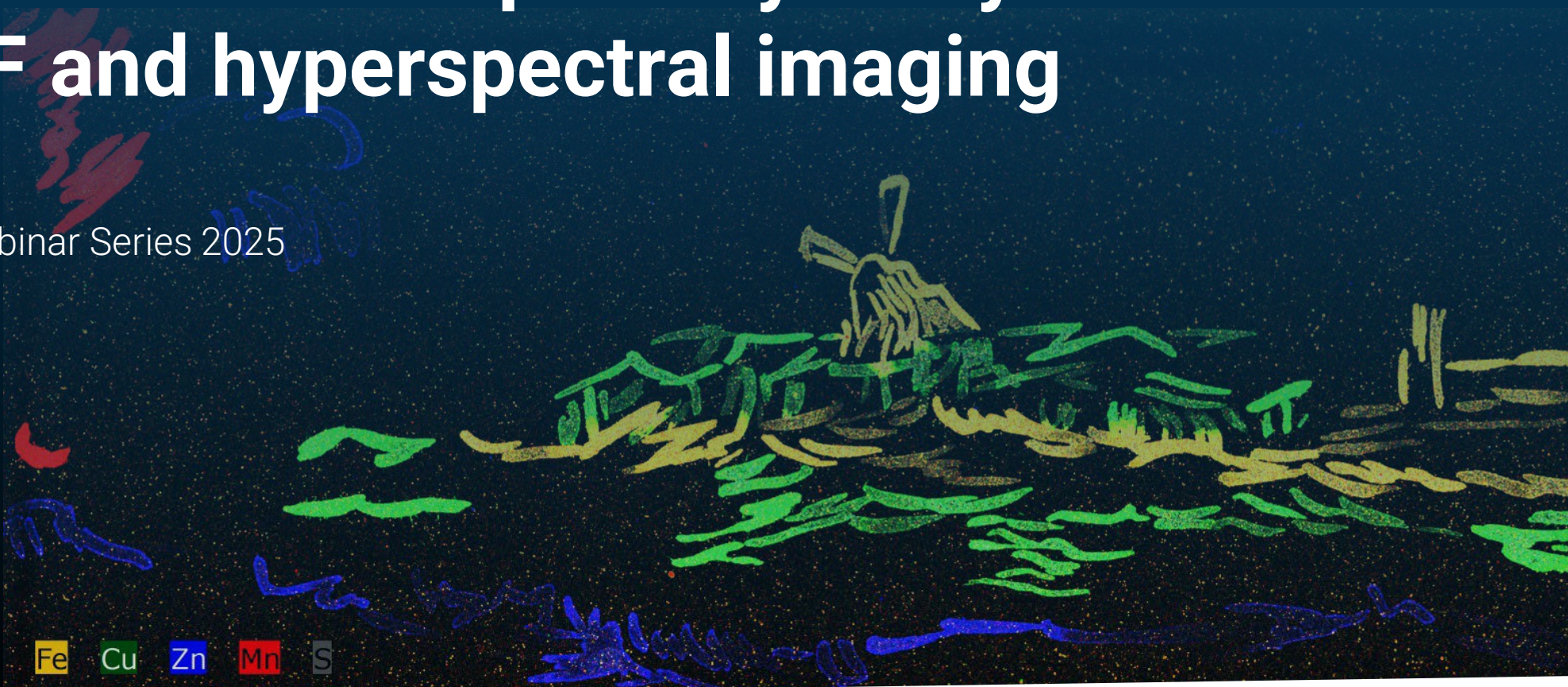


BRUKER PRESENTS: CONSERVING KNOWLEDGE

Non-invasive manuscript analysis by means of micro-XRF and hyperspectral imaging

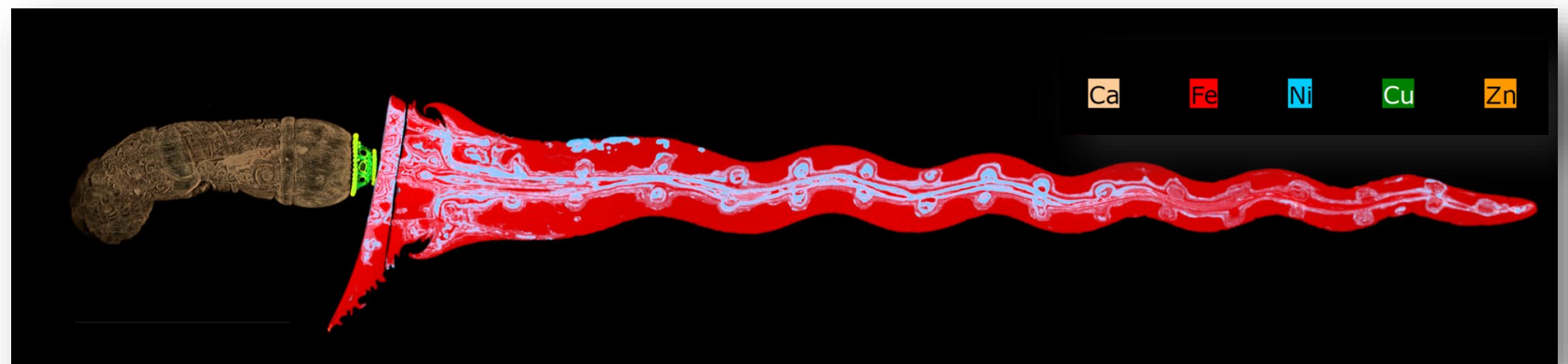
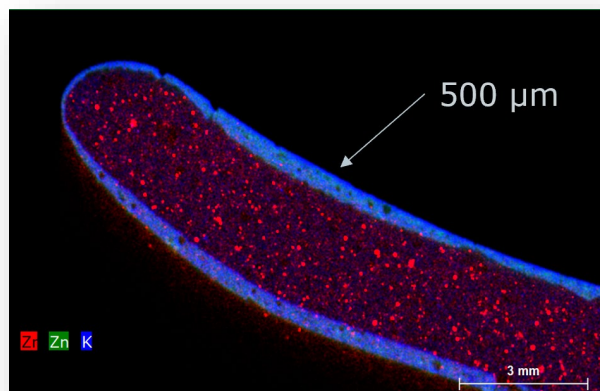
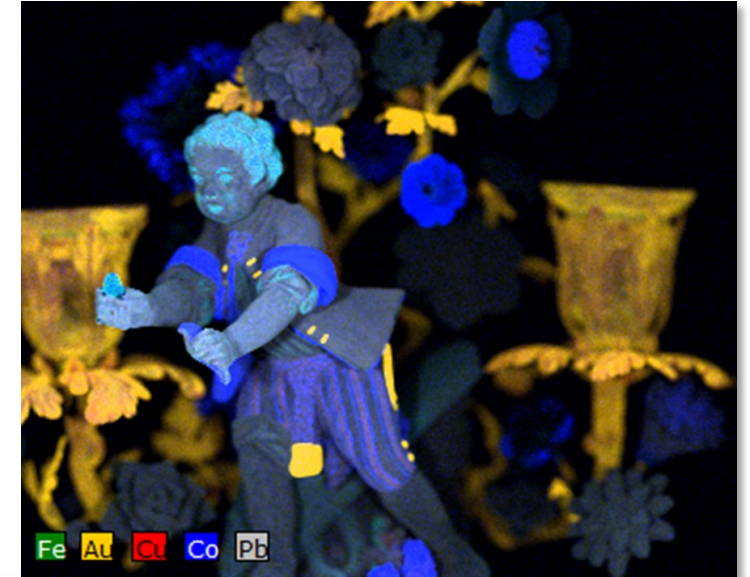
Art & Conservation Webinar Series 2025



Fe Cu Zn Mn S

Art & Conservation Webinar Series Overview

- This webinar discusses the analysis of manuscripts and written Heritage.
- In June 2025, we will dedicate a webinar to the analysis of porcelain and ceramics using micro-XRF.
- In November 2025, we will explore novel approaches to the quantitative analysis of pesticides.



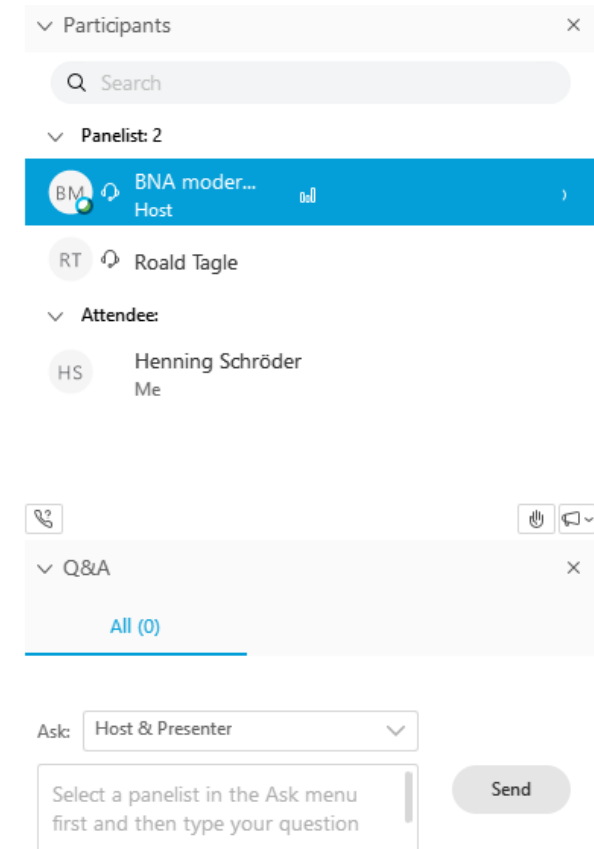


Art & Conservation Webinar Series

Quantification by means of XRF in Cultural Heritage Studies

If you have questions during this webinar,
please **type your questions**, thoughts, or comments in the
Q&A box and **press Send**.

We ask for your understanding, if we do not have time to
discuss all comments and questions within the session.
Any unanswered questions or comments will be answered
and discussed by e-mail or in another WebEx session.



Art & Conservation Webinar Series

The Speakers



Dr. Roald Tagle

- Head of XMP Application, Bruker Nano Analytics, Berlin, Germany



Mareike Gerken M.A.

- Application Scientist XMP for Cultural Heritage, Bruker Nano Analytics, Berlin, Germany

CONSERVING KNOWLEDGE: NON-INVASIVE MANUSCRIPT ANALYSIS

An introduction to Historical writing inks

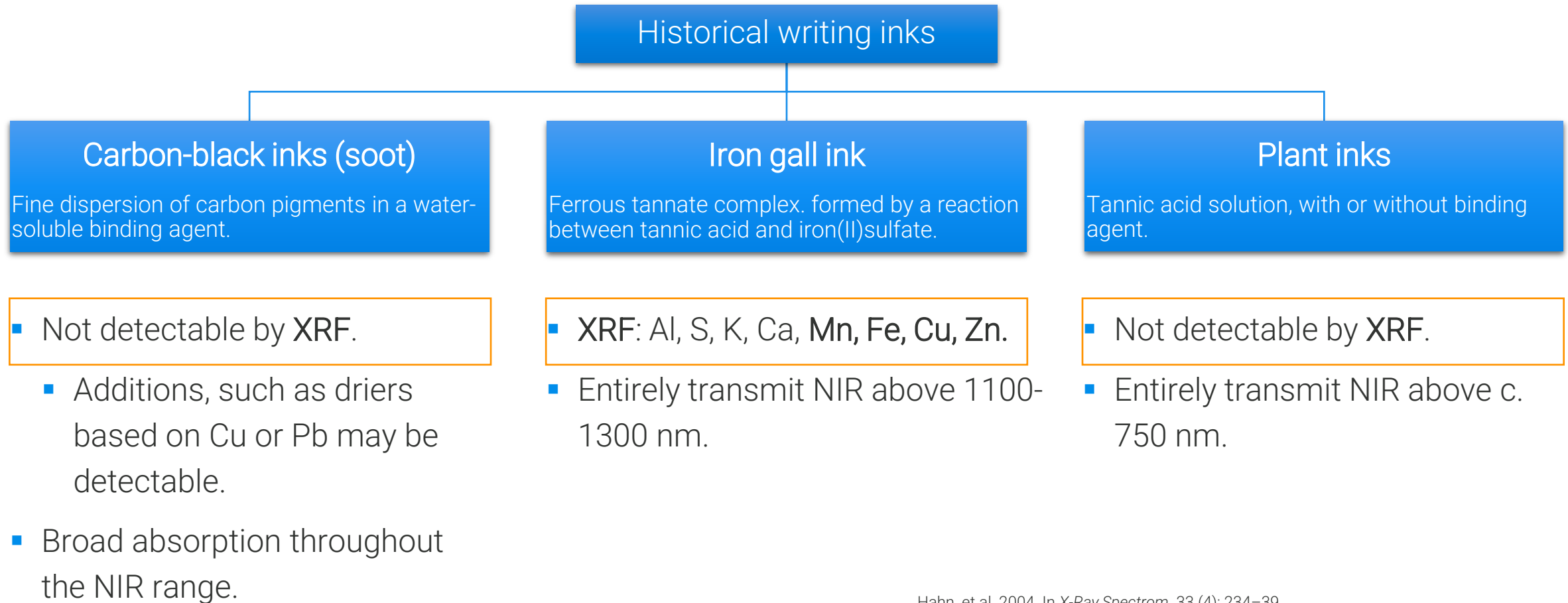
An introduction to Historical writing inks



- Oldest preserved documents are written in Carbon inks.
 - China 3rd millennium BCE.
 - Ancient Egypt.
 - Medieval manuscripts.
- Chemical reaction known in antiquity.
- First identifications 3rd /4th c. CE.
- From Middle Ages to 19/20th cent. It is the most common ink in Europe.
- Theophilus 12th cent. treatise *De diversis artibus*: thorn bark ink.
- Also identified in Near East MS.

Hahn, et al. 2004. In *X-Ray Spectrom.* 33 (4): 234–39.
 Krekel, Christoph. 1999. In *International Journal of Forensic Document Examiners* 5: 54–58.
 Nehring et al. 2021. In *Archaeological and Anthropological Sciences.* 13:71.
 Rabin, Ira. 2021. In *Traces of Ink*, ed. L. Raggetti, 70–78. Experiences of Philology and Replication: Brill.

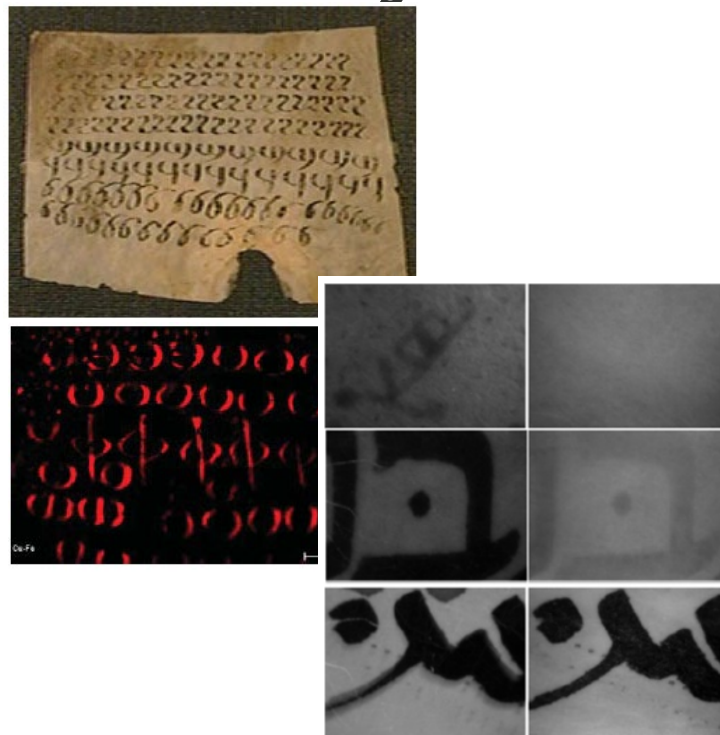
An introduction to Historical writing inks



Hahn, et al. 2004. In *X-Ray Spectrom.* 33 (4): 234–39.
 Krekel, Christoph. 1999. In *International Journal of Forensic Document Examiners* 5: 54–58.
 Nehring et al. 2021. In *Archaeological and Anthropological Sciences.* 13:71.
 Rabin, Ira. 2021. In *Traces of Ink*, ed. L. Raggetti, 70–78. Experiences of Philology and Replication: Brill.

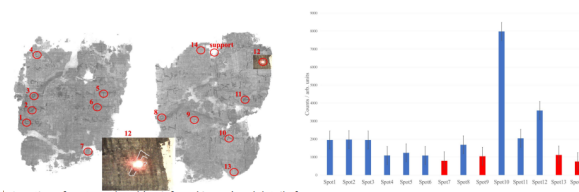
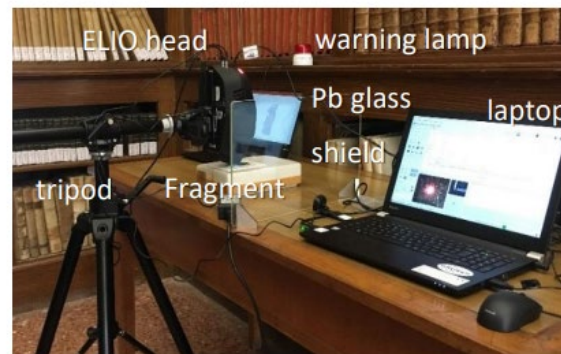
An introduction to XRF for the study of historical writing inks

Identifying and classifying historical writing inks



Rabin et al. 2012. In *COMSt* 3: 26-30.
 Rabin, Ira. 2021. In *Traces of Ink*, ed. L. Raggetti, 70–78. Experiences of Philology and Replication: Brill.

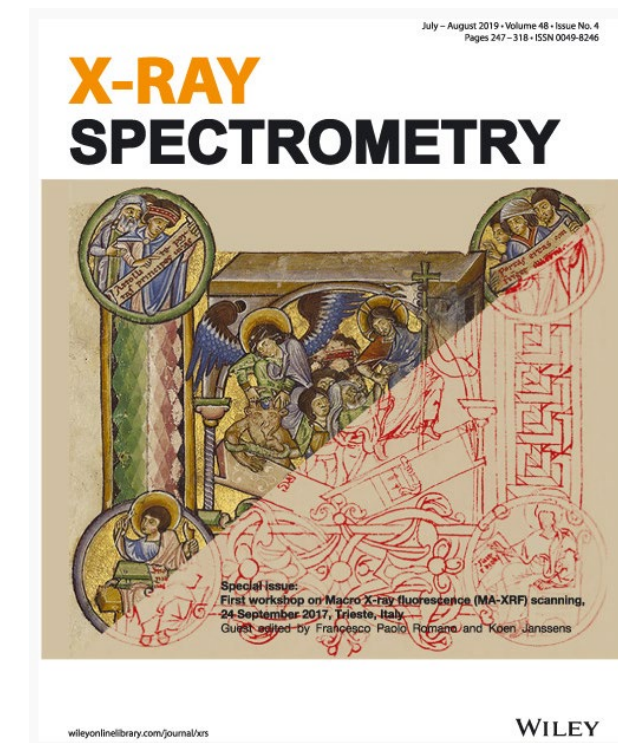
Carbonized papyrus scrolls from Herculaneum



Location of spots analysed (on infrared image) and detail of spot 12 (taken from the Elio in-built camera during analysis) for PHERC. 254. Infrared image by S.W. Booras (Chabries et al. 2003). © National Library, Naples - Brigham Young University, Provo (USA).

