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

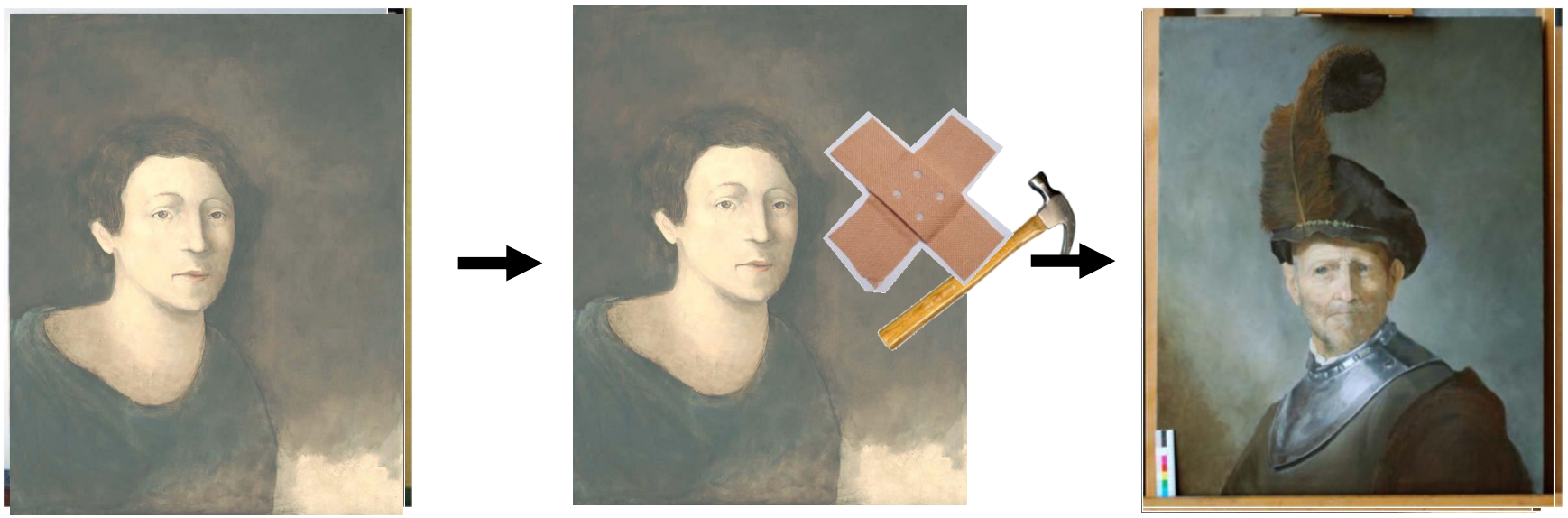
Matthias Alfeld

Joint ICTP-IAEA Workshop on Advances in X-ray Instrumentation for Cultural Heritage Applications
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



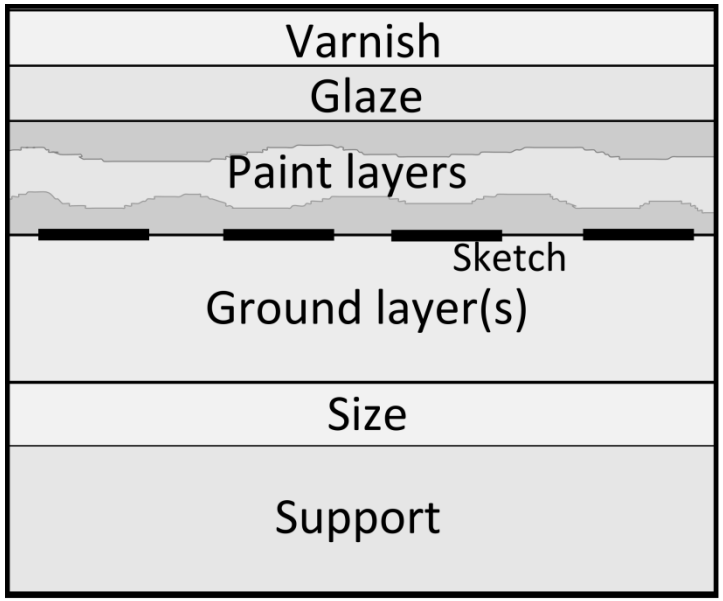
-Investigate the creation process (*pentimenti*)
    ->Contribute to discussions of authenticity and painting technique
-Visualize later restorations and degradation processes
    ->Support the conservation of artworks
-Visualize overpainted works
    ->Fill gaps in the oeuvre of an artist
-Identify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

Images: A. Sartorisus. From: M. Alfeld, et al., J. Anal. At. Spectrom. (2013) **28**, 40-51.

Scientific investigation of historical paintings

- Structure of a easel painting

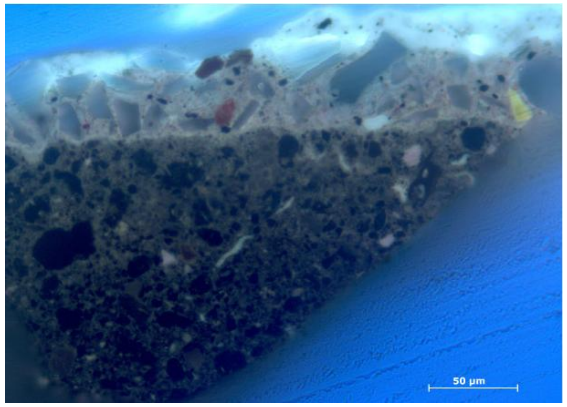
  It is of highest importance that as much of the painting's original structure is **preserved**, so that all investigations must be **nondestructive** and sampling limited as far as possible.



Scientific investigation of historical paintings

- 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.

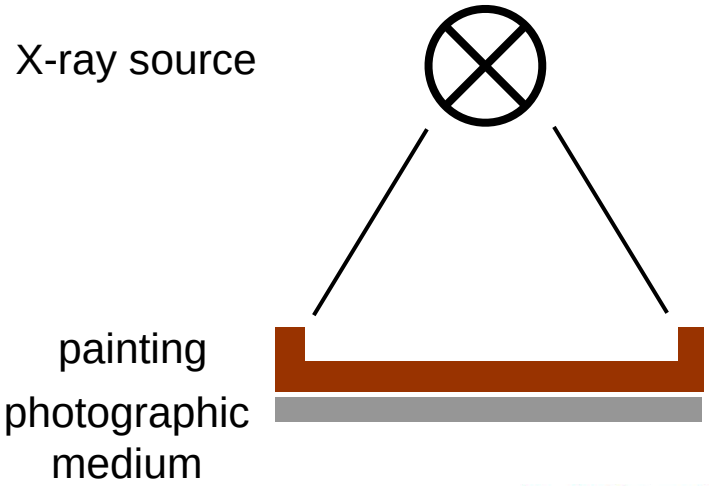
microscopic



macroscopic

Scientific investigation of historical paintings

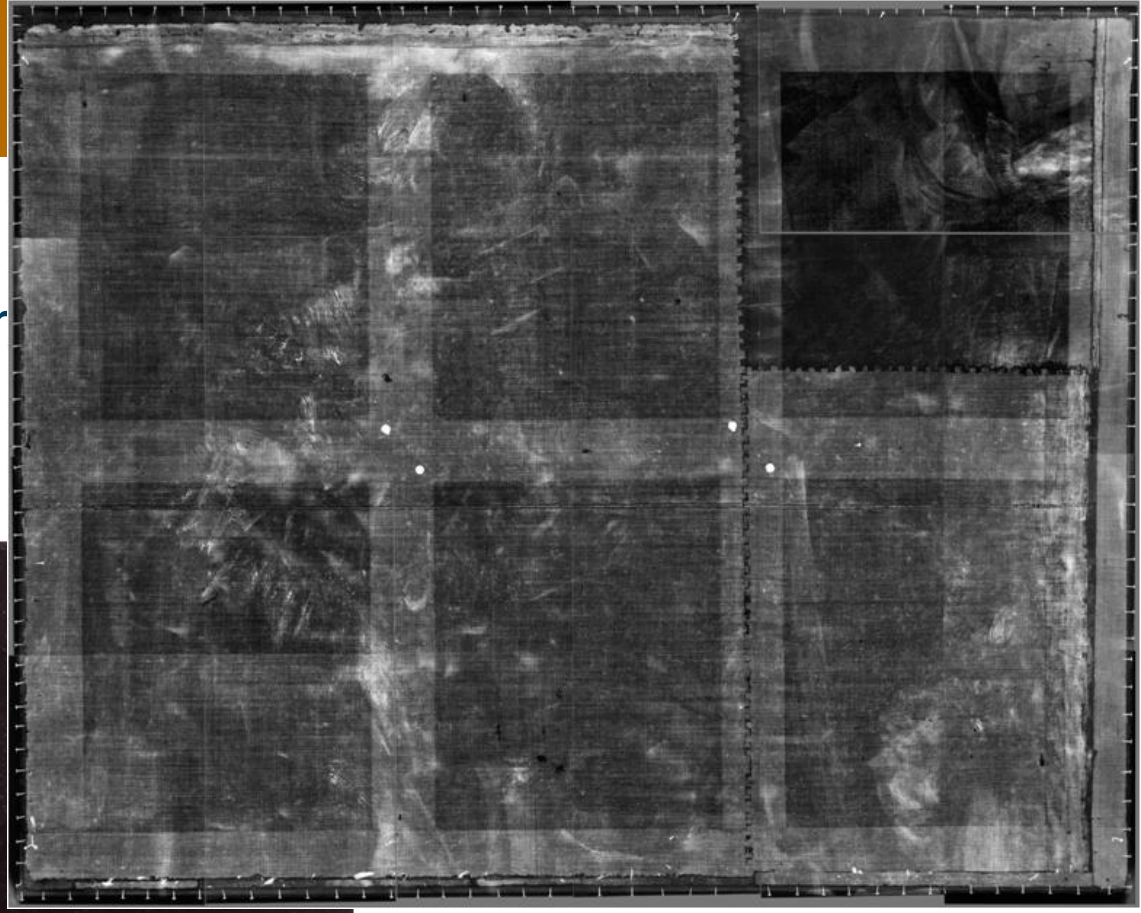
- XRR: X-ray Radiography
  - No elemental contrast
  - Often dominated by the lead white distribution
  - Can contain strong contributions from the support



Scientific investigation

- XRR: X-ray Radiogr

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



P. Noble, A. van Loon, M. Alfeld, K. Janssens, J. Dik, *Techné* (2012). **35**, 36-45.

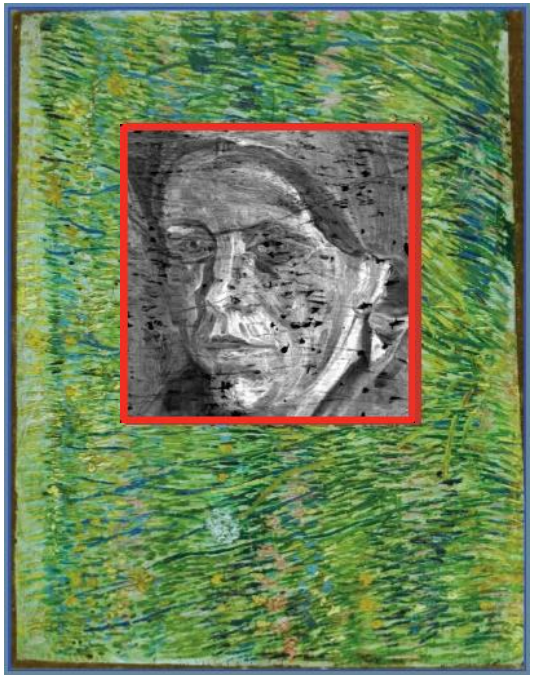
Scientific investigation of historical paintings

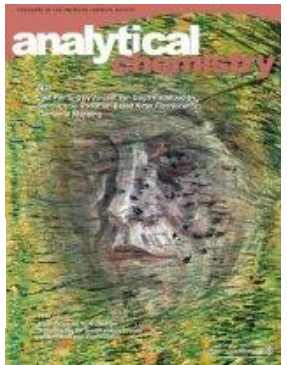
- Elemental contrast would allow to distinct between paint layers containing pigments of different elemental composition.
- For a long time no method allowing to obtain elemental distribution images was available for the investigation of historical paintings.
- Only Neutron-Activation Autoradiography (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.

Scientific investigation of historical paintings

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





J. Dik, K. Janssens, G. Van der Snickt, L. van der Loeff, K. Rickers, M. Cotte, *Anal. Chem.* (2008) **80**, 6436 – 6442.

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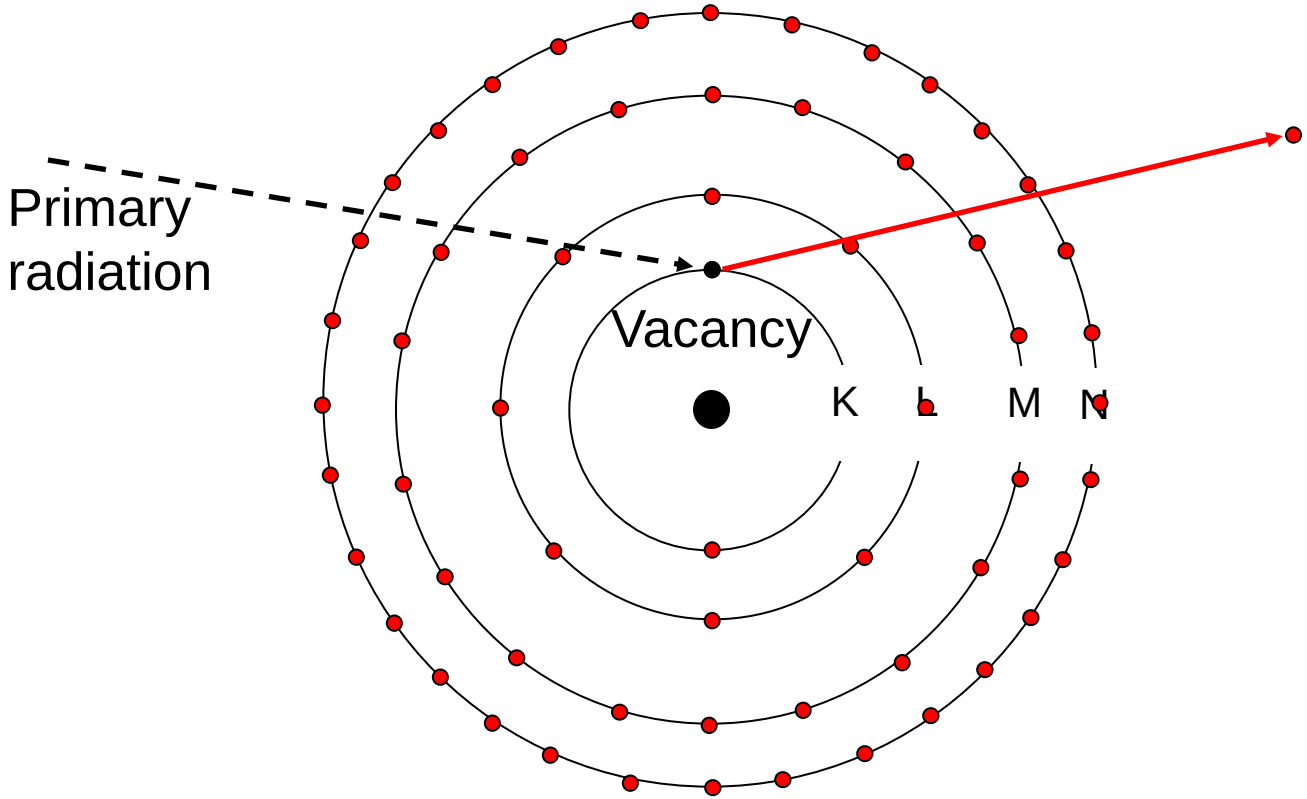
Introduction: XRF



