5 mm resolution, 2 days

in situ results (variant of Instrument D)
1 mm resolution, 6 days

World’s largest object entirely mapped with XRF
Composed of 12 individual scans with Instrument D
2032 x 1456 pixel
1 mm step size
~0.4 s/pixel
=> 2 Weeks
XRF imaging of historical paintings on the macro-scale: Capabilities and limitations.

XRF imaging of historical paintings: mobile instruments.
Fe: Earth pigments
Mn: Earth pigments
Hg-L: Vermilion (HgS)
Pb-L: Lead white
Rest on the flight to Egypt, Caravaggio, 135 x 167 cm, Oil on canvas, Galleria Doria Pamphilj, Rome
These findings are significant as, based on Giovan Battista Bellori’s “Vite de’ Pittori, Scultori et Architetti moderni” (Rome, 1672), a number of art historians assumed that Caravaggio never:
- Used Cu containing blues in pure form
- Used Vermilion in pure form in flesh tones
- Adjusted the composition during its execution

In collaboration with: emmebi diagnostica artistica s.r.l., Roma, Italy
XRF imaging of historical paintings: mobile instruments

Name: Bruker M6 Jetstream
Source: 30 W Rh X-ray tube
Optic: Polycapillary (>50 µm beam size)
Detectors: 1 SDD
Range: 60 x 80 cm²
Speed: >100 pixel/sec

Mobile instrumentation: comparison

Sensitivity measured on NIST SRM 611 - Trace Elements in Glass

- DESY, 38.5 keV
- Instrument D, 45 kV, 0.2 mA
- M6 Jetstream, 50 kV, 0.6 mA

Sensitivity [cps/(mg/g)] vs Atomic number

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XXX PC vs PH???
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XRF imaging of historical paintings on the macro-scale: Capabilities and limitations

Flower Still Life, unknown artist, begin 20th century
Oil on canvas, 100 x 80 cm
Kröller-Müller Museum, Otterlo, the Netherlands
KM 100.067

Before 1920 L. C. Enthoven collection
1974 Kröller-Müller Museum
2003 Dismissed for:
- Signature
- Format
- Composition

Flower Still Life, Vincent van Gogh, summer 1886
Oil on canvas, 100 x 80 cm
Kröller-Müller Museum, Otterlo, the Netherlands
KM 100.067, F 278, JH 1103
“This week I painted a large thing with two nude torsos — two wrestlers, a pose set by Verlat. And I really like doing that.”
Vincent van Gogh, Letter Nr. 555, Antwerp, 26.01.1886
- The whereabouts of the painting described were not known.

Questions:
- Can the underlying composition be better visualized by MA-XRF?
- Can further arguments for or against Van Gogh’s authorship be found?

Flower Still Life,
unknown artist, begin 20th century
Oil on canvas, 100 x 80 cm
Kröller-Müller Museum, Otterlo, the Netherlands
KM 100.067

1998: X-ray radiography (XRR)
Flower still life

Wrestlers

Original Canvas

Double Canvas

Stretcher

Chalk Ground

Glue and Pb white

Primary beam

Fluorescence radiation
XRF imaging of historical paintings

Beamline L
HASYLab@DESY
Hamburg, Germany
38.5 keV Energy (collimated by slit system)
3 Si-Drift-detectors
0.25-0.525 s/pixel
1 mm step size
Two additional areas were scanned by means of Instrument D with a dwell time of 3.6 s/pixel.
XRF imaging of historical paintings: comparison

Zn-Ka: Zinc white
XRF imaging of historical paintings: comparison

Ba-Ka: Barium sulfate as extender for red lake(?)
Sensitivity measured on NIST SRM 611 - Trace Elements in Glass

Sensitivity [cps/(mg/g)]

Z

| Instrument D, 45 kV, 0.2 mA, 0.8 mm Collimator |
| DESY, 38.5 keV, 4 SDD |

XRF imaging of historical paintings: comparison
XRF imaging of historical paintings: comparison

Ba-Ka: Barium sulfate as extender for red lake(?)
Vincent van Gogh, *Potatoeaters*

XRF imaging of historical paintings: comparison

- Zn
- Ba
- Hg-L

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Sample taken in the flesh tone (arm) of a wrestler
XRF imaging of historical paintings: comparison

XRadiography
XRF imaging of historical paintings: comparison

Flower still life

Pb distribution

Zn distribution

200 μm
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XRF imaging of historical paintings: comparison

Flower Still Life, unknown artist, 20th century
Oil on canvas, 100 x 80 cm
Kröller-Müller Museum, Otterlo, the Netherlands
KM 100.067

Still life with meadow flowers and roses,
Vincent van Gogh, summer 1886
Oil on canvas, 100 x 80 cm
Kröller-Müller Museum, Otterlo, the Netherlands
KM 100.067, F 278, JH 1103


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Limitations: Absorption

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Thickness of lead white paint layer absorbing 90% of the emitted radiation (80 mass% lead white, 20 mass% linseed oil)
Limitations: No depth sensitivity

The position of the vermilion-containing paint layer cannot be directly determined from elemental distribution images and other methods are needed to determine it.

Limitations: No chemical contrast

Questions:
- Are parts of the original composition hidden behind a later added curtain?
- To which extend is original paint still present?

Limitations: No chemical contrast

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Other groups

> The Bruker M6 Jetstream has been sold several times, no exact numbers are available.

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Conclusions

> MA-XRF allows for the (comparatively) fast acquisition of images indicating the distribution of elements in surface and sub-surface paint layers.

> These images feature contrast complimentary to other imaging techniques and provide insight in:
  - The creation process of the painting
  - Previous conservation treatments
  - Overpainted works

> Large elemental distribution images can provide information how representative local information provided by other techniques is.

> MA-XRF is limited by:
  - Absorption effects
  - Lack of depth sensitivity
  - Lack of chemical contrast
Conclusions

Where are we eight years after „Patch of grass“?

- A large number of paintings has been investigated by MA-XRF (more than 15 at SR sources, more than 150 with mobile instruments).

- Mature and commercial instruments are available. The development of new instruments in research groups is ongoing.

- SR-based and mobile, X-ray tube bases scanners are both used as they are complimentary.

- Major developments are expected not in the improvement of pure XRF-scanners, instead a combination with other methods (confocal XRF, XRD, IR, THz) is expected to constitute the major development of the next years.
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You – Attention!