Bonnerot et al. 2025 (Poster) *International Symposium on Archaeometry*.

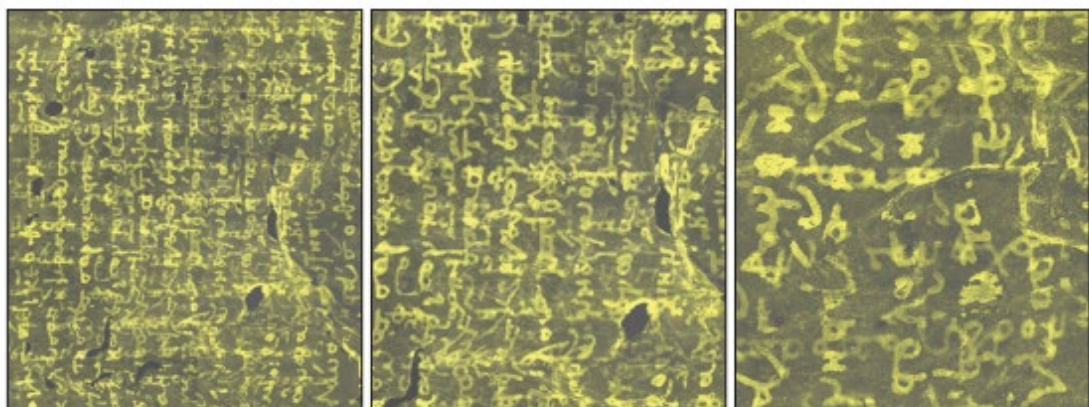
Underdrawings below MS illuminations



Turner et al. 2018 *X-Ray Spectrom.* 48: 4 251–261. DOI 10.1002/xrs.2956.

An introduction to XRF for the study of historical writing inks

Visualizing palimpsests



Archimedes brought to light

Uwe Bergmann describes how physicists have used X-ray fluorescence to uncover some of Archimedes' oldest writings that were hidden from sight in an ancient medieval prayer book

Bergmann, Uwe 2007 *Phys. World* 20 (11) 39. DOI 10.1088/2058-7058/20/11/39


Provenance analysis using elemental ratios

X-RAY SPECTROMETRY



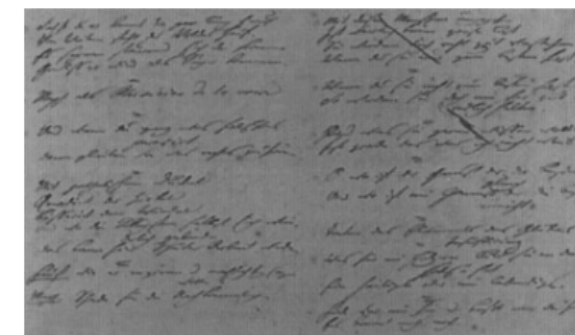
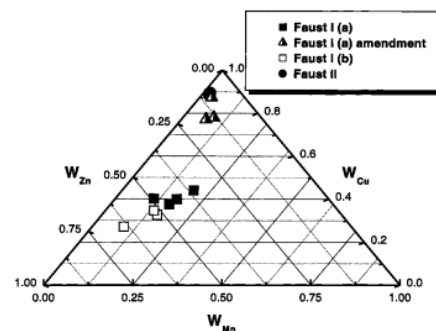
Research Article

Characterization of iron-gall inks in historical manuscripts and music compositions using x-ray fluorescence spectrometry[†]

O. Hahn , W. Malzer, B. Kanngiesser, B. Beckhoff

First published: 10 February 2004 | <https://doi.org/10.1002/xrs.677>  | Citations: 88

[†] Presented at the European Conference on EDXRS, Berlin, Germany, 16–21 June 2002



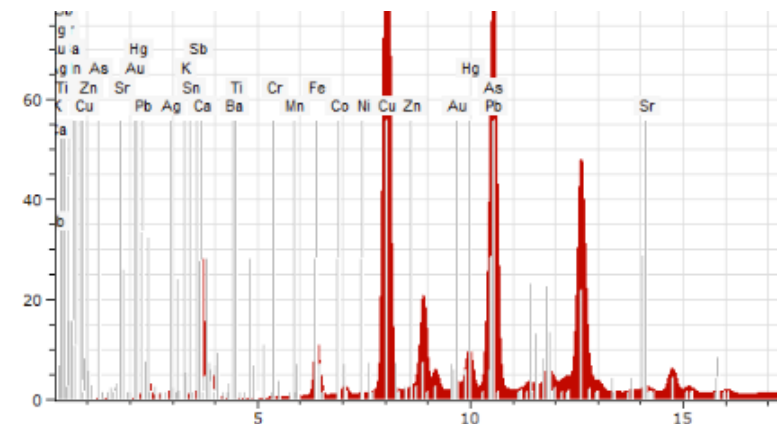
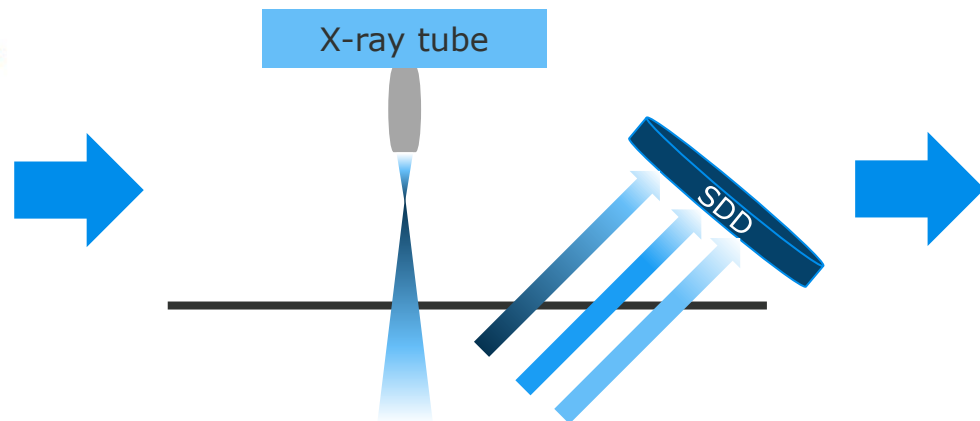
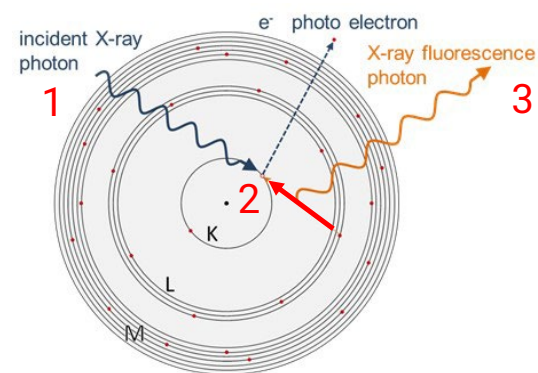
Hahn et al. 2004 *X-Ray Spectrom.* 33: 234–239. DOI 10.1002/xrs.677

CONSERVING KNOWLEDGE: NON-INVASIVE MANUSCRIPT ANALYSIS

All instruments at hand XRF devices for manuscript analysis



An introduction to Spatially resolved micro-X-ray fluorescence analysis



XRF, Art and Collections Management

Mapping



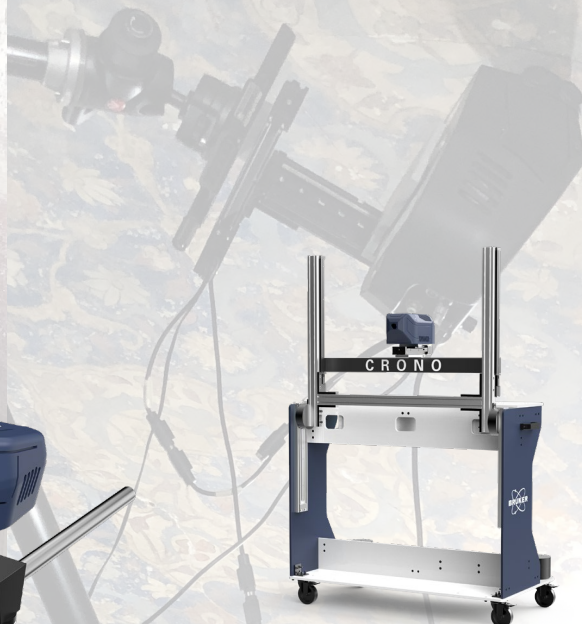
Spot



TRACER



ELIO



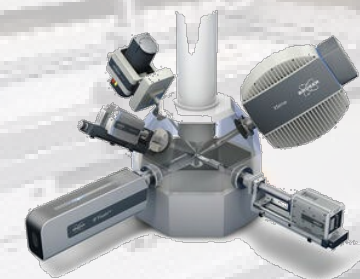
CRONO



M6
JETSTREAM

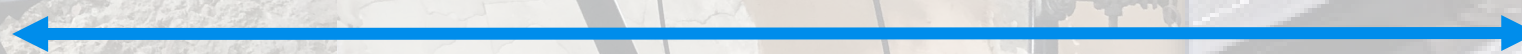


M4 TORNADO



SEM
EDS-WDS- μ XRF

Portable



Lab based

Instrumentation TRACER 5

The standard in
handheld-XRF
analysis for
cultural heritage



Instrumentation

ELIO

Flexibility of approach and positioning – ideal for different objects on-site and in the lab



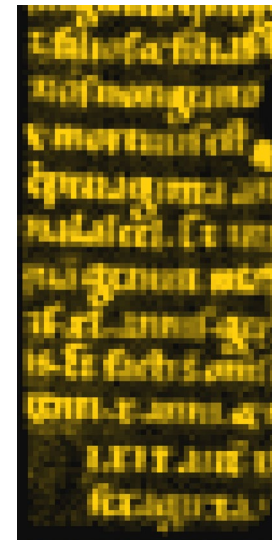
20 kV 200 μ A, 1 mm spot, c. 5 h
1 mm pixel size, 2 s dwell time



Mesoamerican manuscripts, Bodleian Library Oxford (see *Grazia et al. 2019*)



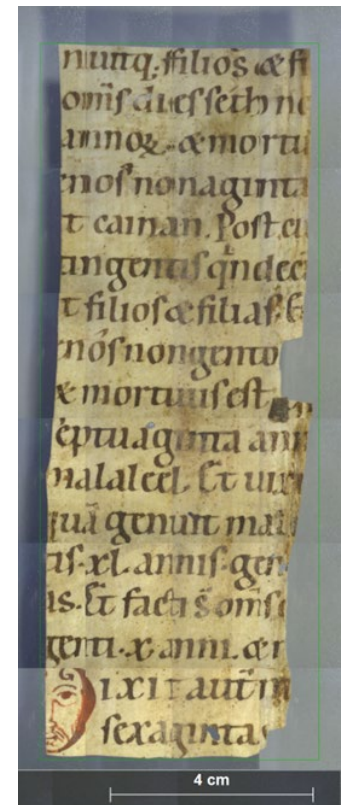
Ca



Fe



Hg

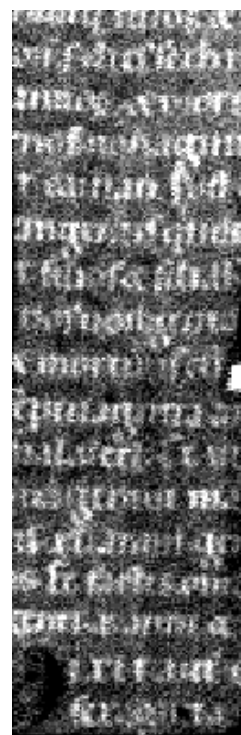
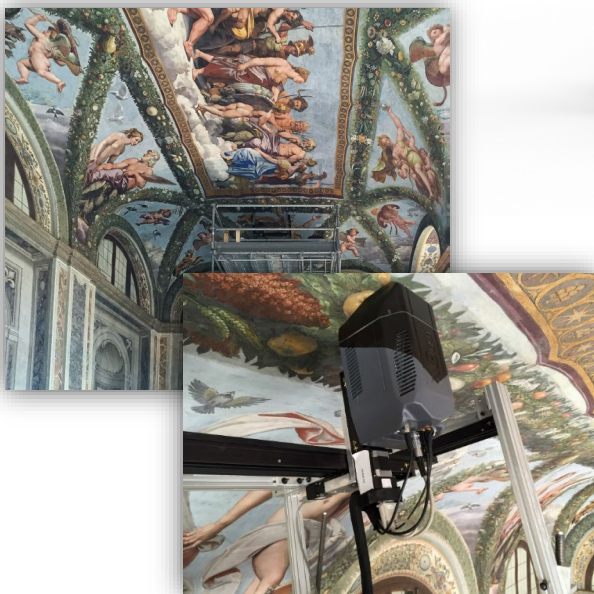


Instrumentation CRONO

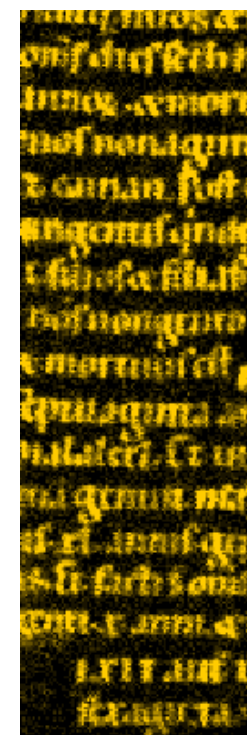
Trolley or frame mounted - lightweight for mobile positioning while retaining mapping micro-XRF capabilities



20 kV 200 μ A, c. 1 h
500 μ m pixel, 100 ms/px



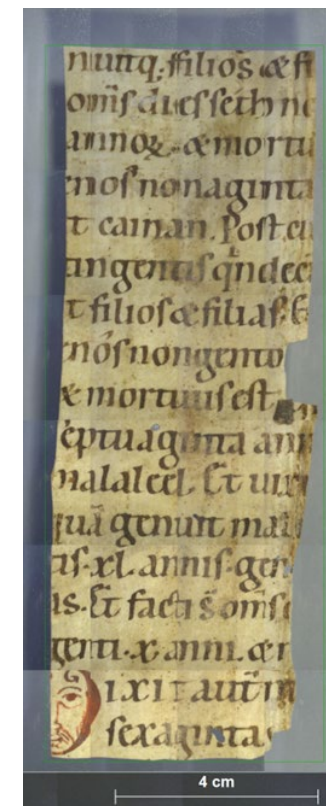
Ca



Fe



Hg

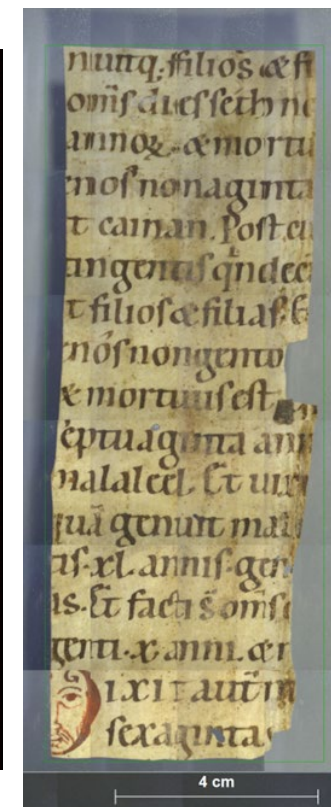
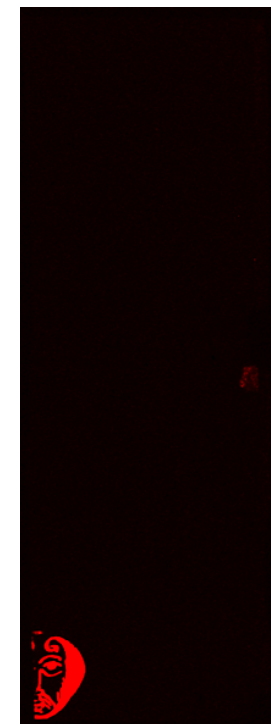
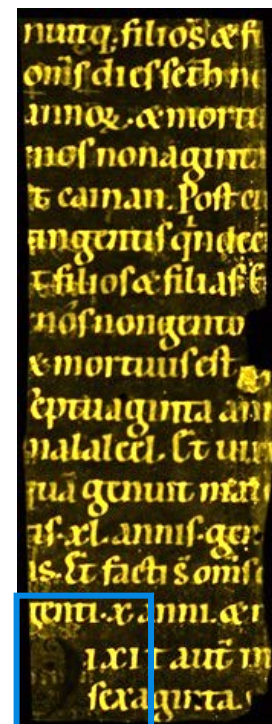
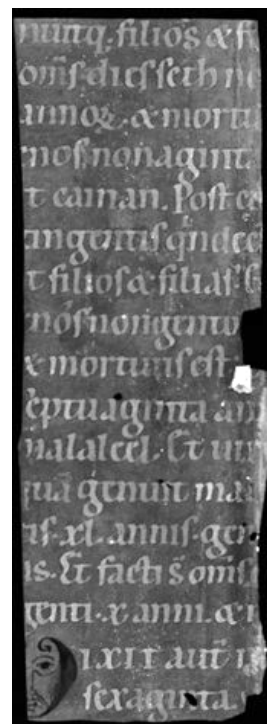
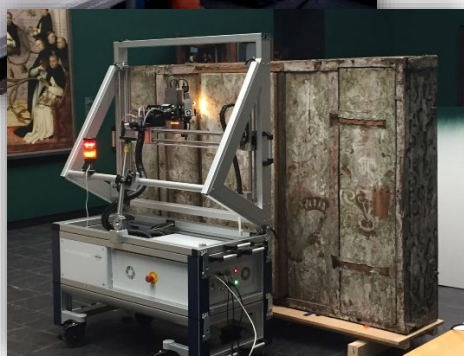


Instrumentation M6 JETSTREAM

Museum- & lab-based mapping solution with large scan area and high resolution.