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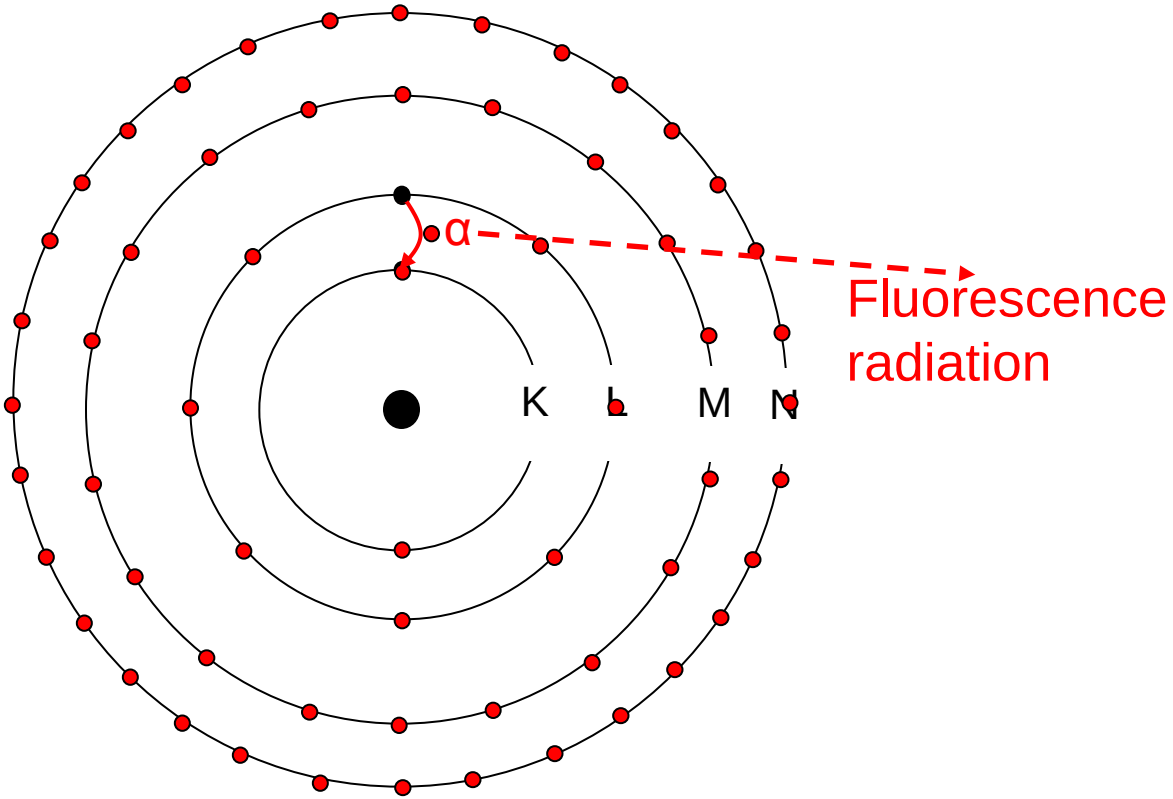
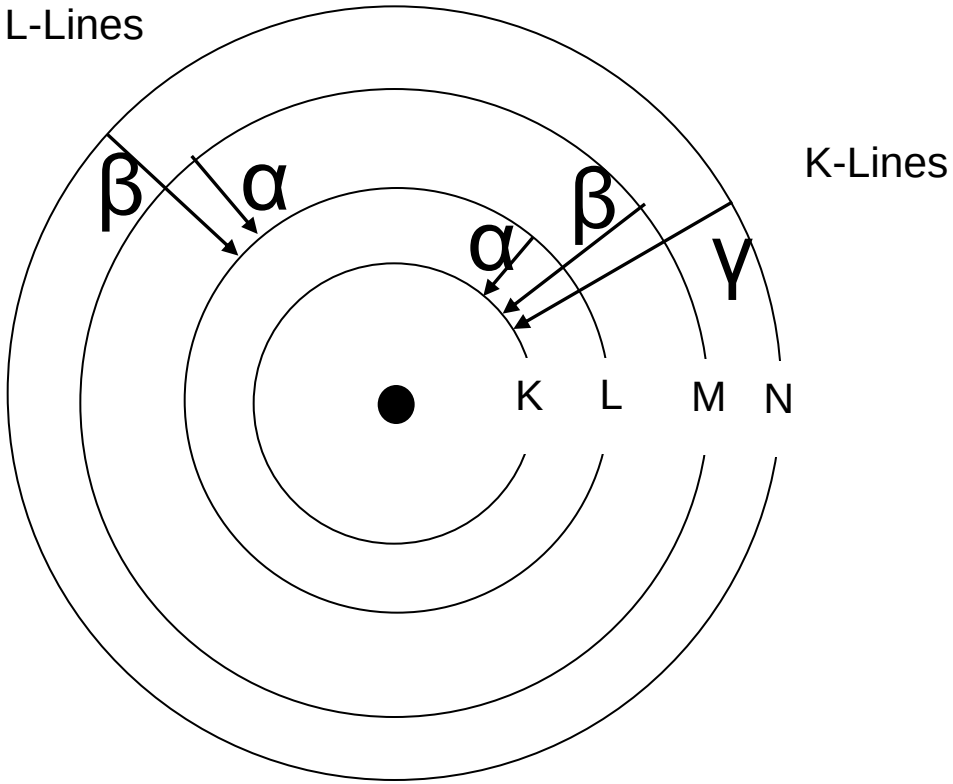
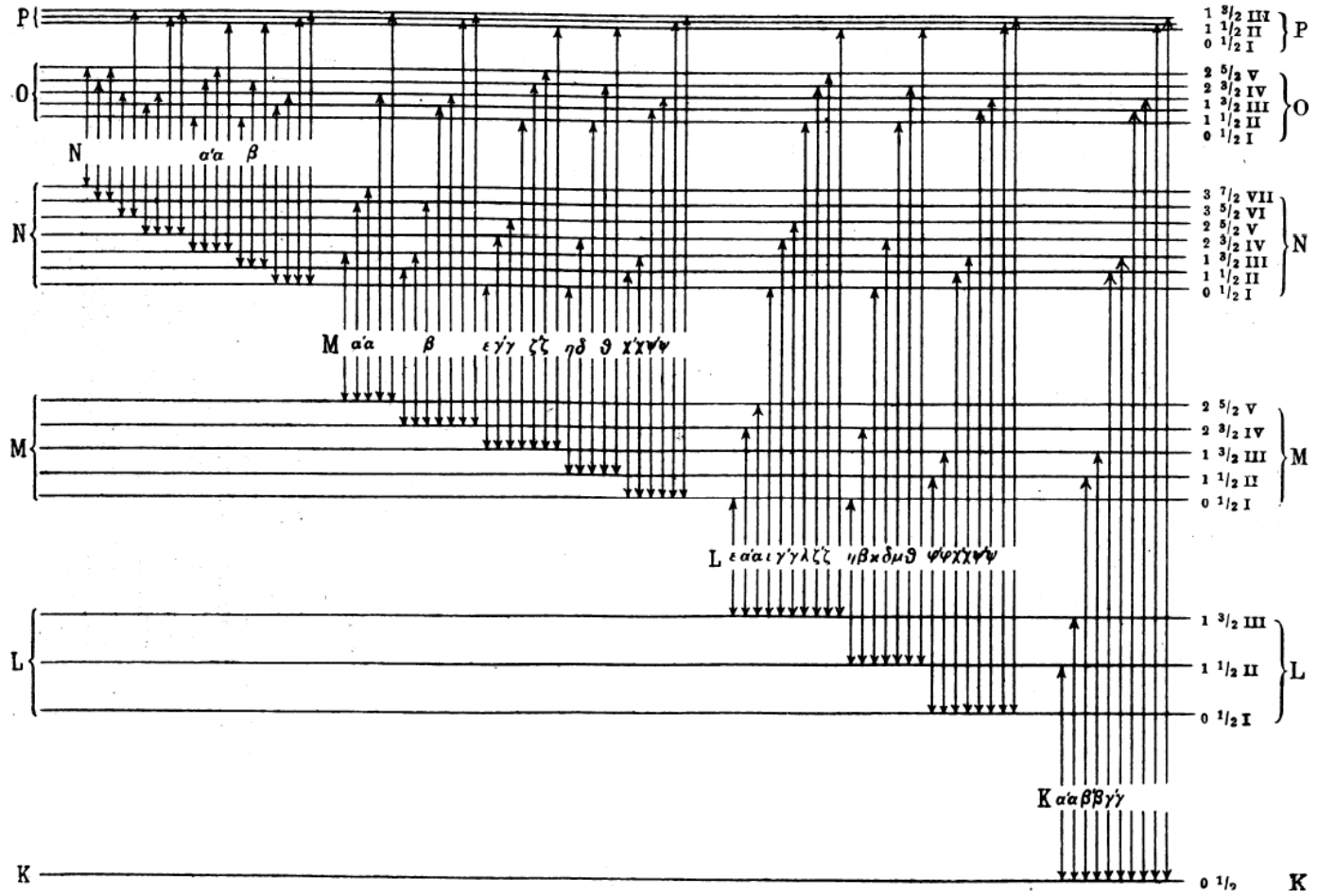


Introduction: XRF



Introduction: XRF

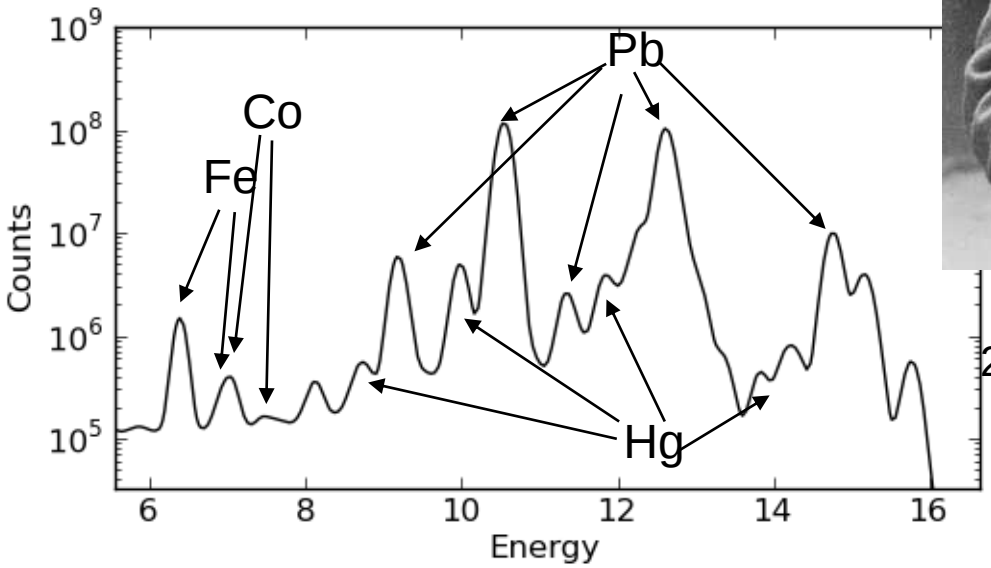


W. Finkelnburg, Einführung in die Atomphysik, 4. Ed. Abb. 67. Cited after D. Freude, Lecture Notes for „Spectroscopy for Physicists“

Introduction: XRF

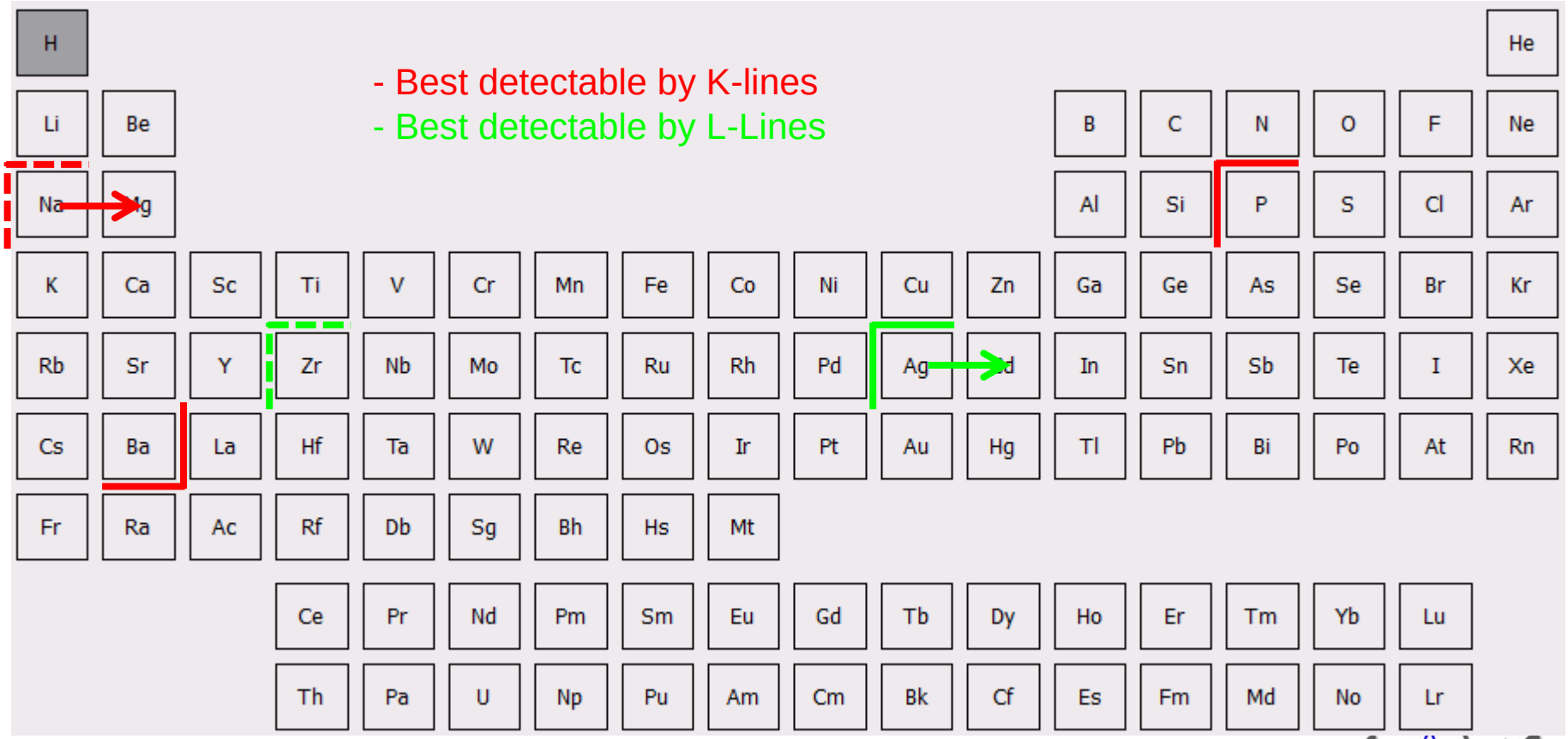
The energy of a fluorescence line is dependent on th
(Z) and line specific constants (Moseley's law):

