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Applications of Synchrotron Light to Cultural Materials Studies

Daryl Howard, XFM Beamline, Australian Synchrotron

AOF School, Melbourne, June 2017

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Cultural Heritage

Its study often involves the chemical analysis of cultural objects (such as books, works of art, artifacts)

Aim to answer: How were they made? Composition? Conservation strategies.

Archimedes palimpsest

Sunflowers, van Gogh

Ancient coin

Ideally a technique for cultural materials analysis should be*:

- Non-destructive (non-invasive) *rare, one of a kind items*
- Fast
- Universal – many different objects may be studied with minimal or no sample pre-treatment
- Versatile – allow local information of small areas and average composition to be obtained (spatial resolution)
- Sensitive – able to detect trace quantities
- Multi-elemental – simultaneously detect multiple components in a single measurement

* According to Lahanier et al. Nuc. Instrum. Meth. B14 (1986) 1-9.

Scanning X-ray Fluorescence Microscopy (XFM)

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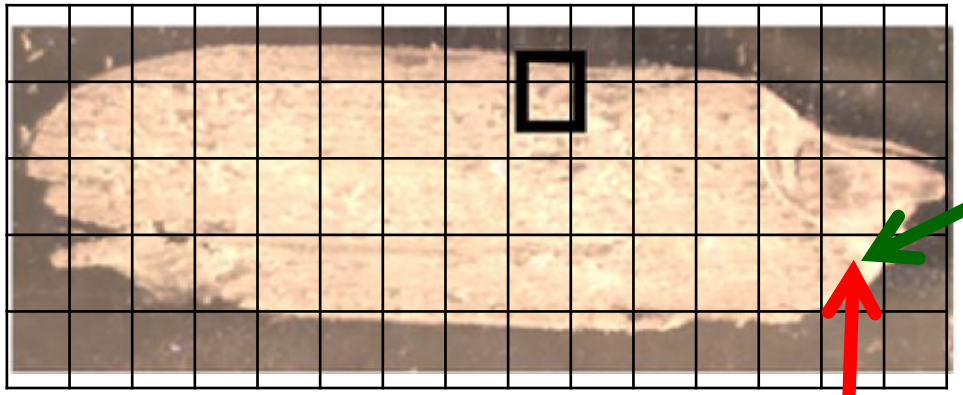
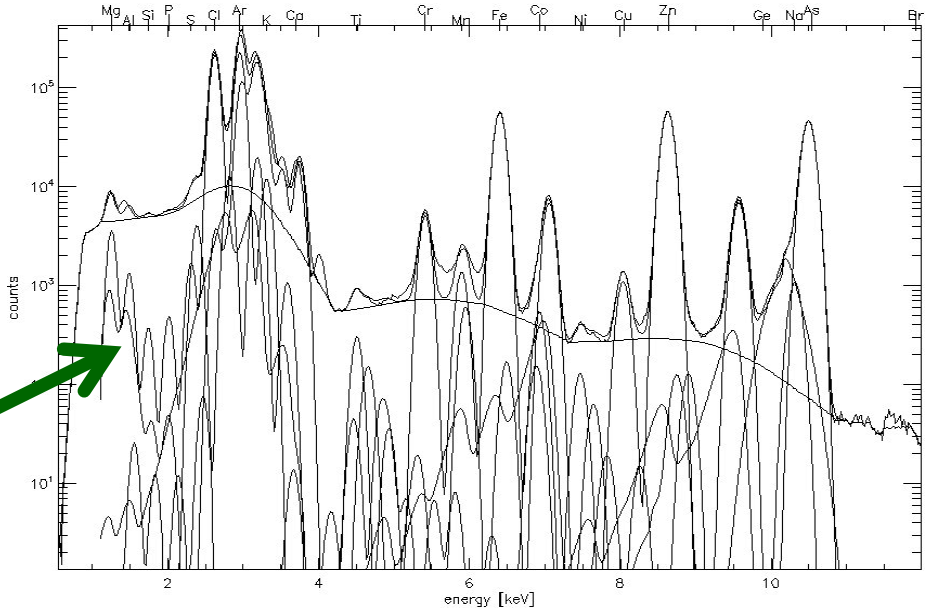
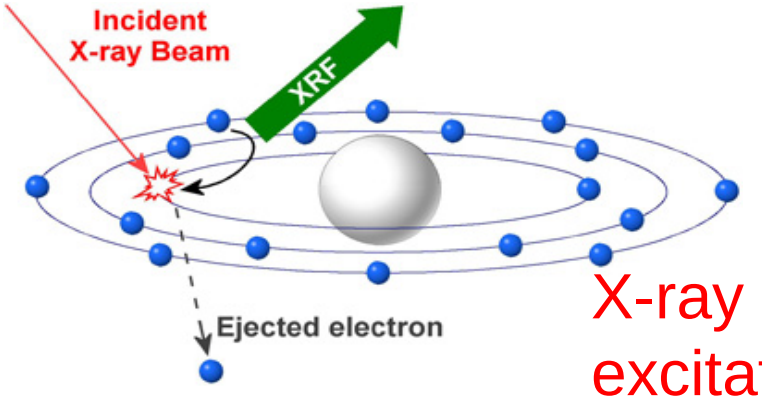
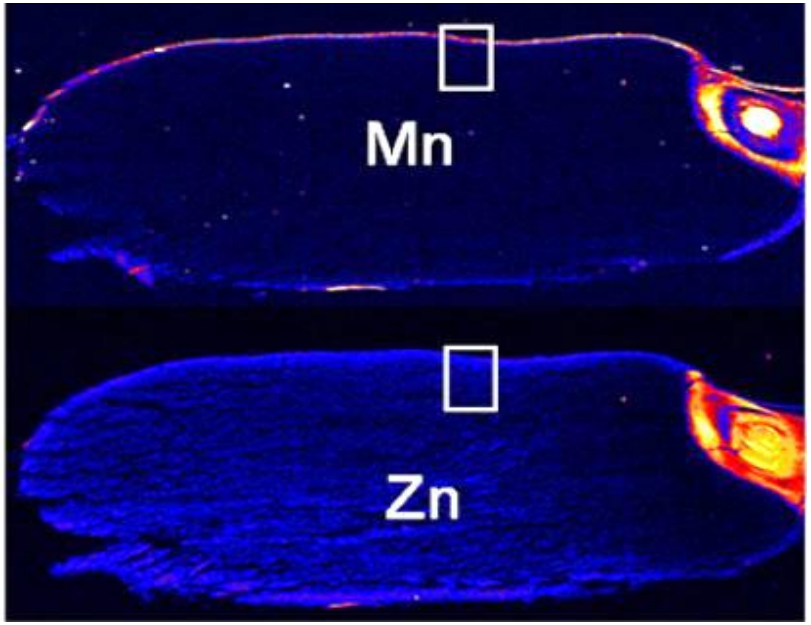
rice grain section







X-ray
excitation beam
(monochromatic)



Hansen et al. J. Cer. Sci. 56 (2012) 307

X-ray Fluorescence Microscopy (XFM)

