Recenti evoluzioni nella strumentazione per analisi non invasive sulle opere d'arte.

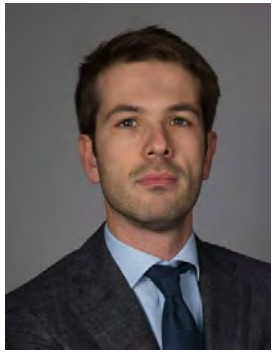
Strumenti portatili, mapping e combinati

Webinar – 25 Maggio 2021

BRUKER

ASSOCIAZIONE ITALIANA DI ARCHEOMETRIA

Speakers



Alessandro Tocchio

Sales Manager

XGLab – Bruker BNA

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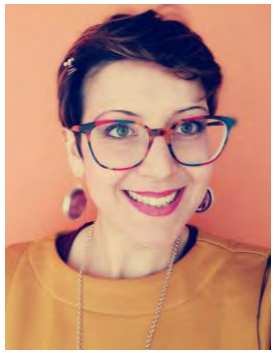
Global Market Segment Manager Art & Conservation

Bruker Nano GmbH

Claudia Sciuto

Dipartimento di Civiltà e Forme del Sapere

Università di Pisa



Simona Raneri

ICCOM-CNR, Pisa

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Agenda

Part I – Recenti evoluzioni nella strumentazione per analisi non invasive sulle opere d'arte

Part II – Novità dai nostri laboratori R&D: combinando l'XRF con tecniche di analisi complementari

Part III – Strumentazione portatile e archeologia da campo: sfide tecniche e prospettive di ricerca

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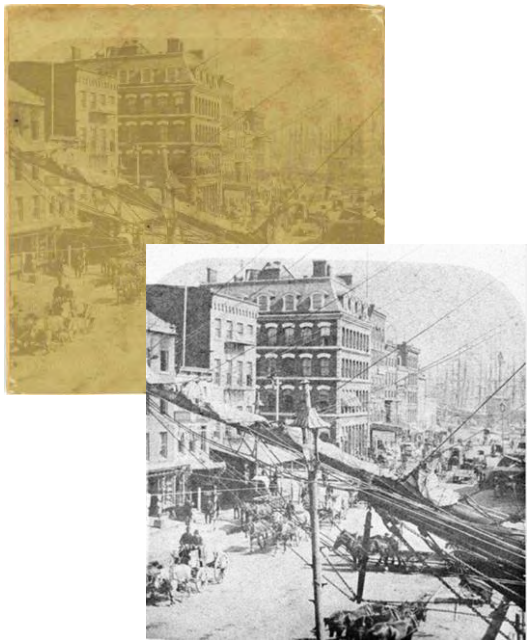
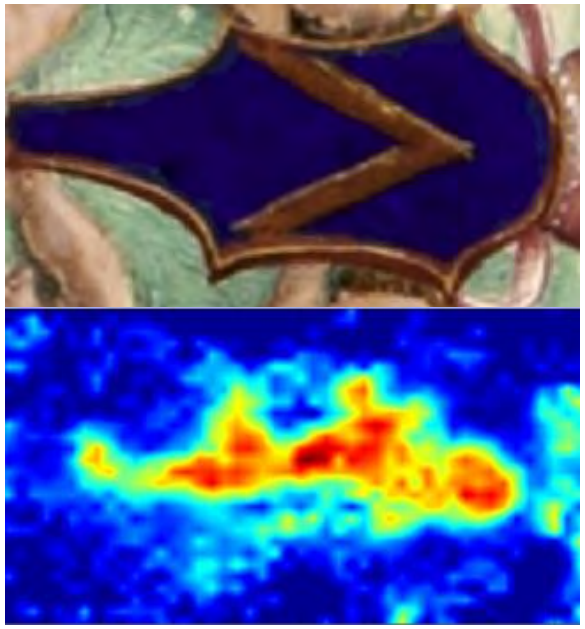
XRF in Art



Trace element sensitive



Information from depth in the sample

No sample preparation

- XRF is an element specific technique as each element absorbs and emits fluorescence at its individual energy
- The element concentration can be determined from this data as XRF spectrometers analyze the fluorescence
- An XRF scanner records the fluorescence on multiple points to determine the element distribution
- In most cases X-rays can penetrate deeper into matter than visible light allowing identification of hidden paintings or faded colors

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XRF in Art

- XRF has proven to be a **core analytical technique** in Cultural Heritage studies
- XRF provides key information on objects: **reliable**, **fast**, and **non-invasive**
- **But** application needs are not always the same. They differ in crucial ways with respect to the **what**, the **where**, and the **how**.
- Bruker offers several instruments for one analytical principle

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XRF, Art and Collections Management

Mapping

Spot

TRACER

ELIO

CRONO

M6
JETSTREAM

M4 TORNADO

SEM
EDS-WDS-µXRF

Portable ⟷ **Lab based**

TRACER 5 Handheld XRF

The standard in handheld-XRF analysis for cultural heritage

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ELIO mapping XRF

Ultra-portable point and mapping XRF

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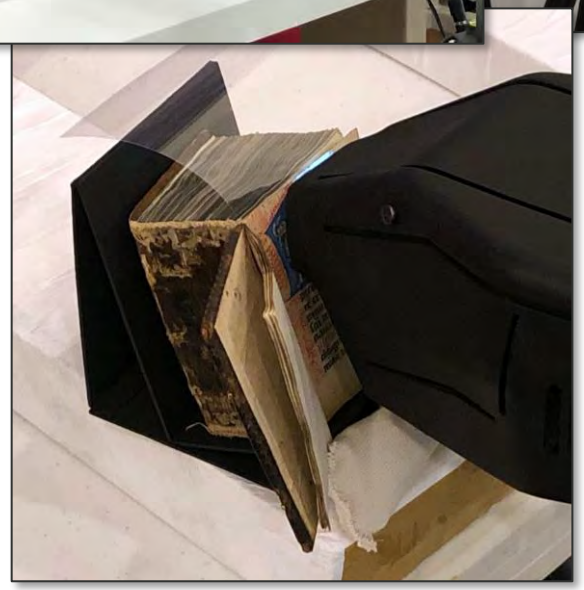
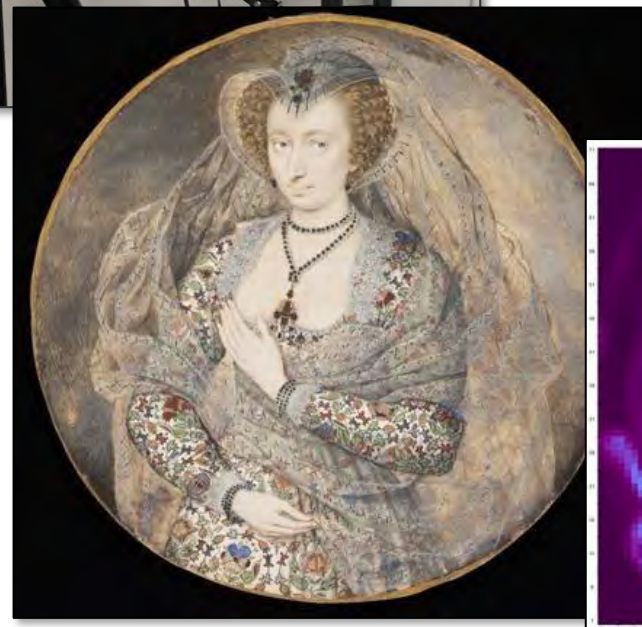
ELIO mapping XRF