$$E(Z) = c_1(Z - c_2)^2$$

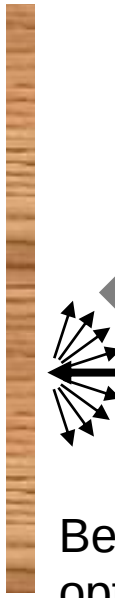


Henry Moseley
23.11.1887 -10.08.1915

Introduction: XRF

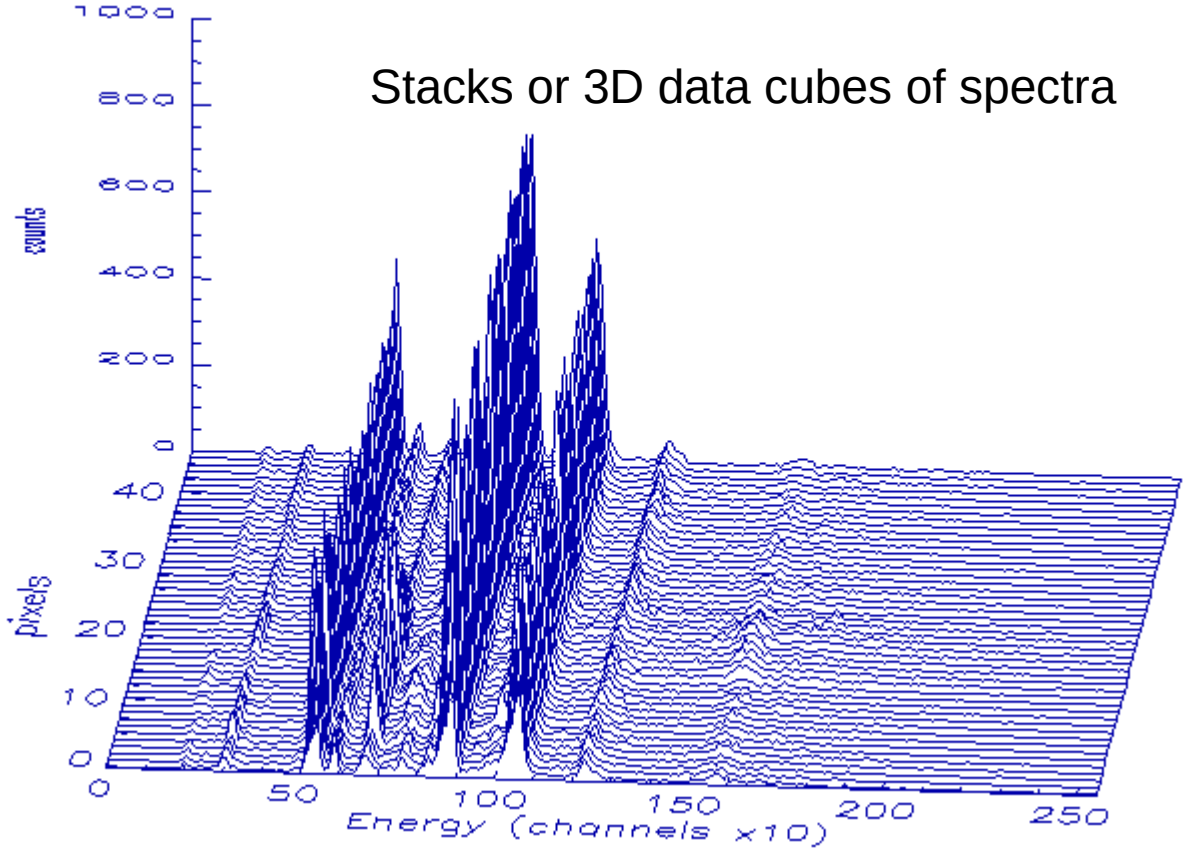


Introduction: XRF imaging



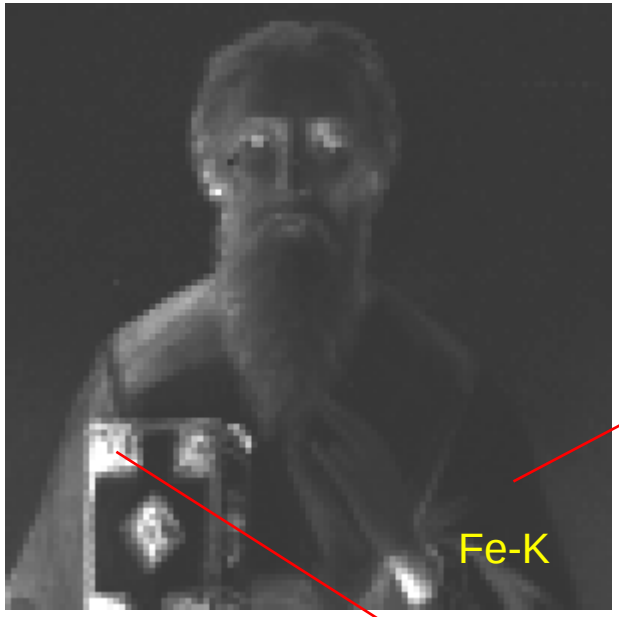
Be
op
painting

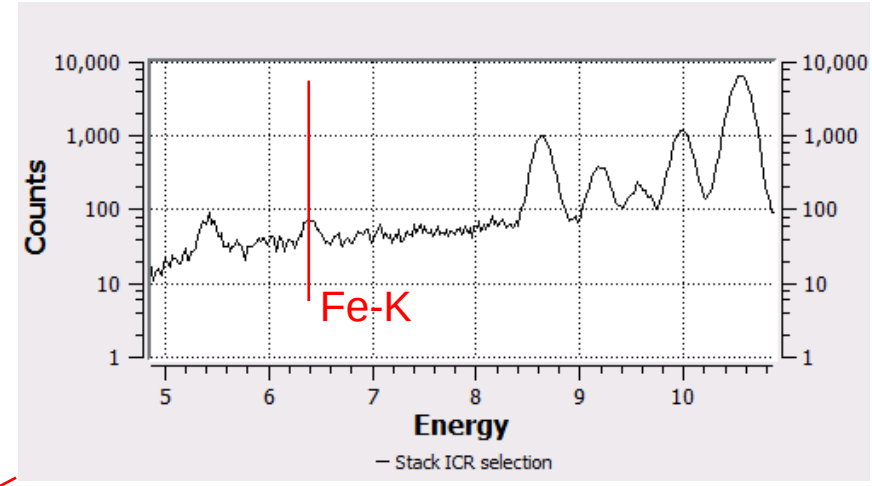
Stacks or 3D data cubes of spectra

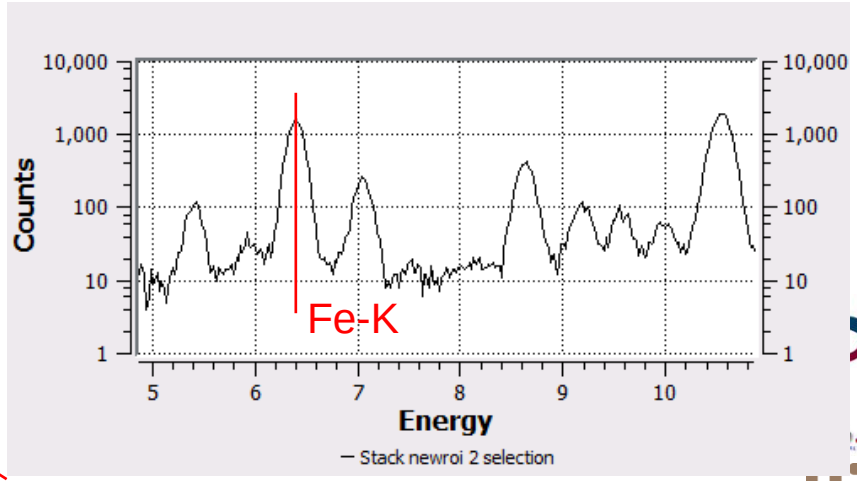


Introduction: XRF imaging

Fe elemental distribution image







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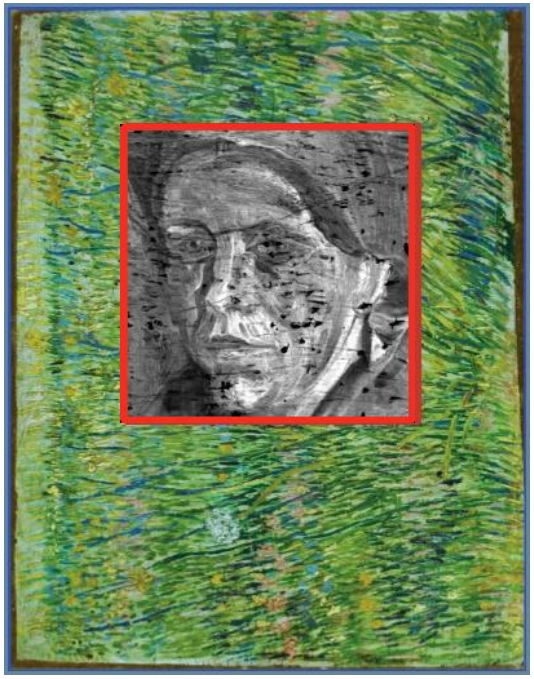
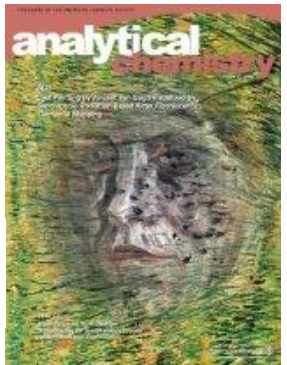
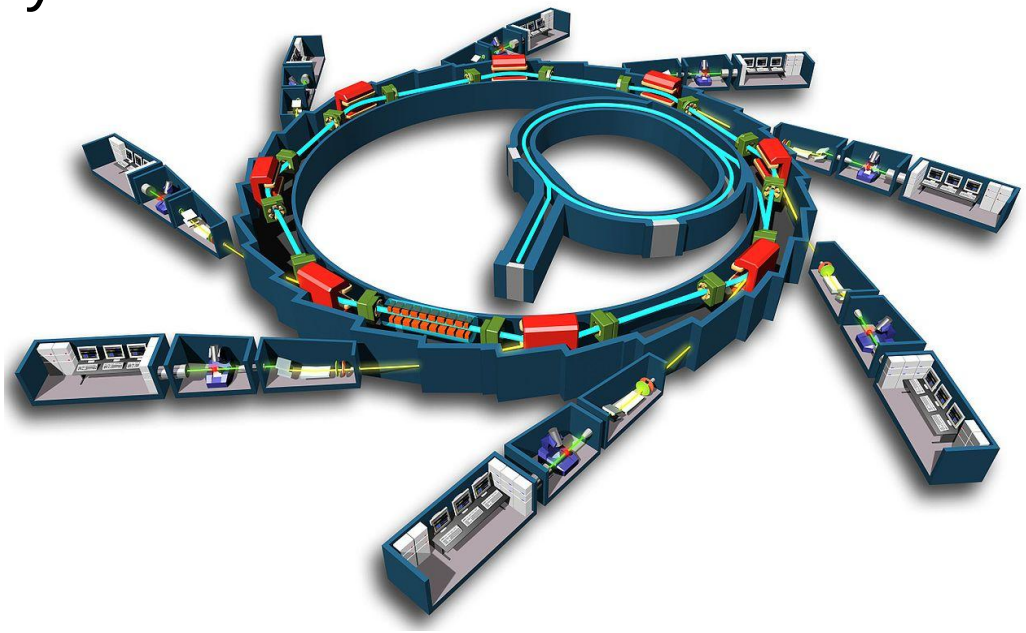




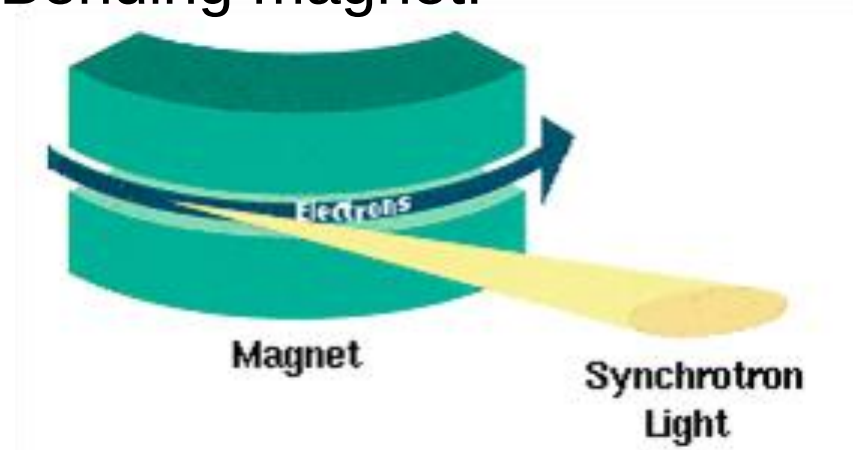
J. Dik, K. Janssens, G. Van der Snickt, L. van der Loeff, K. Rickers, M. Cotte, *Anal. Chem.* (2008) **80**, 6436 – 6442.

XRF imaging of historical paintings: SR

Synchrotron:

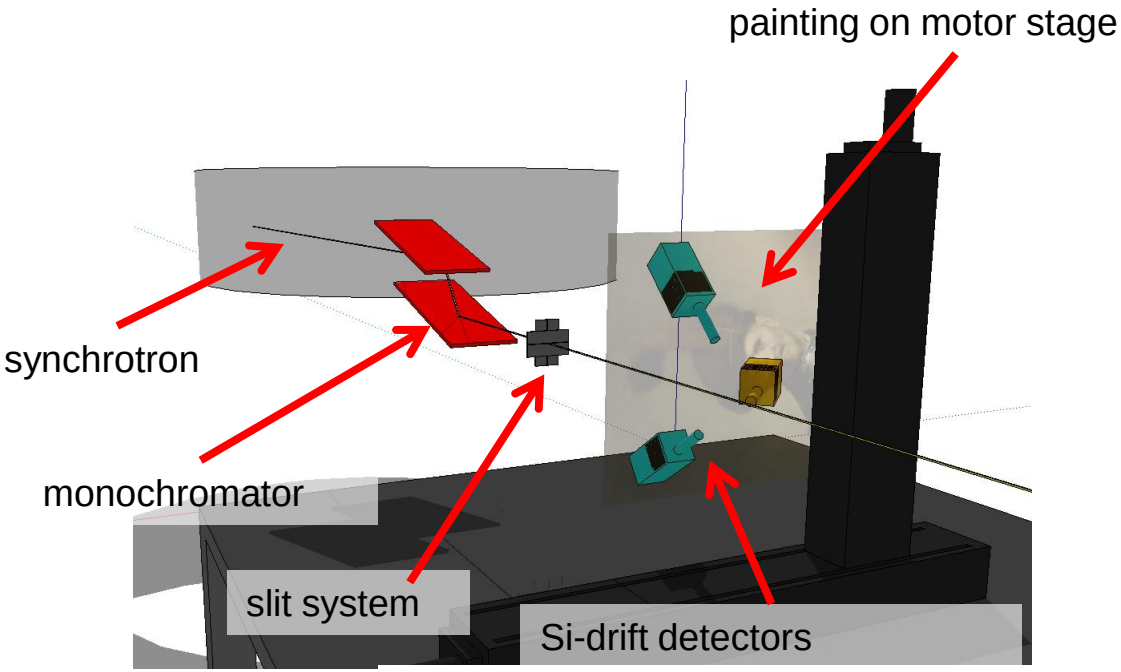


Bending magnet:



Images: www.wikipedia.org

XRF imaging of historical paintings: SR



Synchrotron sources
- High intensity
- Monochromatic
- (Coherent radiation)
- (Polarized radiation)
- Stationary
- Limited availability

Name:	DESY scanner
Radiation:	monochromatic radiation 27-38.5 keV
Optic:	Collimating slits
Detectors:	1-4 SDDs

M. Alfeld, et al., *J. Anal. Atom, Spectrom.* (2013) ***28,*** 40-51.

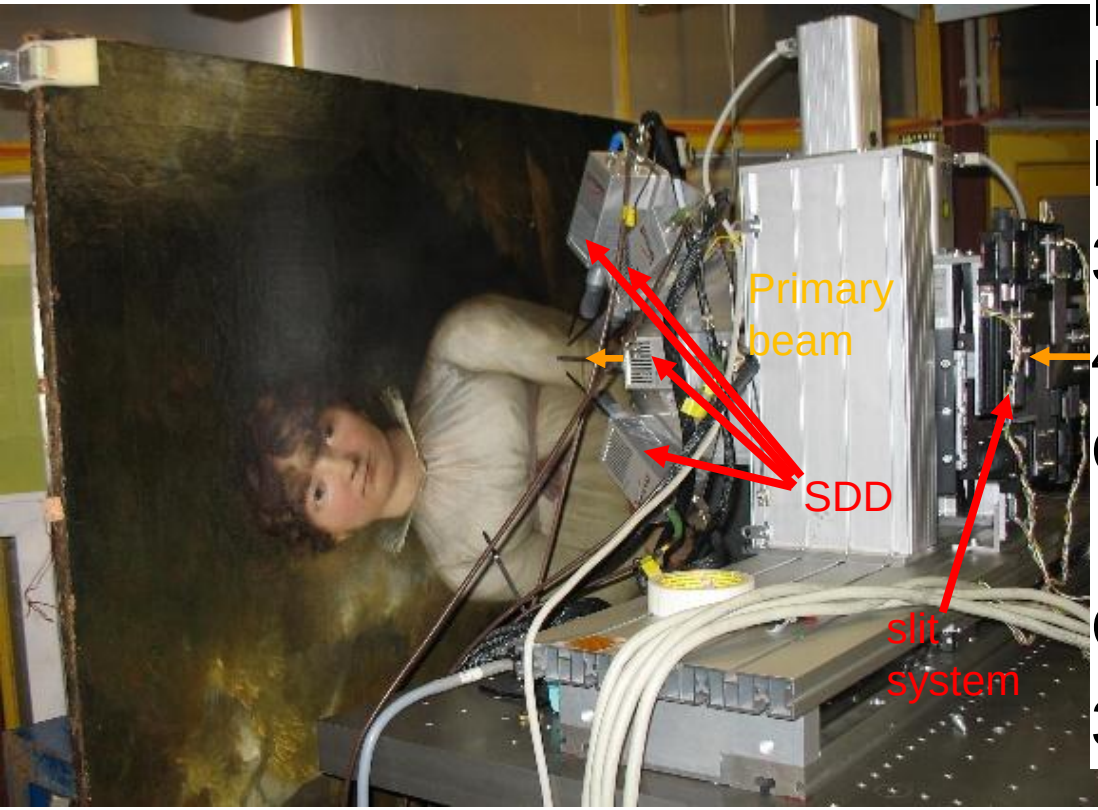
XRF imaging of historical paintings: SR

> 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

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 cm^2

3.5 days

XRF imaging of historical paintings: SR

Fe: Earth pigments

XRF imaging of historical paintings: SR

Pb-L: Lead white

XRF imaging of historical paintings: SR

Co: Cobalt blue

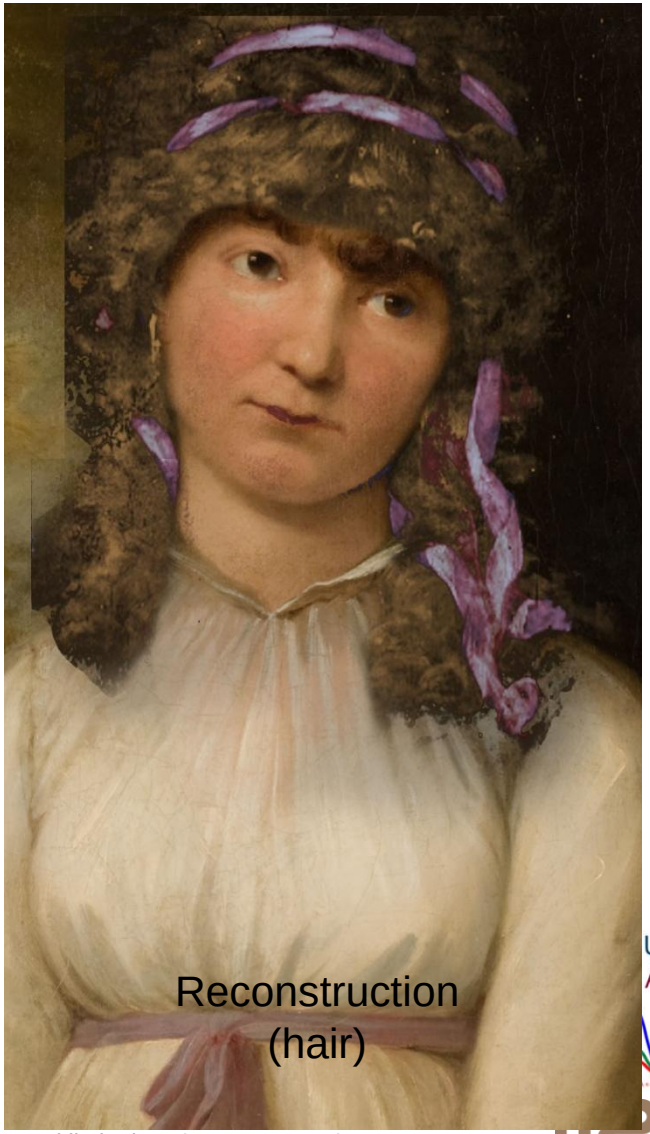
XRF imaging of historical paintings: SR

Hg-L: Vermilion

XRF imaging of historical paintings: SR

Sb: Naples Yellow

XRF imaging of historical paintings: SR



XRF imaging of historical paintings: SR

reconstruction (hair)

radiograph

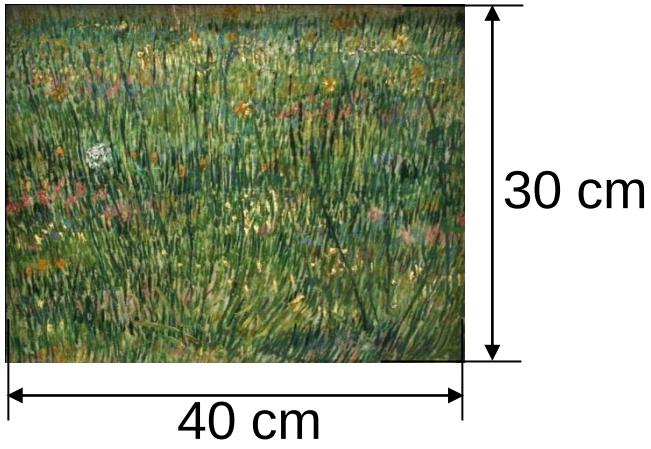
Drawing by Philipp Otto Runge (ca. 1805)

M. Alfeld, K. Janssens, K. Rickers, B. Thijsse, J. Blaas, J. Dik, “A portrait by Philip Otto Runge? Visualizing modifications to the painting using synchrotron-based X-ray Fluorescence elemental Scanning”, Z. Kunsttechnol. Konserv. (2011) **25**, 157-163.