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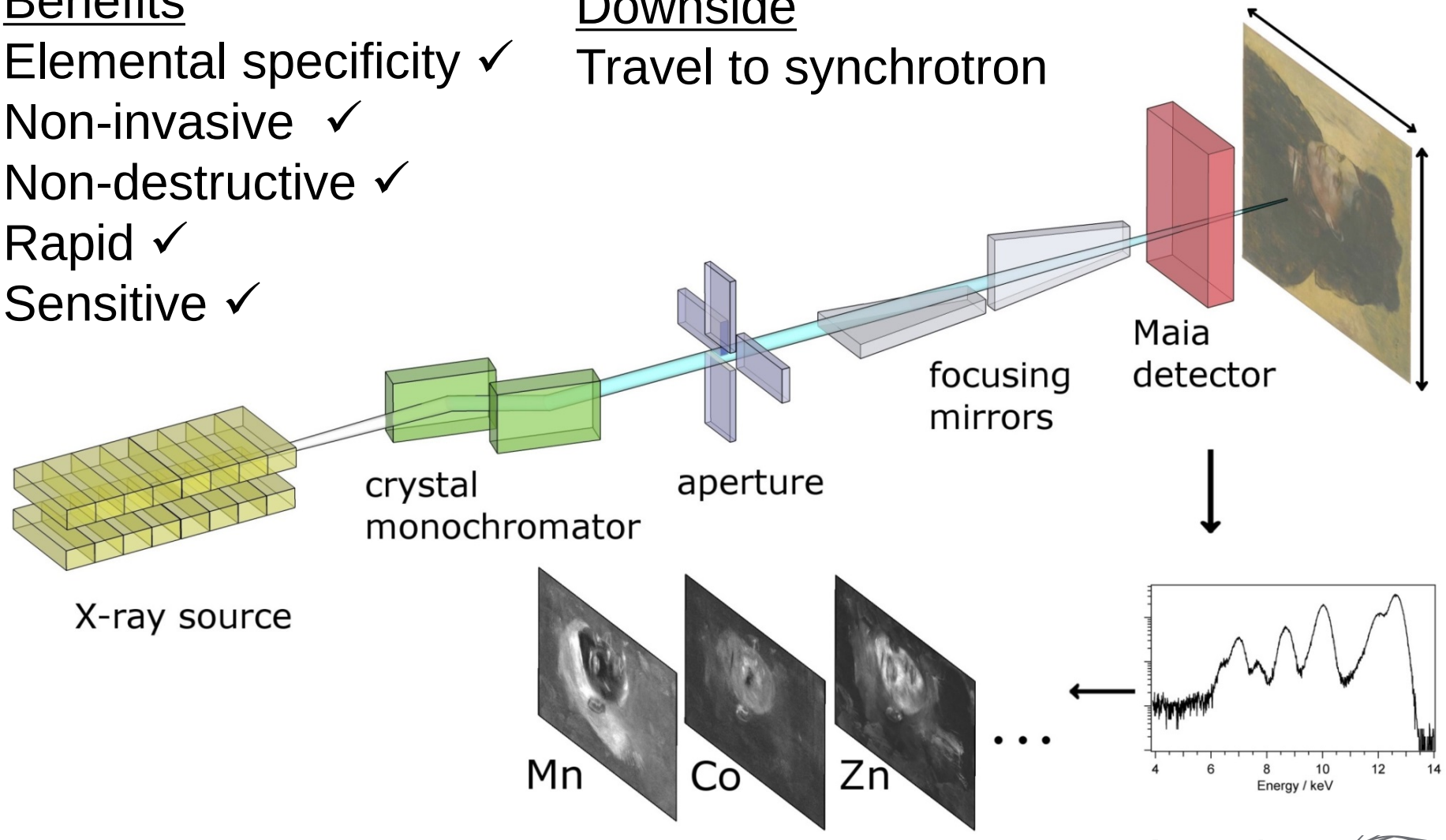
Benefits

Elemental specificity ✓
Non-invasive ✓
Non-destructive ✓
Rapid ✓
Sensitive ✓

Downside

Travel to synchrotron



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Synchrotron Radiation Advantages

- Monochromatic
- Brilliance
- Tunable source

Things to keep in mind:

- Is the sample sensitive to radiation damage?

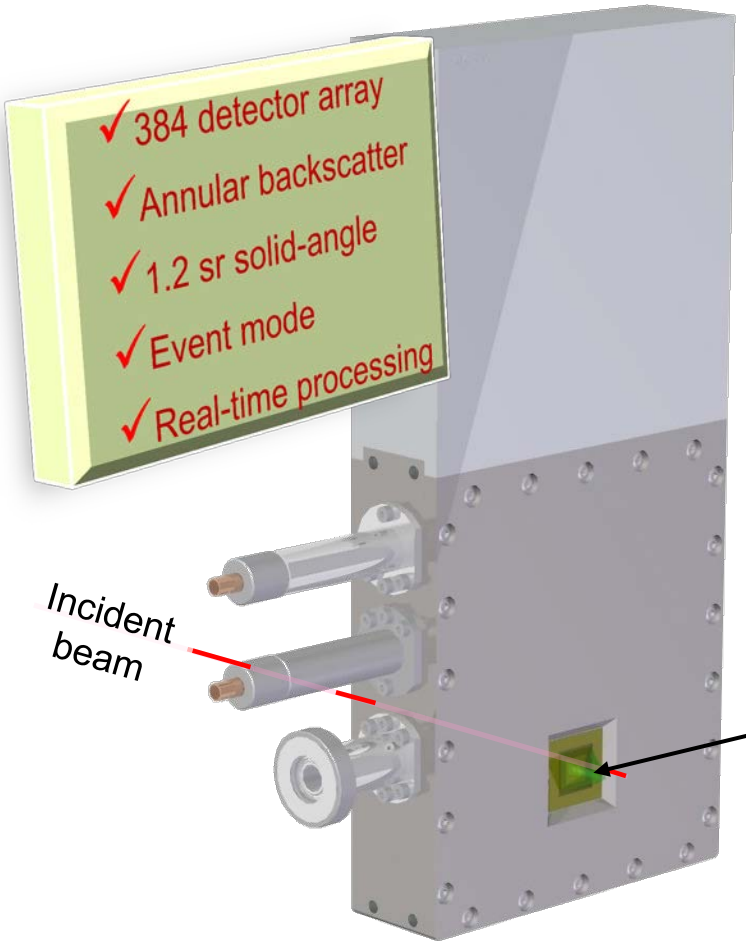
Testing of representative material may be required.

Minimise potential radiation damage with short dwell time (fast detection methods)

Keep radiation As Low As Reasonably Achievable (ALARA)

Bertrand, L. *et al.* Mitigation strategies for radiation damage in the analysis of ancient materials. *Trends Analyt. Chem*. **66,** (2015) 128–145

Fast detection - Maia Detector Array



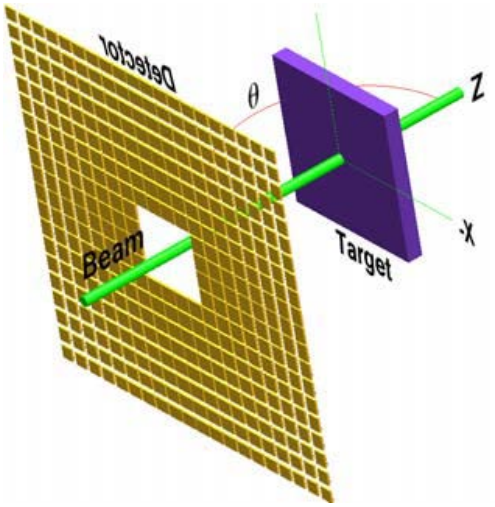
Maia 384 detector array

Brookhaven National Lab (USA) & CSIRO (Australia)

- Fly-scanning ~1 ms dwell per pixel

- Full XRF spectrum saved per pixel

- Large area, high-definition mapping



Kirkham *et al.*, AIP Conf. Series 1234 (2010) 240.