35 kV 800 μ A, 40 μ m spot, c. 8 h
50 μ m pixel, 20 ms/px



Ca

Fe

Hg

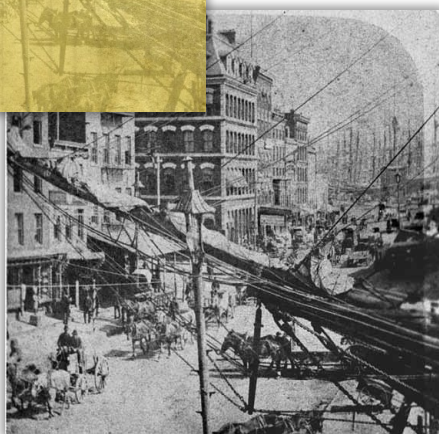
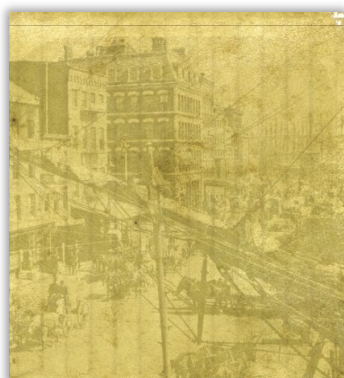
Instrumentation

M4 TORNADO

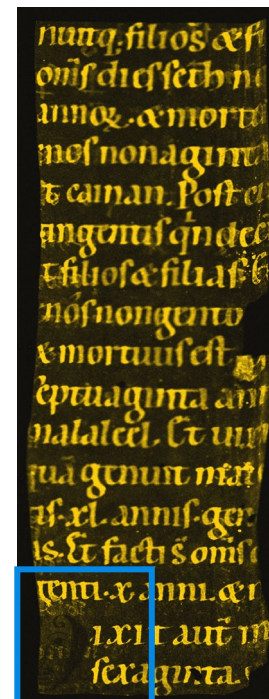
Smallest spot and high light element sensitivity with special atmospheres



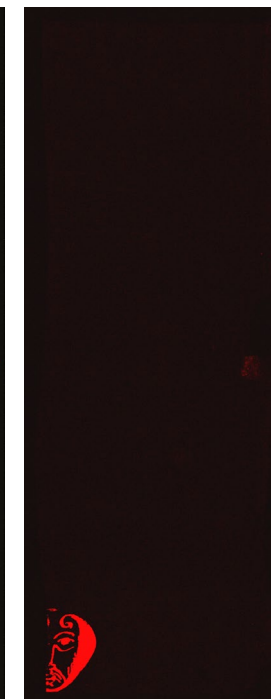
50 kV 600 μ A, 20 μ m spot, c. 10 h
50 μ m pixel, 10 ms/px



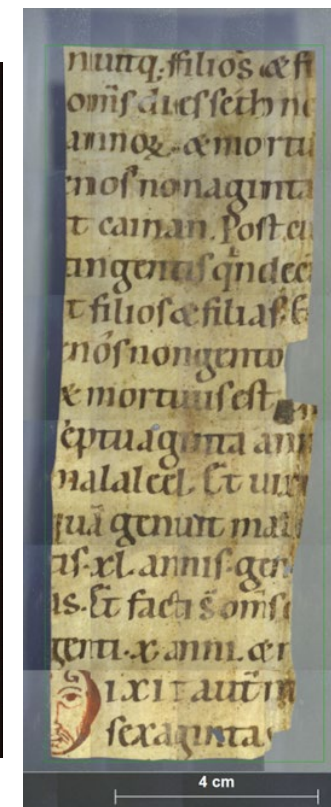
Ca



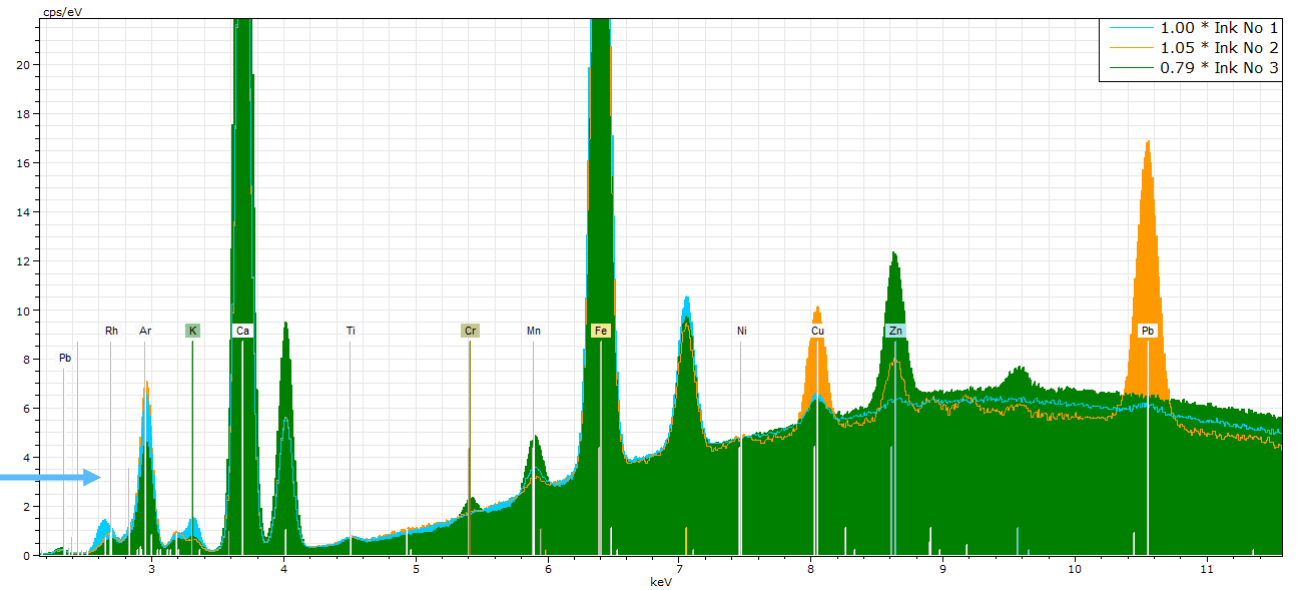
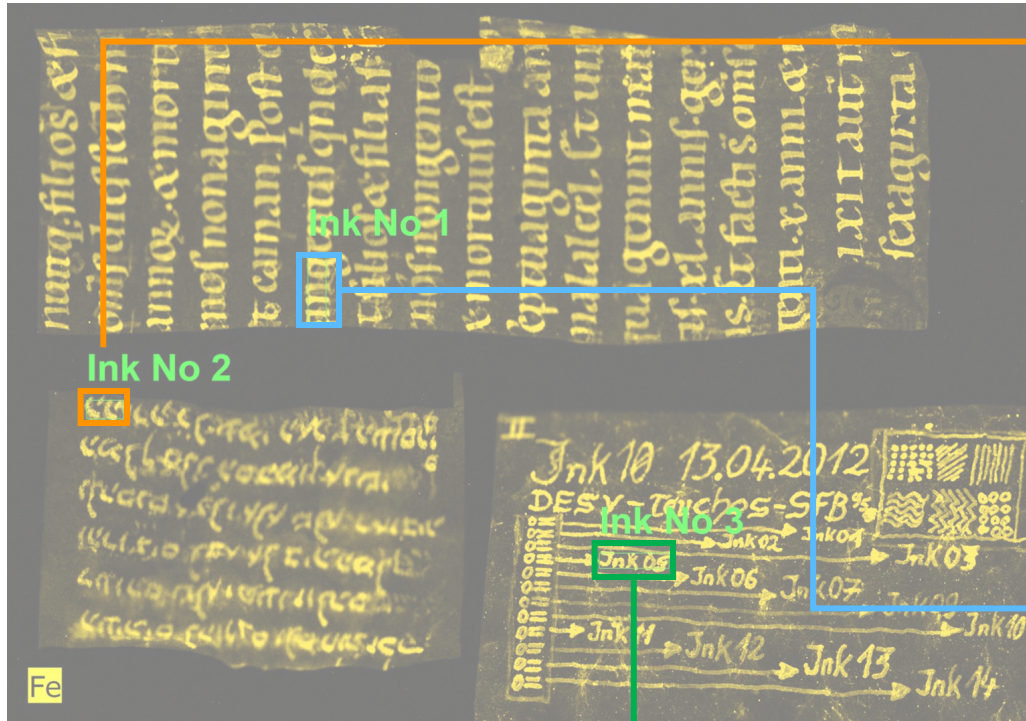
Fe



Hg

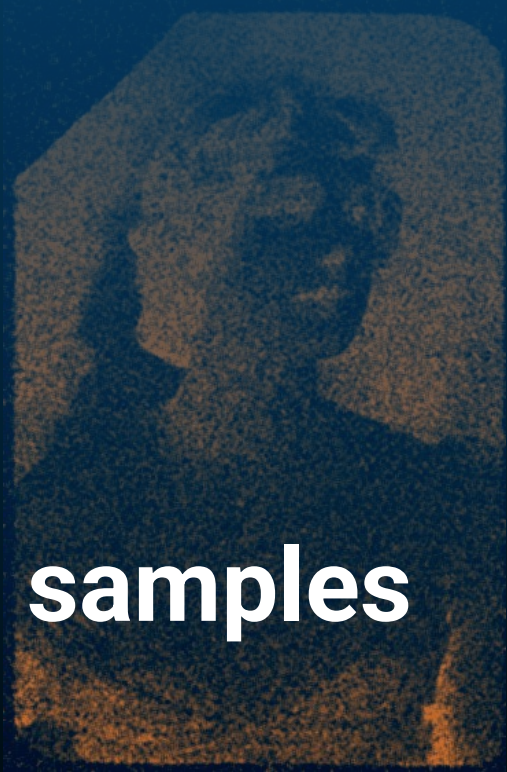
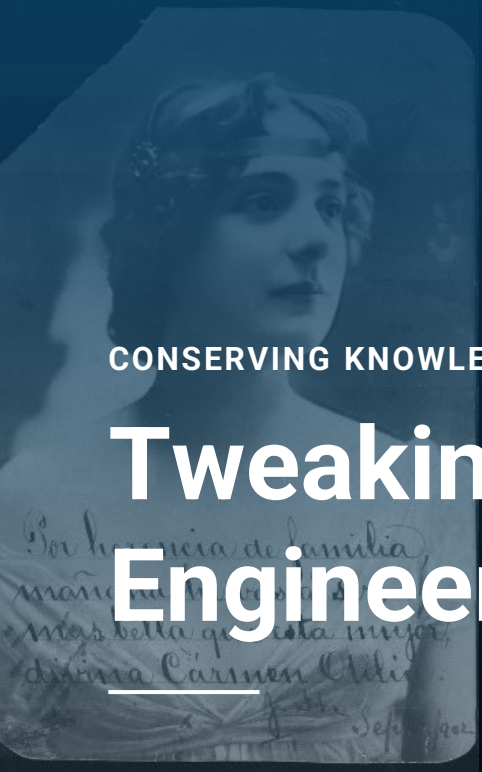


Sophisticated software options Enhanced data processing features



CONSERVING KNOWLEDGE: NON-INVASIVE MANUSCRIPT ANALYSIS

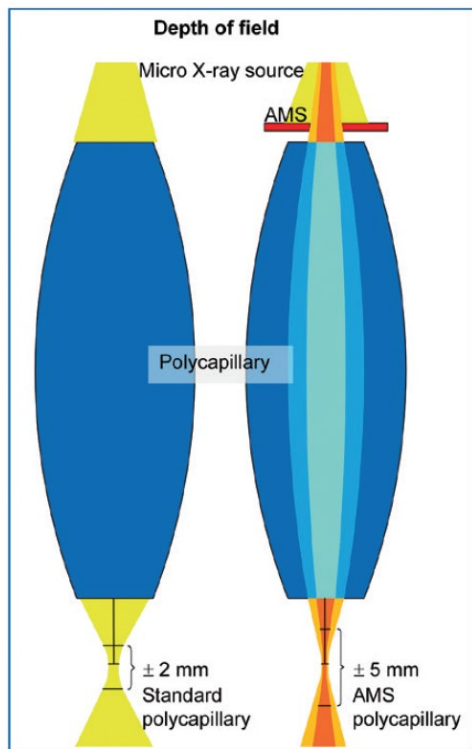
Tweaking the machine: Engineering specials for special samples



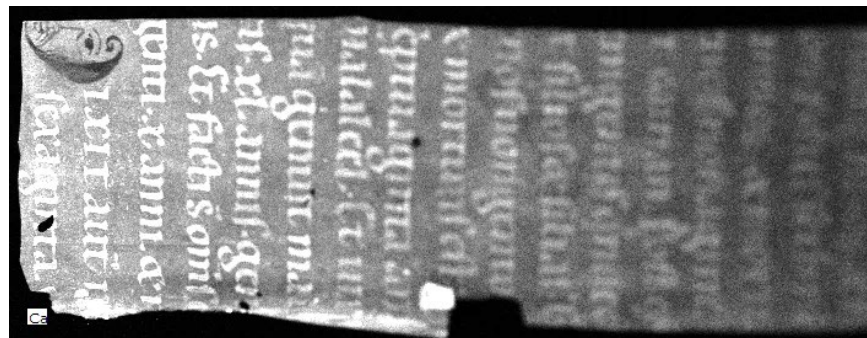
The Aperture Management system (AMS) Maintaining a high spatial resolution in areas out of focus



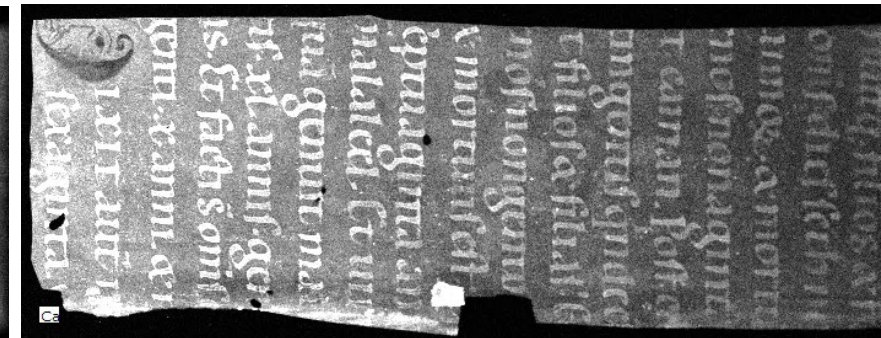
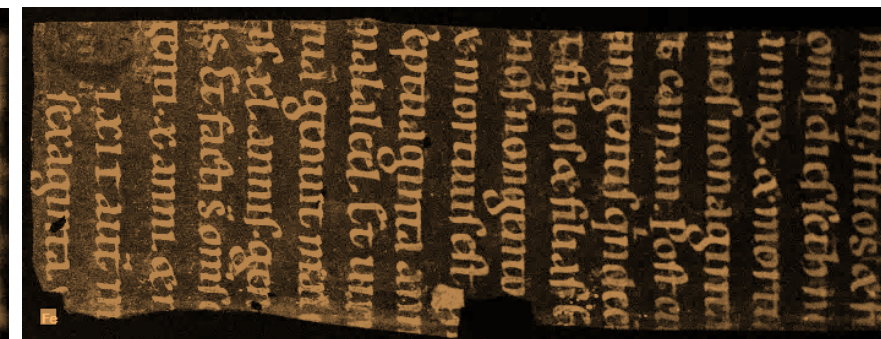
The AMS is a patented solution that reduces the divergency of the polycapillary beam. Because it reduces the photon flux, it is only integrated into 2x 60 mm² SDD systems.



No AMS

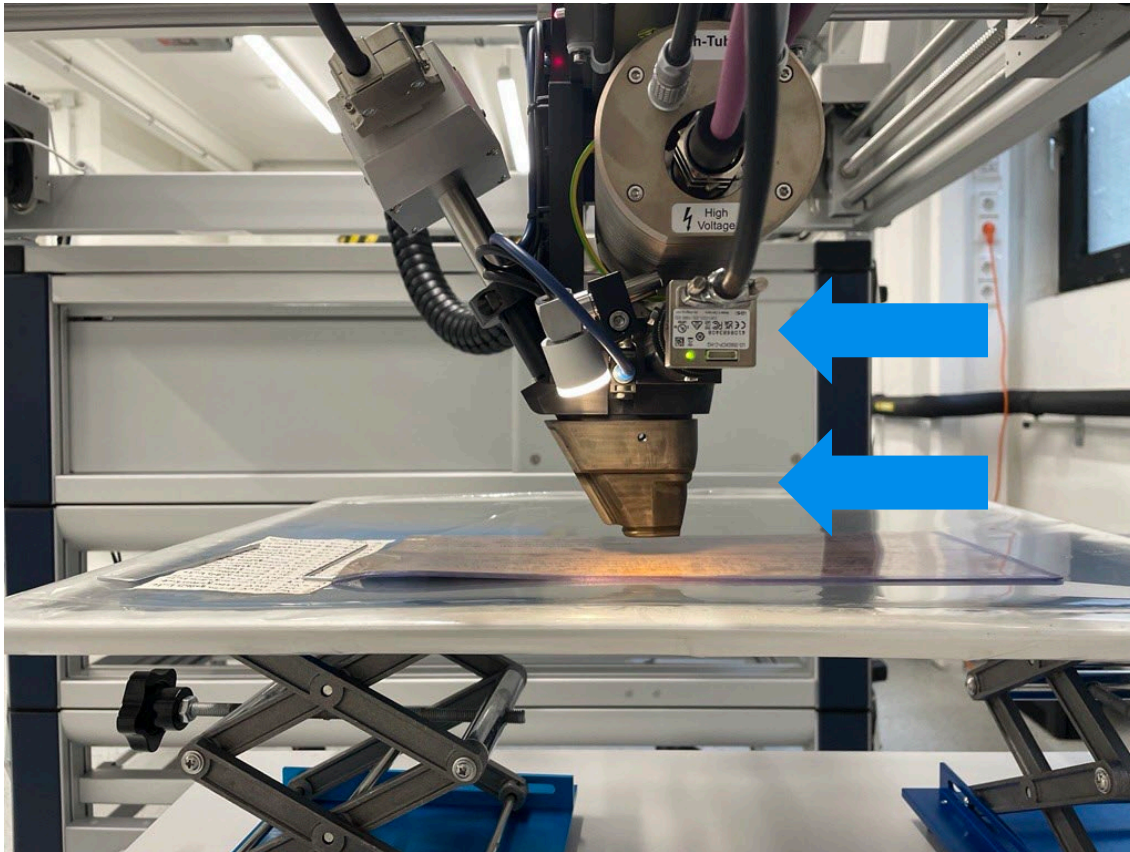


AMS 500



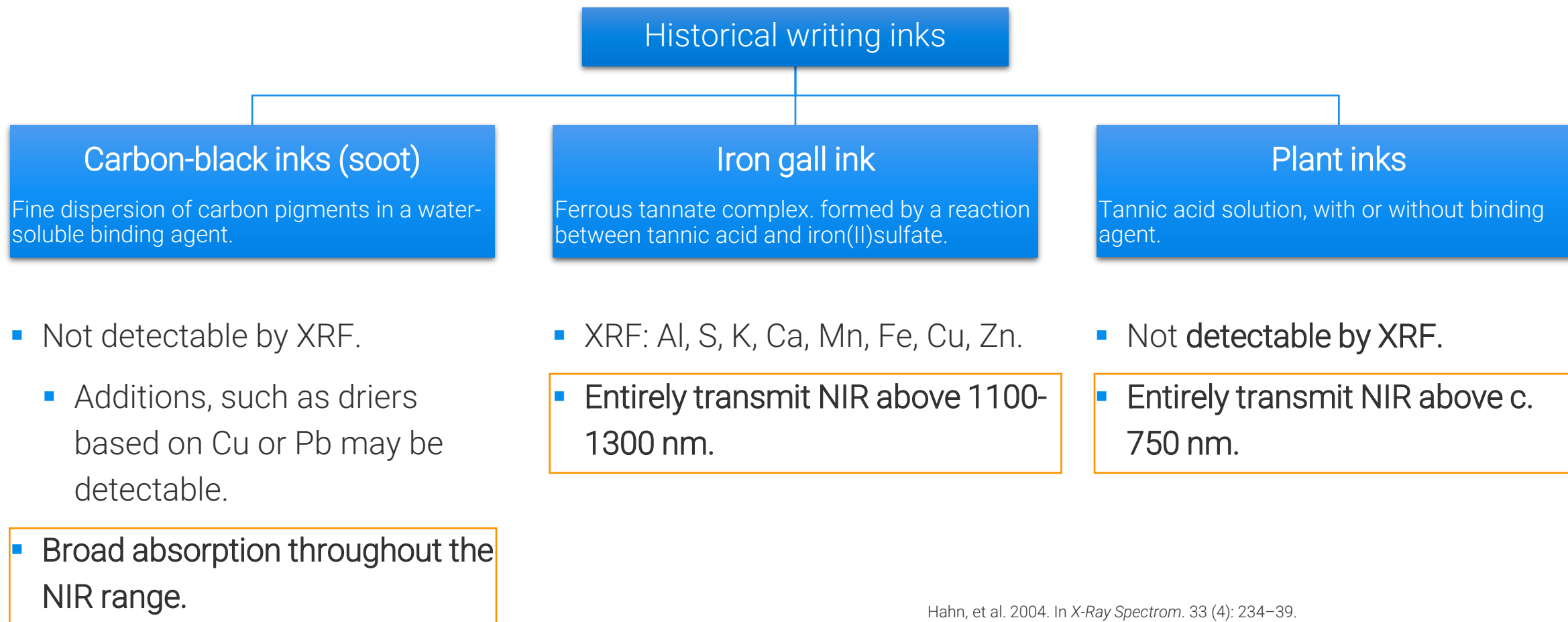
Manuscript sample out of focus (~2 cm).