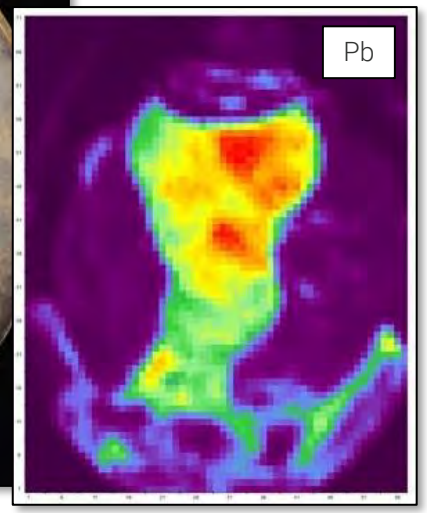
Flexibility of approach and positioning – ideal for manuscripts, books and other documents

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





Isaac Oliver miniatures, Fitzwilliam Museum, Cambridge University (*Dr. Paola Ricciardi*)



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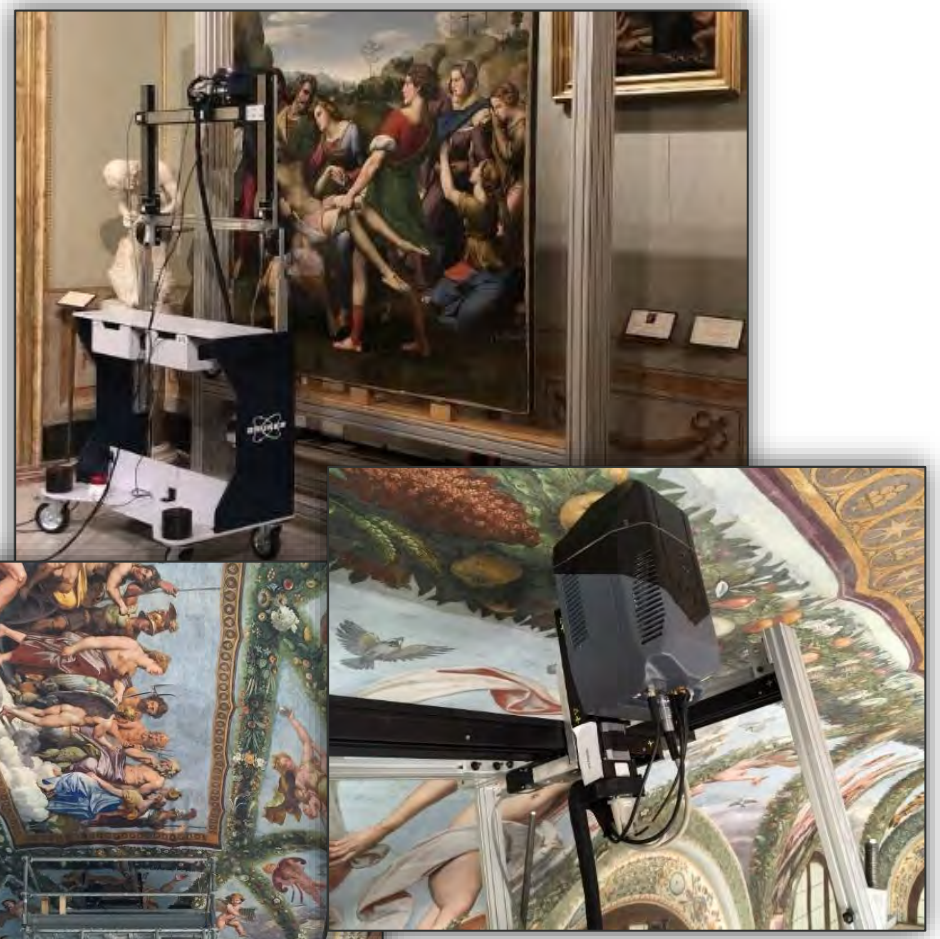
CRONO mobile large-area micro-XRF mapping

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



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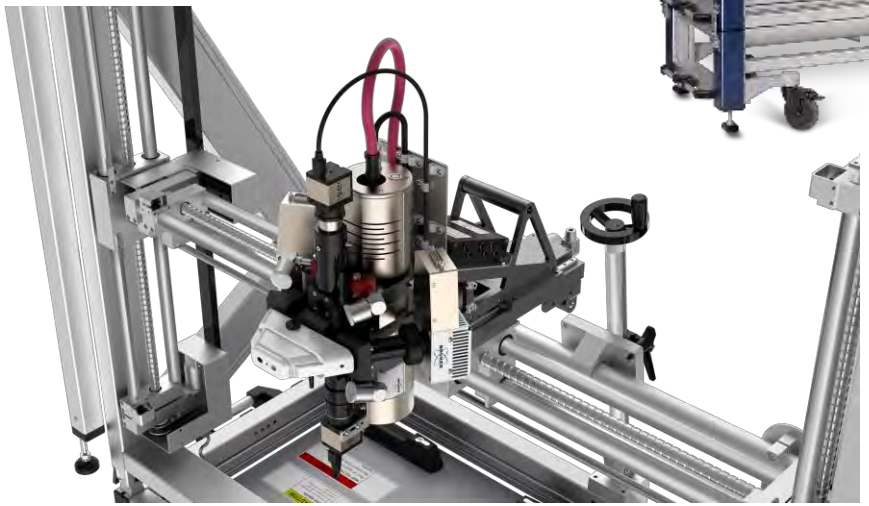
M6 JETSTREAM large-area micro-XRF mapping