Pigments

Pigment – ground coloured material that forms the basis of paints

– early pigments were ground earth or clay
(XRF, XRD, IR often used for analysis)

Paint – pigments suspended in a binder

– common binders: oil, egg yolk, acrylic
(binders suitable for infrared analysis)

Synchrotron

Pigments - Whites

Lead white, $2PbCO_3 \cdot Pb(OH)_2$
Used since antiquity

Zinc white, ZnO
Introduced 19th century

Titanium white, TiO_2
Introduced 20th century

Dates of manufacture can help with authentication

Pigments – examples

Vermilion – HgS, from the mineral cinnabar

Red ochre – Fe_2O_3

Red lead – $2PbO \cdot PbO_2$

The Seine at Asnières, Renoir (1879)

Cobalt blue
$CoAl_2O_4$

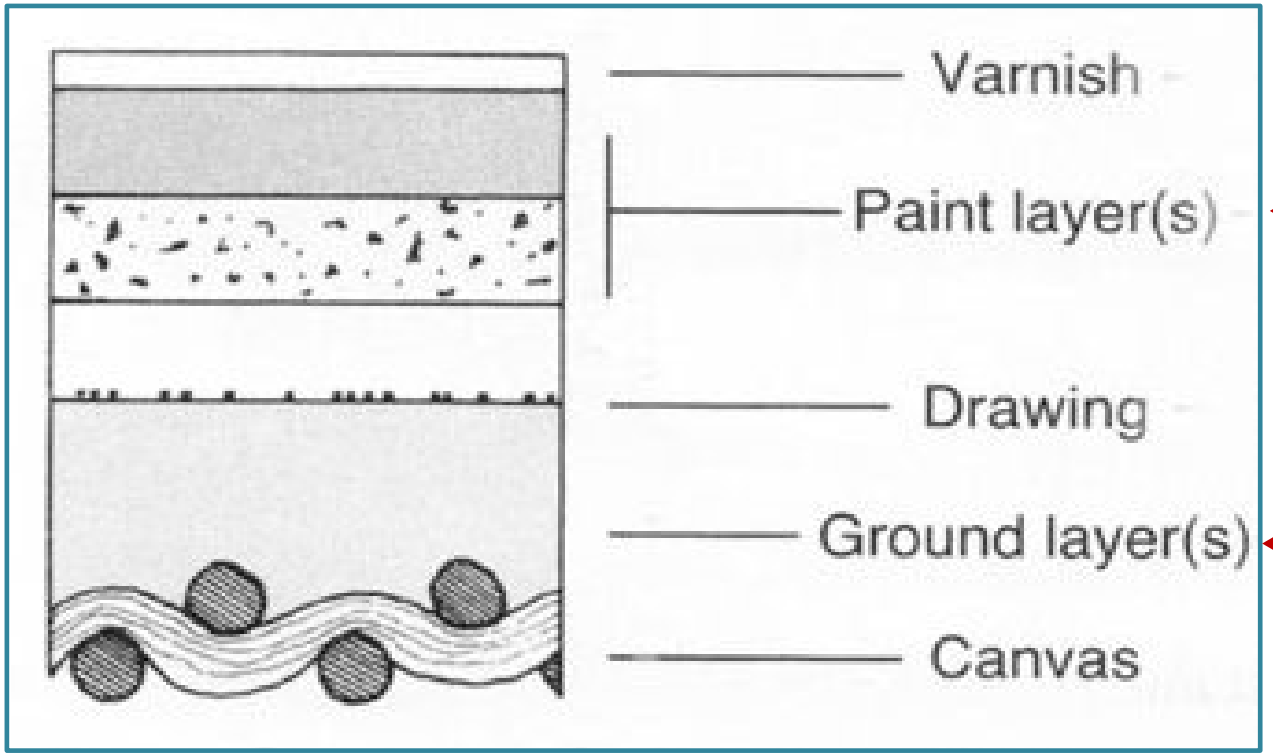
The Red Studio, Matisse

Cadmium red
CdSe

Prussian blue
$Fe_4[Fe(CN)_6]_3$
Iron(II,III) hexacyanoferrate(II,III)

XRF is suited for identification of the metallic elements in many pigments

Painting Construction



Ca, Ti, Cr, Mn, Fe, Co, Cu, Zn, As, Hg, Pb, …

often lead white (~70 wt% Pb)

XRF frequently used to analyse subsurface layers

Lead can be a problem

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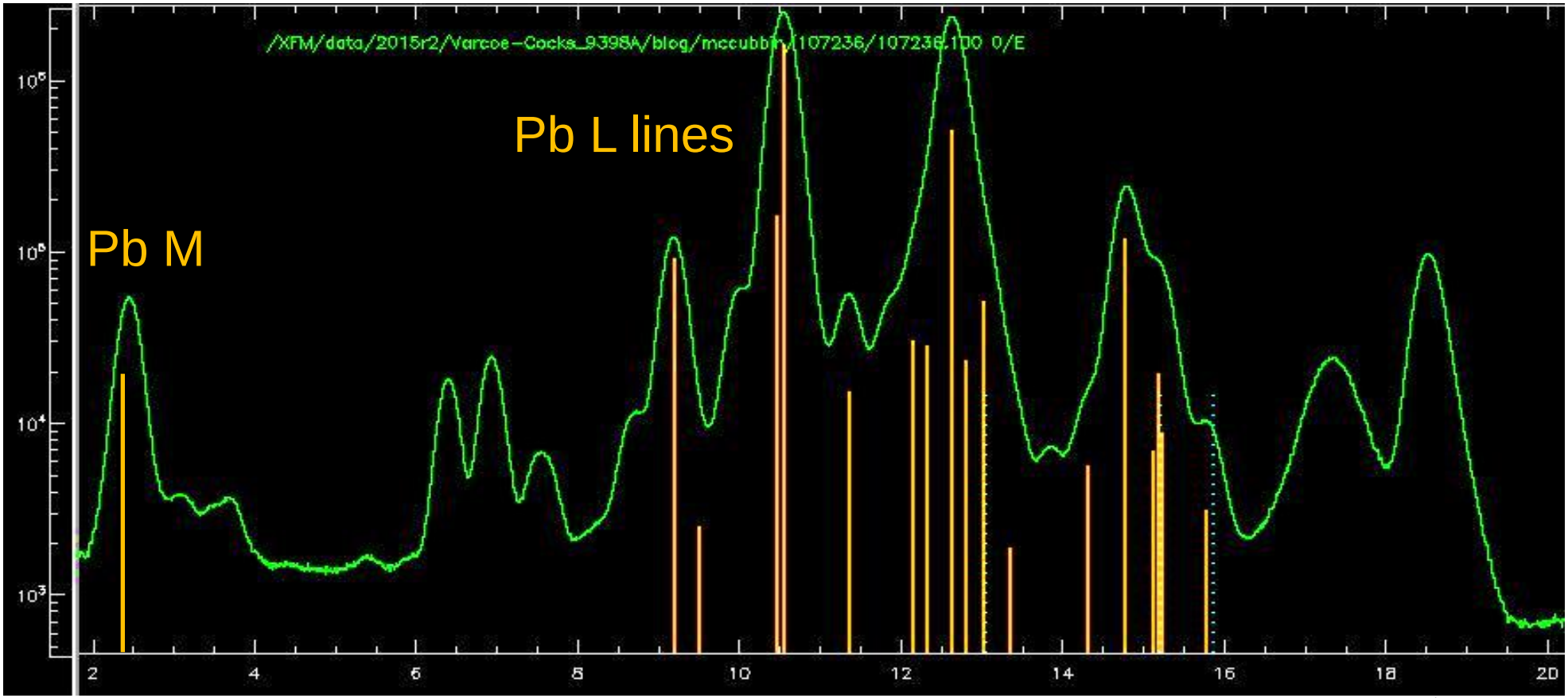
Pb commonly found in historic materials.

Pb acts as a shield and its fluorescence masks other elements of interest.