XRF imaging of historical paintings: SR

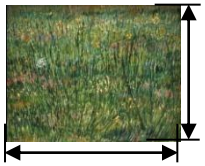
The applications for scanning macro-XRF with synchrotron sources is limited by several factors:

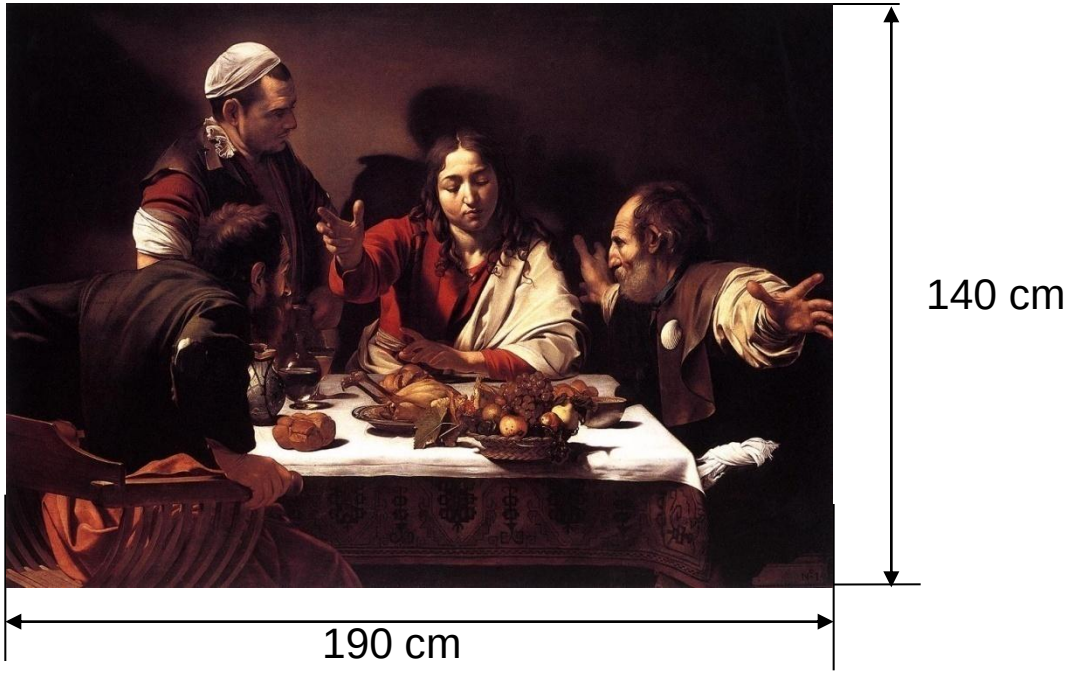
- Beamtimes are not easily available and are of limited duration
- The painting has to be transported and moved through the beam
- The size of the painting is limited



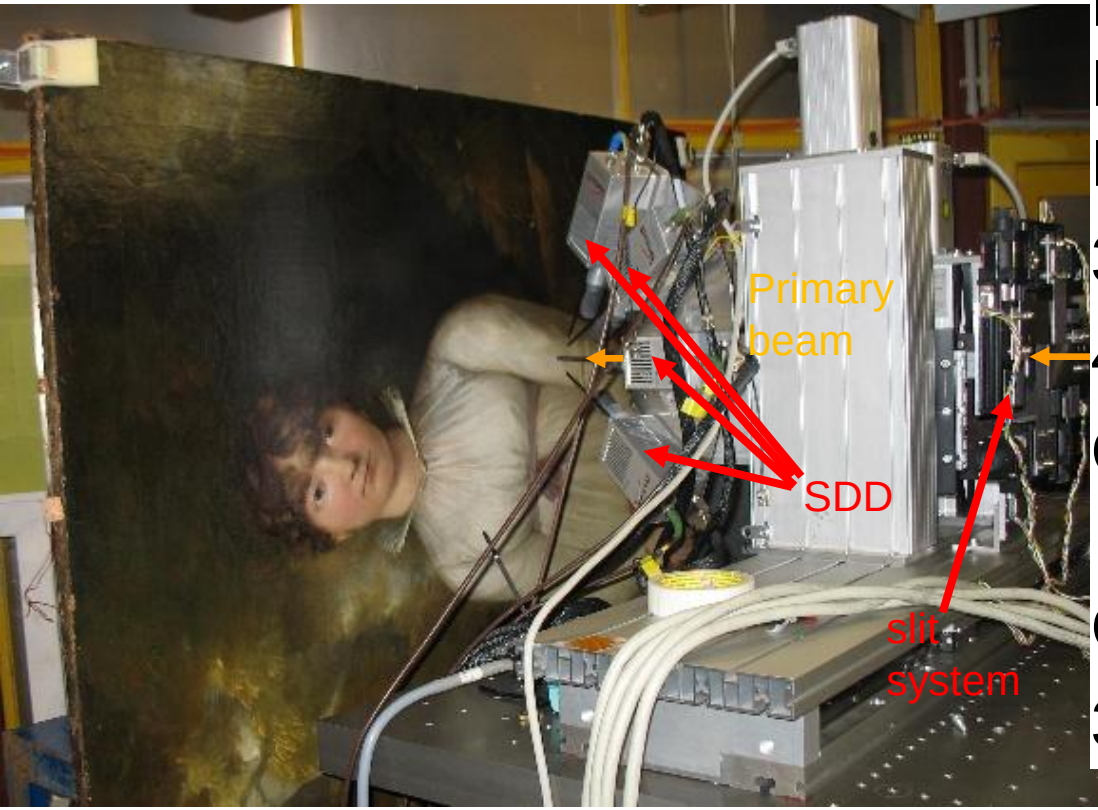
XRF imaging of historical paintings: SR

“Supper at Emmaus”, Caravaggio





XRF imaging of historical paintings: SR



Beamline L, HASYLab@DESY Hamburg, Germany

35 keV Energy

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Collimated beam: 0.5x0.3 mm

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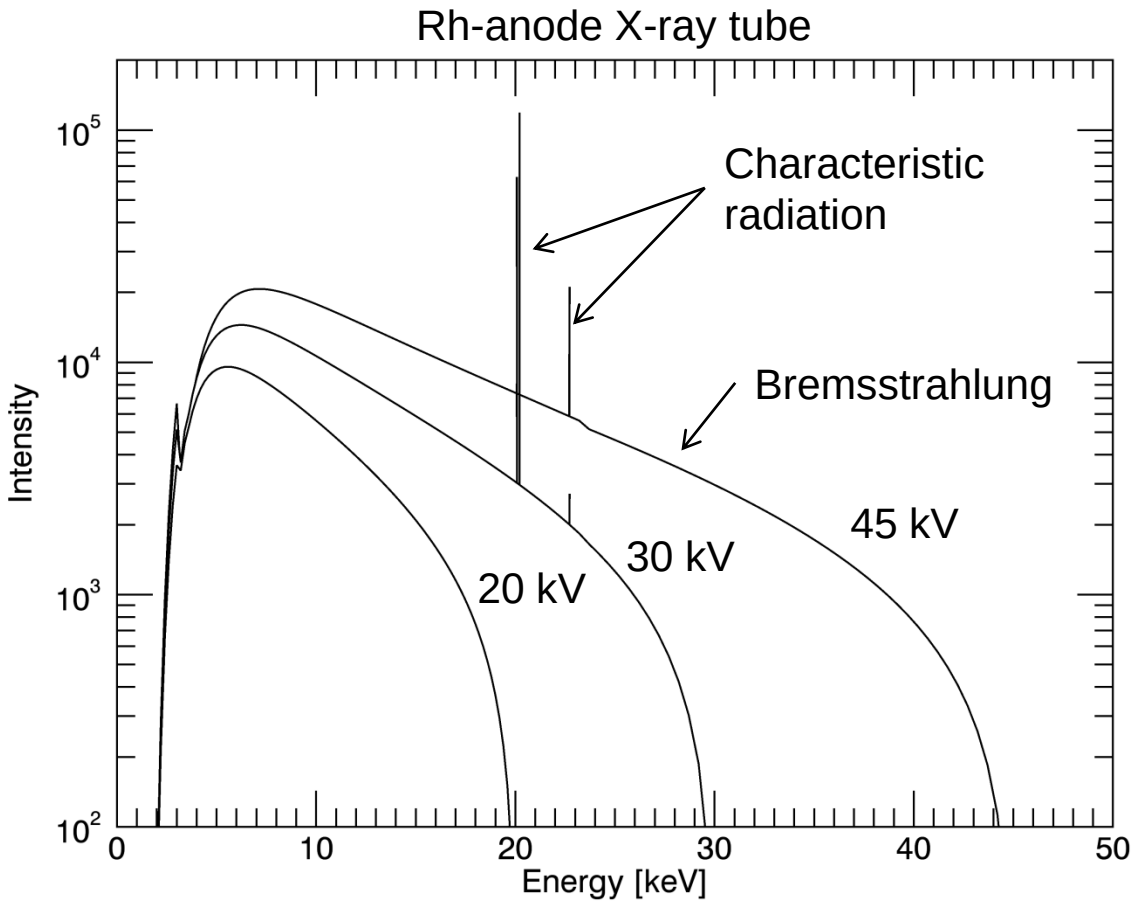
XRF imaging of historical paintings: mobile instruments



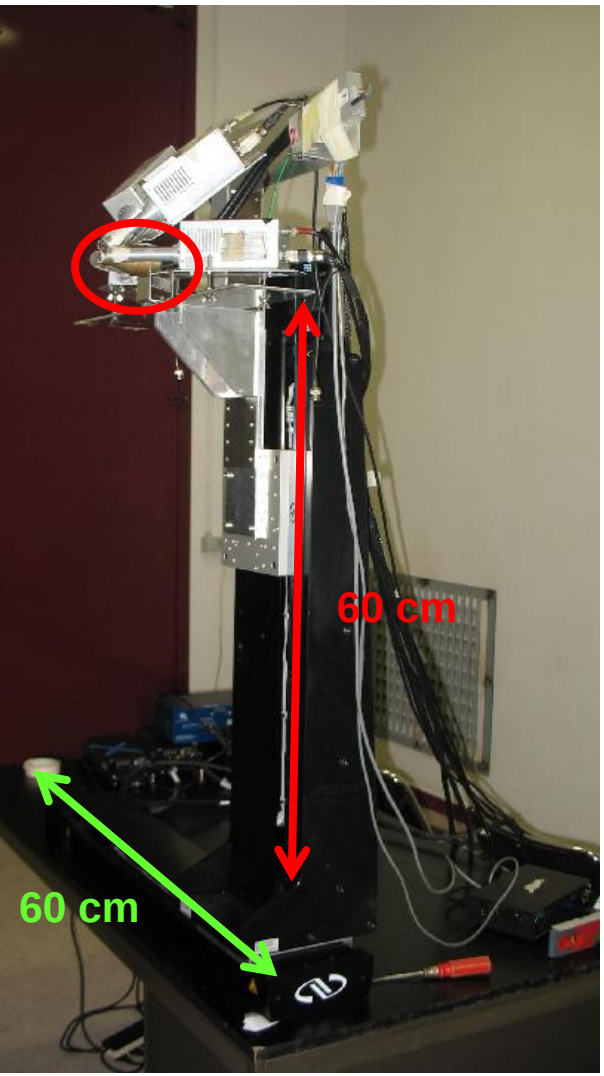
X-ray tube sources

- Easily available
- Transportable
- Polychromatic
- Limited intensity

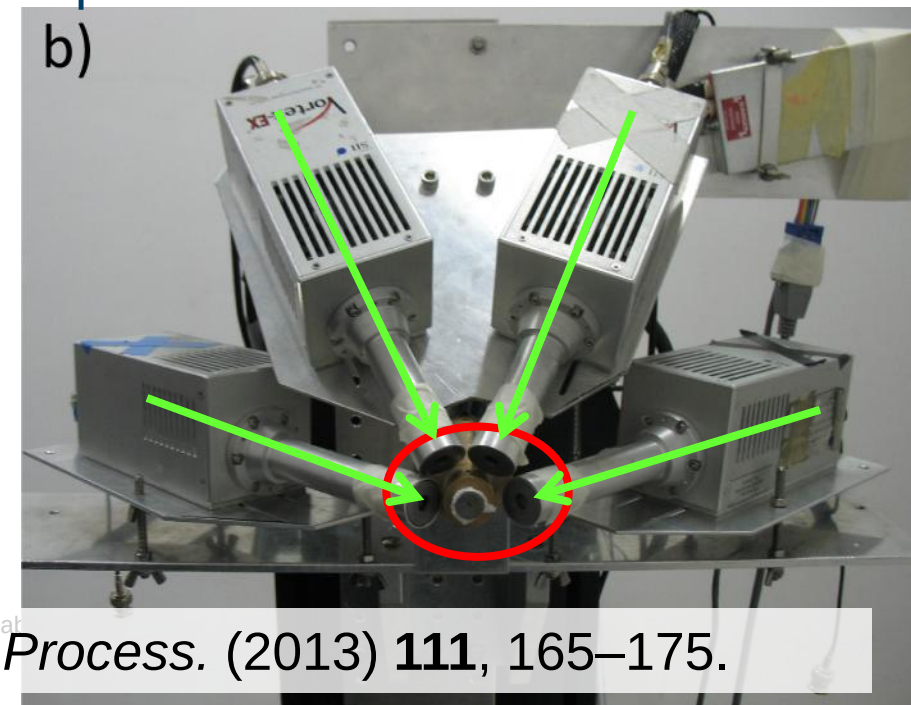
www.moxtek.com

Image X-ray tube: www.wikipedia.org

XRF imaging of historical paintings: mobile instruments

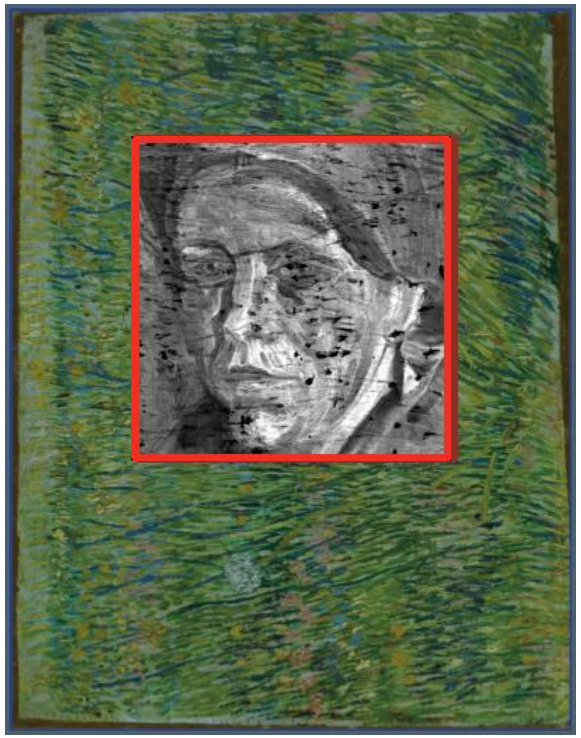


Name:	Instrument D (University of Antwerp)
Source:	10 W Rh X-ray tube
Optic:	0.5 or 0.8 mm Pb pinhole
Detectors:	4 SDDs
Range:	60 x 60 cm^2
Speed:	10 pixel/s



M. Alfeld, et al., *Appl. Phys. A: Mater. Sci. Process.* (2013) **111**, 165–175.

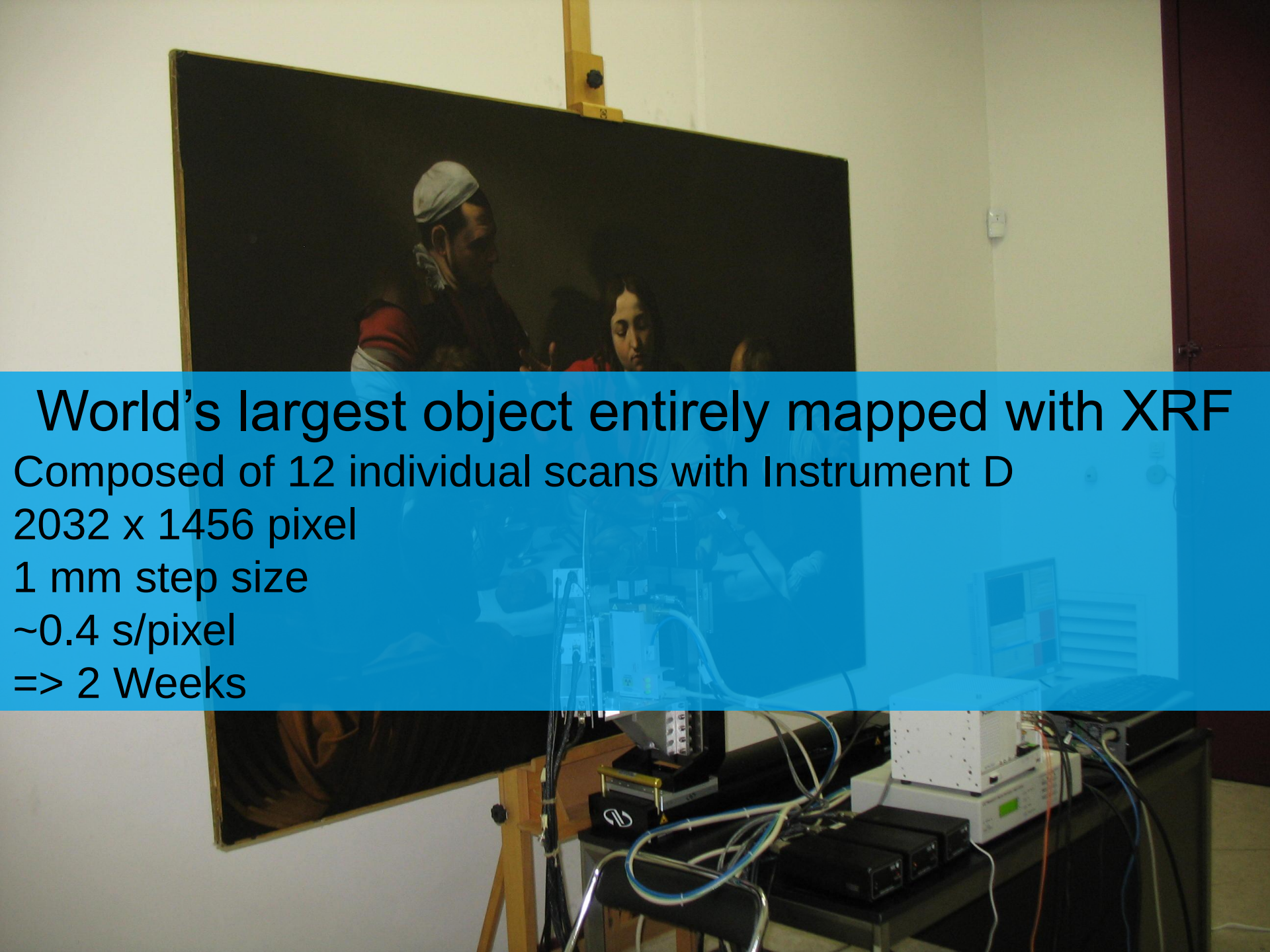
XRF imaging of historical paintings: mobile instruments