Museum- & lab-based mapping solution



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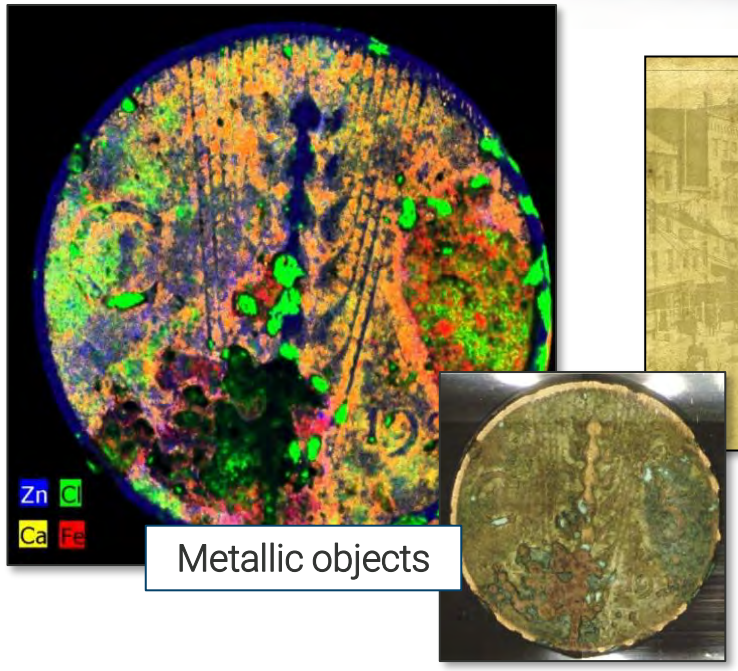
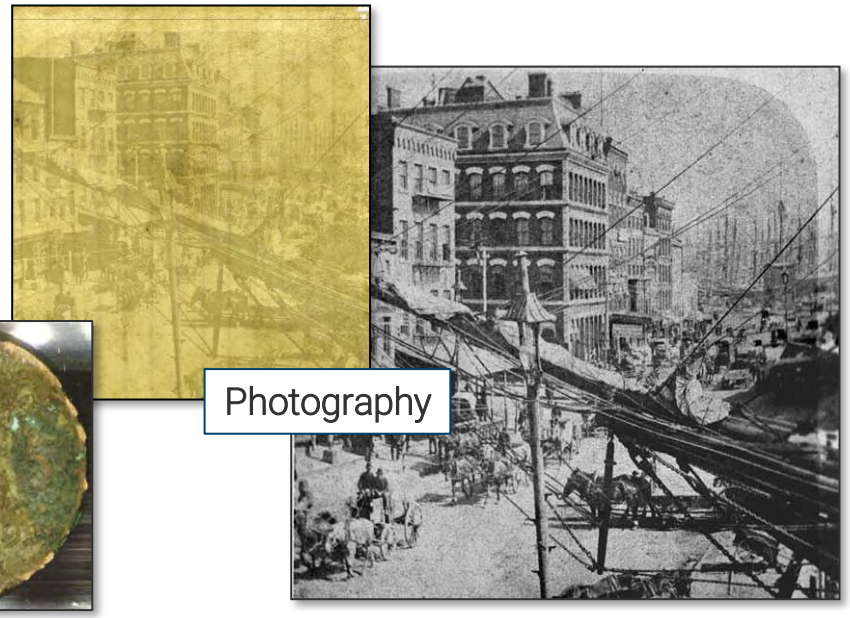
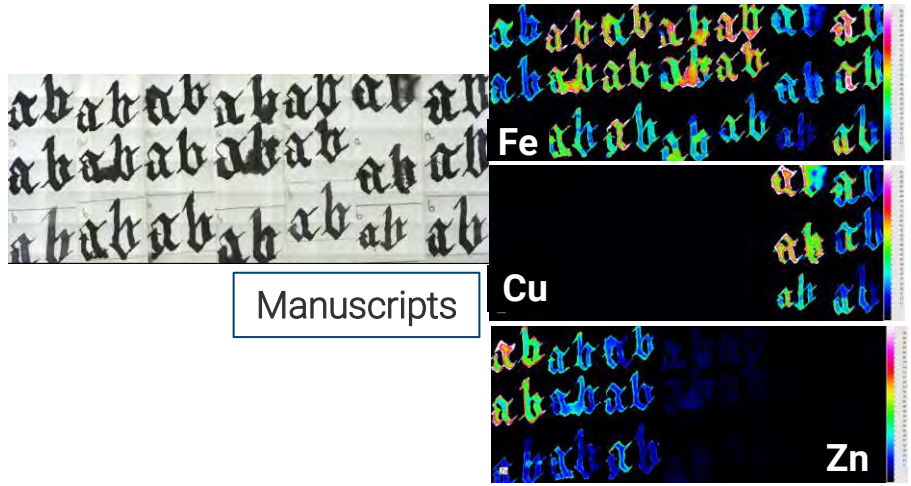
M4 TORNADO micro-XRF

Small spot, closed-beam µXRF







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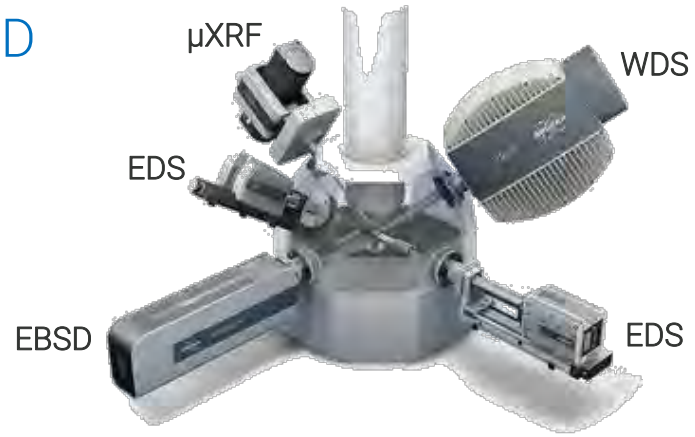
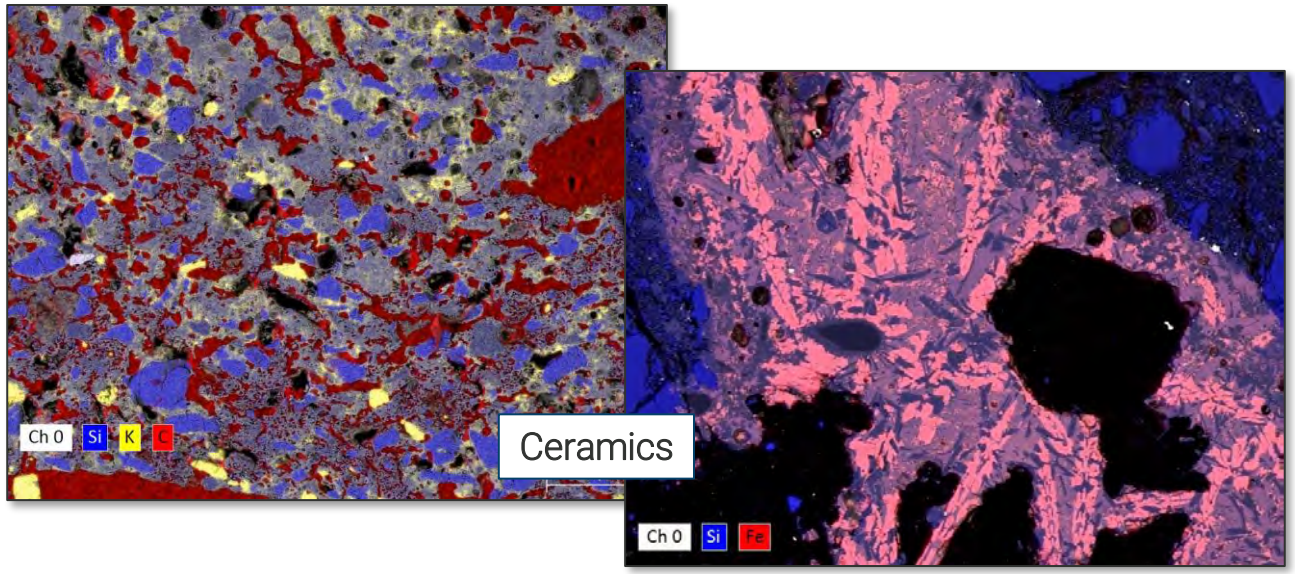
QUANTAX detectors for Scanning Electron Microscopes