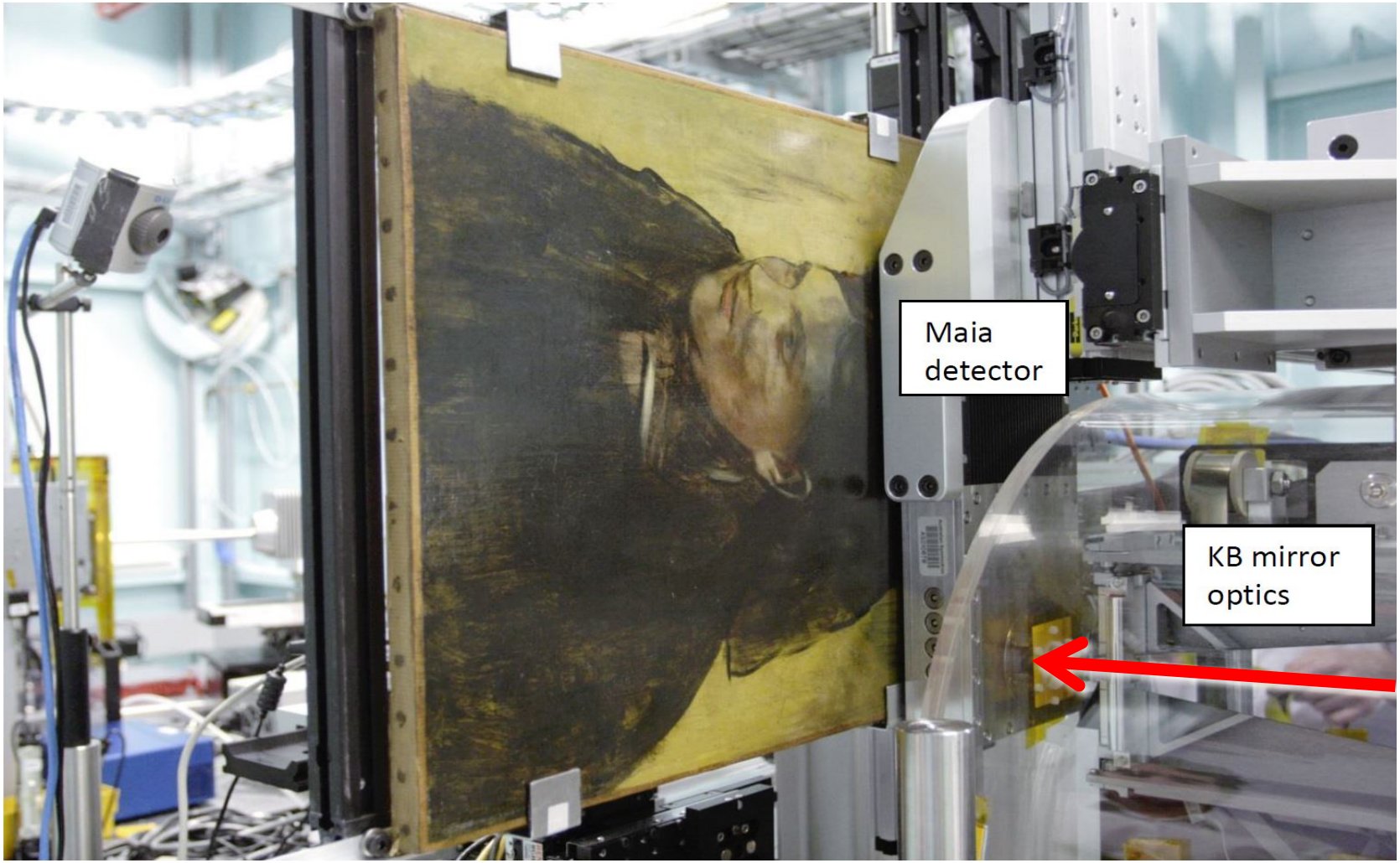


Portrait of a Woman by Edgar Degas

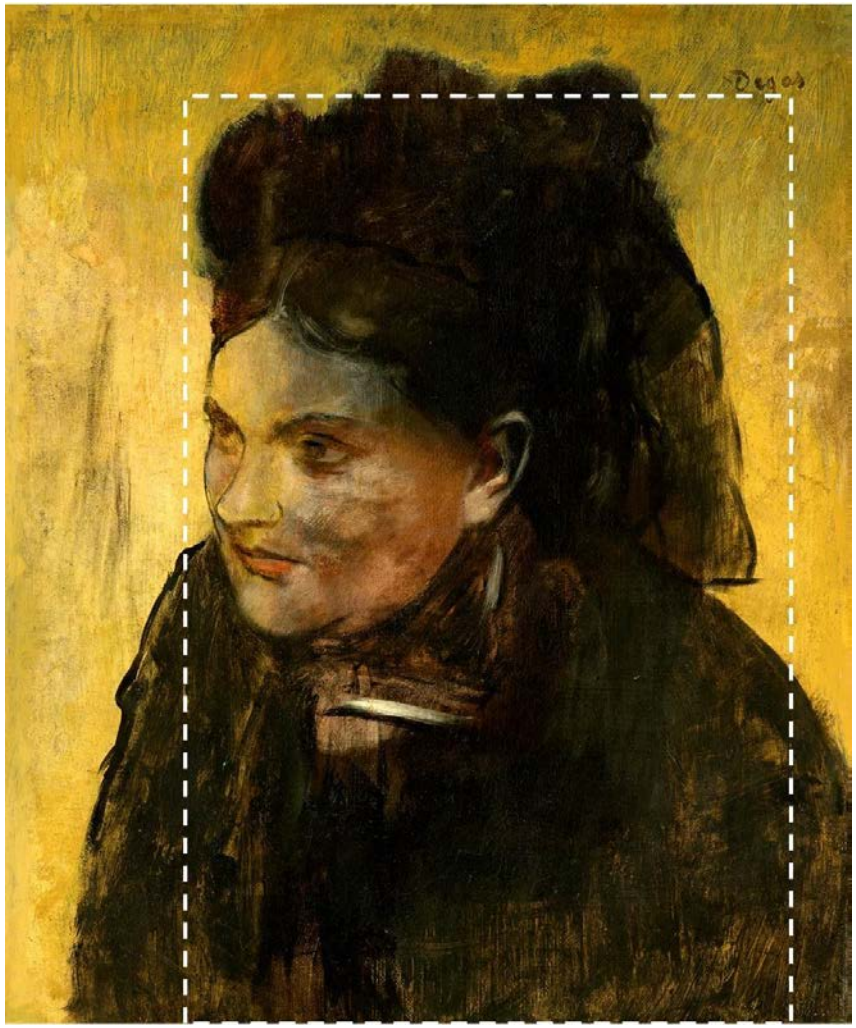
Portrait of a Woman (Portrait de Femme), c. 1876-80, oil on canvas, 46.3 × 38.2 cm, National Gallery of Victoria, Melbourne, Felton Bequest, 1937

X-radiograph and Infrared image

Mounting the painting



Scan parameters



scan area highlighted

60 µm pixel (approx size of a brush hair)

3.7 ms dwell

426 x 267 mm^2 scan area

31.6 megapixel maps

33 hour collection time

Energy 12.6 keV
(below Pb L_3 absorption edge)