DESY results
0.5 mm resolution, 2 days

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

M. Alfeld, et al., *J. Anal. Atom, Spectrom.* (2011) ***26,*** 899-909.



World’s largest object entirely mapped with XRF

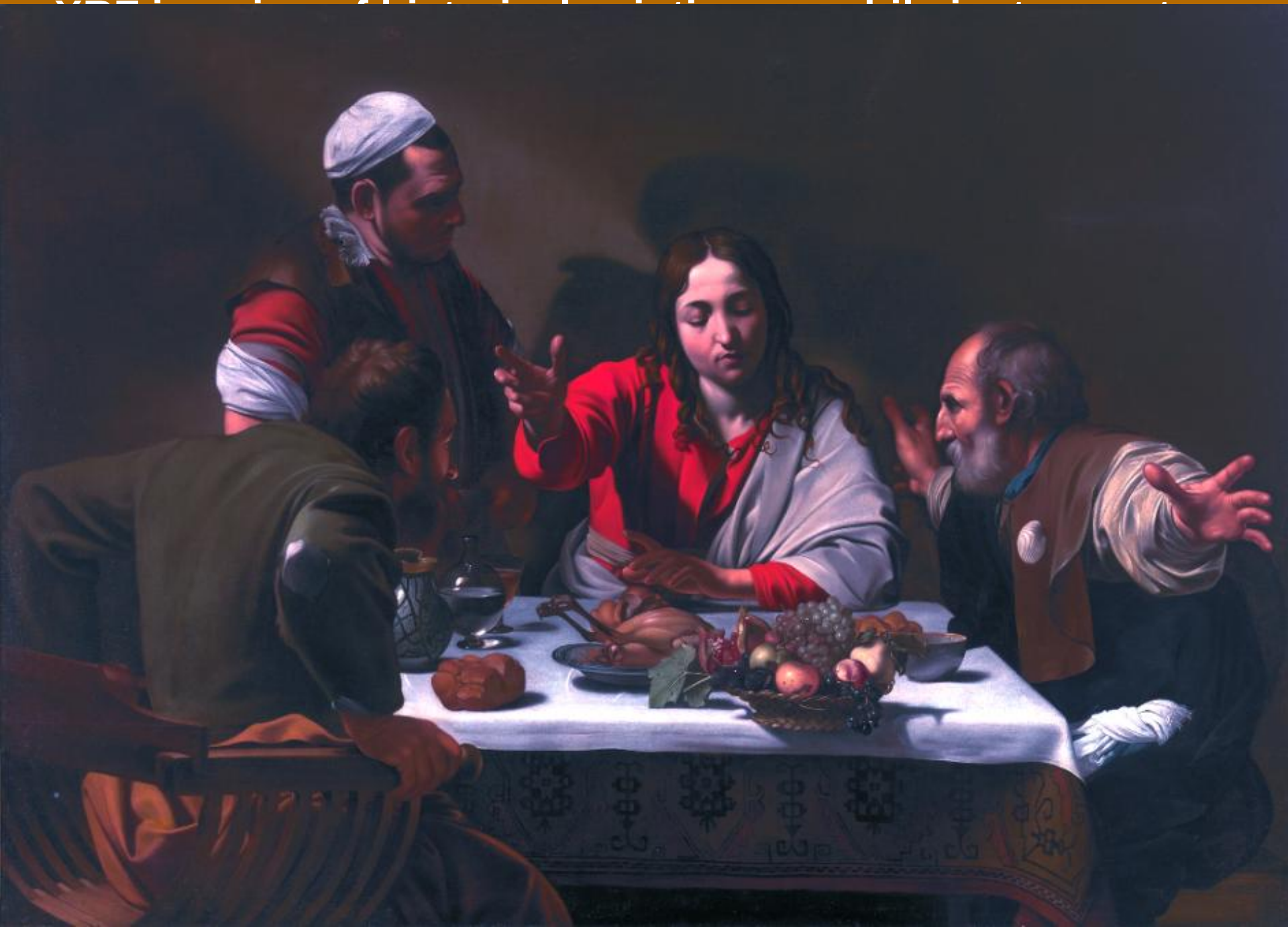
Composed of 12 individual scans with Instrument D

2032 x 1456 pixel

1 mm step size

~0.4 s/pixel

=> 2 Weeks



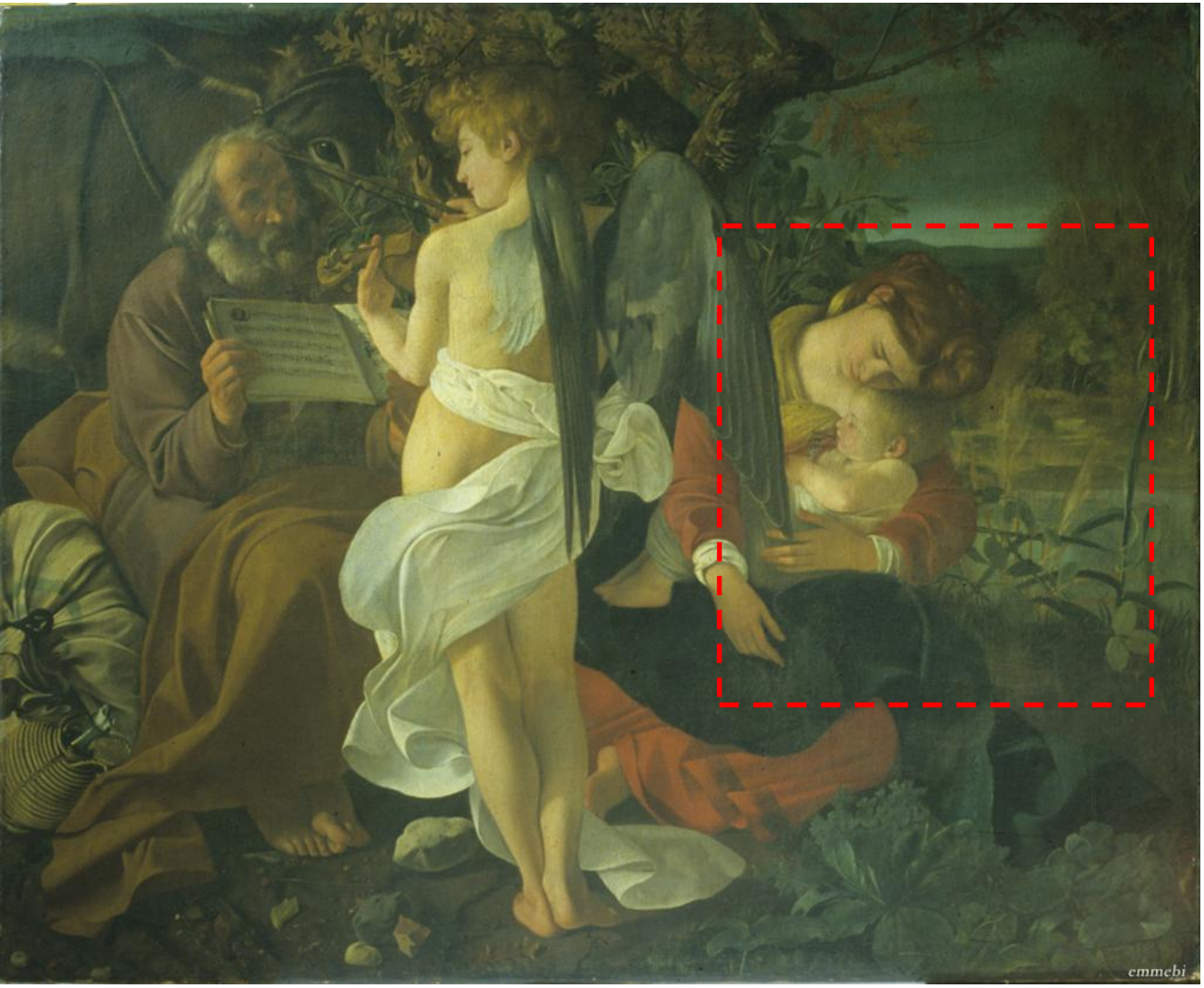
XRF imaging of historical paintings: mobile instruments

XRF imaging of historical paintings: mobile instruments


Hg-L: Vermilion (HgS)


Pb-L: Lead white

XRF imaging of historical paintings: mobile instruments



Rest on the flight to Egypt, Caravaggio,
135 x 167 cm, Oil on canvas
Galleria Doria Pamphili, Rome

In collaboration with: emmebi diagnostica artistica s.r.l., Roma, Italy

XRF imaging of historical paintings: mobile instruments

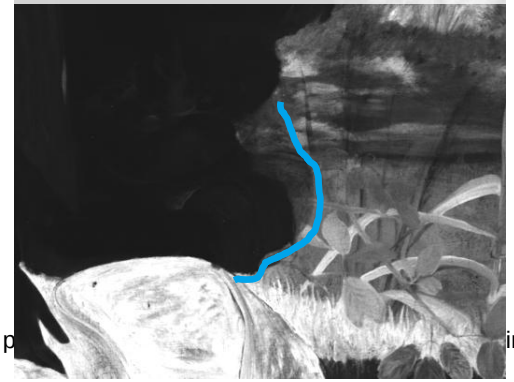
These findings are significant as, based on Giovan Battista Bellori's "Vite de' Pittori, Scultori et Architetti moderni" (Rome, 1672), a number of art historians assumed that Caravaggio never:

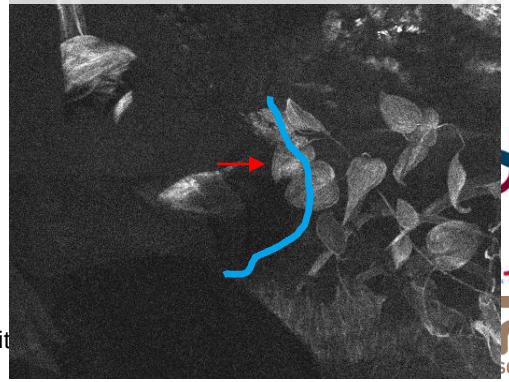
-Used Cu containing blues in pure form

-Used Vermilion in pure form in flesh tones

-Adjusted the composition during its execution

Rest on the flight to Egypt,
Caravaggio,
135 x 167 cm, Oil on canvas
Galleria Doria Pamphili,
Rome, Italy





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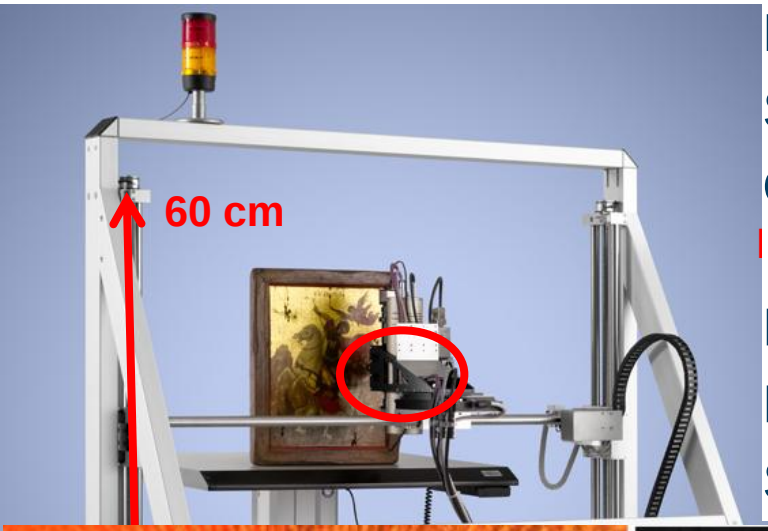
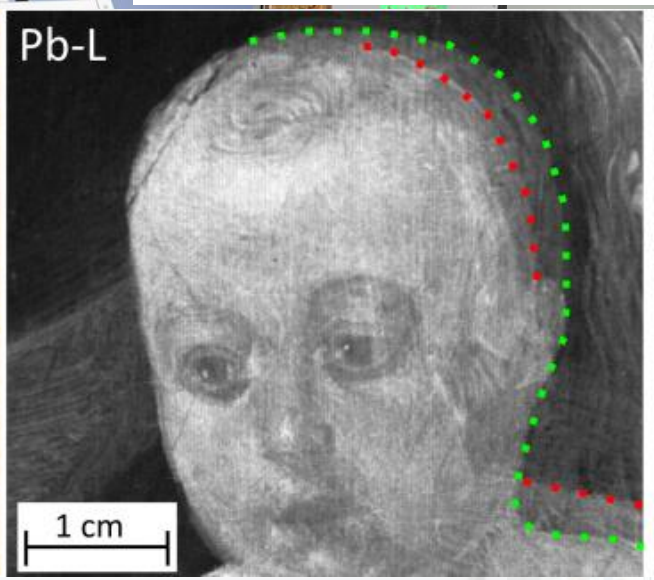
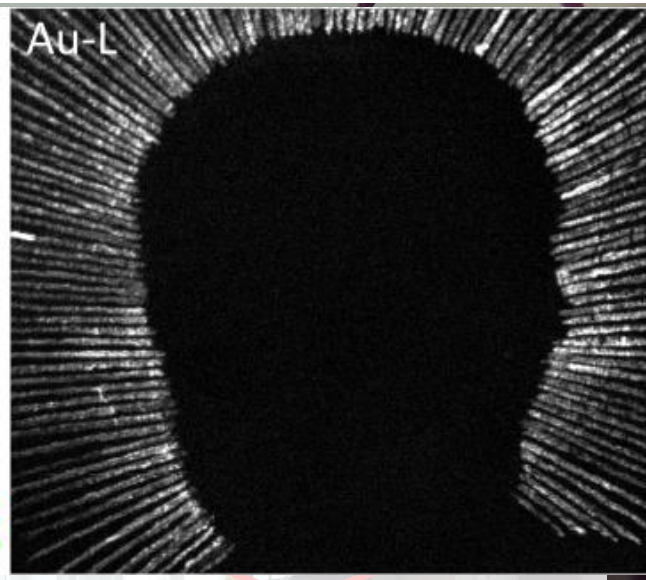
XRF imaging of historical paintings: mobile instruments



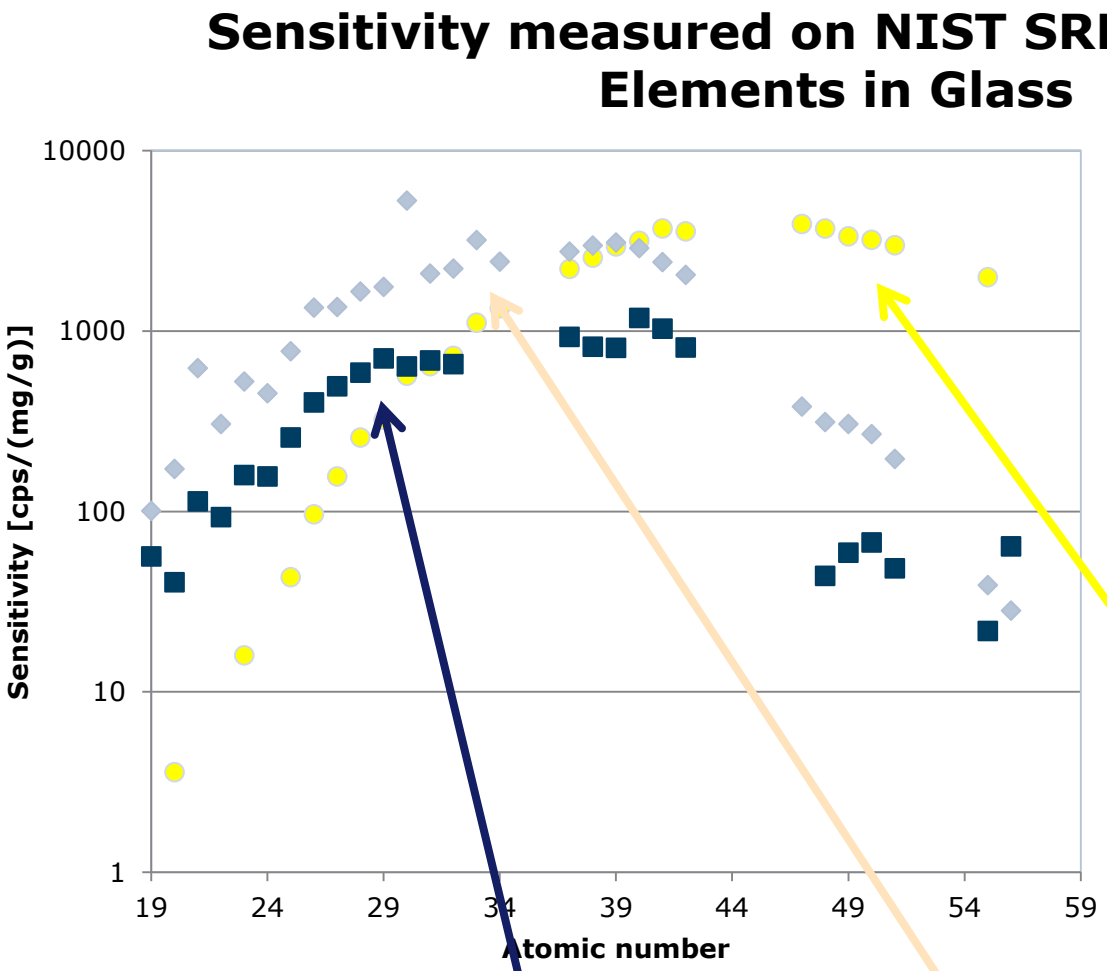
Name:	Bruker M6 Jetstream
Source:	30 W Rh X-ray tube
Optic:	Polycapillary (>50 µm beam size)
Detectors:	1 SDD
Range:	60 x 80 cm^2
Speed:	>100 pixel/sec