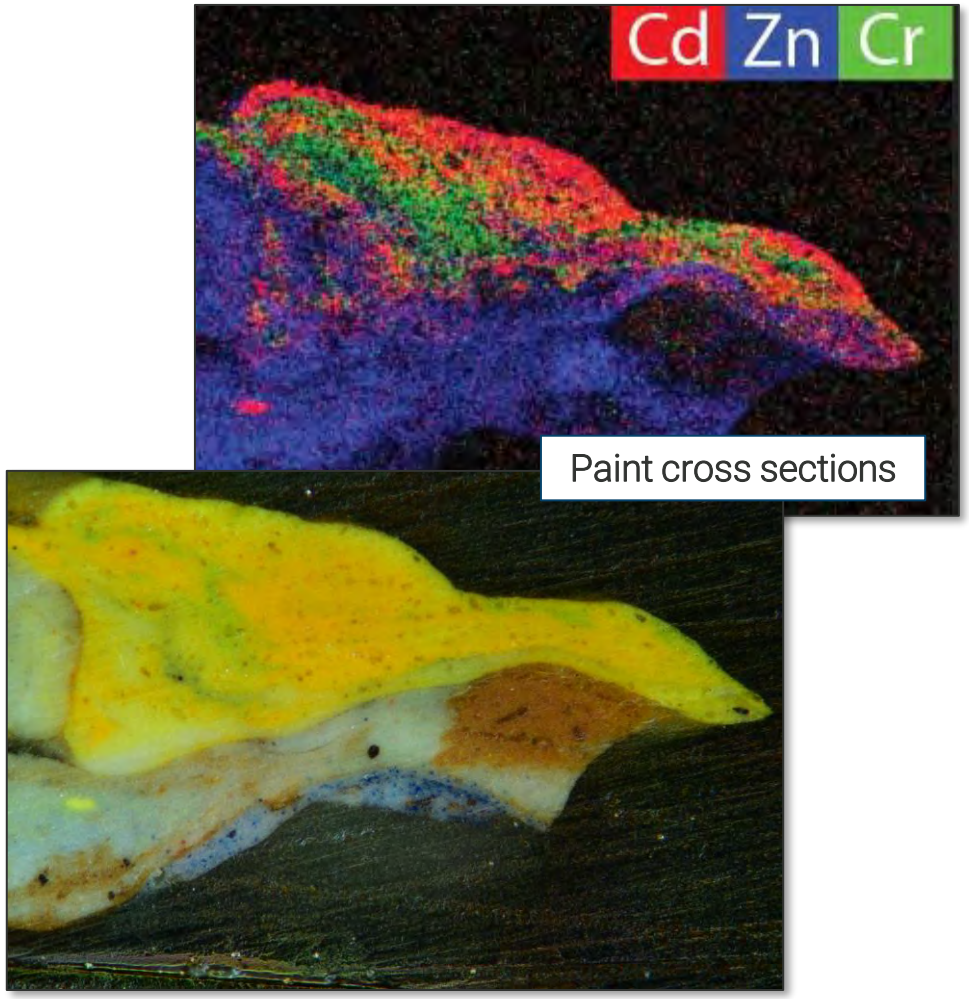
EDS, WDS and EBSD detectors for SEM

XTrace micro-XRF source for SEM





Ceramics



Paint cross sections

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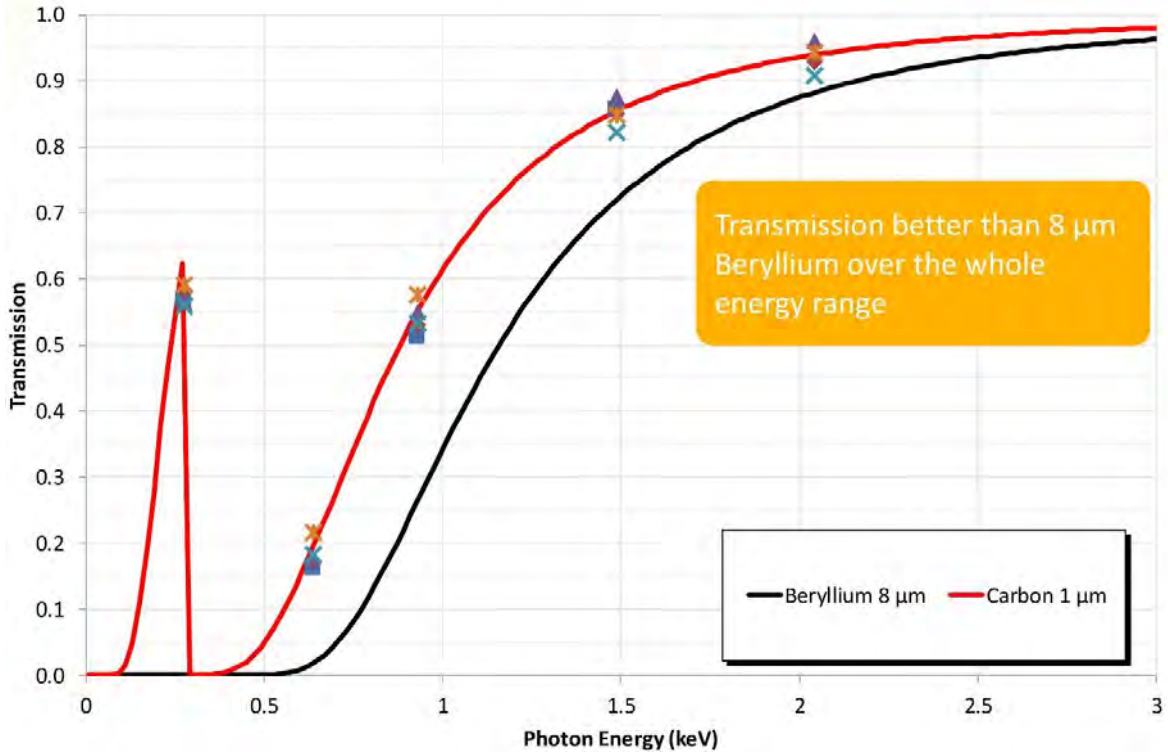
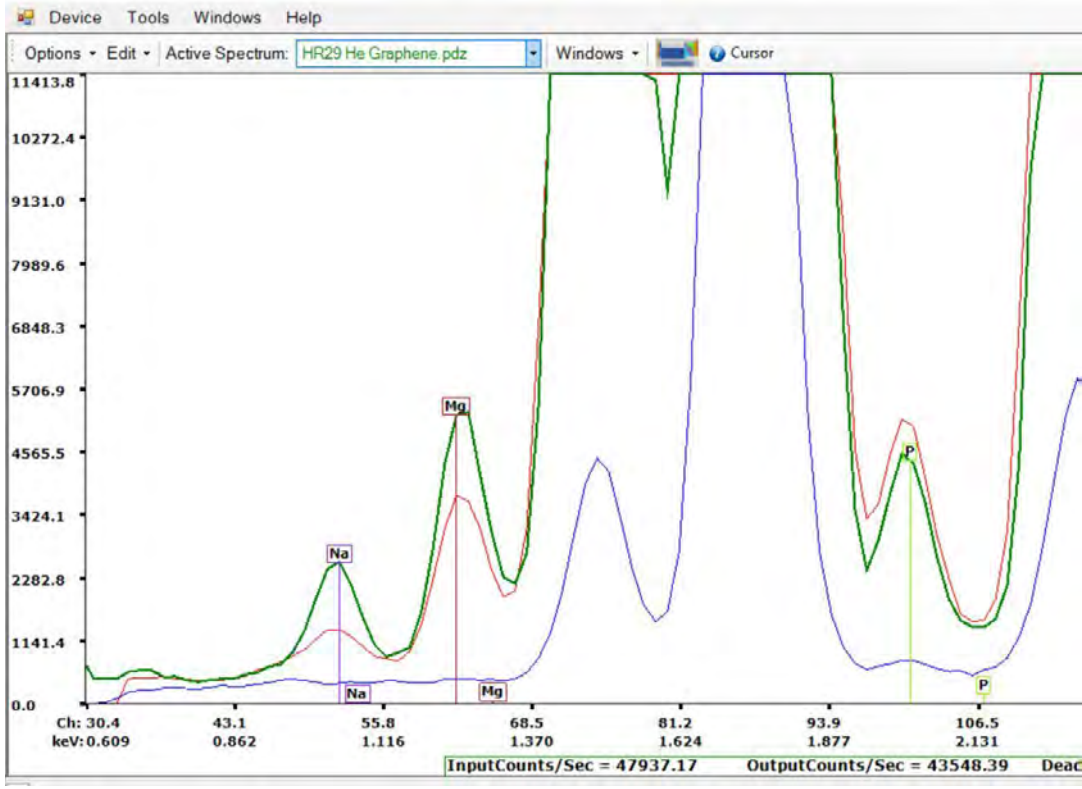
Novelties – TRACER 5g