Modifying the set-up of the probe Conducting measurements in areas difficult to reach



By NYC Wanderer (Kevin Eng) - originally posted to Flickr as Gutenberg Bible, CC BY-SA 2.0, <https://commons.wikimedia.org/w/index.php?curid=9914015>

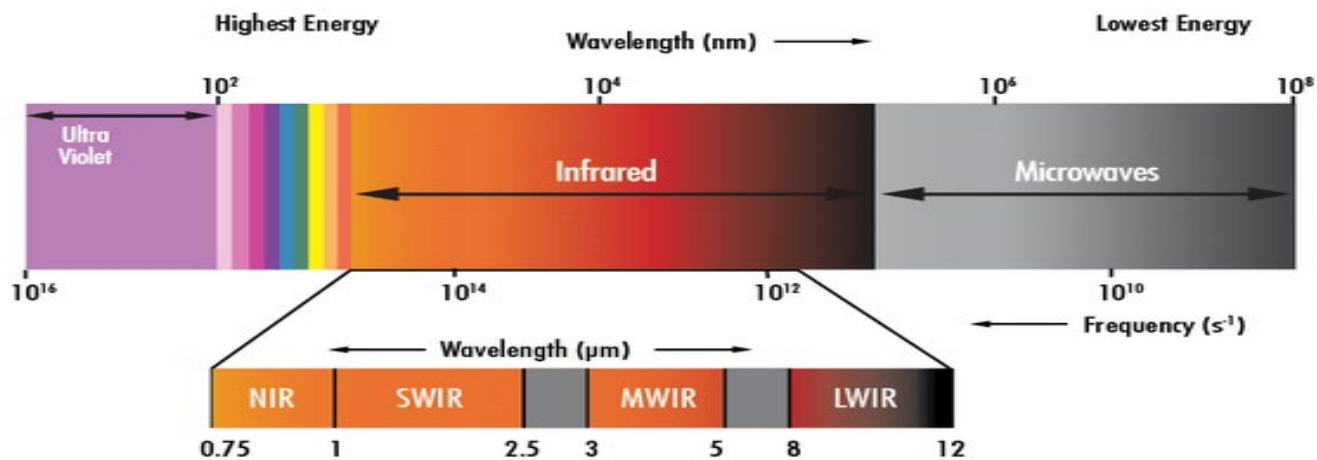
An introduction to Historical writing inks



Hahn, et al. 2004. In *X-Ray Spectrom.* 33 (4): 234–39.
 Krekel, Christoph. 1999. In *International Journal of Forensic Document Examiners* 5: 54–58.
 Nehring et al. 2021. In *Archaeological and Anthropological Sciences.* 13:71.
 Rabin, Ira. 2021. In *Traces of Ink*, ed. L. Raggetti, 70–78. Experiences of Philology and Replication: Brill.

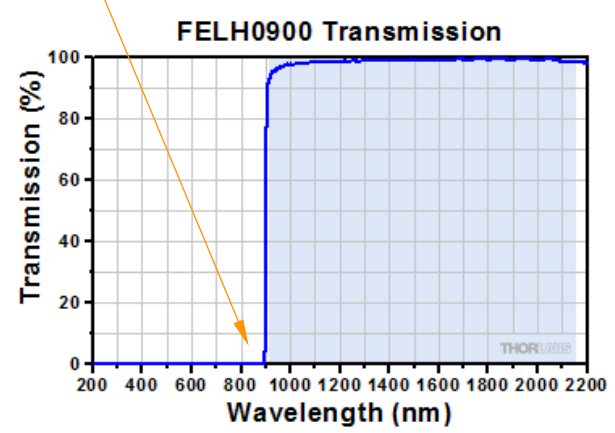
Modifying the illumination of the M6 JETSTREAM

Combining XRF with near infrared transmission properties

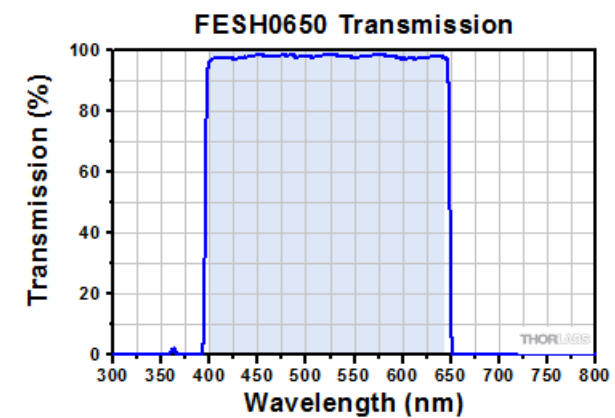


940 nm LED

Longpass-Filter for NIR-Mode



Alternative IR cut filter for VIS mode



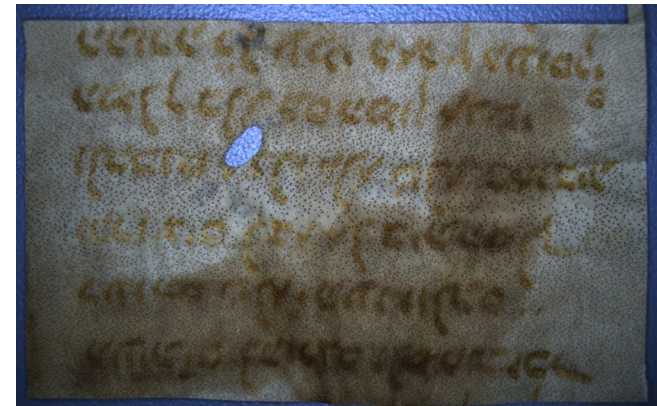
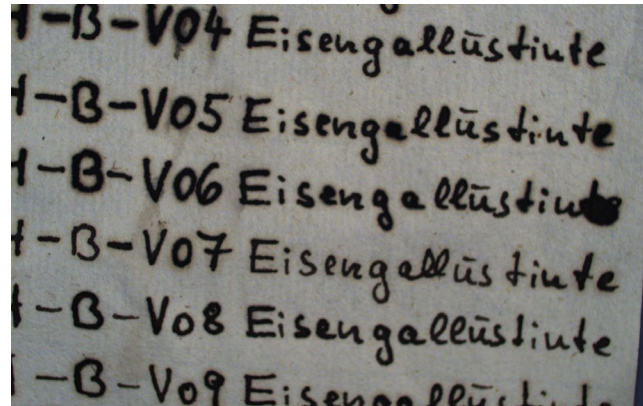
CMOS-Camera without IR cut filter



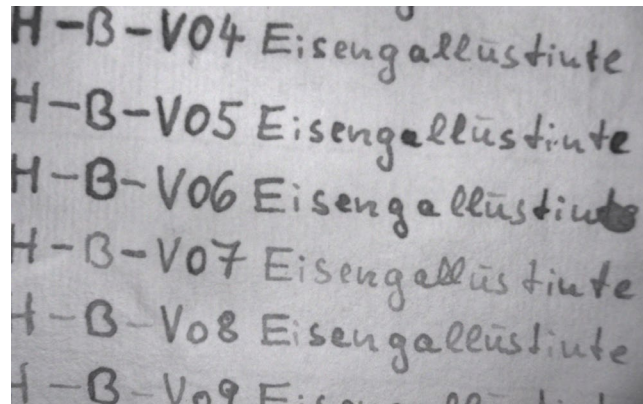
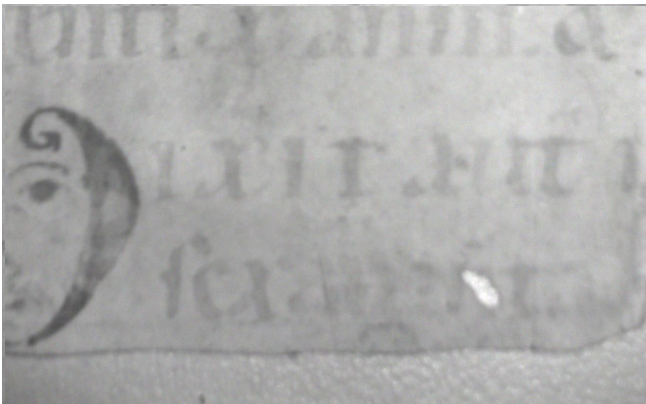
Modifying the illumination of the M6 JETSTREAM Visualising the NIR: Iron gall inks



VIS



NIR



CONSERVING KNOWLEDGE: NON-INVASIVE MANUSCRIPT ANALYSIS

From counting atoms to absolute numbers: Quantitative analysis of iron gall inks

From counting atoms to absolute numbers: Quantitative analysis of iron gall inks

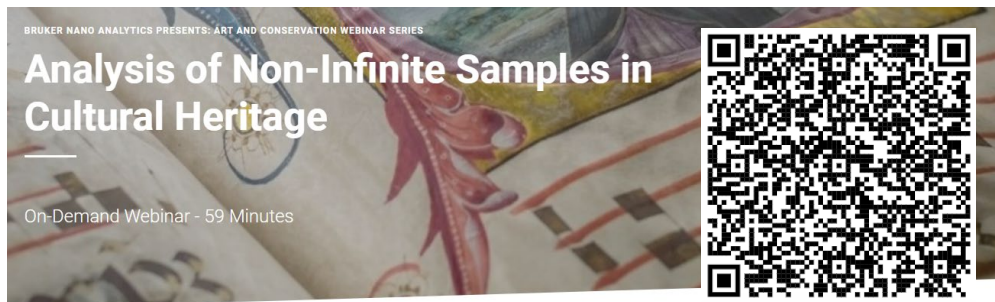
Ink quantification

Standard-based

- Reference materials can be used directly:
 - ✓ to determine the sensitivity of the instrument
 - ✓ and apply these to the unknown sample.
 - ✓ Using the **Standard Addition Method**, matrix effects are negligible.

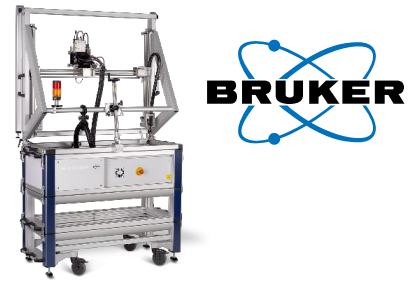
Standard-less

- Calibrations based on **Fundamental parameters** (FP), combined with a **layer analysis software** (XMethod):
 - ✓ Physics are well-described.
 - ✓ FP algorithm includes inter-element effects, such as absorption or secondary excitation!
 - ✓ Determination of mass deposition (g/m^2).



Quantitative analysis of iron gall inks

Standard-based approaches

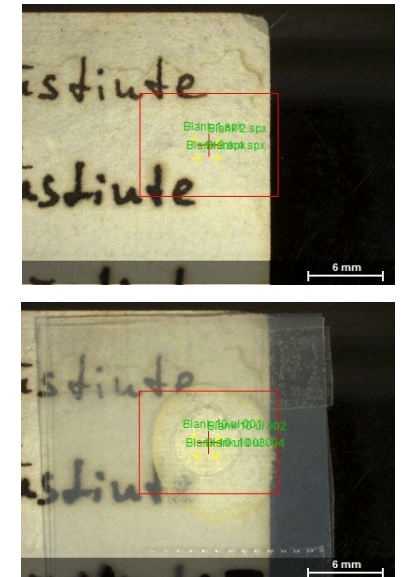
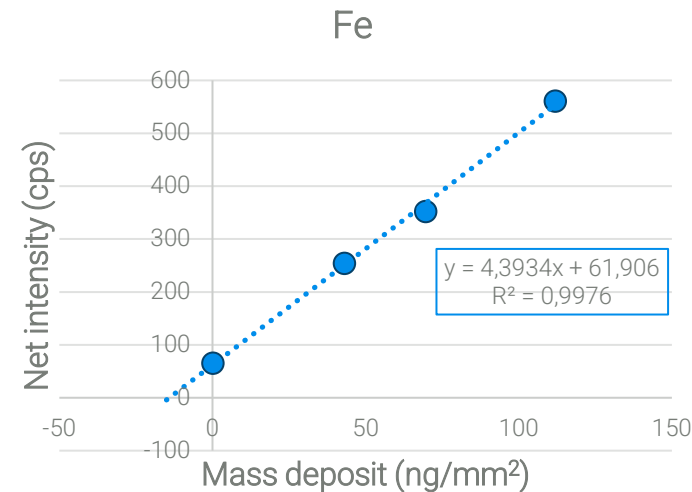


- A multi-element reference sample set was created and the mass deposition (ng/mm^2) determined.
- Thin filter papers loaded with varying amounts of Mn, Fe, Cu and Zn.
- These were placed on a transparent holder leaving the central area uncovered for analysis.

- Four points were measured on the paper with and without the references.
- Using the results from the correlation and knowing that the Blank is not 0 ng/mm^2 , we can determine the instruments sensitivity for the standards and measurement conditions.

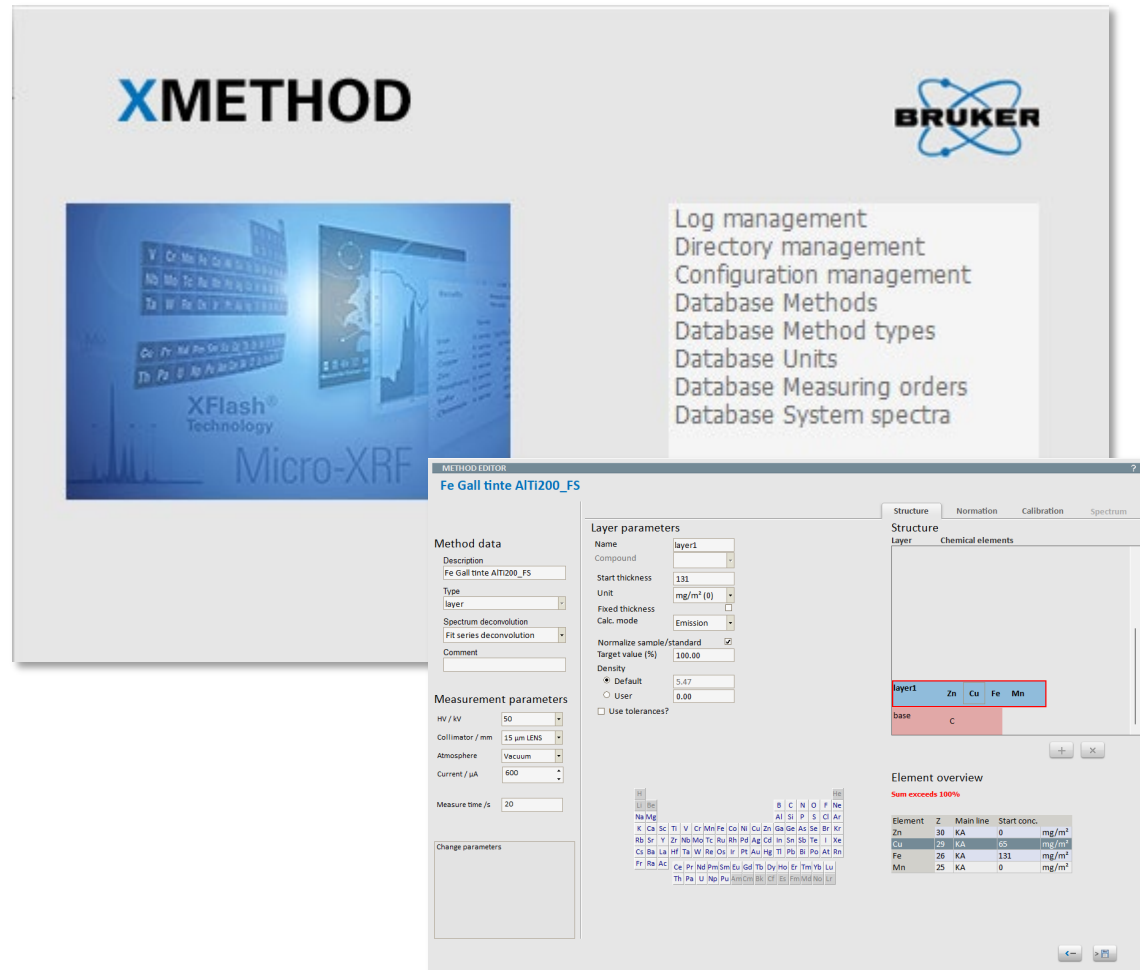


Final set of reference materials.



Quantitative analysis of iron gall inks

Standard-free approaches using XMethod



XMETHOD

BRUKER

Log management
Directory management
Configuration management
Database Methods
Database Method types
Database Units
Database Measuring orders
Database System spectra

METHOD EDITOR
Fe Gall tinte AIT1200_FS

Method data
Description: Fe Gall tinte AIT1200_FS
Type: layer
Spectrum deconvolution: layer
Fit series deconvolution: layer
Comment:

Measurement parameters
HV / kV: 50
Collimator / mm: 15 µm LENS
Atmosphere: Vacuum
Current / µA: 600
Measure time / s: 20

Layer parameters
Name: layer1
Compound:
Start thickness: 131
Unit: mg/m² (0)
Fixed thickness:
Calc. mode: Emission
Normalize sample/standard:
Target value (%): 100.00
Density:
* Default: 5.47
o User: 0.00
 Use tolerances?