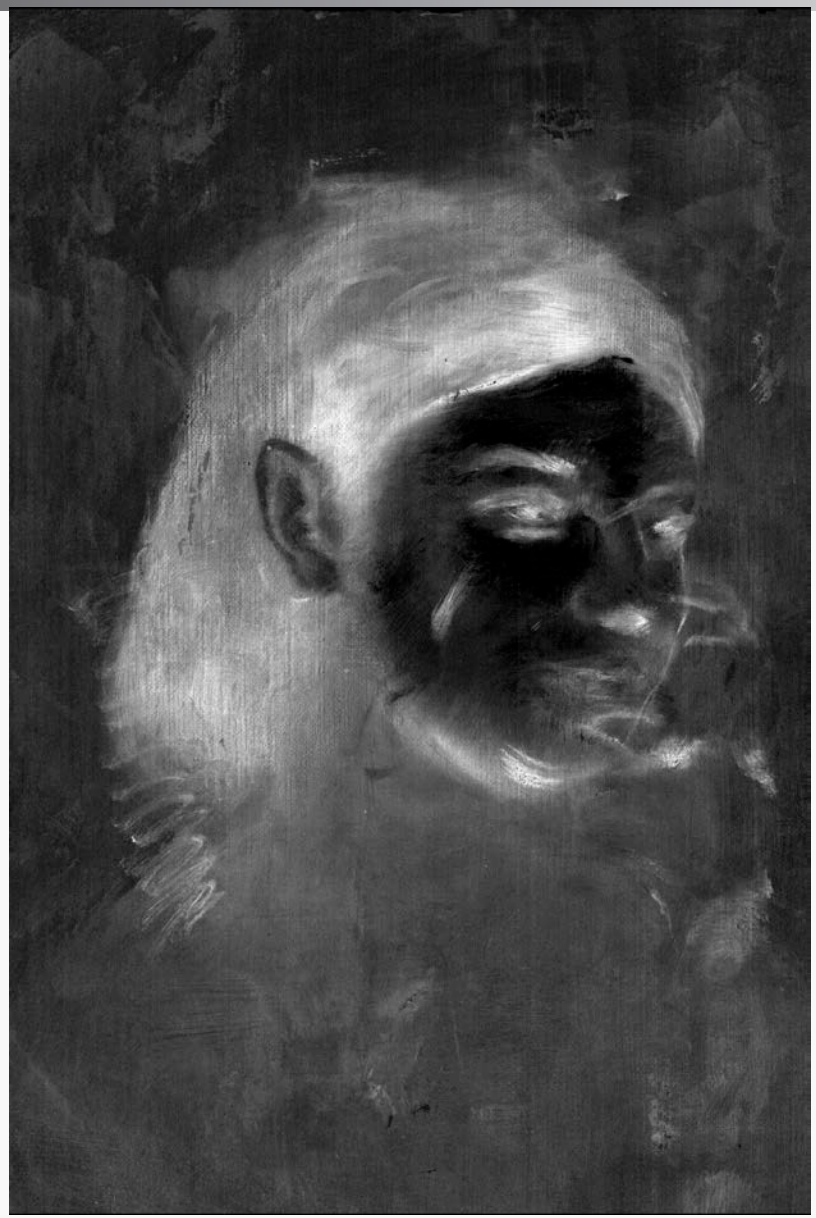
Thurrowgood et al. “A Hidden Portrait by Edgar Degas”
Scientific Reports (2016) 6:29594

Elemental Maps

Zinc

Zn detail

Elemental Maps



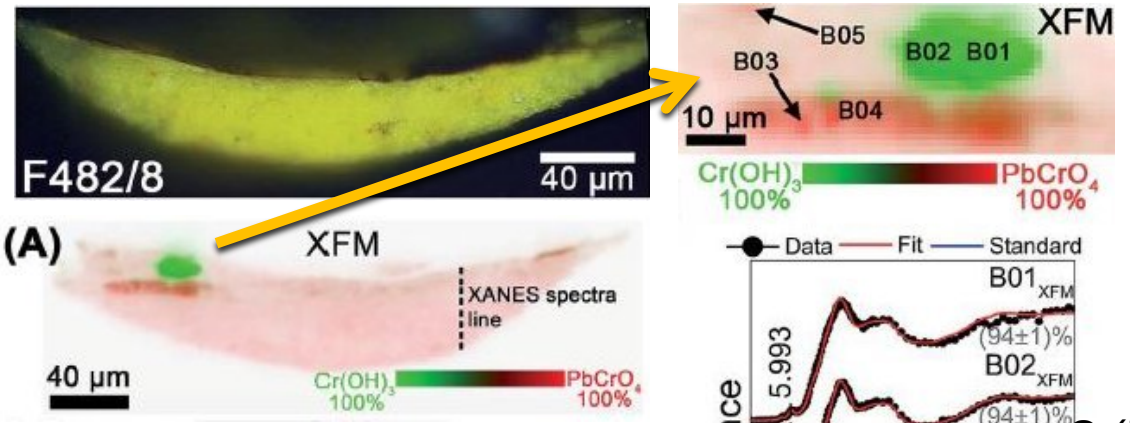
Mn Fe

XANES XRF imaging

Darkening of chrome yellow pigments

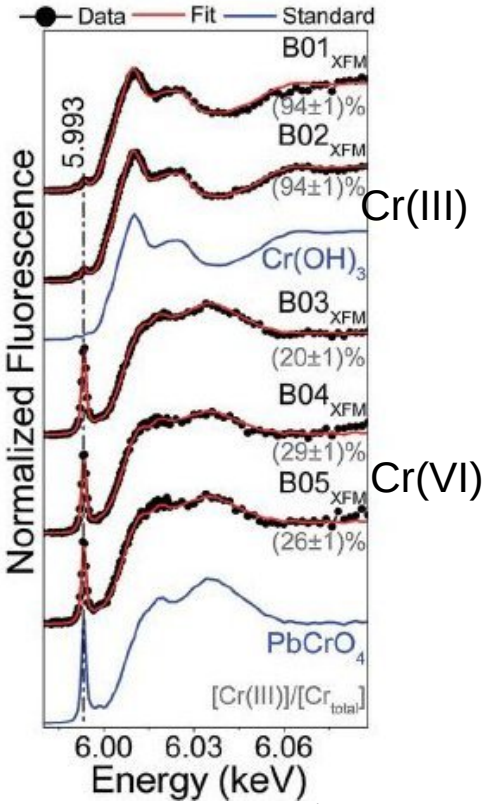
Cr (VI) yellow → photo-reduction → Cr (III) brown

The Bedroom, van Gogh, 1888



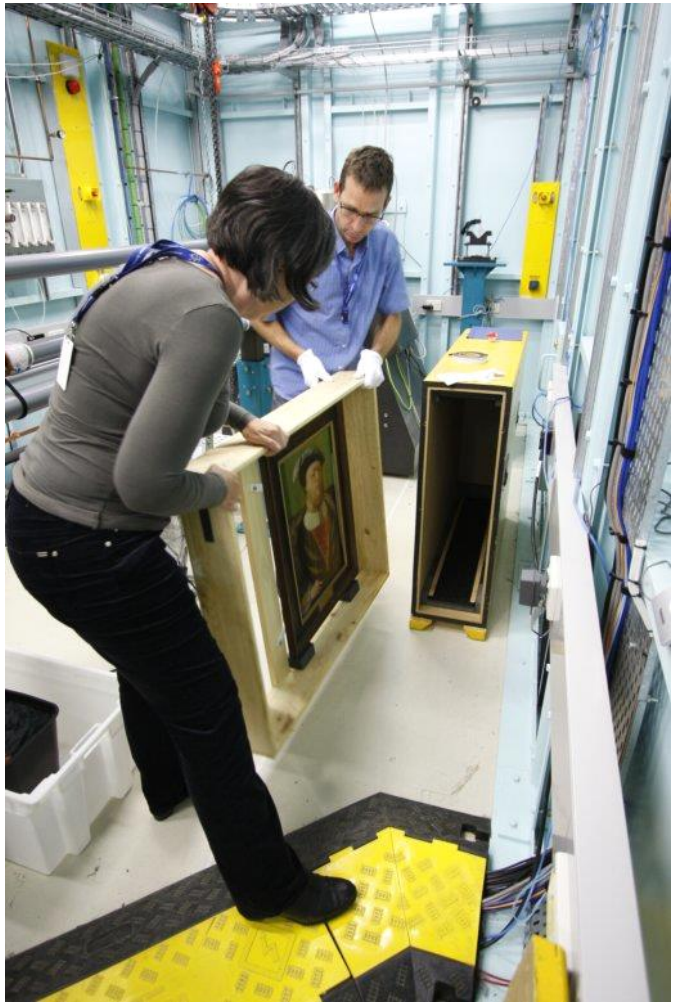
Stack of 126 maps measured across the Cr edge