- Incorporates new Graphene window detector
- Dramatically improves the low energy sensitivity of the instrument





- 3x Sensitivity for Na
- 2x sensitivity for Mg

In Nose down; no window; He flush (60 sec)

- LOD Na <300 ppm
- LOD Mg <100 ppm

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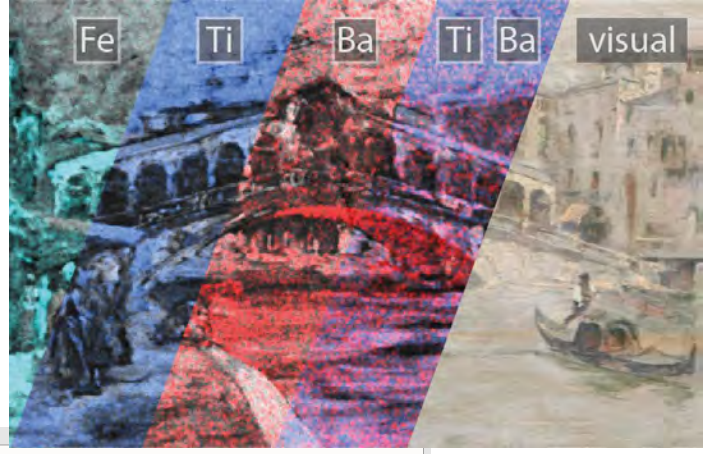
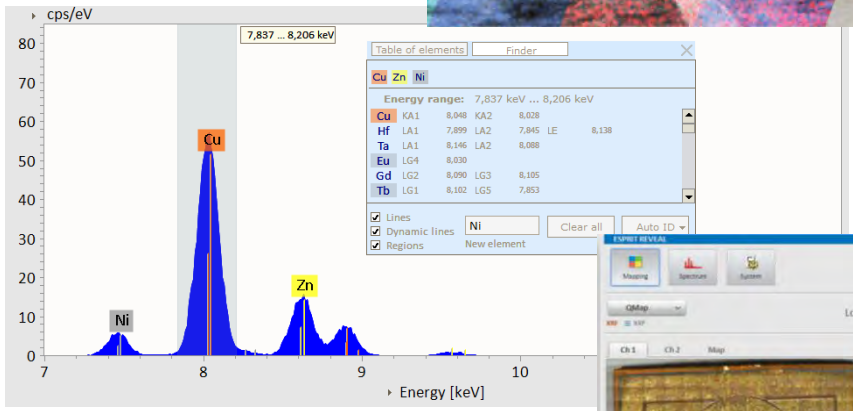
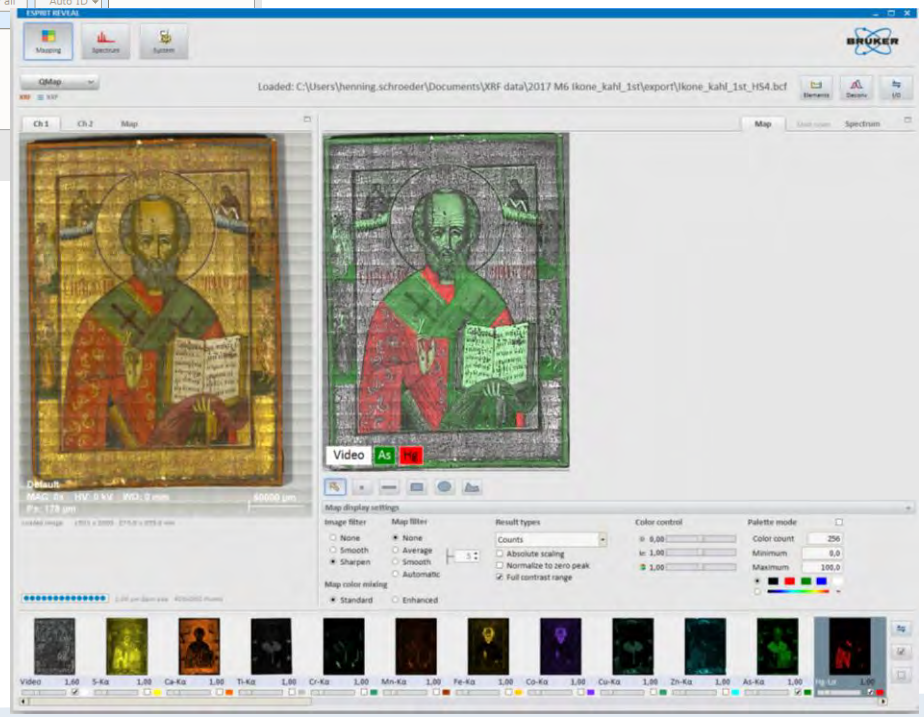
Novelties – ELIO & CRONO: ESPRIT Reveal



- easy manual and automatic peak identification
- compare spectra
- background subtraction and deconvolution / peak fitting
- spectra quantification with selectable and customizable evaluation methods





- visualization and overlay of sample images and hypermaps for multi-element display
- cut and extract object spectra
- maximum pixel analysis
- background subtraction and deconvolution

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Study of historic photography Elemental analysis by micro-XRF

Why scan historic photography?

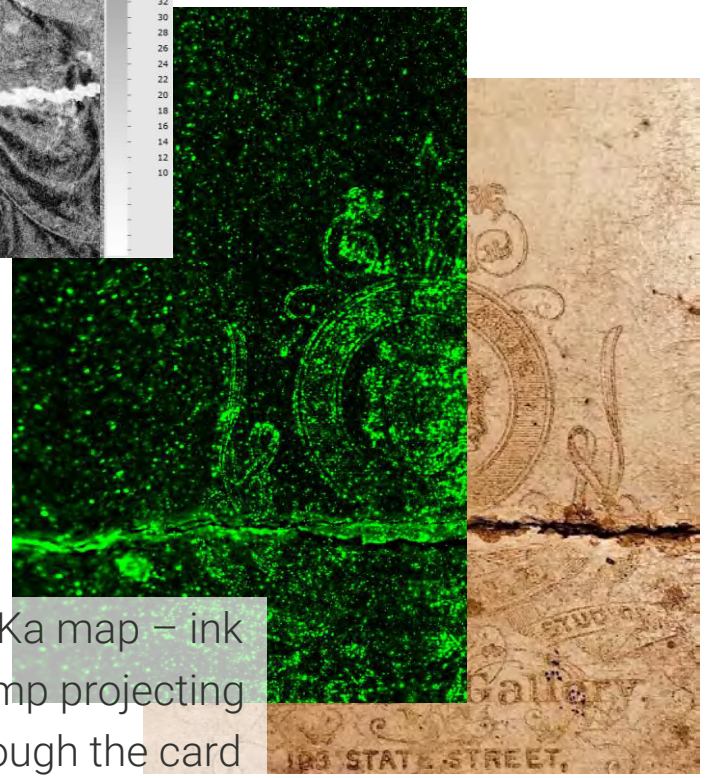
- Recovery of damage, accessing the original image when no longer easily visible optically
- Understanding historic photographic processes, including materials and methods
- "Seeing through" later retouching and overpainting