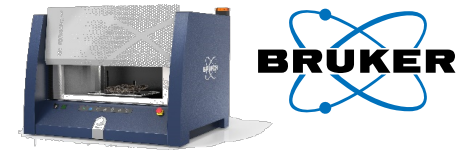
Structure
Layer: Chemical elements
layer1: Zn, Cu, Fe, Mn
base: C

Element overview
Sum exceeds 100%

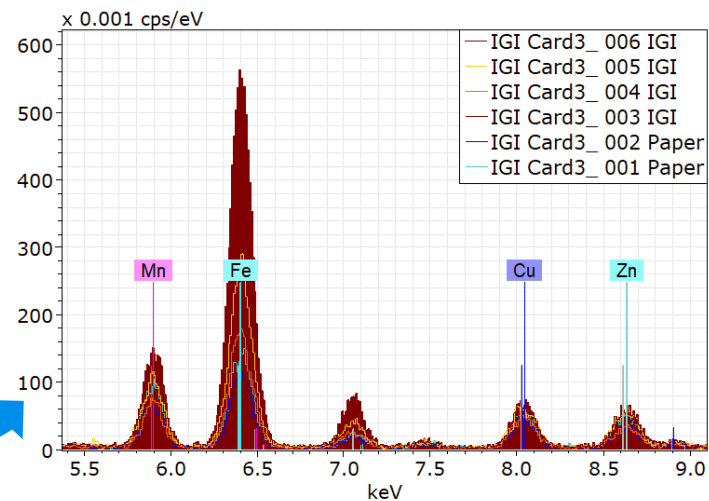
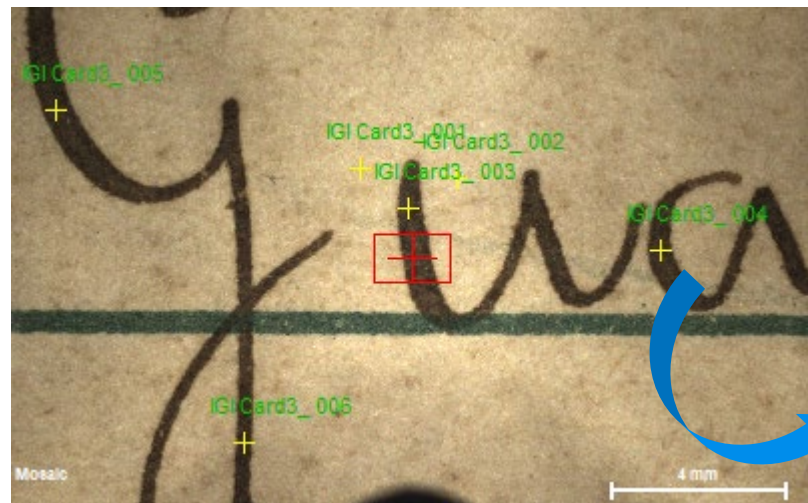
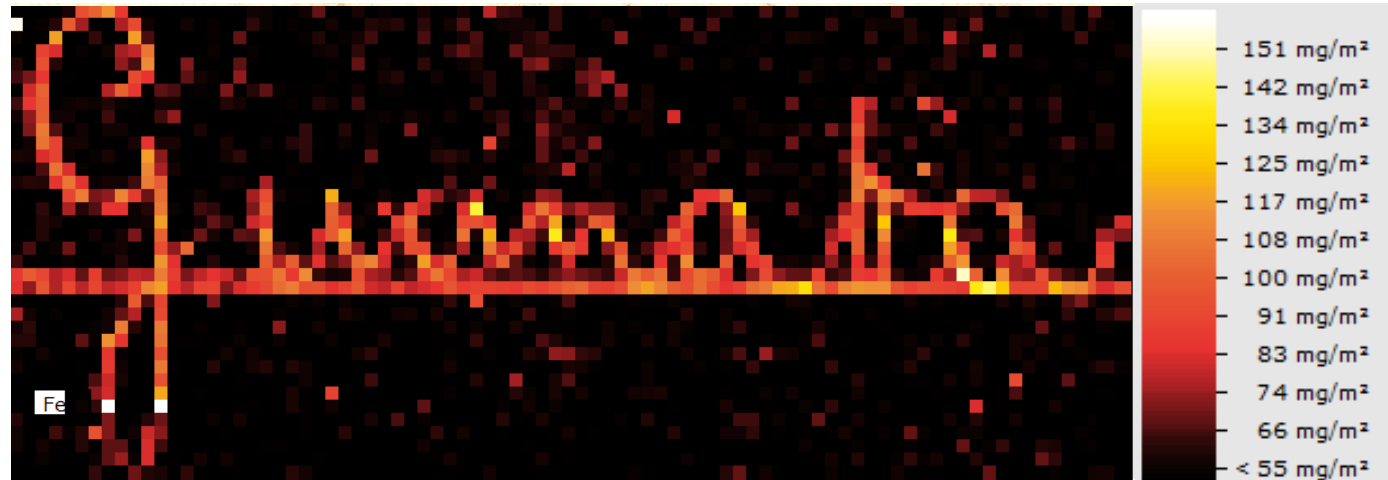
Element	Z	Main line	Start conc.
Zn	30	KA	0 mg/m²
Cu	29	KA	63 mg/m²
Fe	26	KA	131 mg/m²
Mn	25	KA	0 mg/m²

- Bruker's instrument FP calibration is very versatile, but was initially built for bulk analysis of heterogeneous samples.
- **XMethod** is the tool to make 'special bits' Methods for particular tasks. Sometimes it is required
 - to input boundary conditions (layer analysis),
 - or a more empirical approach to calibration might be beneficial.





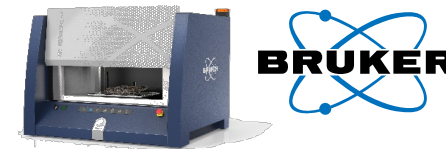
Quantitative analysis of iron gall inks Standard-free approaches using XMethod



TECHNART 2025 ≡

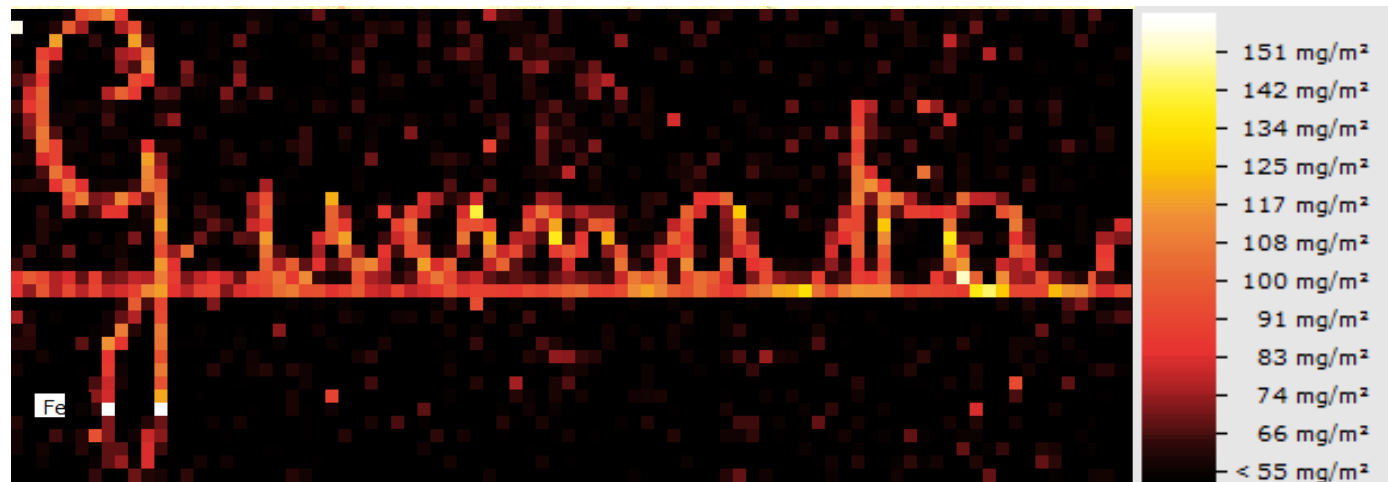
International Conference on Analytical Techniques for Heritage Studies and Conservation.

Perugia, Italy
6th–9th May, 2025

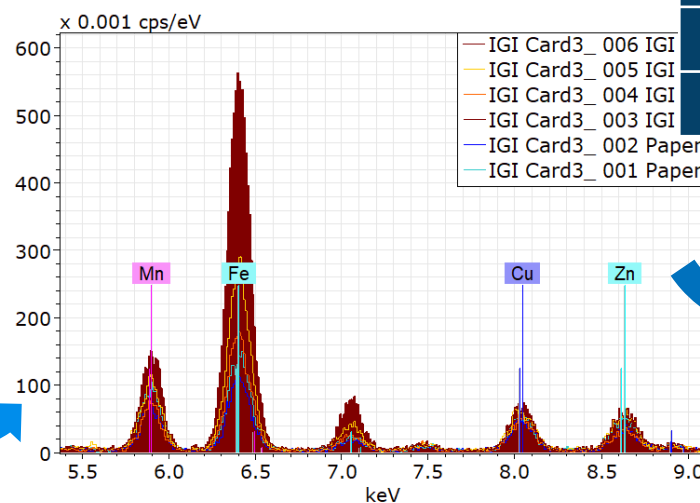
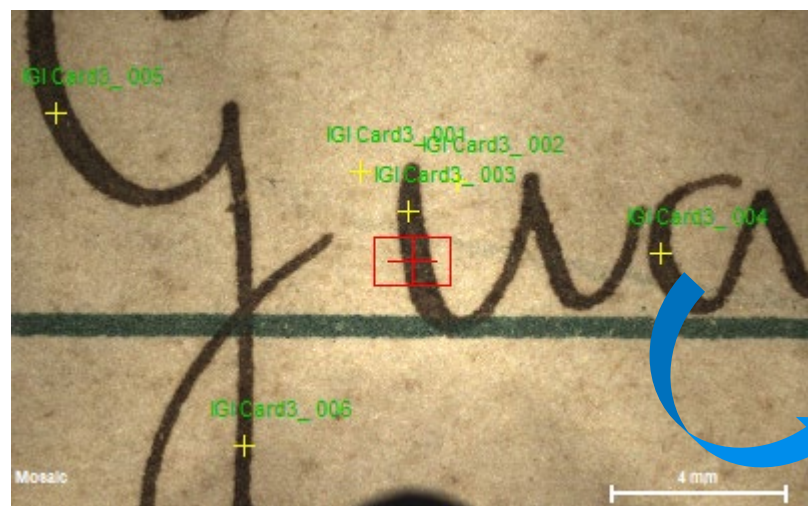


Quantitative analysis of iron gall inks

Standard-free approaches using XMethod



Spectrum	Mn [mg/m ²]	Fe [mg/m ²]	Cu [mg/m ²]	Zn [mg/m ²]
IGI Card3_1	58	183	15	11
IGI Card3_2	40	89	12	10
IGI Card3_3	27	56	10	6
IGI Card3_4	28	96	13	7
IGI Card3 Average	38	106	13	8
Paper Card3_1	26	35	9	6
Paper Card3_2	37	45	10	9



CONSERVING KNOWLEDGE: NON-INVASIVE MANUSCRIPT ANALYSIS

Combining spatially resolved micro-XRF with hyperspectral imaging: Introducing the IRIS

Fe Cu Zn Mn S

IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER

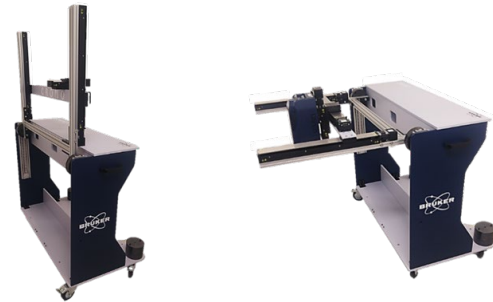


XRF

- Excitation: compact tube (10 W, 50 kV)
- Detection: SDD 50 mm², from **Na** to **U** (with optional He flux)

Reflectance Spectroscopy

- Excitation: Halogen Lamp
- Detection: two spectrometers covering 400 nm to 2500 nm



Scanning parameters

- Area: 60 cm x 45 cm
- Max Speed: 42 mm/s

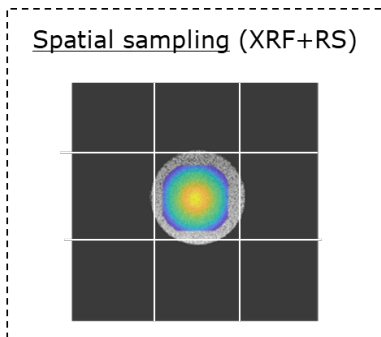
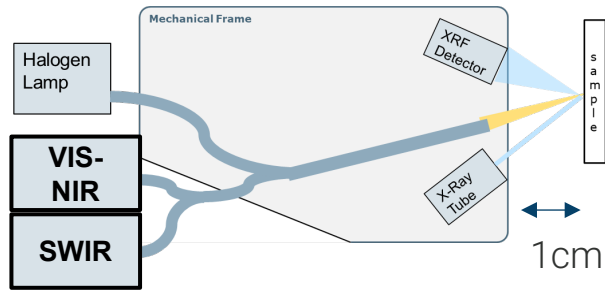
Configurations

- Easily transportable
- Tilt angle from 0° to 90°

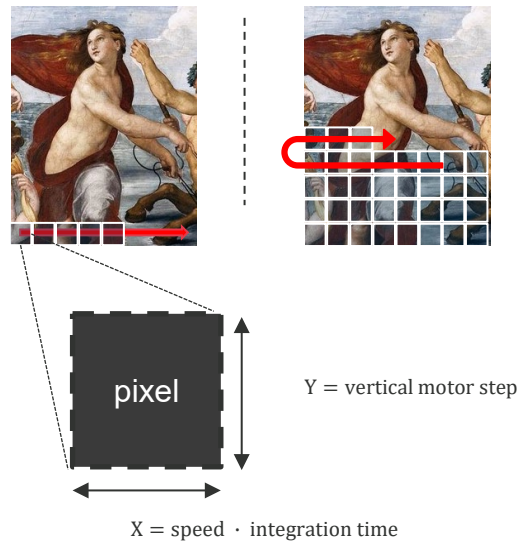
Instrument developed under the project "MOBARTECH", co-financed by Regione Lombardia (POR FESR 2014 – 2020)4

IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER

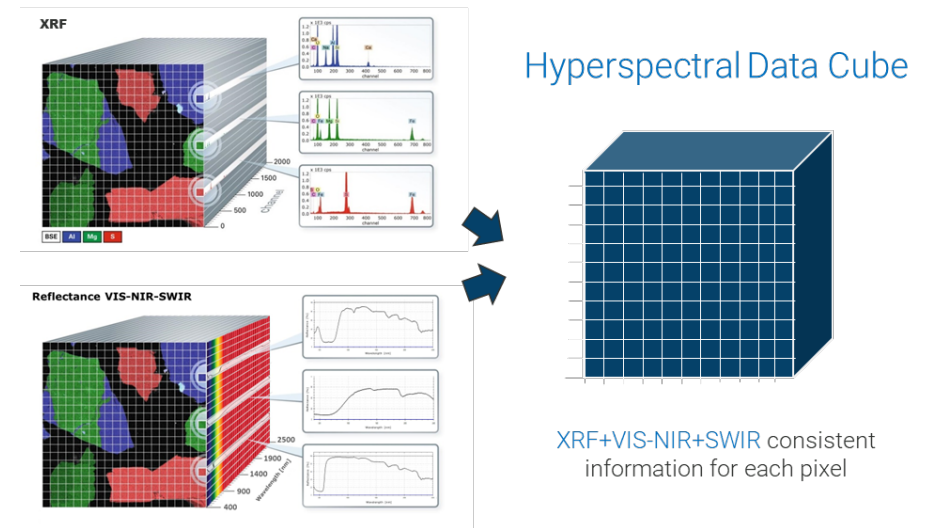
Overlapped XRF-RS spot of analysis



Whisk broom scanning



Data output

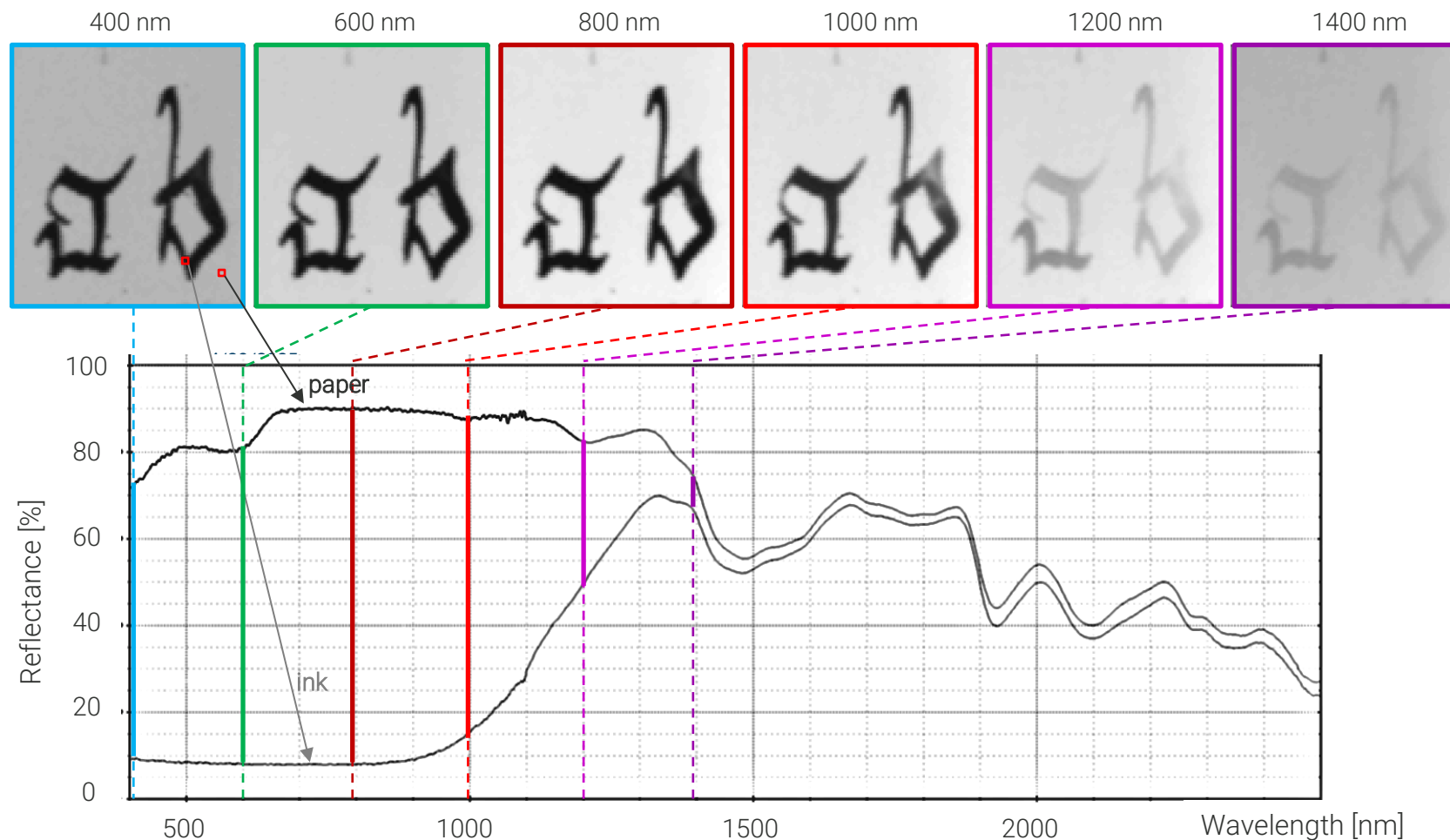
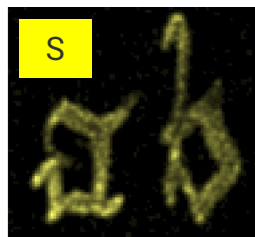
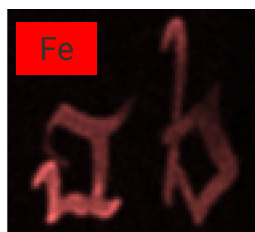
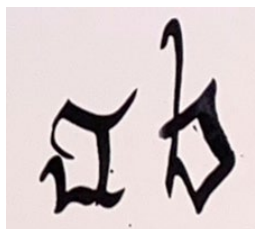


- ✓ No need for pixel stretching or map alignment!
- ✓ Minimized photo-induced aging or modification!

IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER

Case Studies: Ink discrimination, aging, ...

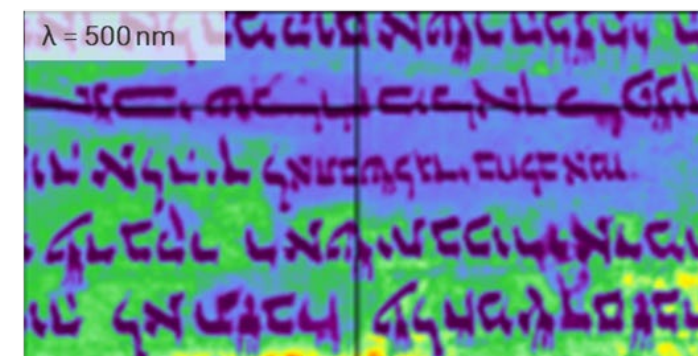
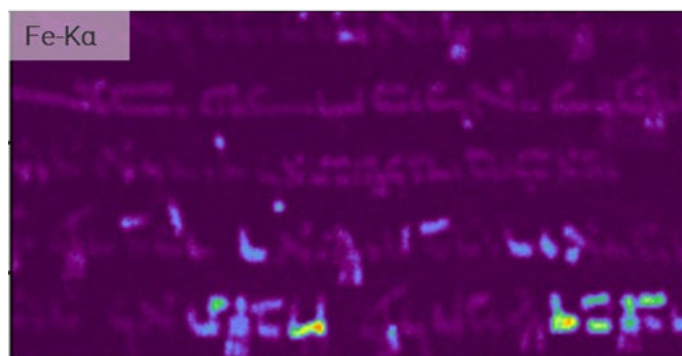
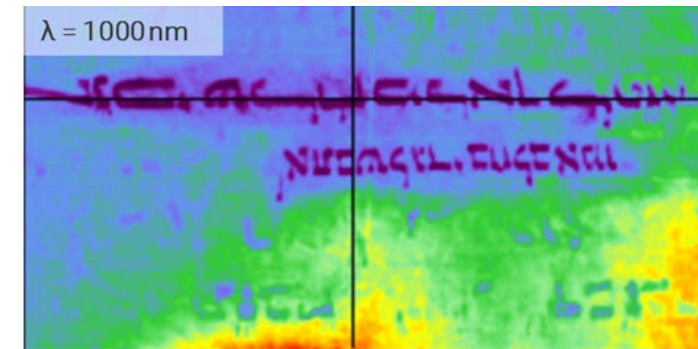
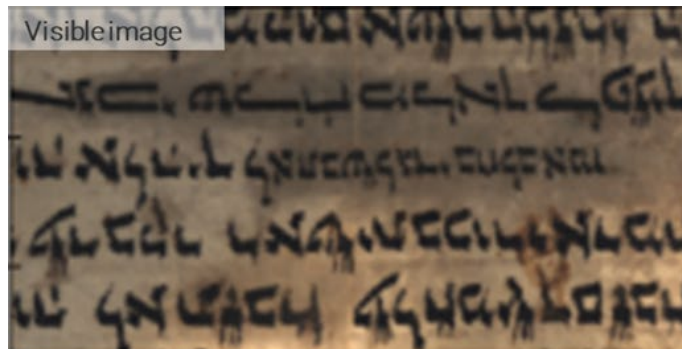
FeSO₄ based ink
Iron Gall



Courtesy of Prof. Dr. Ira Rabin, Federal Institute for Materials Research and Testing (BAM), Berlin, Germany.

IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER

Case Studies: Manuscript analysis



Courtesy of Prof. Dr. Ira Rabin, Federal Institute for Materials Research and Testing (BAM), Berlin, Germany.

IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER

Case Studies: Manuscript analysis

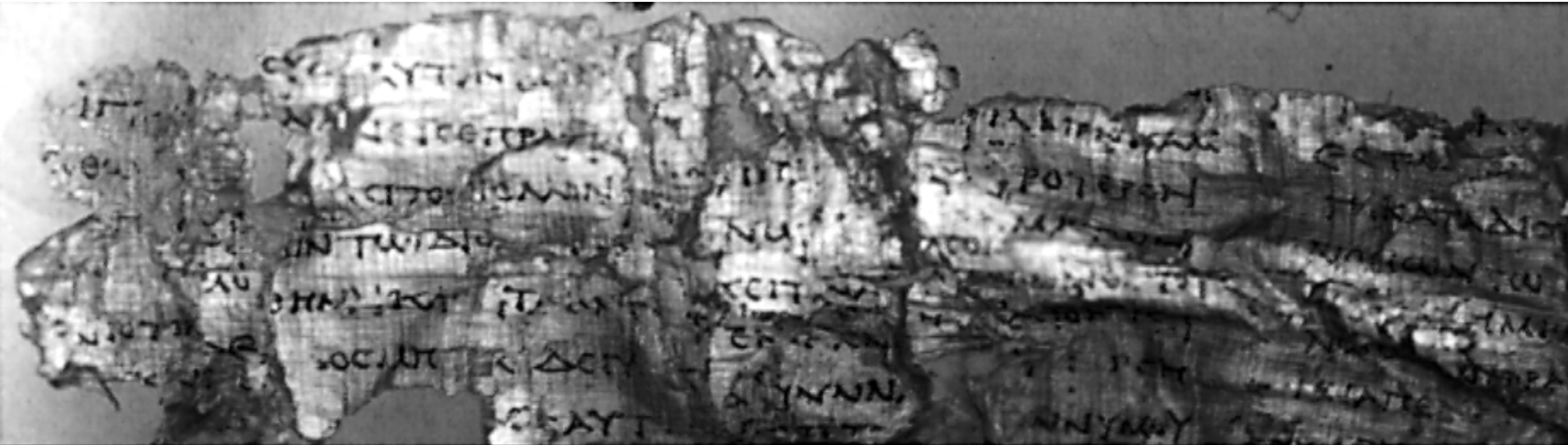


The **Herculaneum papyri** are more than 1,800 papyri found in the Herculaneum Villa of the Papyri in the 18th century, carbonized by the eruption of Mount Vesuvius in AD 79.

Courtesy of Biblioteca Nazionale di Napoli,
Istituto di Scienze del Patrimonio Culturale
Consiglio Nazionale delle Ricerche

IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER

Case Studies: Manuscript analysis



Hyperspectral @ 1920nm

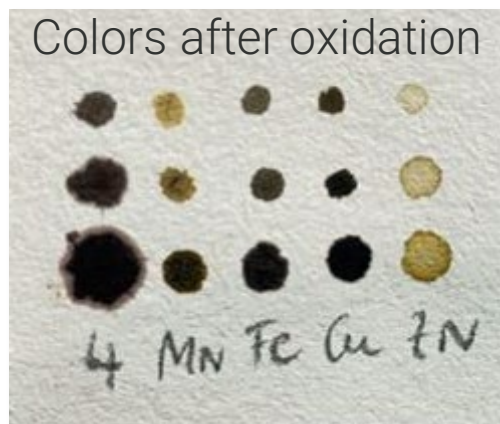
Courtesy of Biblioteca Nazionale di Napoli,
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IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER

What do we see on a mock-up after making our own iron gall ink?



Adding metal ions to the solution



Preparing a mock-up using the solution without and with different metal ions to scan with IRIS – XRF/VIS-NIR-SWIR



IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER

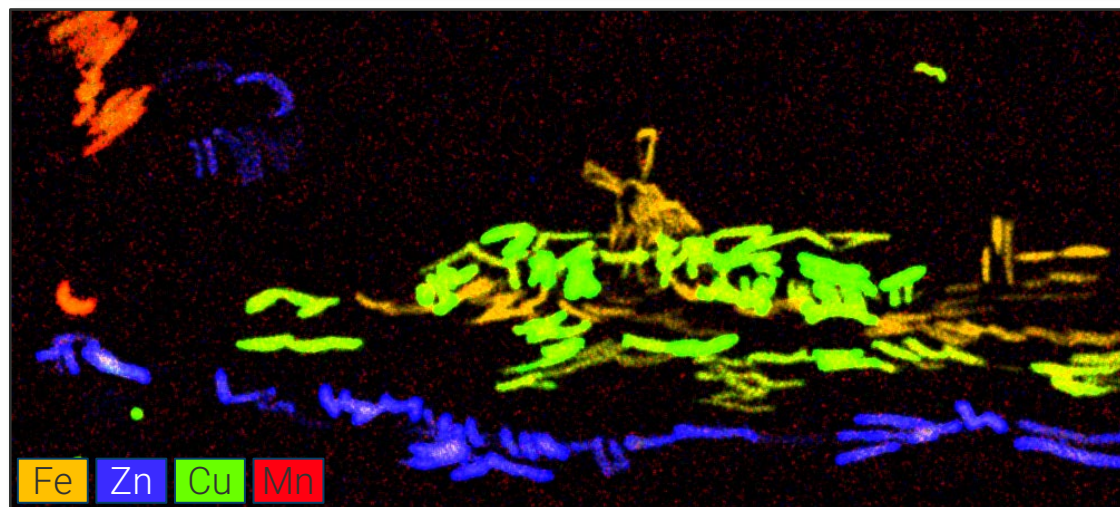
Onto new horizons in the analysis of historical inks



All inks visible at 625 nm.



Ink with no metal ions invisible at 900 nm.



S from the metal sulfates.

Onto new horizons in the analysis of historical inks

Summary and Conclusion

- The combination of spatially-resolved micro-XRF with the study of NIR transmission characteristics offers non-invasive classification of the most common historical writing inks.
- The measurement methodology must be chosen according to the hardware of the system used.
- Using special instrument designs and technical solutions, even areas difficult to approach can be measured with high spatial resolution.
- Micro-XRF further offers the possibility to quantify the amount of ink deposited:
 - Standard-based approaches rely on 1. the range and 2. the accuracy of the reference materials available.
 - Standard-less approaches offer vast possibilities reaching even into visualization of the amounts deposited.
- The IRIS system offers co-registered XRF and hyperspectral information.





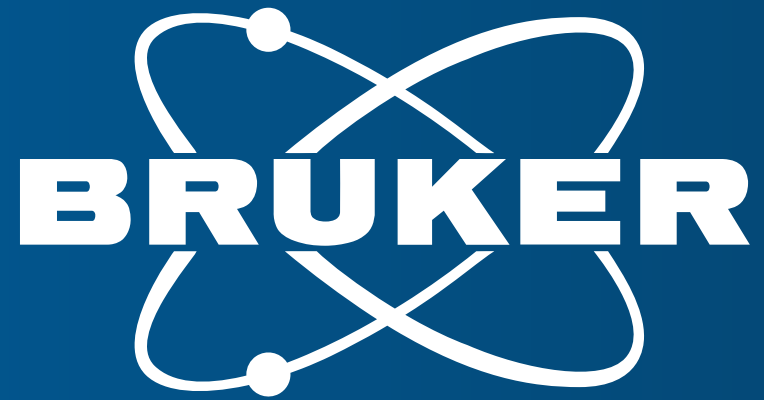
Art & Conservation Webinar Series

Quantification by means of XRF in Cultural Heritage Studies

If you have questions during this webinar,
please **type your questions**, thoughts, or comments in the
Q&A box and **press Send**.

We ask for your understanding, if we do not have time to
discuss all comments and questions within the session.
Any unanswered questions or comments will be answered
and discussed by e-mail or in another WebEx session.

A screenshot of a WebEx interface. At the top, there is a "Participants" section with a search bar and a list of participants: "Panelist: 2" (BNA moder... Host), "Roald Tagle", and "Attendee: Henning Schröder Me". Below this is a "Q&A" section with a search bar and a list of questions (currently empty, showing "All (0)"). At the bottom, there is an "Ask:" dropdown menu set to "Host & Presenter", a text input field with a placeholder "Select a panelist in the Ask menu first and then type your question", and a "Send" button.



Innovation with Integrity

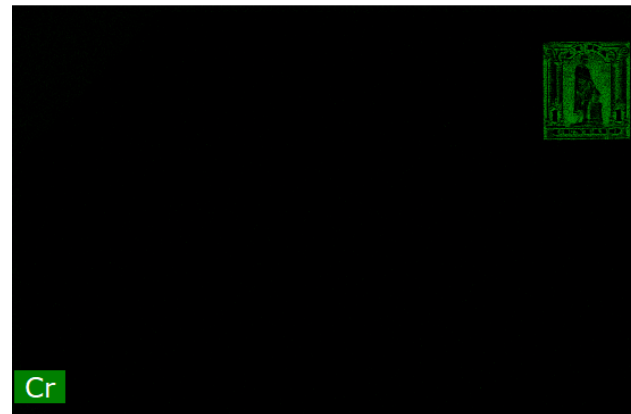
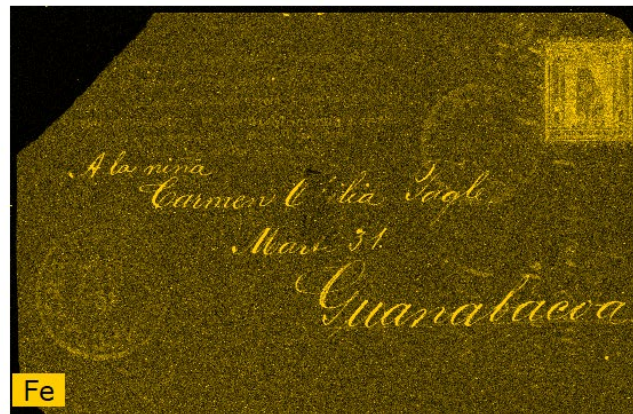
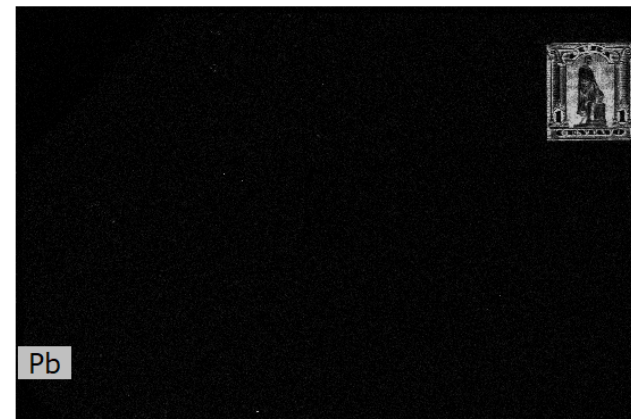
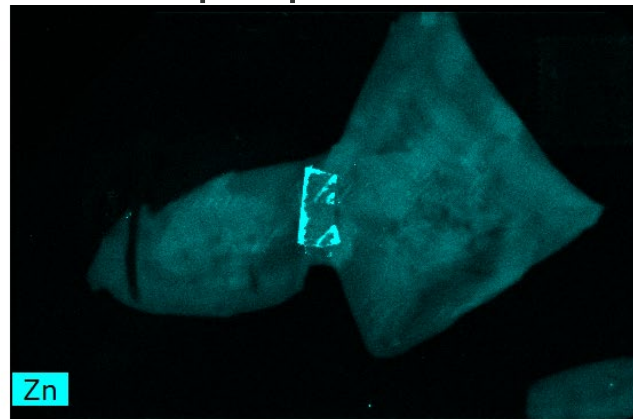
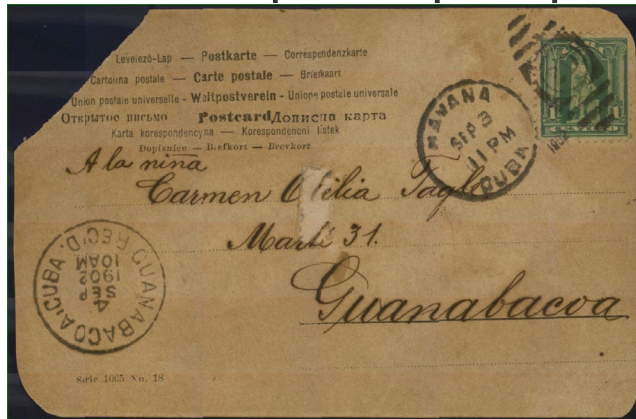
Polycapillary lens vs. Collimator

Visualizing a covered iron gall ink



M6 JETSTREAM (56 min)

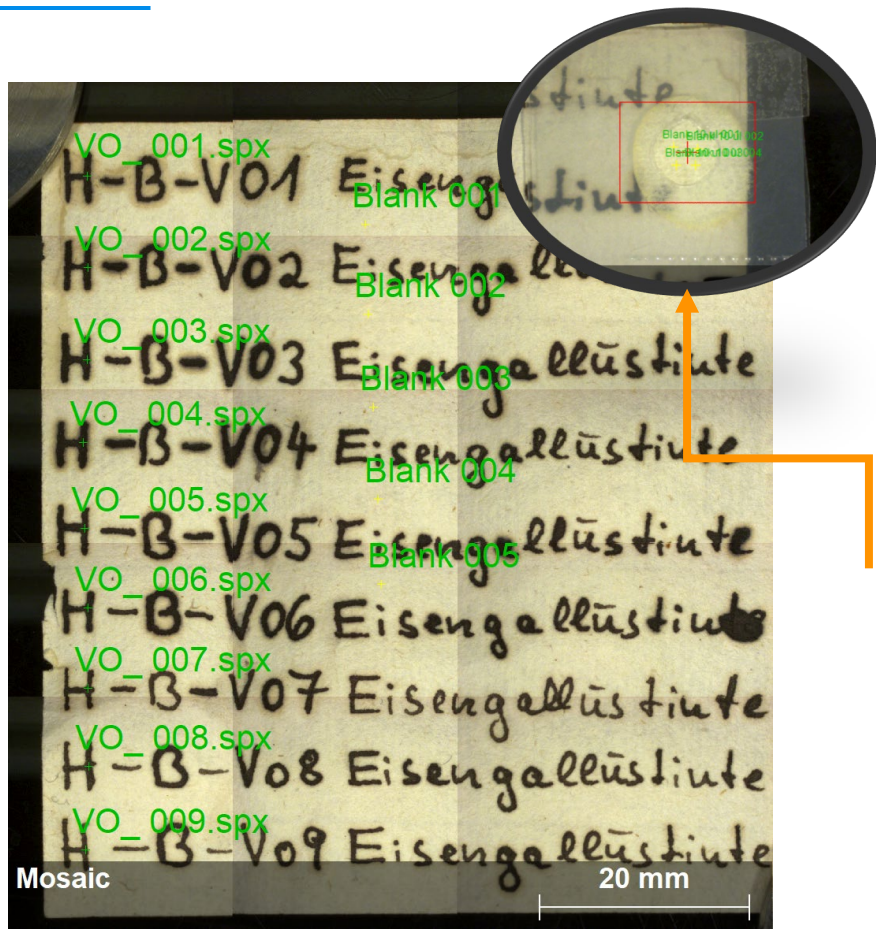
35 kV, 800 μ A, 35 μ m spot size, 150 μ m pixel size, 10 ms





Finally, applying the method to a sample

From counting atoms to determining mass deposition on paper



Iron gall ink mock-ups with varying content of Fe, Mn, Zn and Cu created by Prof. Dr. rer. nat. habil. Oliver Hahn, BAM, Berlin, Germany.