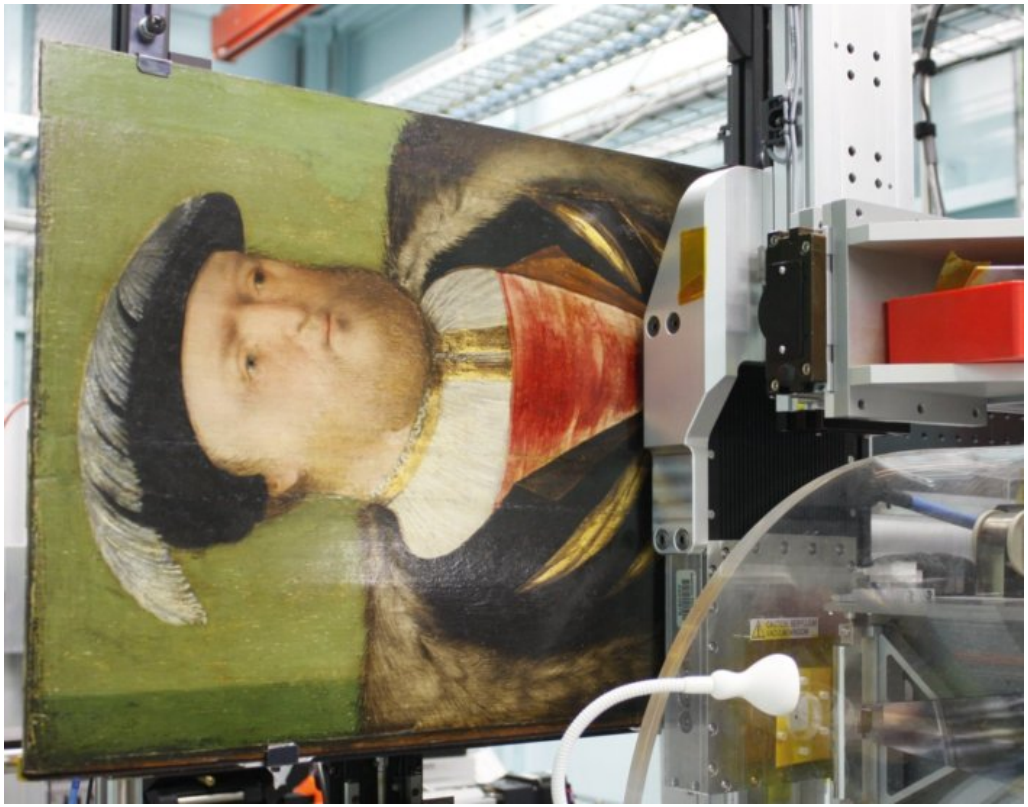
0.5 ms dwell per 1 µm pixel



Monico et al. JAAS (2015)

Tudor Painting of Henry VIII - Art Gallery NSW





Oil on wood panel, 545 x 380 mm^2
c. 1535

Paula Dredge, Simon Ives

Henry VIII

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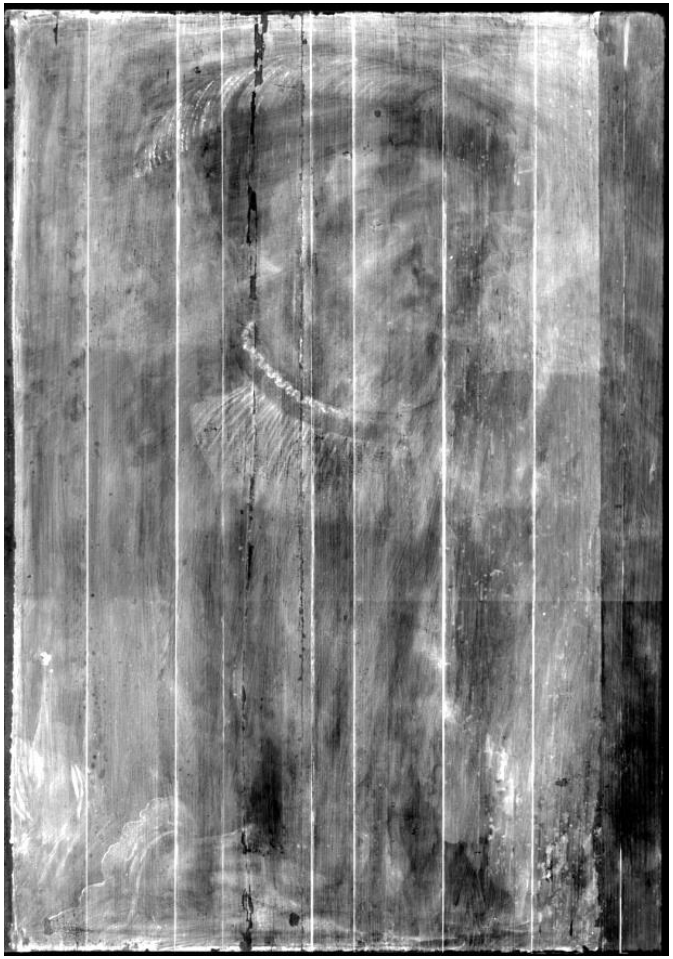
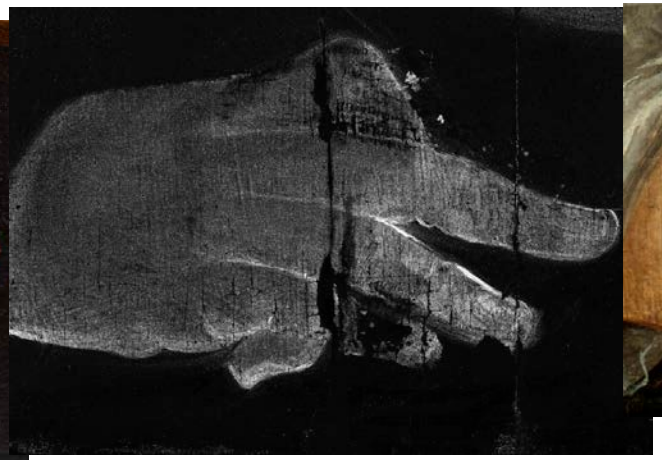
Before restoration