M4 TORNADO micro-XRF

- Recovery of fine elemental detail

Optical image of late 1800's B&W print on card

Ag-La element map (gradient inverted) to show "positive" image



Cu-Ka map – ink stamp projecting through the card

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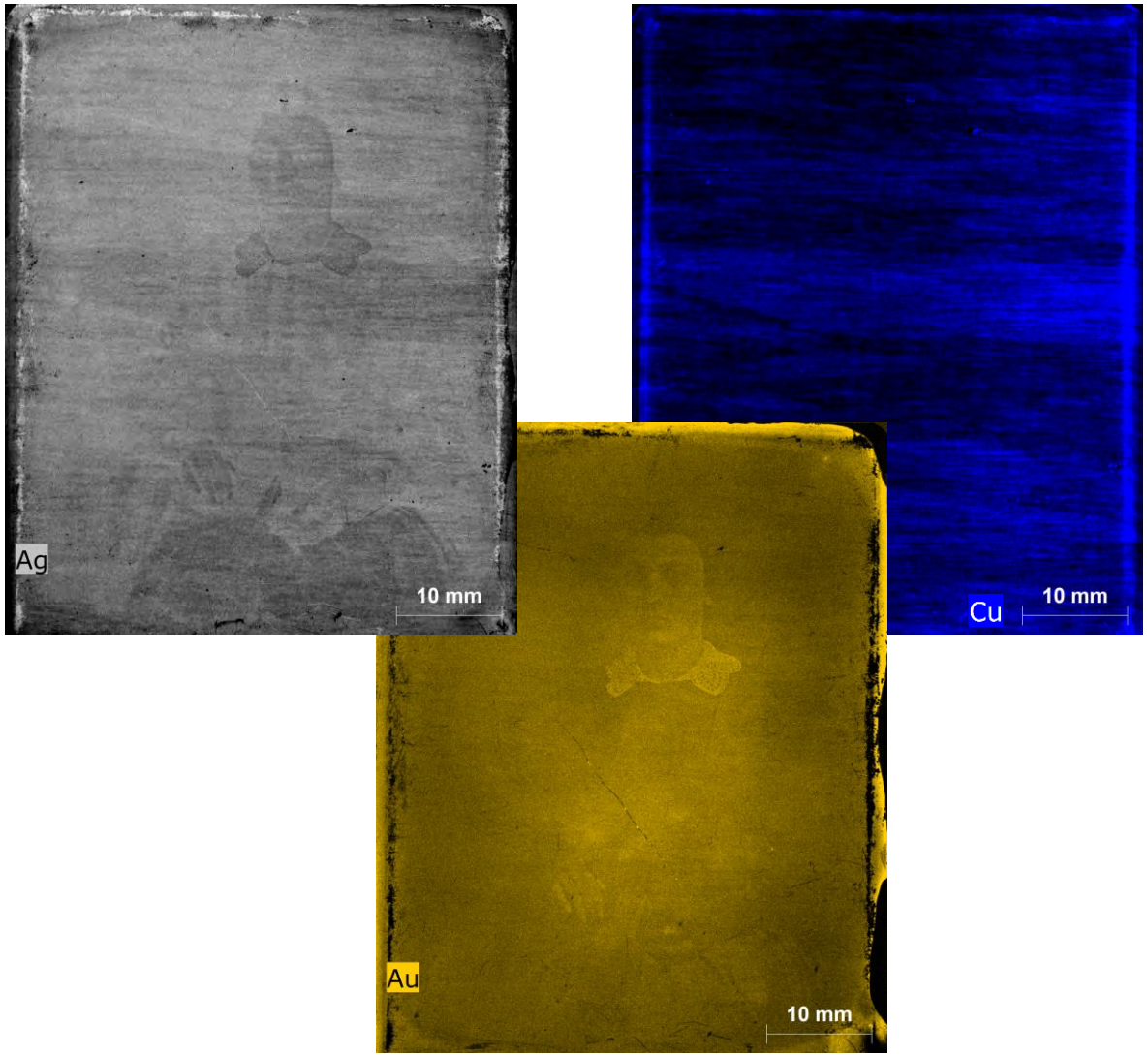
Study of historic photography Elemental analysis by micro-XRF

- Recovering images from a damaged daguerreotype

Optical image of a 1/9 plate daguerreotype photo that is mildly scratched and tarnished

Hg image occurs as a "positive" due to the daguerreotype process, recovering fine detail



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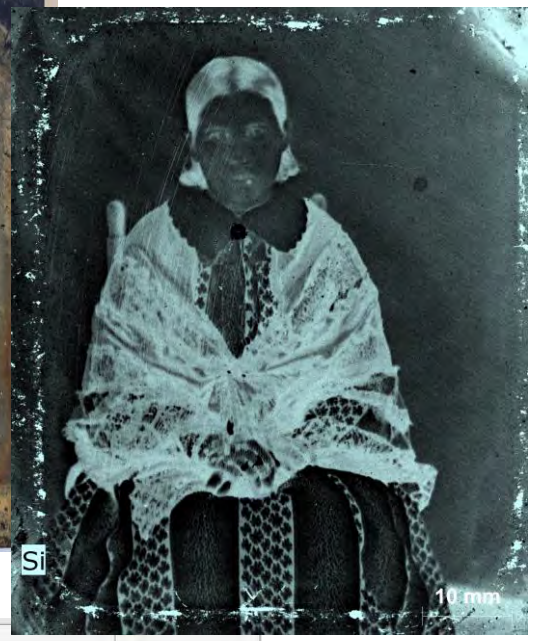
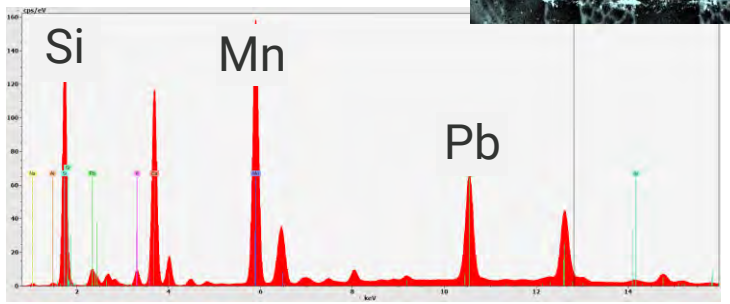
Study of historic photography Elemental analysis by micro-XRF

- Tin-type photograph on a base of Si-Pb-Mn glass

Optical image





Si-map appears as a "negative" due to shielding by the Ag that defines the image

The photograph was retouched with Au-paint to "create" jewelry, which is lacking in the original image

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Novelties – M6 JETSTREAM : Double Detector