Chemical element	Mn	Fe	Cu	Zn
Conversion factors	176	166	102	132
ng/mm ²	Mn	Fe	Cu	Zn
Blank_1	7.0	16.6	2.0	1.3
Blank_2	10.6	23.2	2.0	2.6
Blank_3	5.3	14.9	2.0	0.0
Blank_4	5.3	13.3	1.0	0.0
Blank_5	7.0	18.2	2.0	1.3
Ave.	7.0	17.2	1.8	1.1
s	2.16	3.82	0.45	1.10
s %	31	22	25	105
Reference location	7.6	14.0	2.2	2.5

Comparing the blank to the reference location

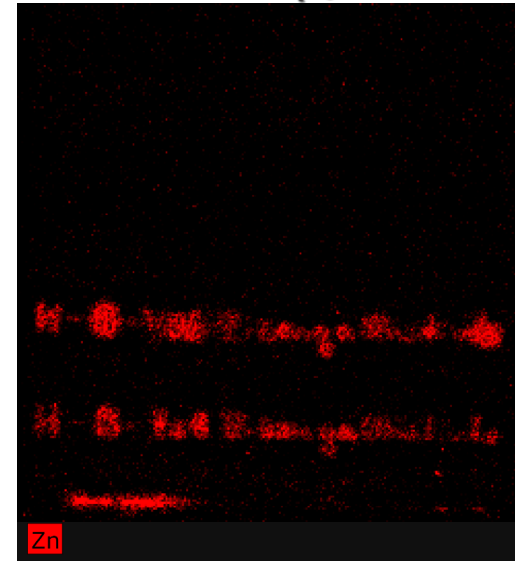
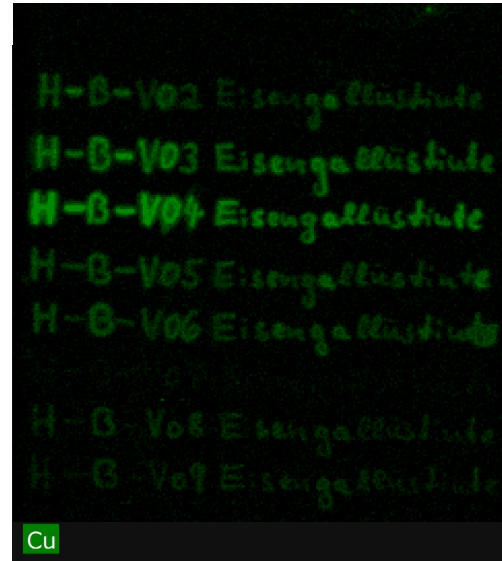
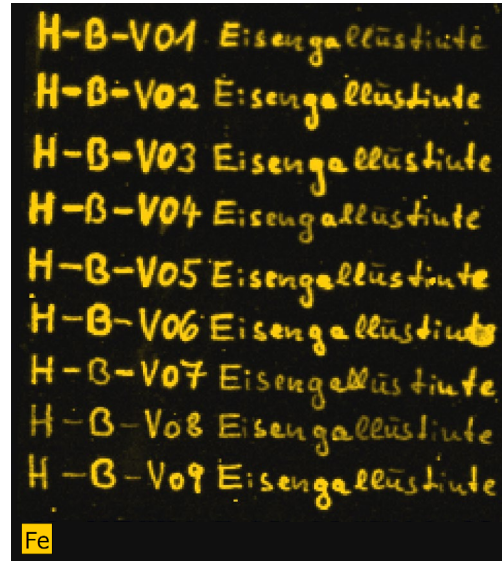
ng/mm ²	Mn	Fe	Cu	Zn
VO_1	0	517	0	0
VO_2	0	434	58	0
VO_3	0	371	102	0
VO_4	0	367	148	0
VO_5	0	293	50	0
VO_6	0	240	39	24
VO_7	0	193	6	0
VO_8	26	170	26	25
VO_9	0	235	25	4

Iron gall ink mock-ups: Final values



Finally, applying the method to a sample

From counting atoms to determining mass deposition on paper

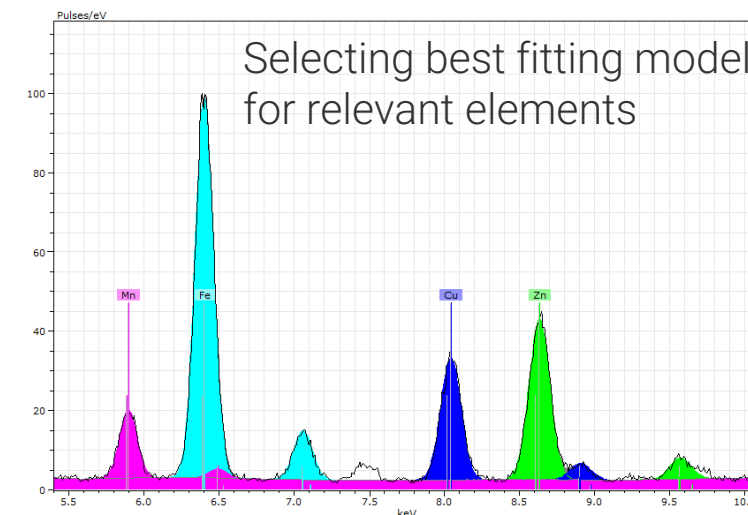
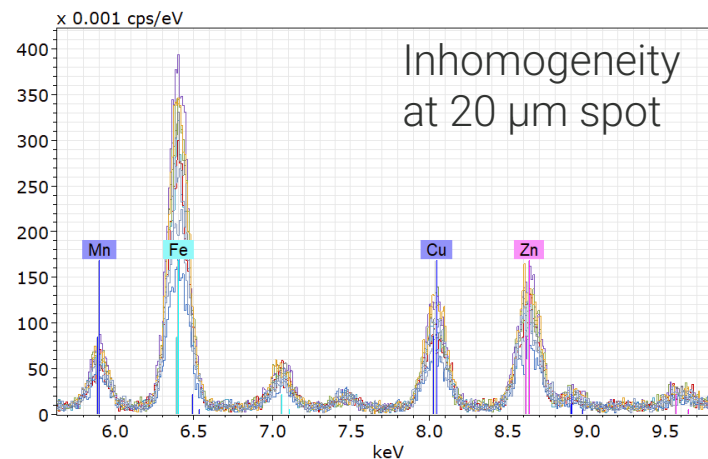
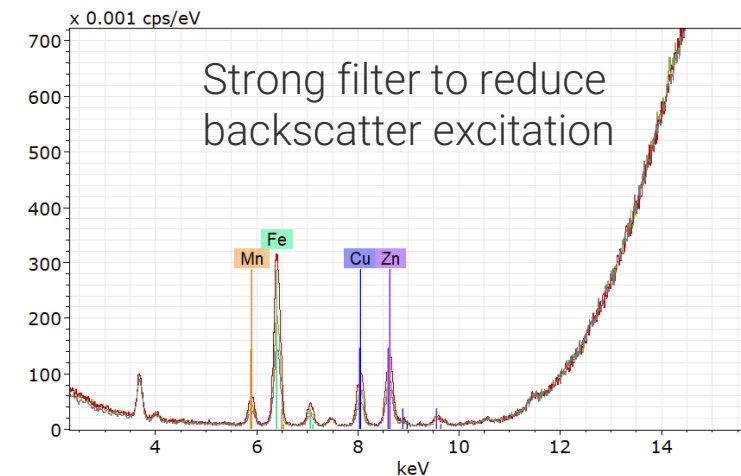
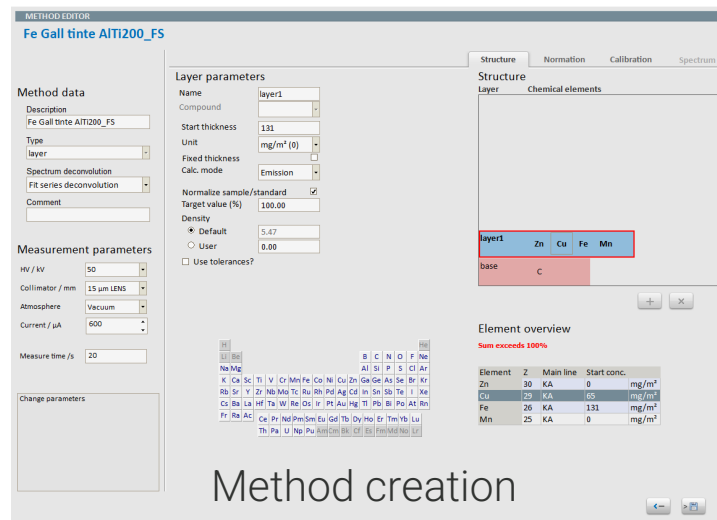


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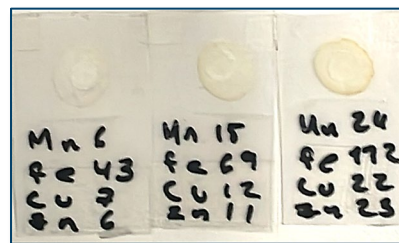
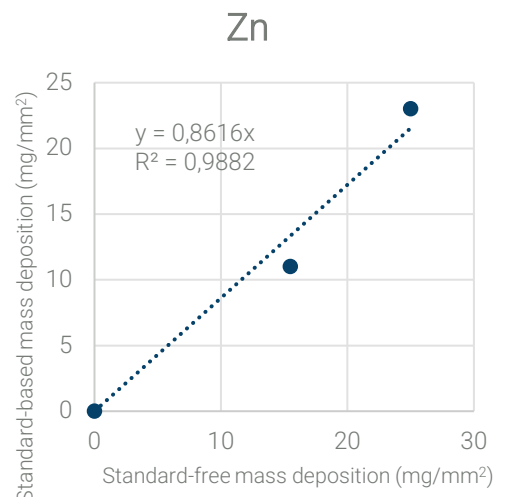
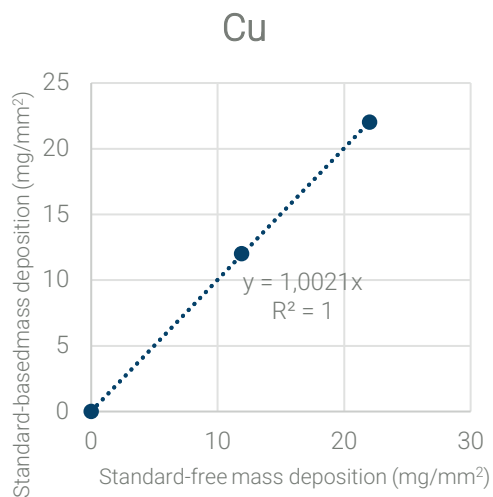
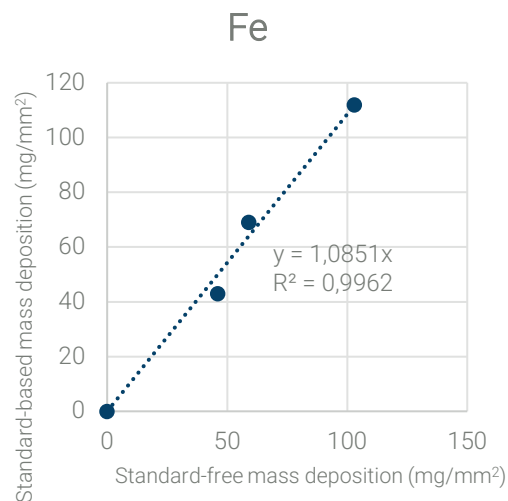
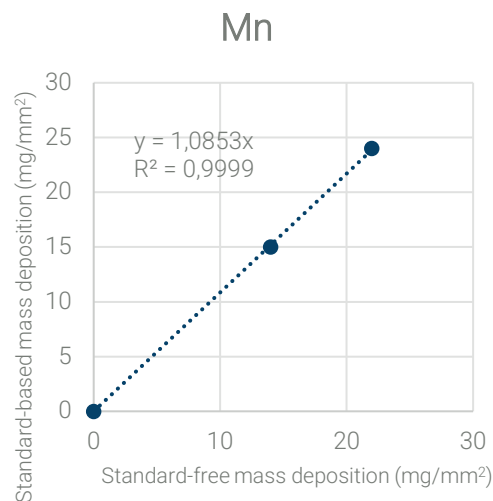
Quantitative analysis of iron gall inks

Creating and improving the quantification using XMethod

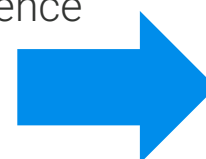




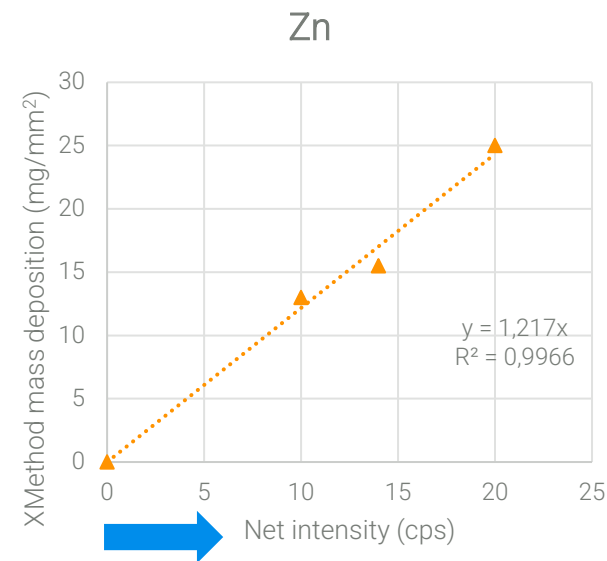
Quantitative analysis of iron gall inks "Validating" standard-free approaches using XMethod



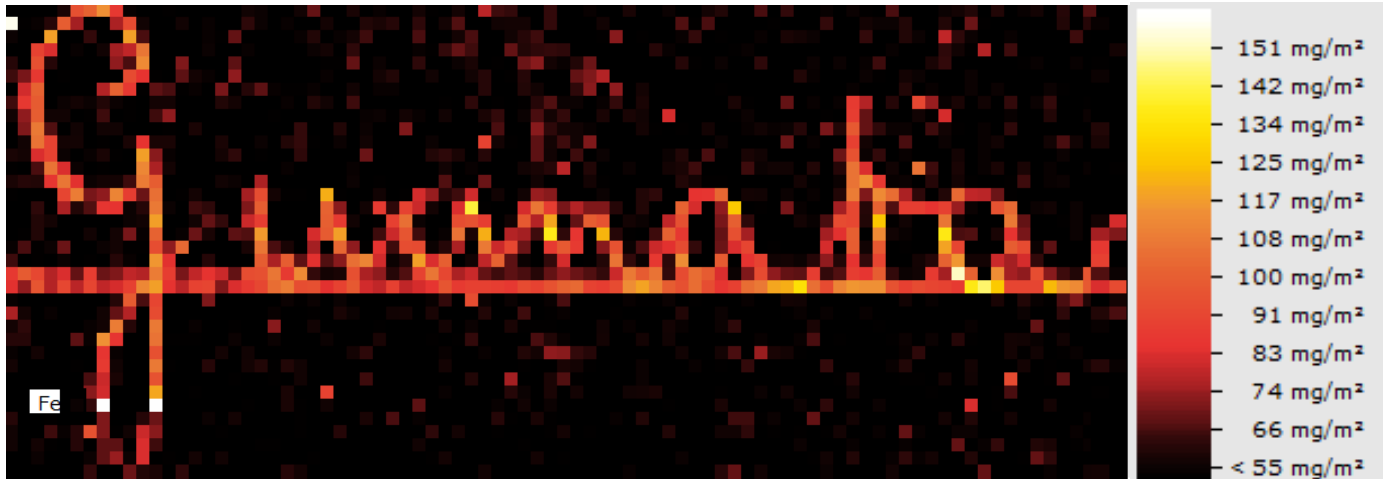
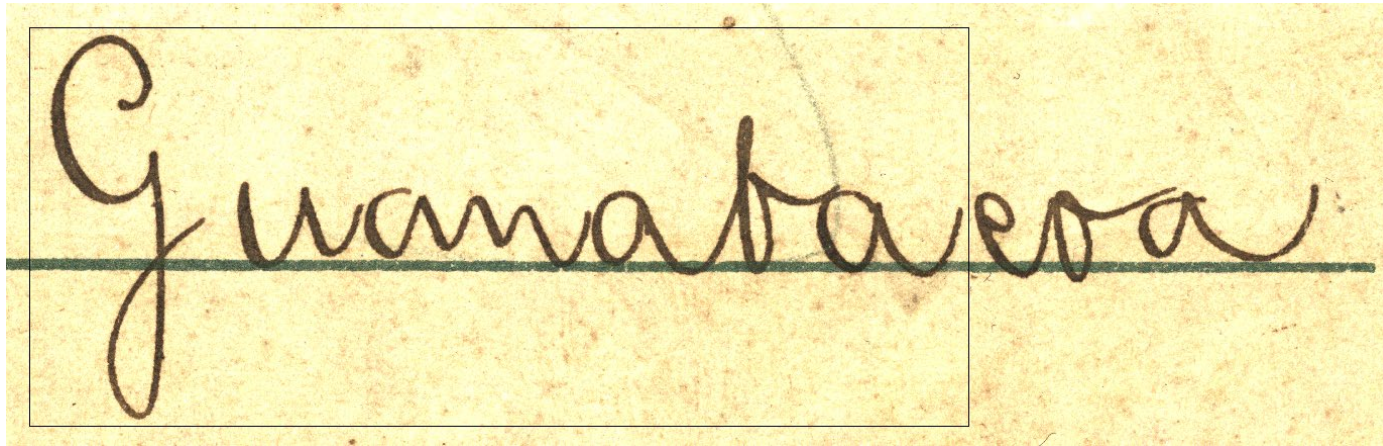
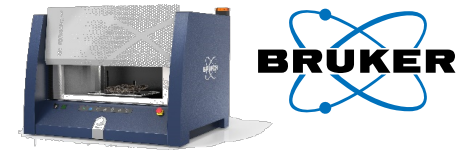
Discrepancy for small values of Mn, Cu and Zn from the self-made reference sample.