X-radiograph
Balsa backing
filled with chalk

XFM Lead map

Henry VIII – Elemental Maps Guide Restoration



Before restoration

Hg map

After restoration

Henry VIII – Restoration

As analysed

After removal of old restorations

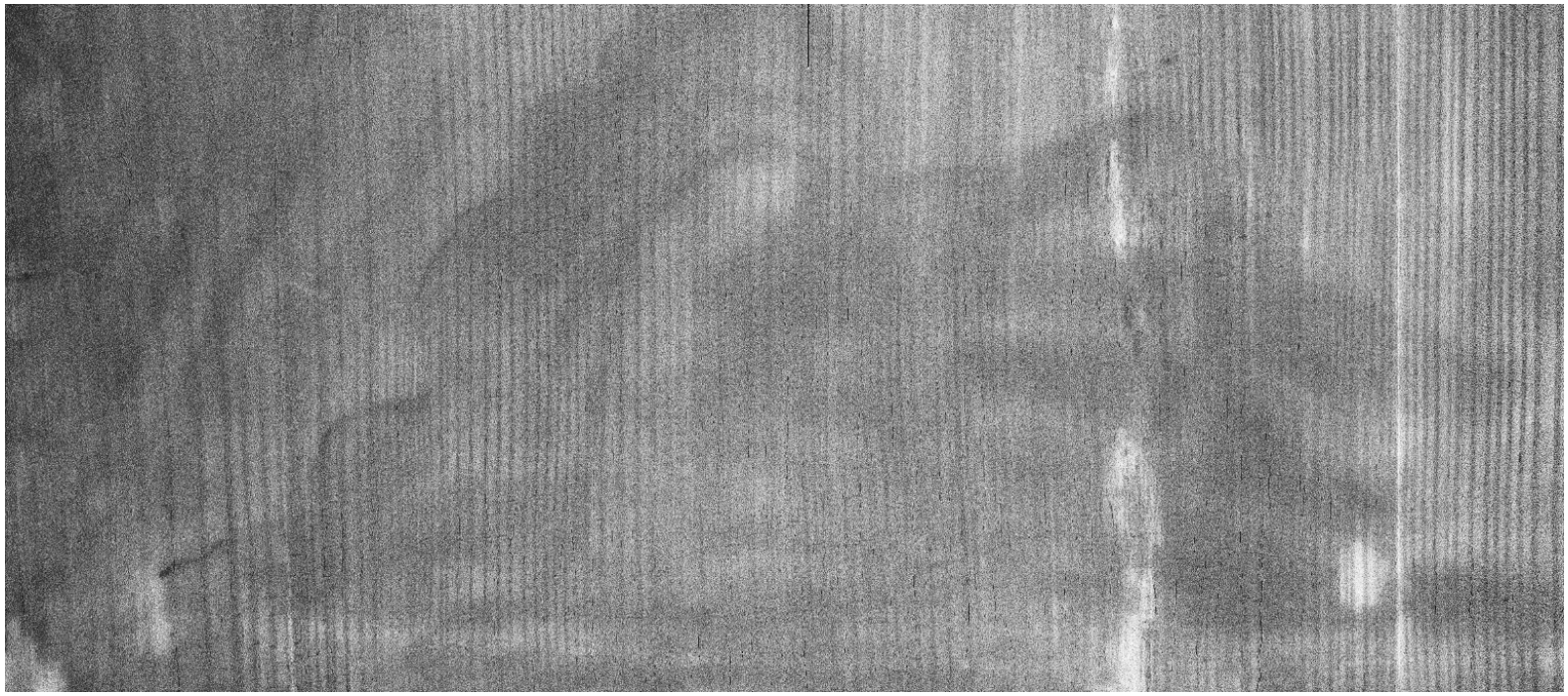
Gold purity can be used as a sign of origin.

Spatial resolution allows Au measurement excluding interference from pigments

<u>Gold foil</u>

Au	: Cu
22	: 1

Henry VIII – Elastic scatter



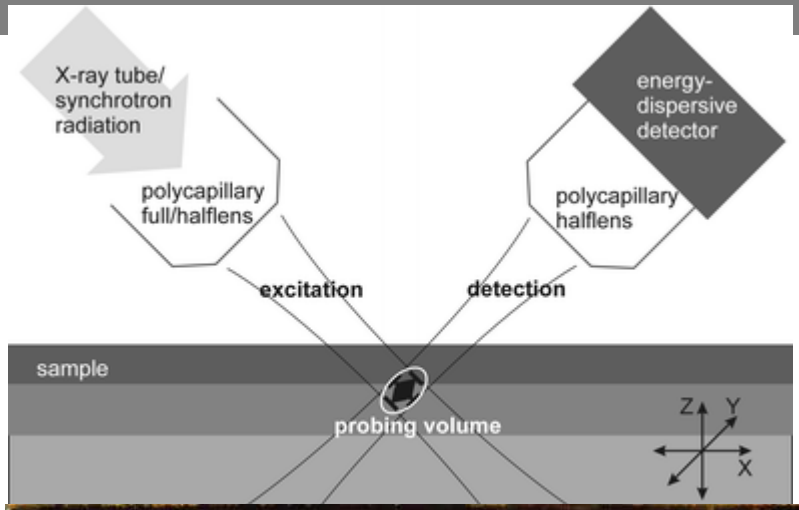
Detail around hand

18.5 keV elastic scatter map reveals wood grain.

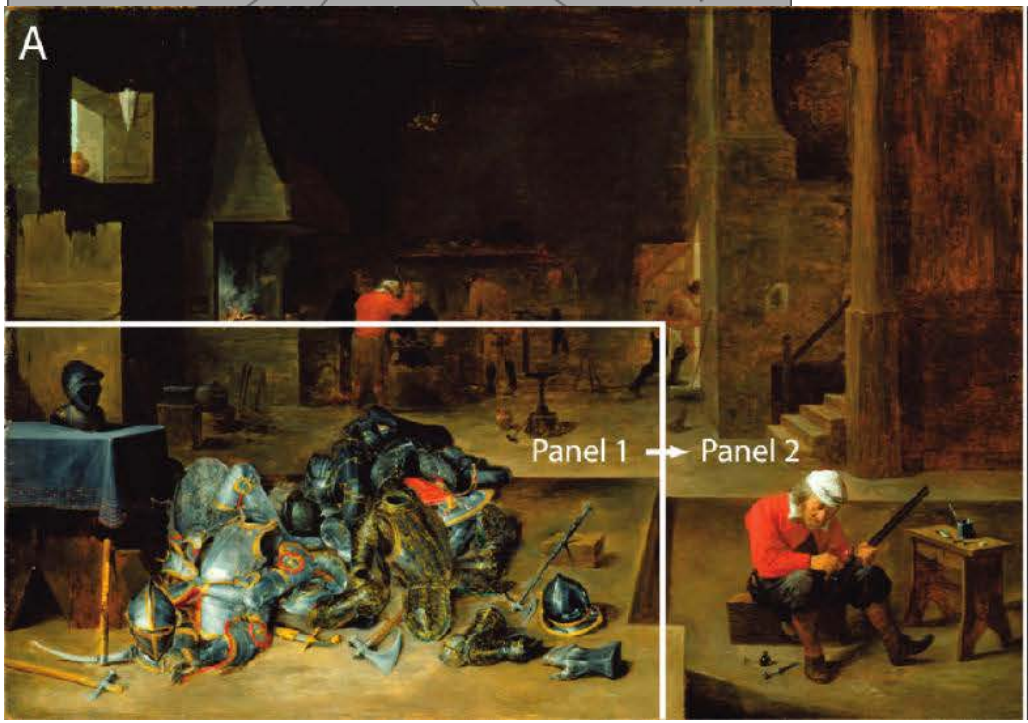
Dendrochronology possible without invasive action.
age circa 1519 for English oak

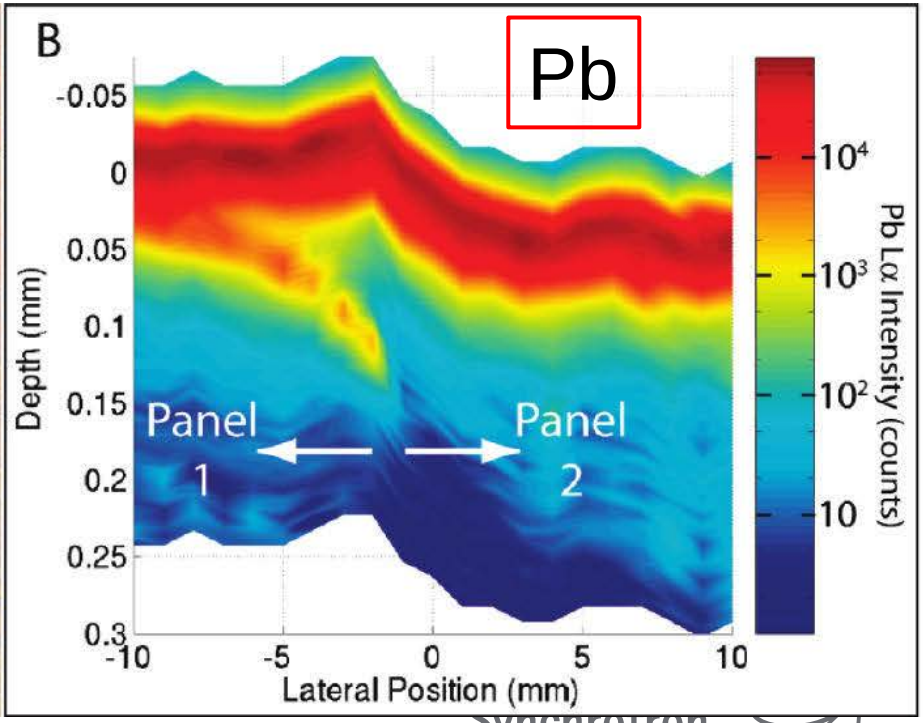
Dredge et al. High-definition synchrotron-sourced x-ray fluorescence mapping of an early Tudor portrait of Henry VIII. Applied Physics A (2015) **121**, 789-900.