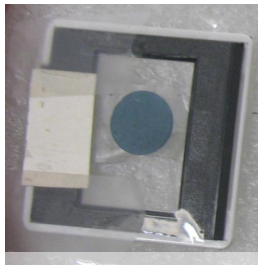


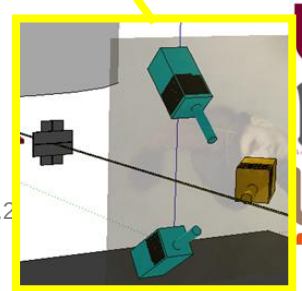


M. Alfeld, et al., *J. Anal. Atom, Spectrom.* (2013) ***28,*** 760-767.

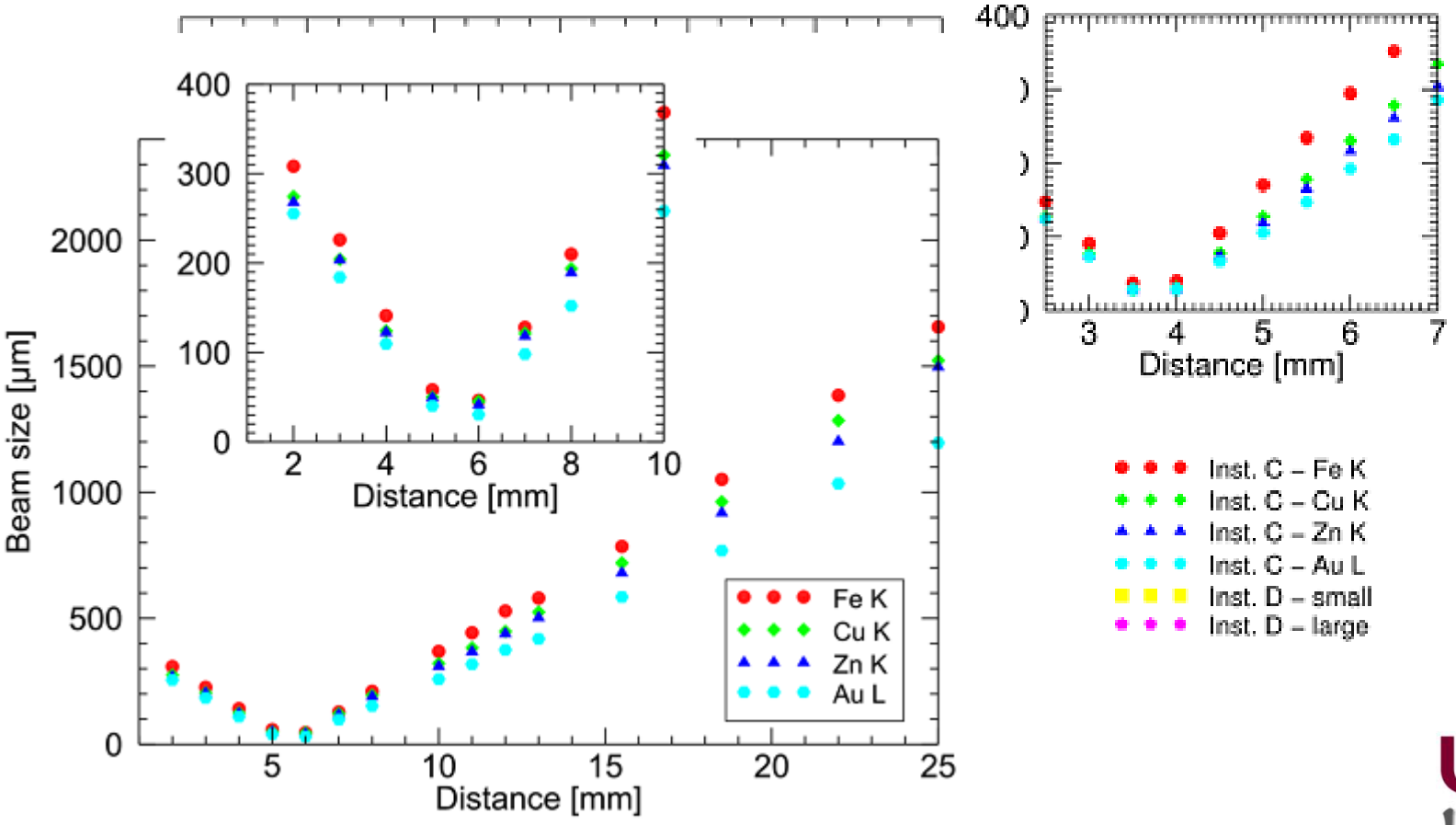
Mobile instrumentation: comparison







XXX PC vs PH???


Beam size [µm]
Distance [mm]
Fe K
Cu K
Zn K
Au L
Distance [mm]
Inst. C – Fe K
Inst. C – Cu K
Inst. C – Zn K
Inst. C – Au L
Inst. D – small
Inst. D – large

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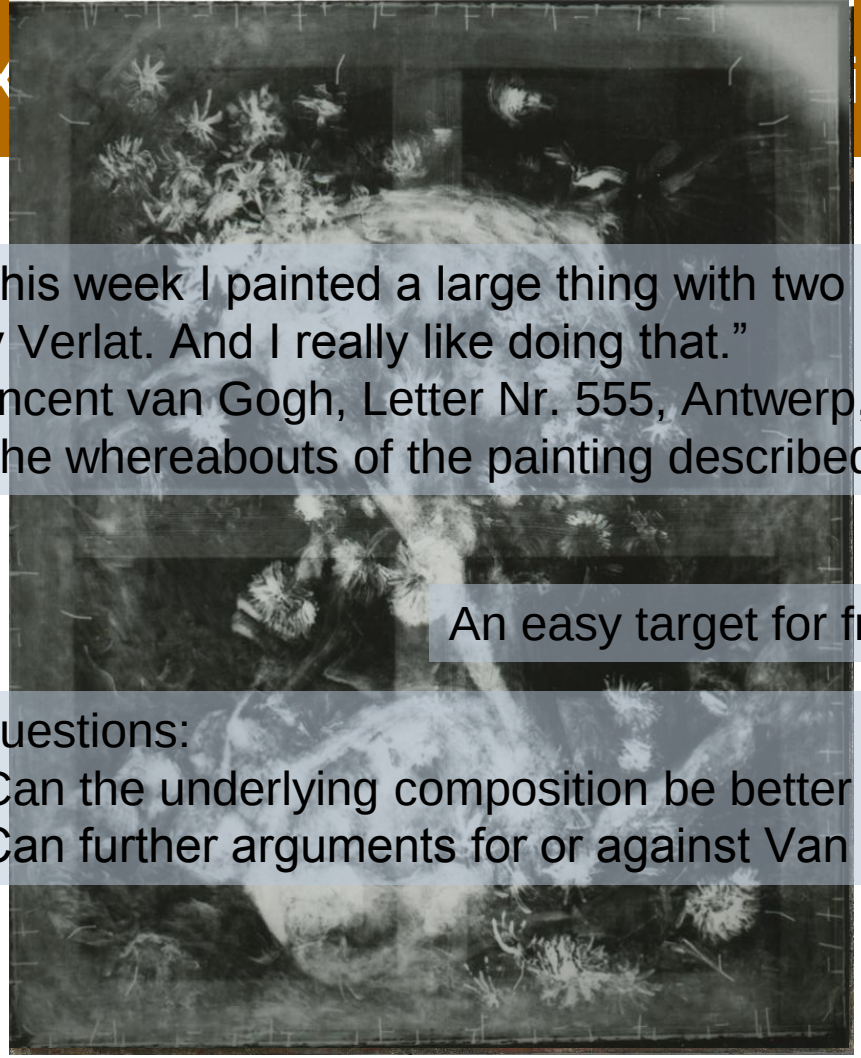
X[illegible]intings: comparison

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

X ntings: comparison



"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.

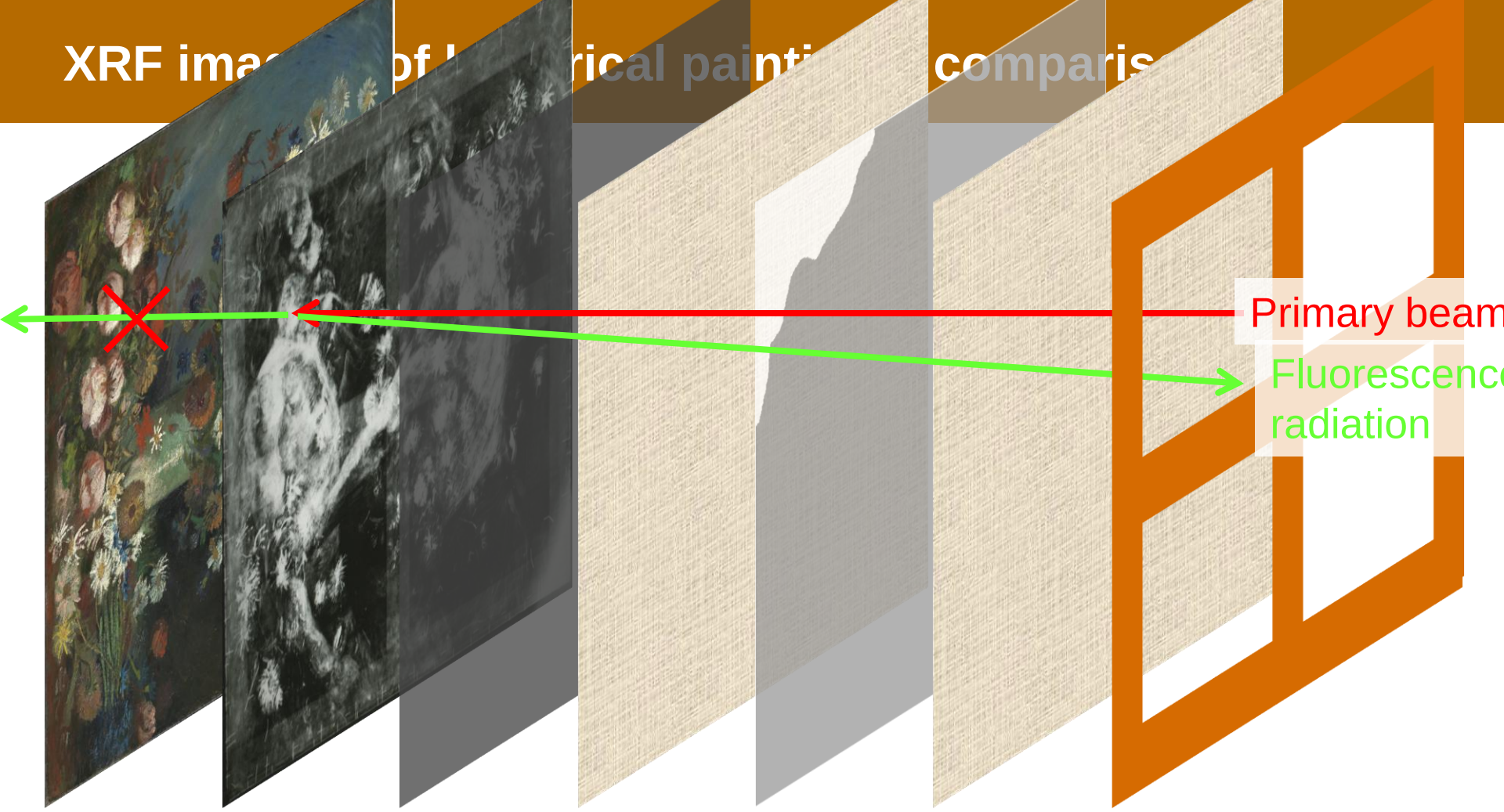
An easy target for fraud?

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

1998: X-ray radiography (XRR)

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

XRF ima[illegible]of h[illegible]rical pai[illegible]nti[illegible] comparis[illegible]



XRF imaging of historical pain

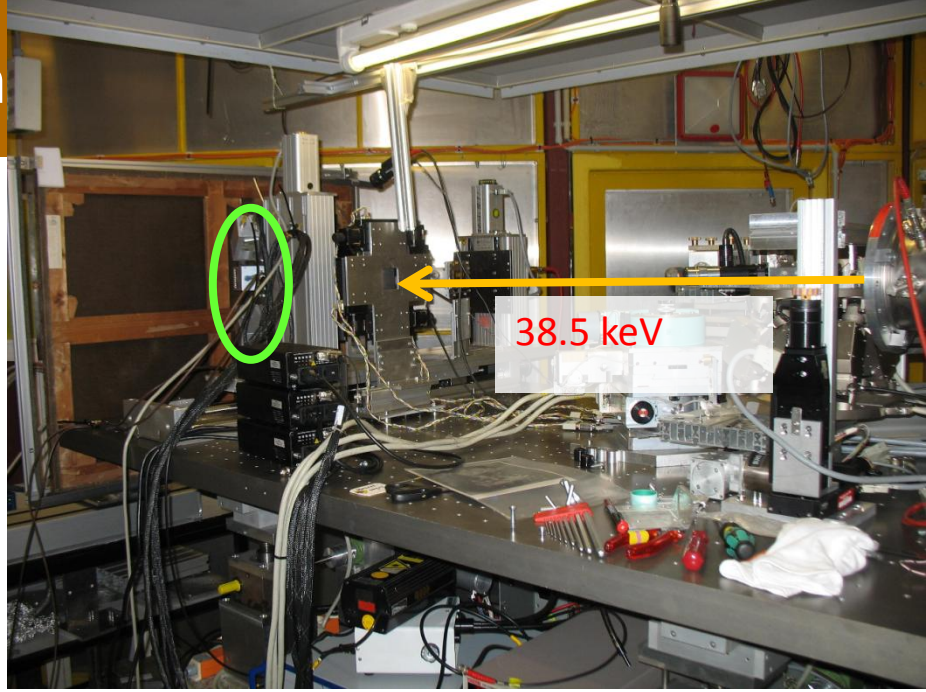
Beamline L
HASYLab@DESY
Hamburg, Germany

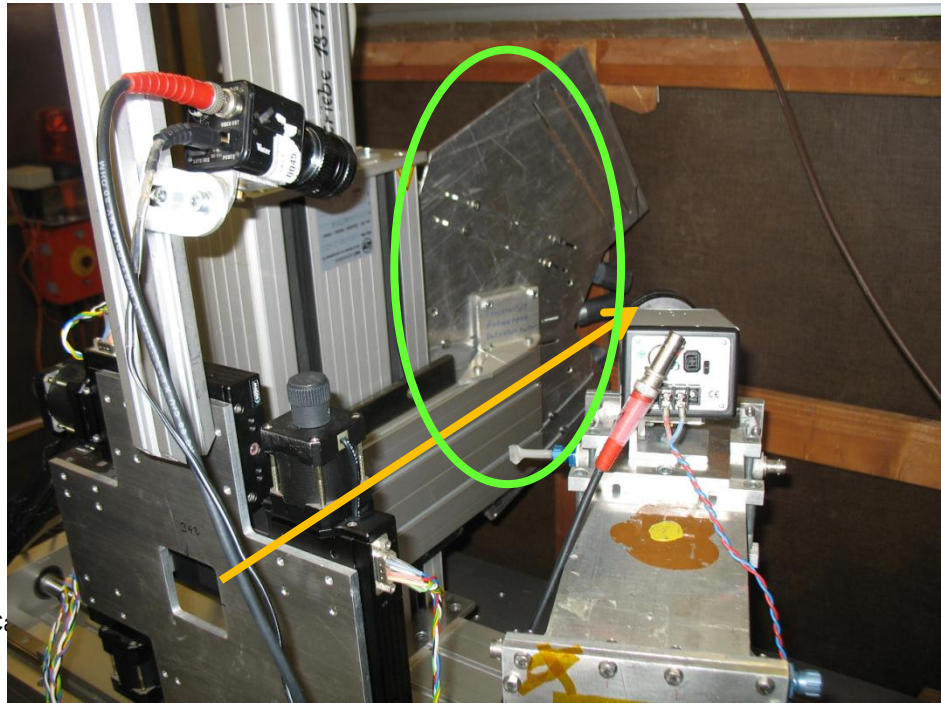
38,5 keV Energy (collimated by slit system)