The uncertainty is NOT related to the sensitivity, but, most likely to sample preparation/evaluation.



Quantitative analysis of iron gall inks Standard-free approaches using XMethod

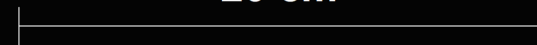


Leaves
Berlin, Germany



K Fe Cl Ca

20 cm



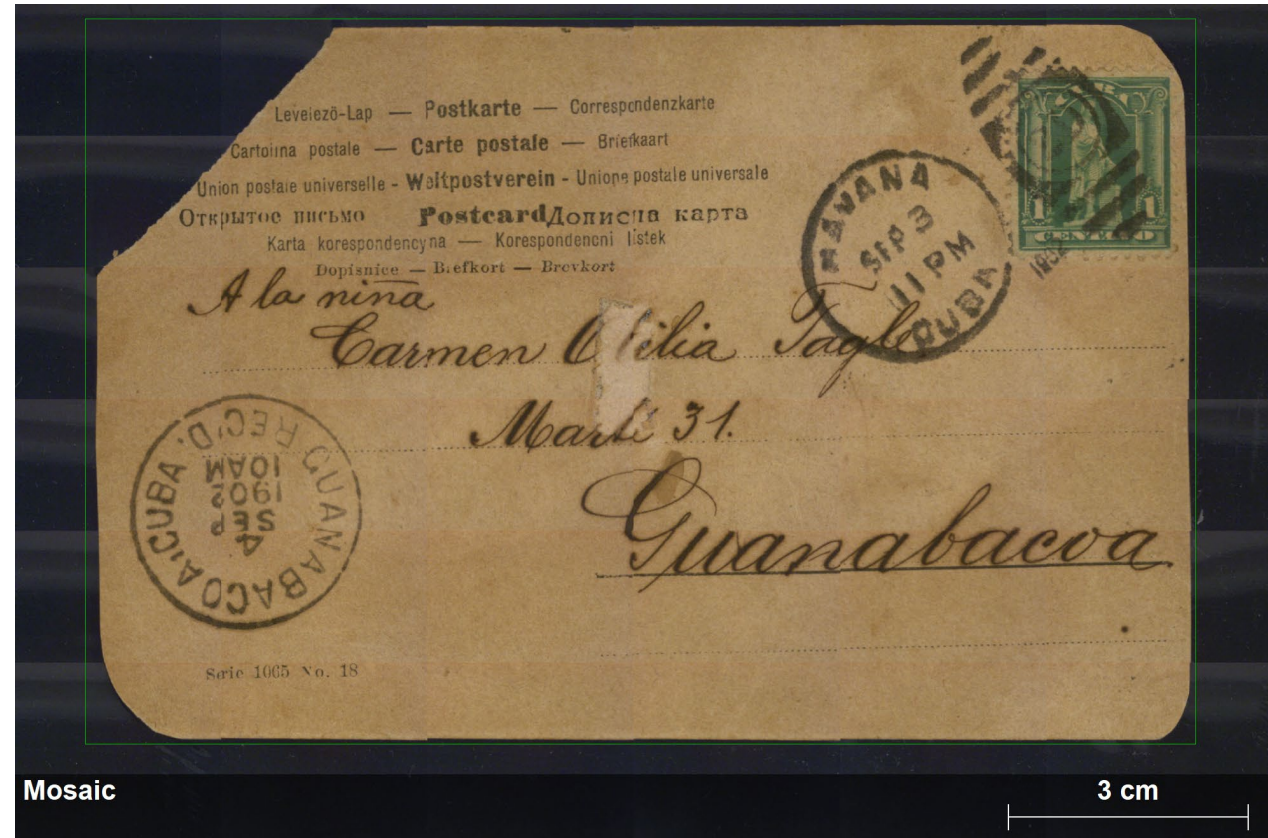
Polycapillary lens vs. Collimator Visualizing a covered iron gall ink



The sample



Recto



Verso

- Postcard, La Habana, Cuba
- Sept 1902
- Photography and iron gall ink writing on Recto
- Iron gall ink writing, stamp and postage stamps on the Verso

Polycapillary lens vs. Collimator

Visualizing a covered iron gall ink

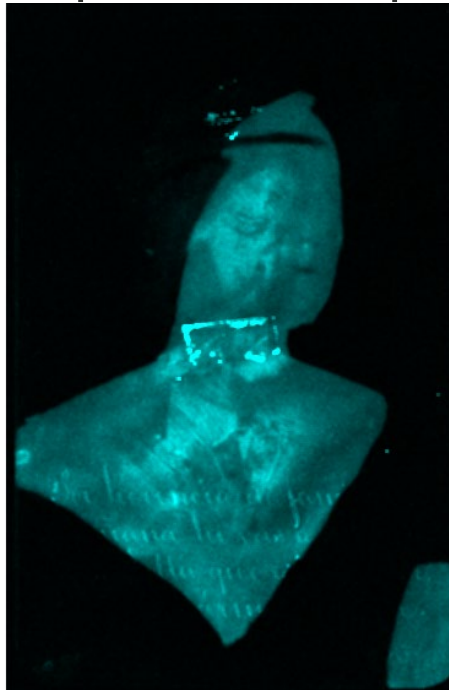


M6 JETSTREAM (56 min)

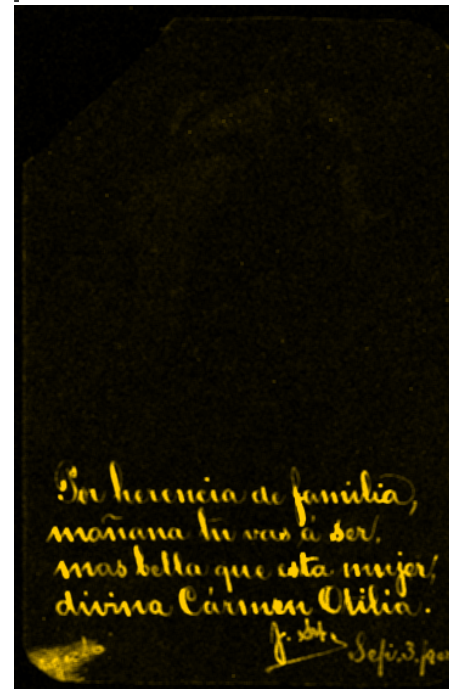
35 kV, 800 μ A, 35 μ m spot size, 150 μ m pixel size, 10 ms



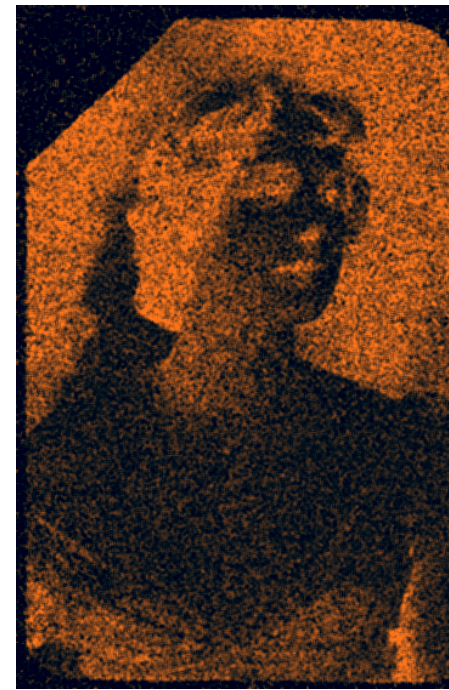
Video



Zn-Ka



Fe-Ka



Ag-Lβ



Pb-Lβ

Iron gall ink contains mainly Fe and Zn sulphates.

Originating from the stamp on the recto.

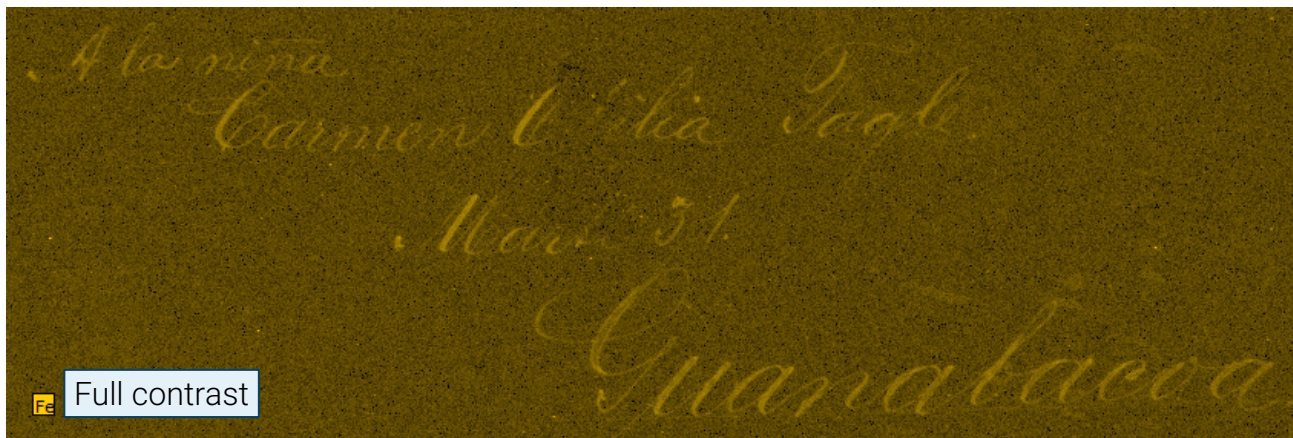
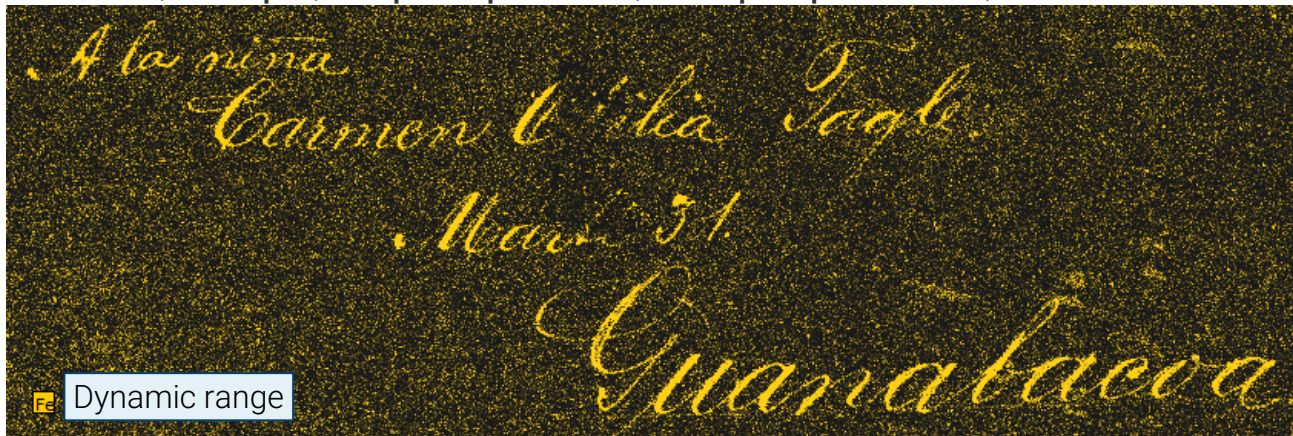
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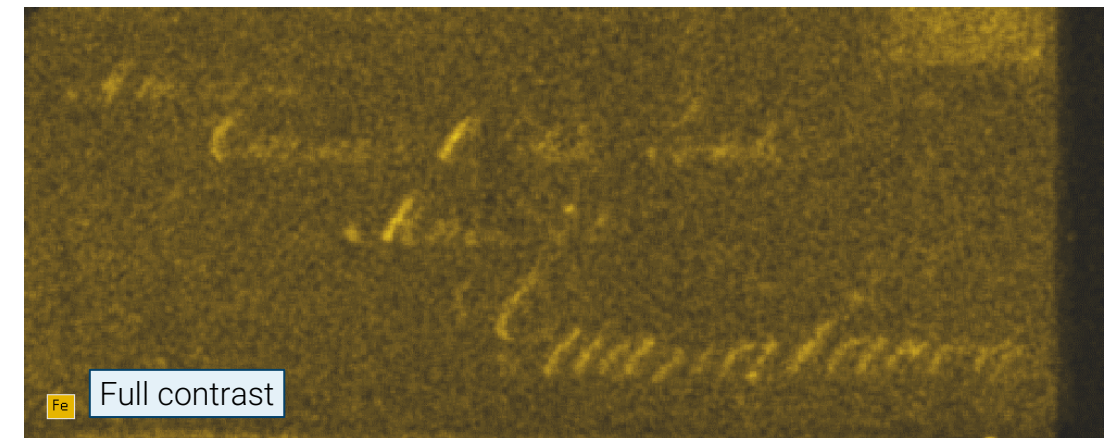
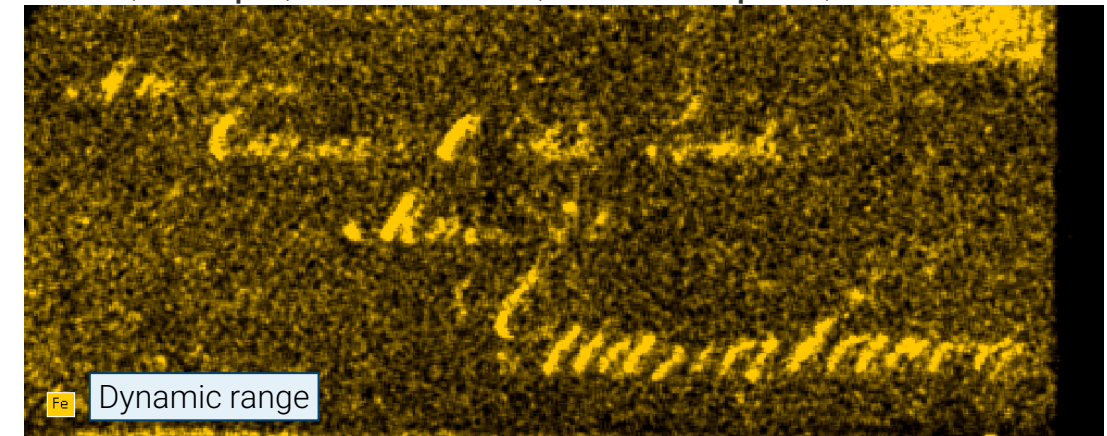
M6 JETSTREAM (56 min)

35 kV, 800 μ A, 35 μ m spot size, 150 μ m pixel size, 10 ms



CRONO (c. 4:10 h)

35 kV, 200 μ A, 0.5 mm colli, 0.25 mm pixel, 100 ms



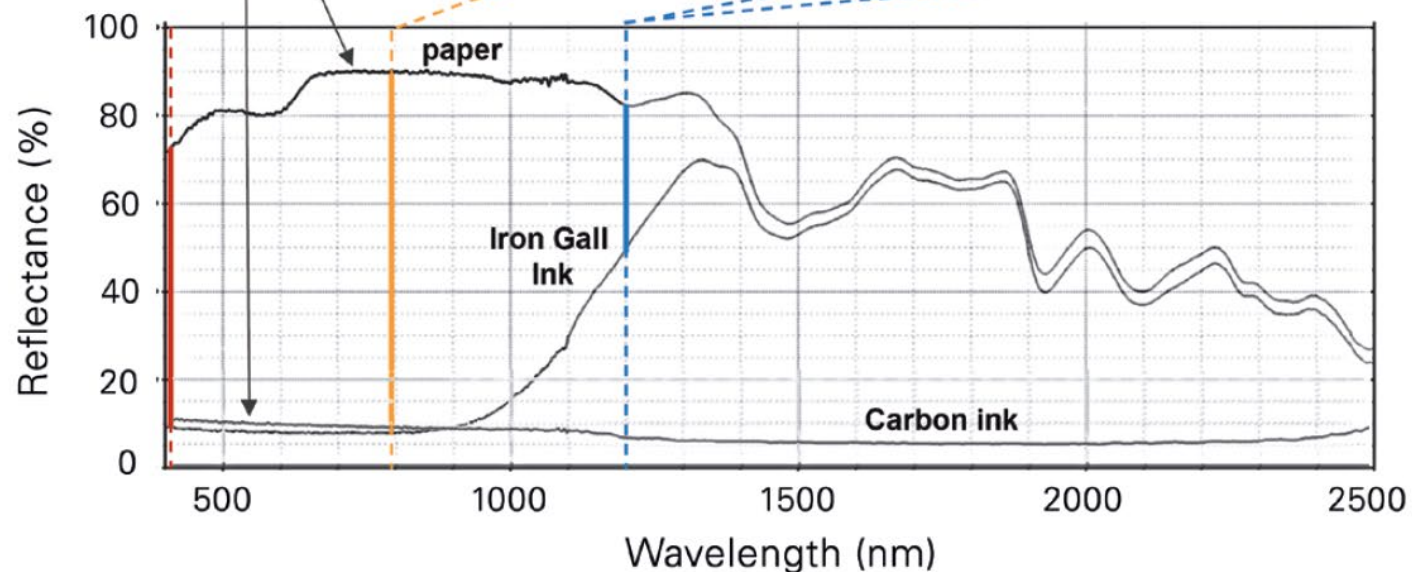
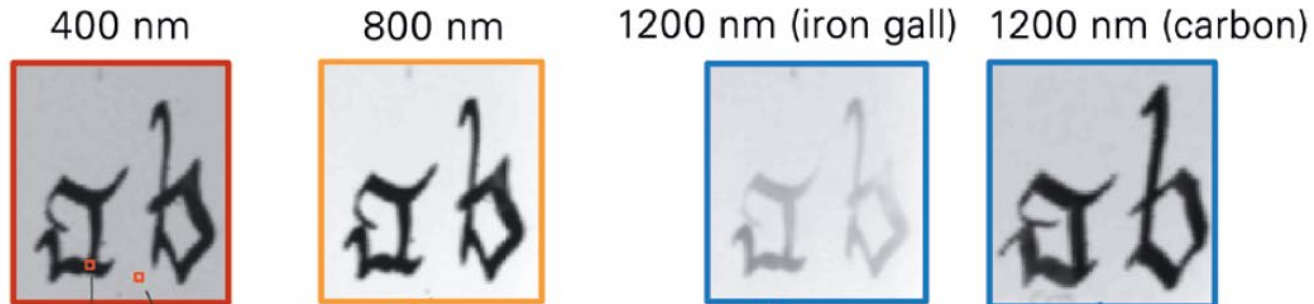
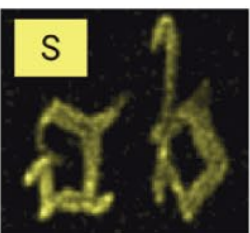
IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER

Case Studies: Ink discrimination, aging, ...

Iron gall ink



Carbon ink



Courtesy of Prof. Dr. Ira Rabin, BAM