Confocal XRF



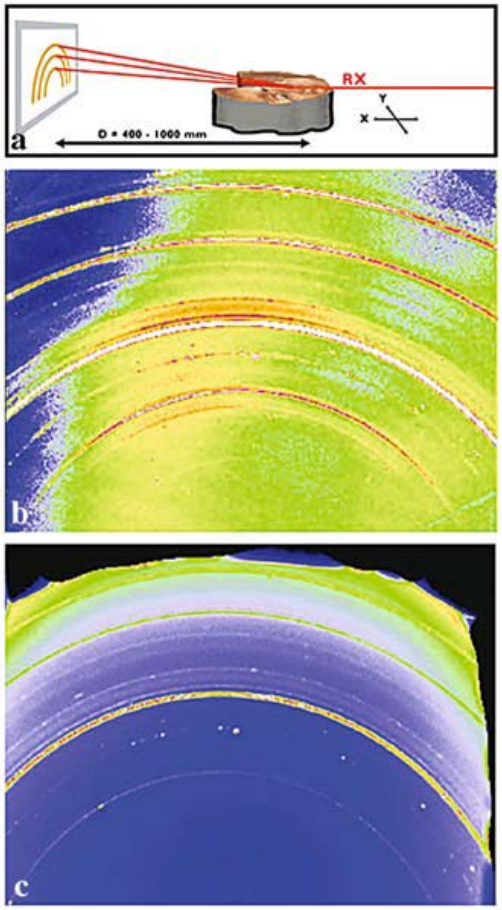
Both source and detector focus on a small volume.
Compositional depth profile is possible.
3D XRF

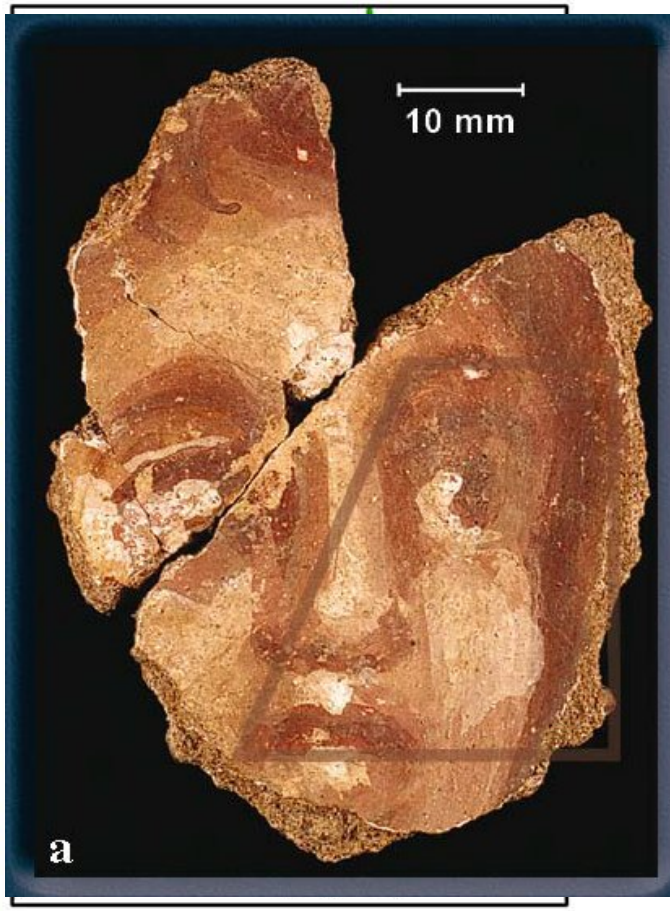


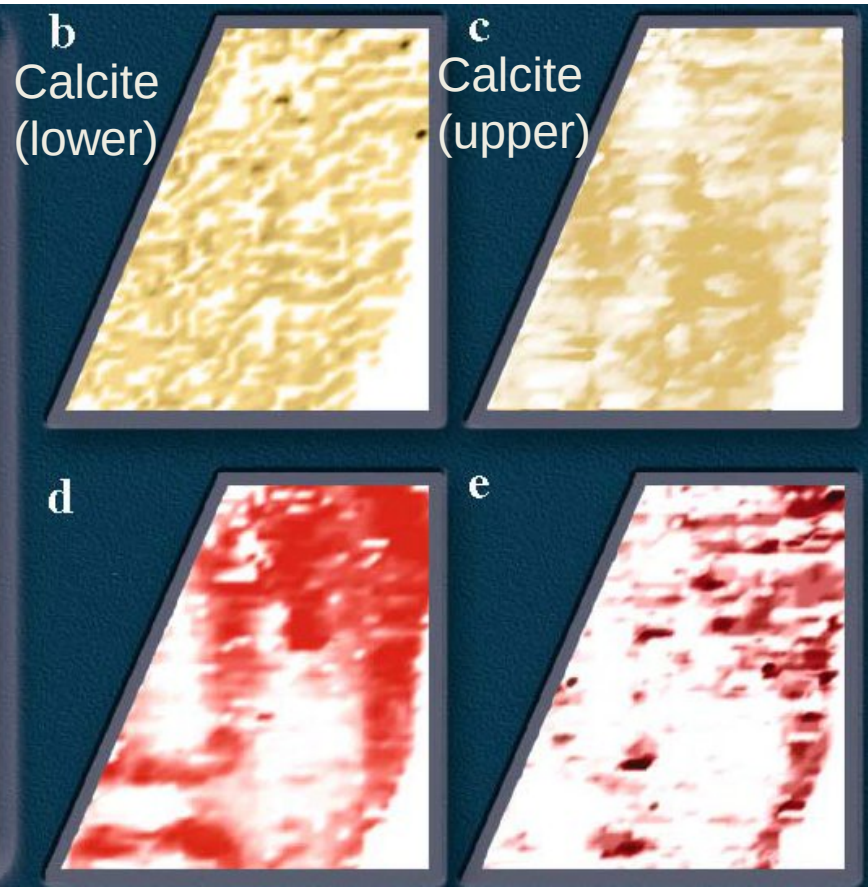


The Armorer's Shop, Woll et al (2008)

X-ray Diffraction







Haematite (Fe_2O_3)

Goethite ($FeO(OH)$)

Identify mineral phases

E. Dooryhee et al. “Non-destructive synchrotron X-ray diffraction mapping of a Roman painting” Appl. Phys. A, 81, 663-667 (2005)

Further References

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U. Bergmann, Archimedes brought to light. Physics World, November 2007, 39-42.

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Favero et al. Reflectance imaging spectroscopy and synchrotron radiation X-ray fluorescence mapping used in a technical study of The Blue Room by Pablo Picasso. Heritage Science (2017) 5:13

Woll et al. The Unique History of The Armorer's Shop. Stud. Cons. 53 (2008) 93-109

Thurrowgood et al. A Hidden Portrait by Edgar Degas. Scientific Reports (2016) 6:29594

Kirkham *et al.* The Maia Spectroscopy Detector System: Engineering for Integrated Pulse Capture, Low-Latency Scanning and Real-Time Processing. AIP Conf. Series 1234 (2010) 240.