Using 2x 60 mm² SDDs results in a significant improvement of signal acquisition

- The Geometry reduces the “shadow” effect
- The dual-detector setup with independent signal processing units allows for maximizing the detectable counts while retaining good spectroscopic resolution and low dead times

More signal per time → faster scanning and/or better signal to noise ratio and lower sample dose → passive improvement without increasing sample irradiation

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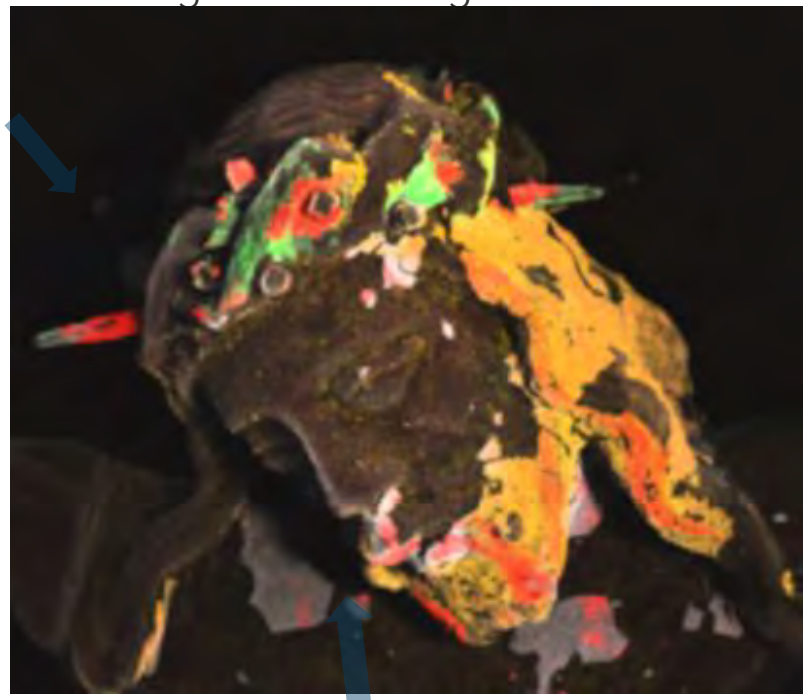
Novelties – M6 JETSTREAM : Double Detector

Single detector
“looking” from the right



Detection “shadow”

Double detector
“looking” from both sides

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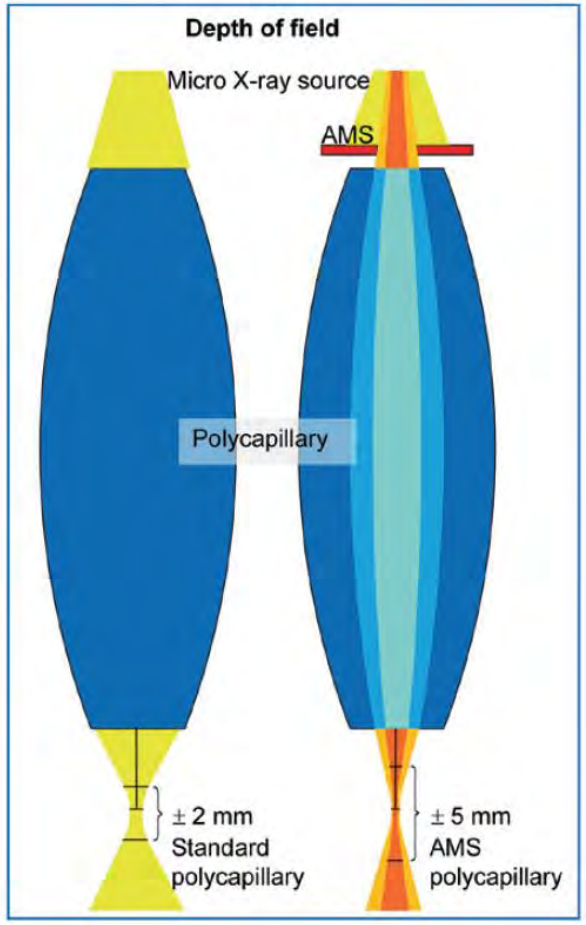
Novelties – M6 JETSTREAM : Aperture Management System



The AMS enables:

- A narrower beam
  - ➔ To keep things in focus, even below and above the analytical distance
- A longer working distance
  - ➔ Less chance of collisions
  - ➔ So variations in sample height are not critical
- Smaller spots for light elements
  - ➔ So lighter elements are resolved better

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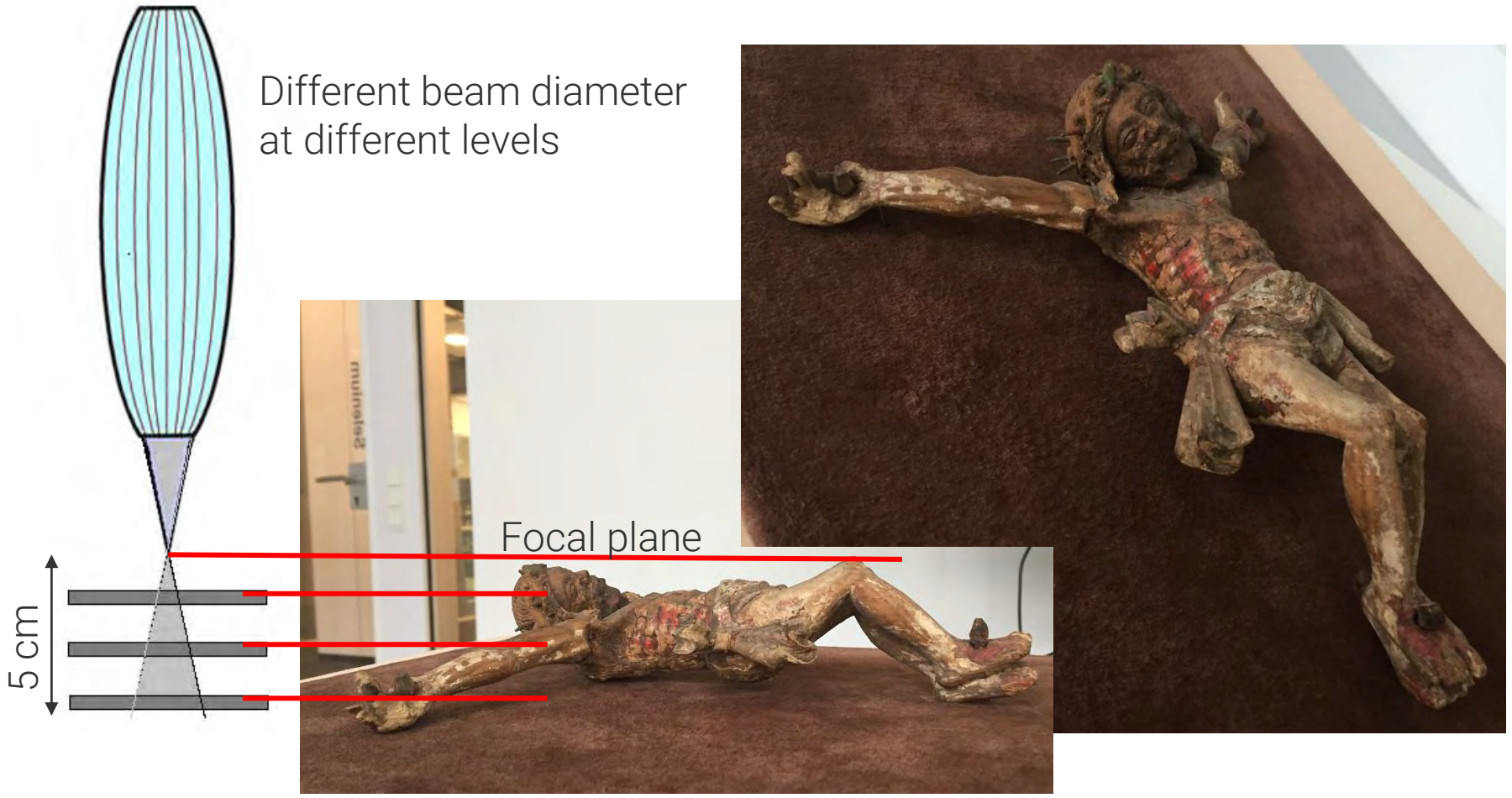
Novelties – M6 JETSTREAM : Aperture Management System