3 Si-Drift-detectors

0.25-0.525 s/pixel

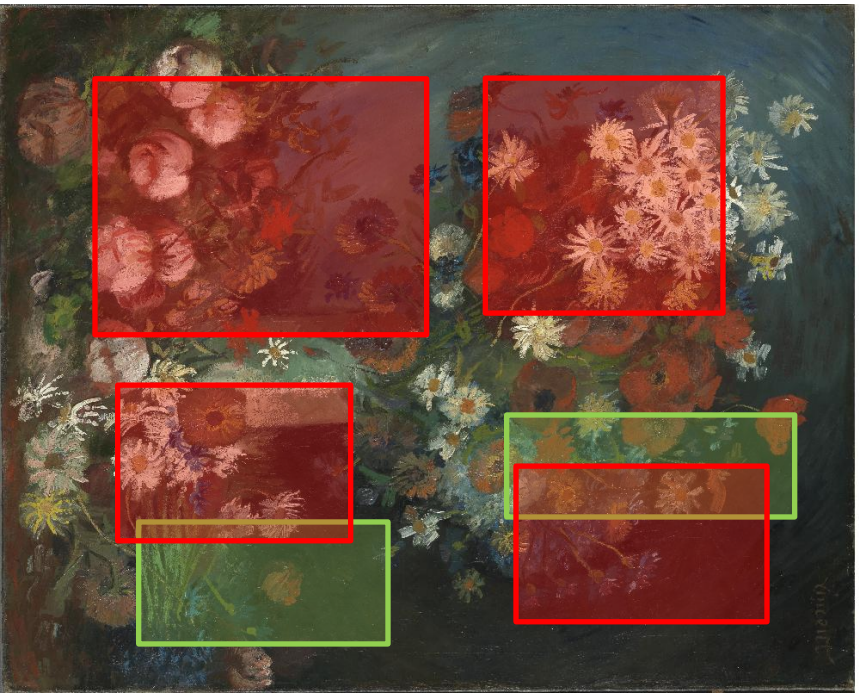
1 mm step size

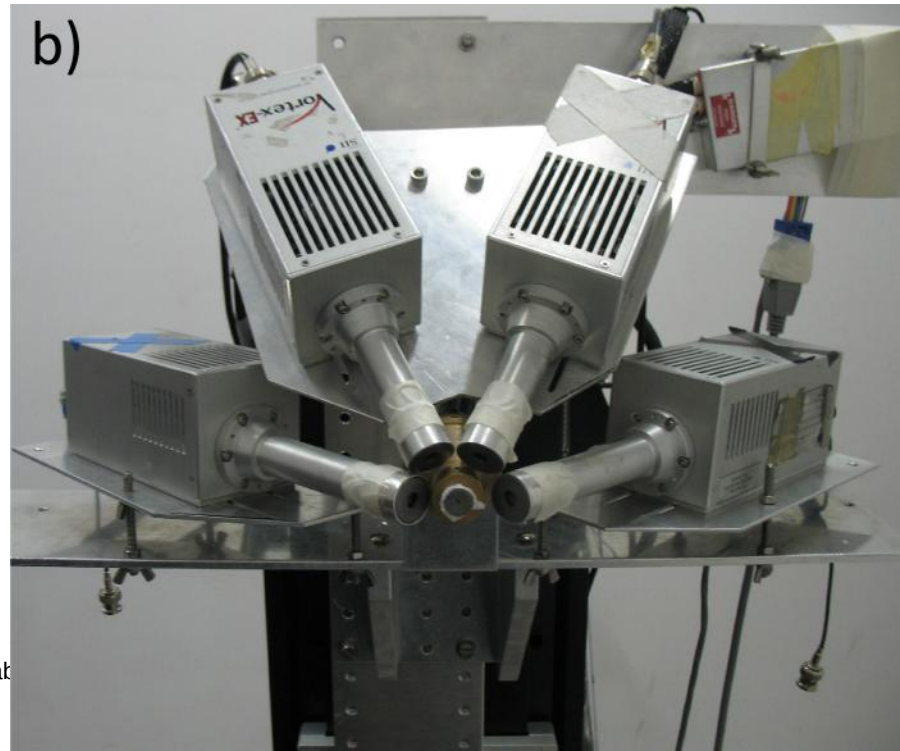




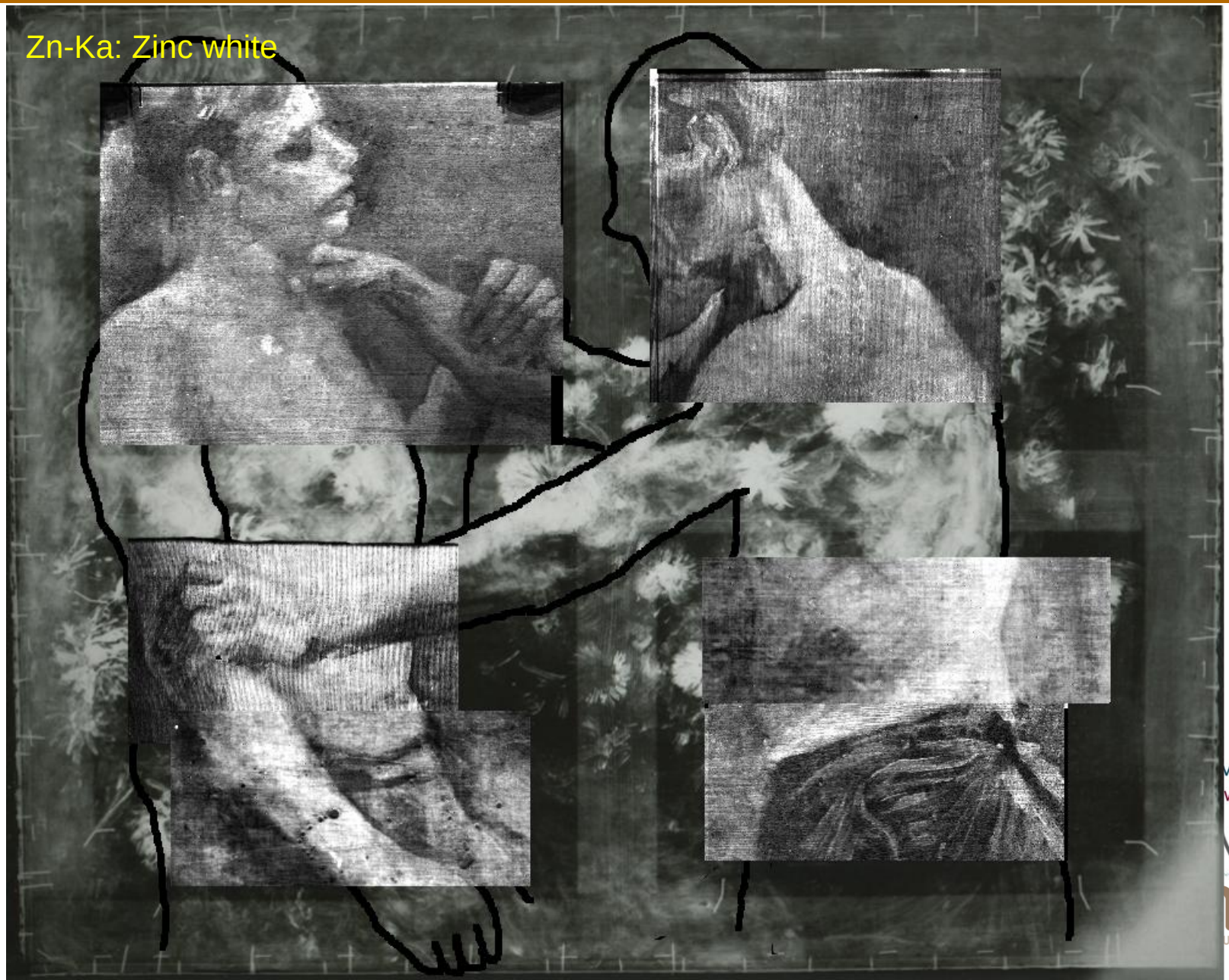
XRF imaging of historical paintings: comparison

- Two additional areas were scanned by means of Instrument D with a dwell time of 3.6 s/pixel.



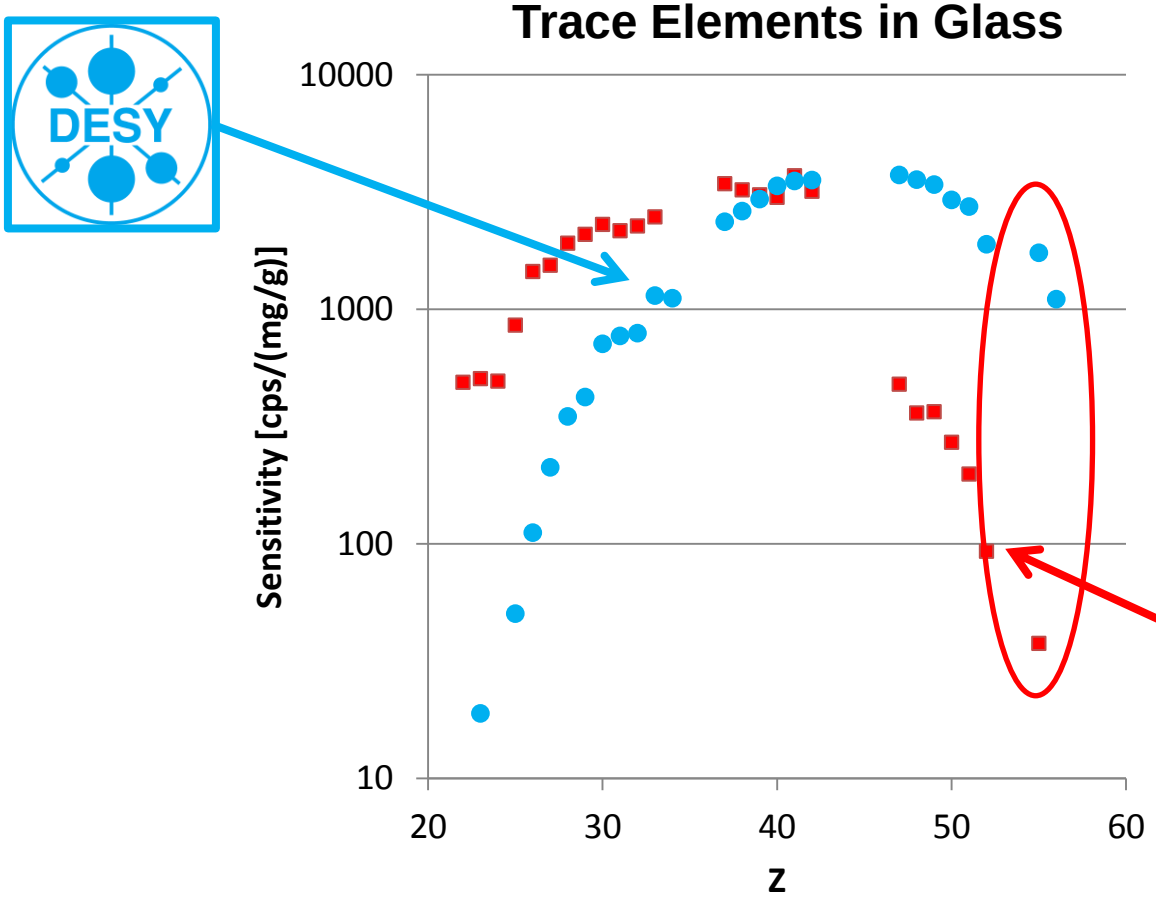


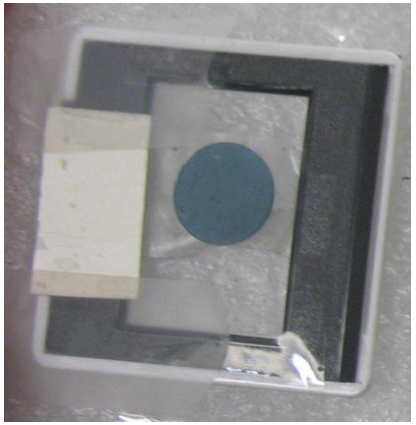
XRF imaging of historical paintings: comparison



XRF imaging of historical paintings: comparison

XRF imaging of historical paintings: comparison

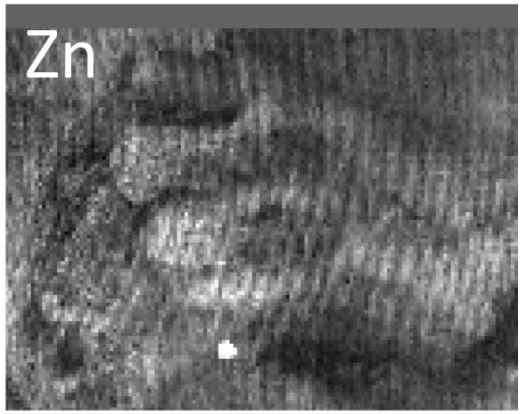


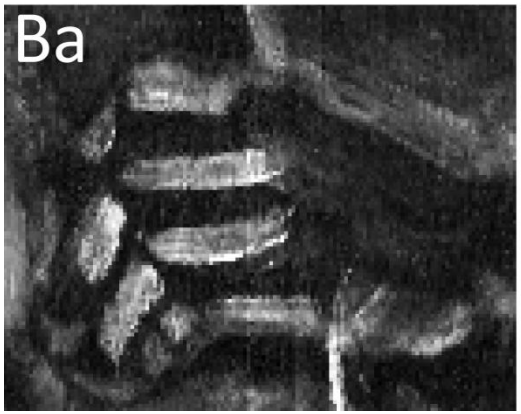


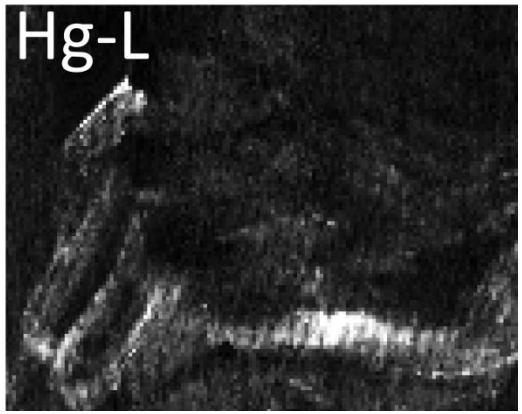
XRF imaging of historical paintings: comparison

XRF imaging of historical paintings: comparison

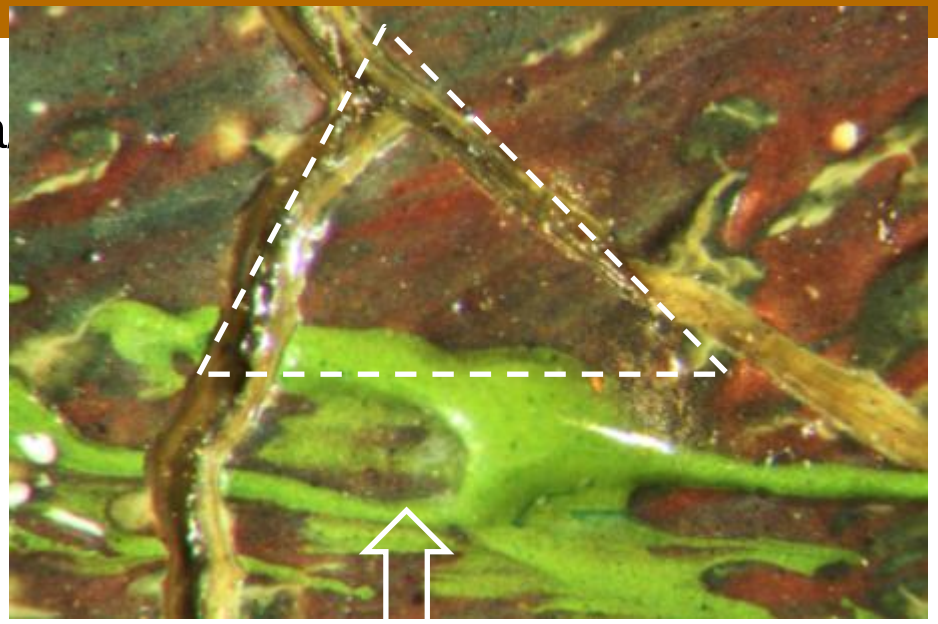
Vincent van Gogh, *Potatoeaters*







XRF imaging of historical paintings: comparison



Sample taken in the flesh tone (arm) of a wrestler

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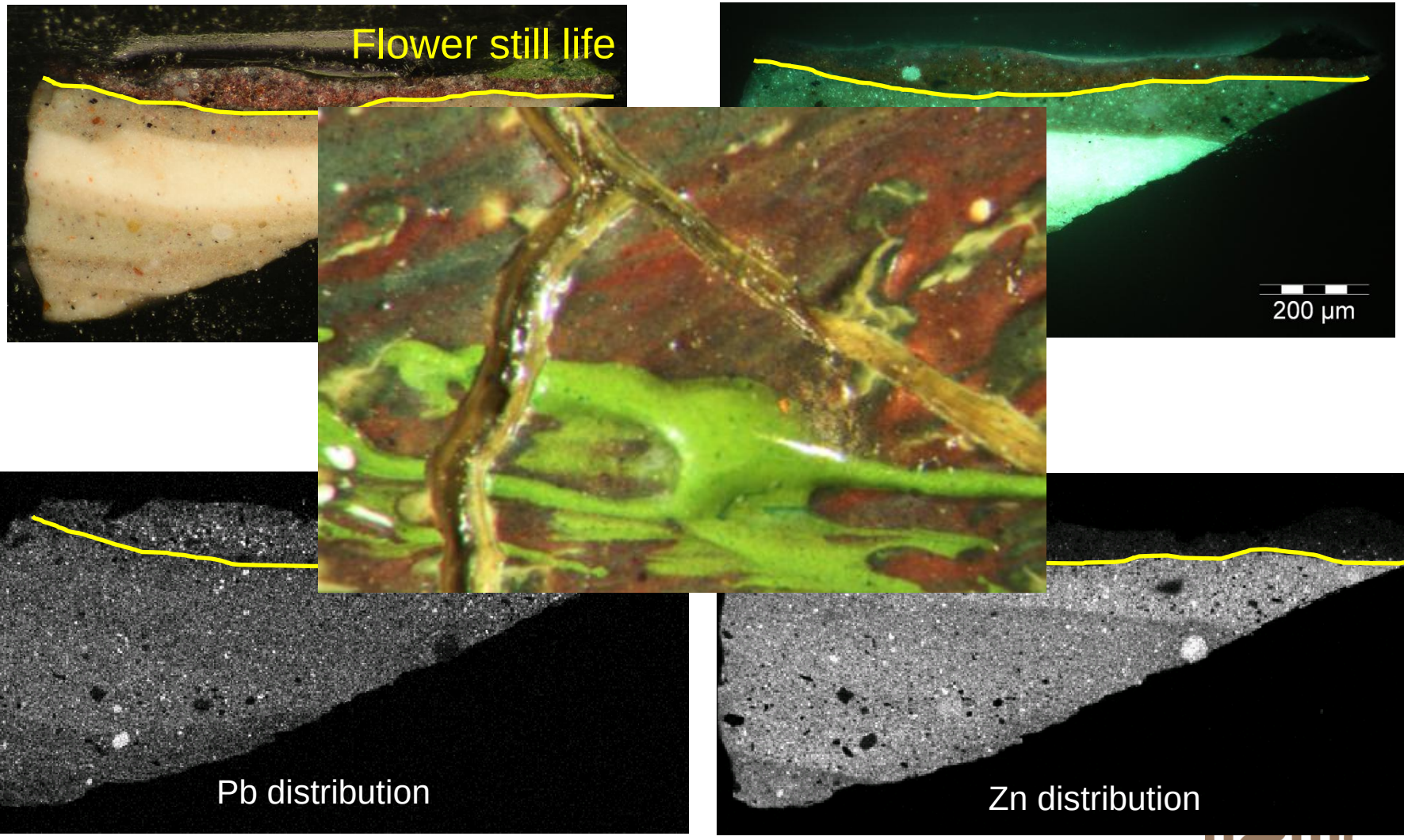
XRRadiography

XRF imaging of historical paintings: comparison



X-ray fluorescence imaging of paintings: comparison

Before 1920 L. C. Enthoven collectio
1920 M. M. Lam collection
1935 A. Philips collection
1970 Heirs of A. Philips
1974 Kröller-Müller Museum
2003 Dismissed
2012 Rehabilitated

L.S. van der Loeff, M. Alfeld, T. Meedendorp, J. Dik, E. Hendriks, G. Van der Snickt, K. Janssens, M. Chavannes, Rehabilitation of a flower still life in the Kröller-Müller Museum and a lost Antwerp painting by Van Gogh, in: L. van Tilborgh, C. Stolwijk (Eds), Van Gogh Studies 4: New Findings, WBOOKS, Zwolle, 2012, pp. 33-53.

M. Alfeld, G. Van der Snickt, F. Vanmeert, K. Janssens, J. Dik, K. Appel, L. van der Loeff, M. Chavannes, T. Meedendorp, E. Hendriks, Appl. Phys. A: Mater. Sci. Process. 111 (2013) 165-175.

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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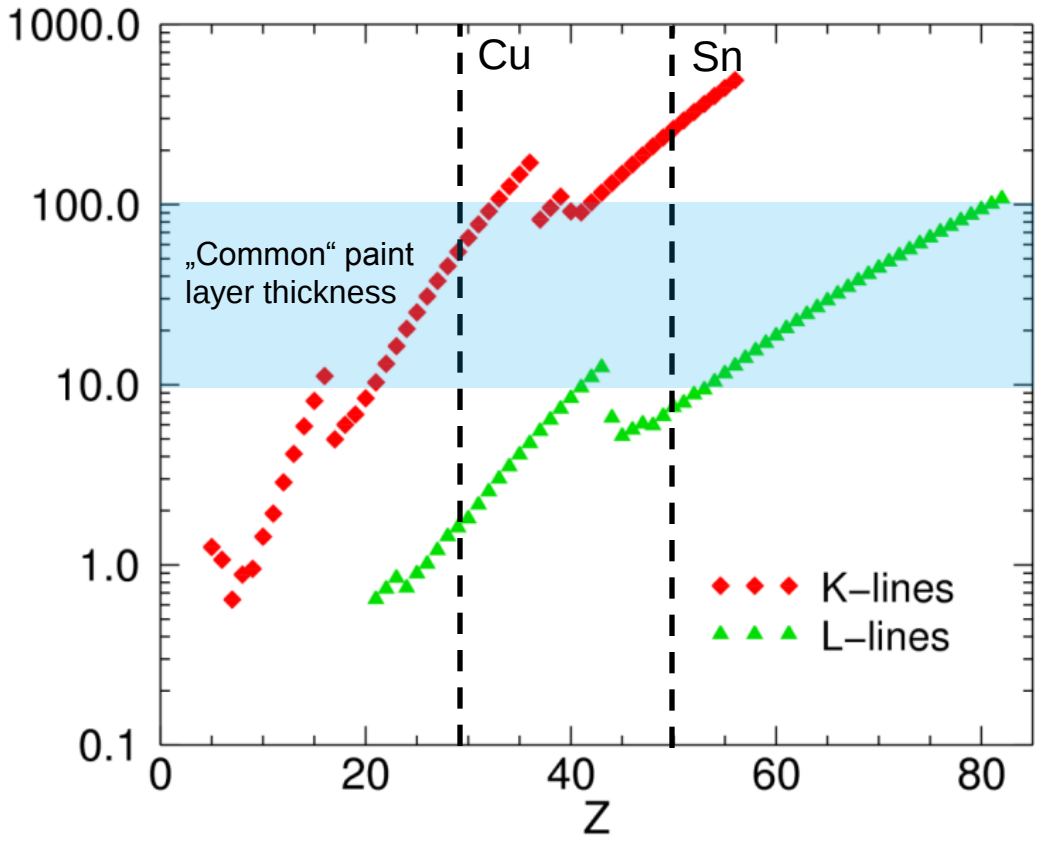
Limitations: Absorption

Lead tin
model le
pigment.

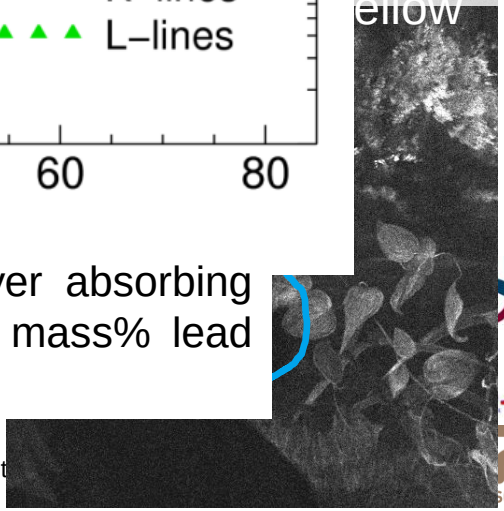
Rest on the flight
Caravaggio,
135 x 167 cm, Oil
Galleria Doria Pa
Rome, Italy



Thickness of lead white paint layer absorbing 90% of the emitted radiation (80 mass% lead white, 20 mass% lineseed oil)

ure form to
containing

ellow



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PMC
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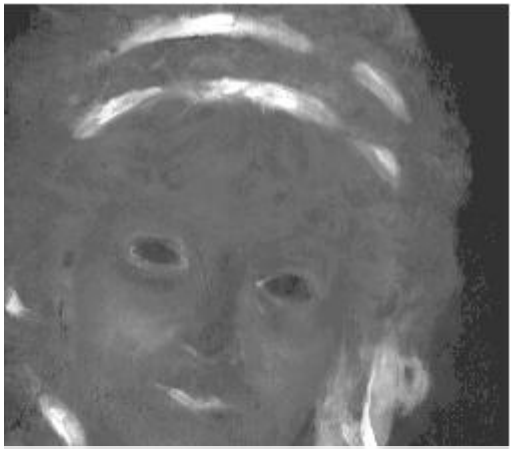
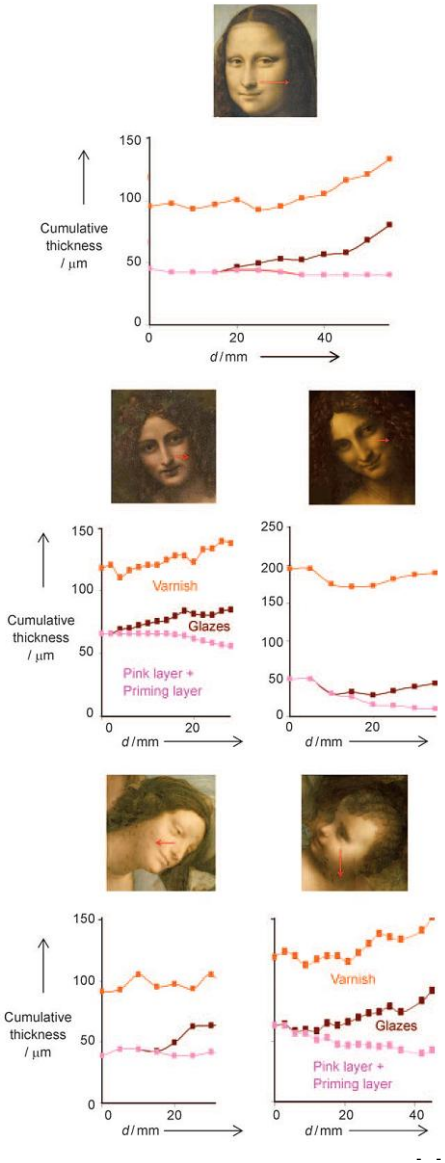
In collaboration with: emmebi diagnostica artistica s.r.l., Roma, Italy

Limitations: No depth sensitivity



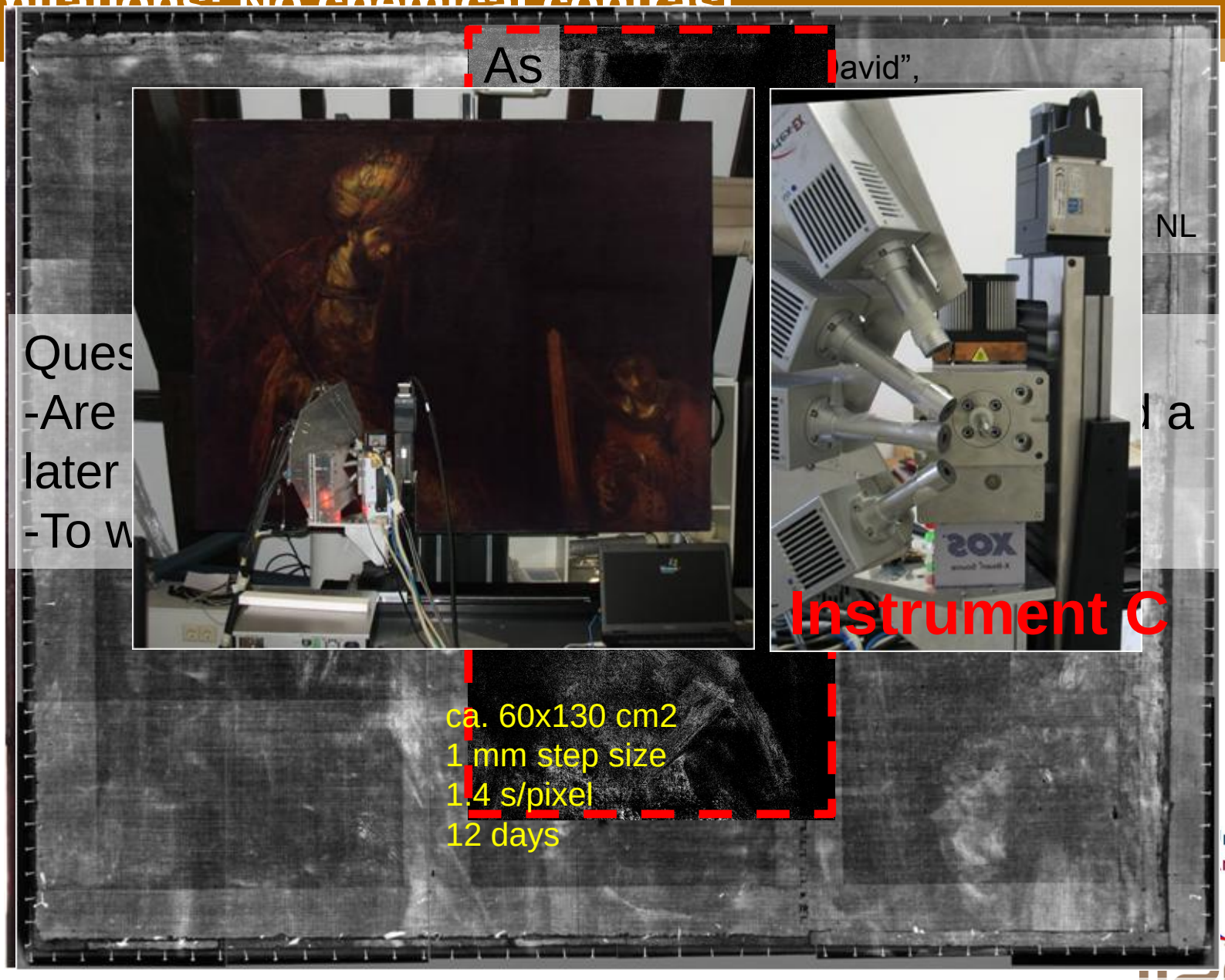
The position of t ontaining paint layer cannot be directly d n elemental distribution images and other r eded to determine it.



-L: Vermilion

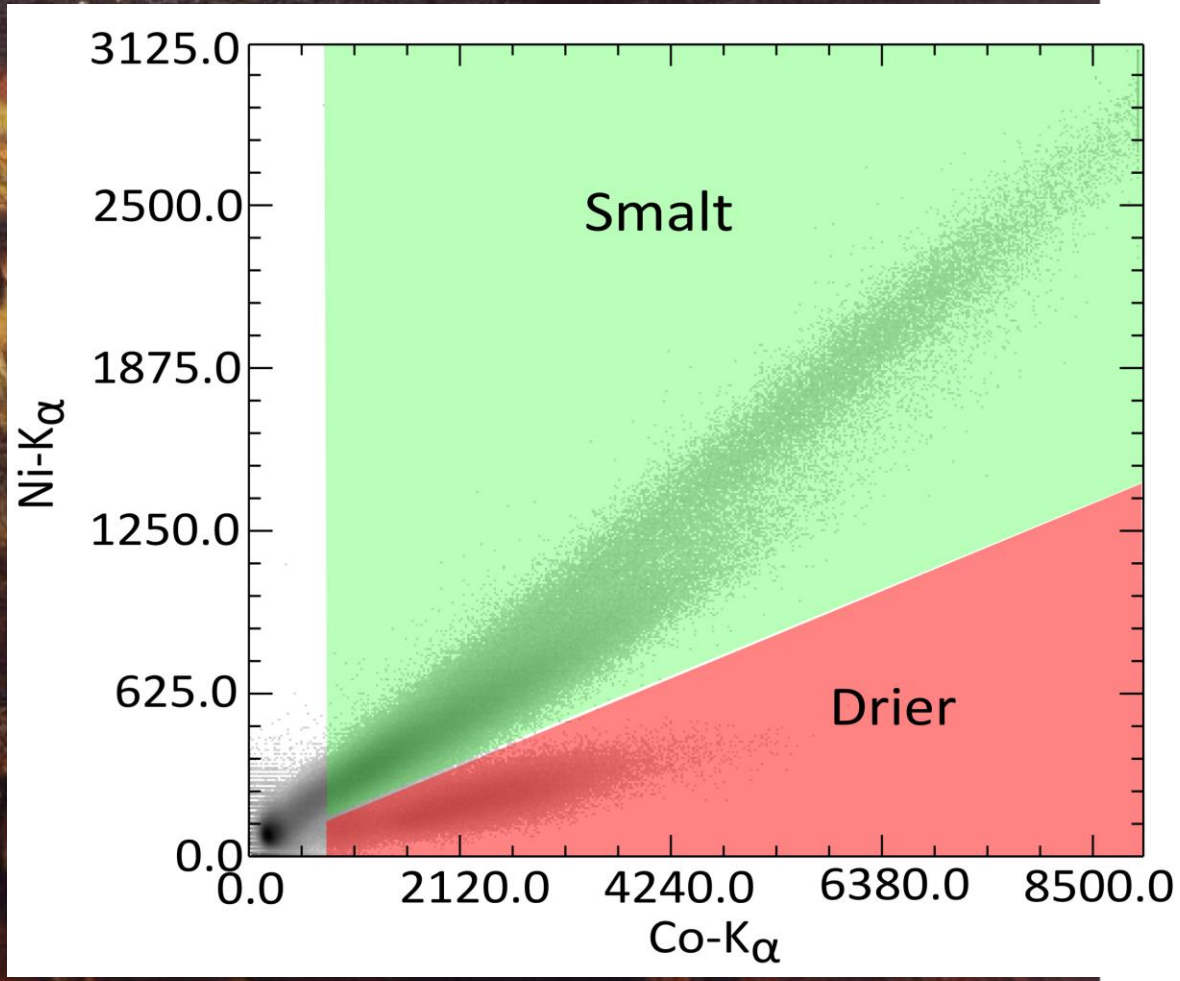
L. de Viguerie, P. Walter, E. Laval, B. Mottin, V.A. Solé, Angew. Chem. Int. Ed. (2010) **49** , 6125–6128.

Limitations: No chemical contrast



P. Noble, A. van Loon, M. Alfeld, K. Janssens, J. Dik, *Techné* (2012). **35**, 36-45.

Limitations: No chemical contrast



P. Noble, A. van Loon, M. Alfeld, K. Janssens, J. Dik, *Techné* (2012). **35**, 36-45.

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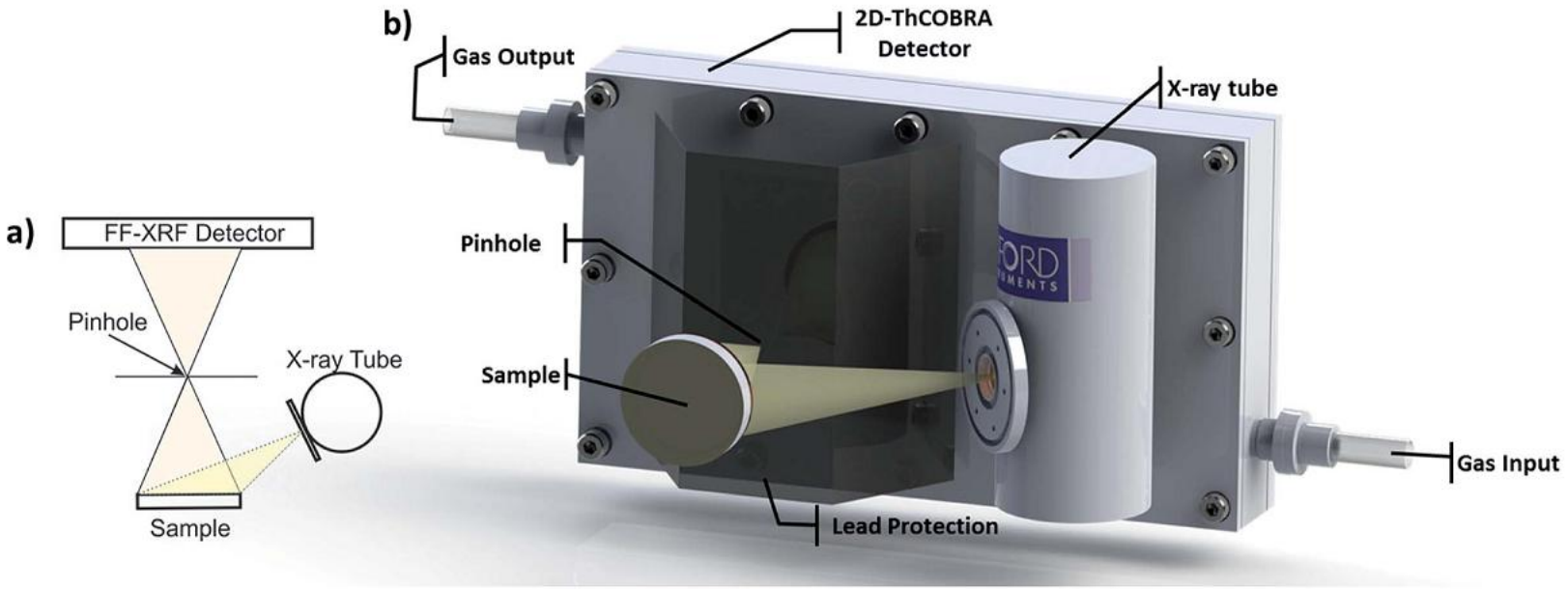
Other groups

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



A. L. M. Silva, M. L. Carvalho, K. Janssens, J. F. C. A. Veloso, *J. Anal. At. Spectrom.* (2015) **30**, 343–352.

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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 tratments
  - 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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Frederik Vanmeert
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Luuk van der Loeff (KMM)
Meta Chavannes (SMBA)
Teio Meedendorp (VGM)
Ella Hendriks (VGM)

emmebi diagnostica artistica s.r.l., Roma, Italy:
M. Cardinali
M. B. De Ruggieri
M. Positano

You – Attention!