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Novelties – M6 JETSTREAM : Aperture Management System

Standard setting

AMS 500 µm

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Novelties – M6 JETSTREAM : Aperture Management System

Standard setting

zoom

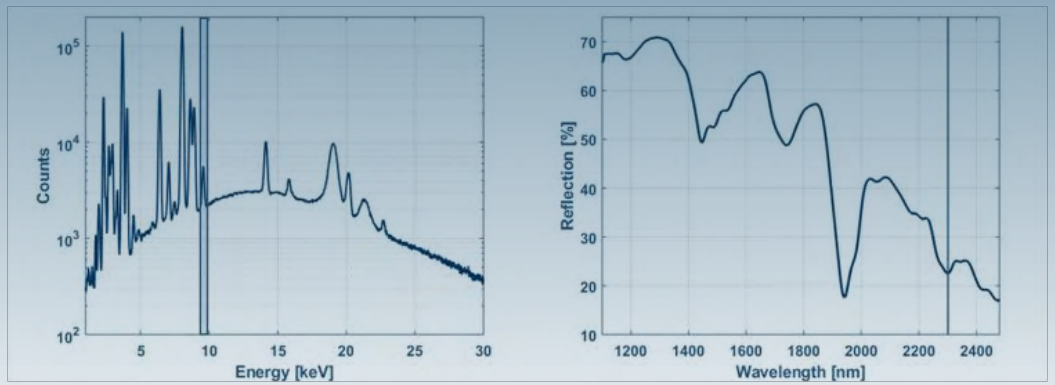
AMS 500 µm

© 2021 Bruker

BNA XGC

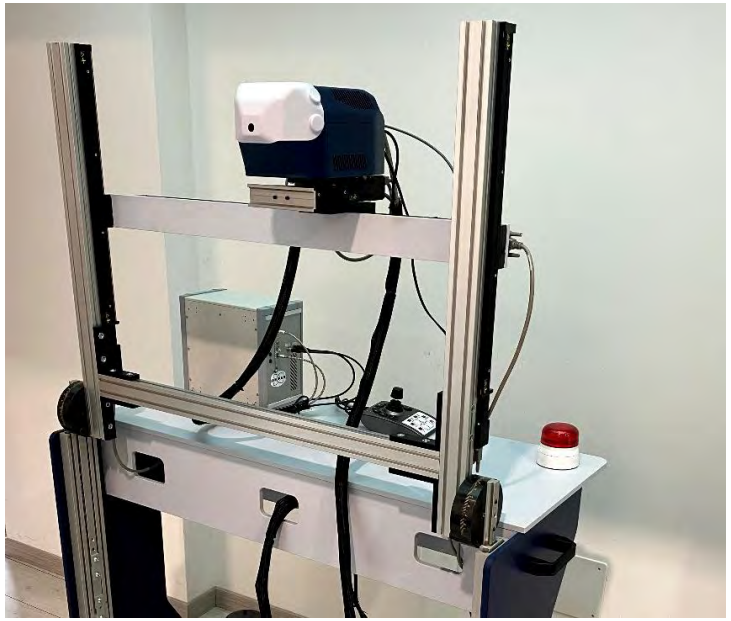
Novità dai nostri laboratori R&D: combinando la tecnica XRF con tecniche di analisi complementari

Alessandro Tocchio



BRUKER Engineering Specials for Art & Conservation

- XRF is a widely adopted technique in Art & Conservation studies, but the data obtained with XRF are often completed by other techniques:



Towards a more comprehensive analysis: XRF combined with complementary techniques

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HYDRA – Portable XRF-XRD

HYDRA Detection head

- X-ray Tube: 30W, 10-50kV (Cu anode)
- XRF detection: SDD with < 135 eV FWHM@Mn Kα
- XRD detection: 2D Photon Counting detector, 20°-55° in 2θ

Vertical Mounting on Tripod

0°-90° Tilt for Horizontal setups

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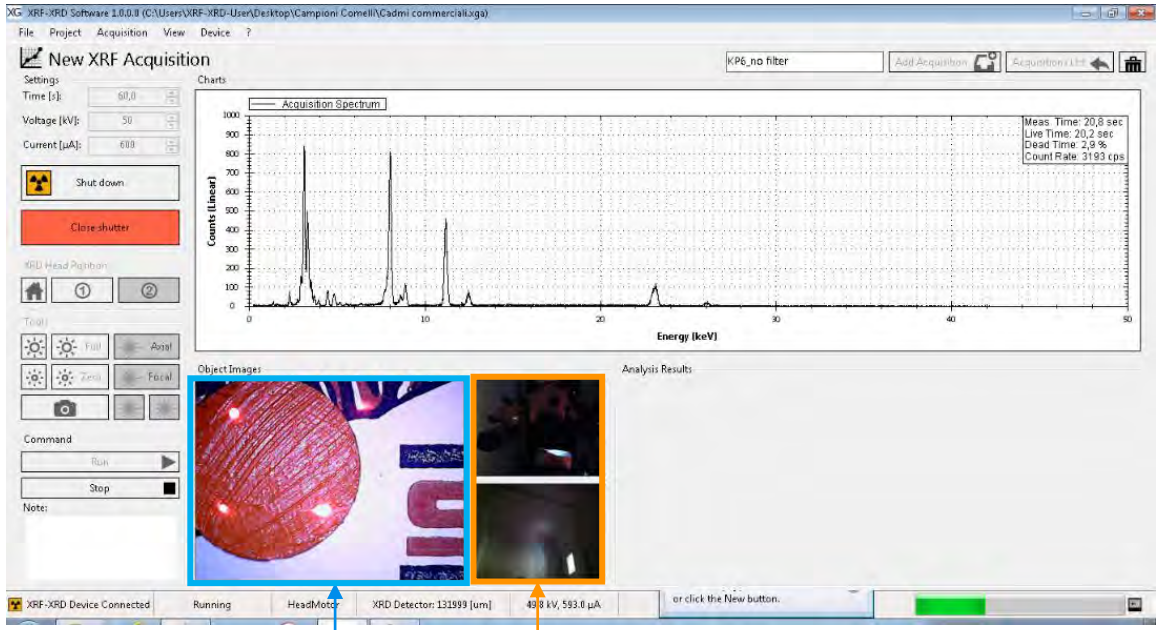
HYDRA – Portable XRF-XRD

- HYDRA Acquisition Software overview

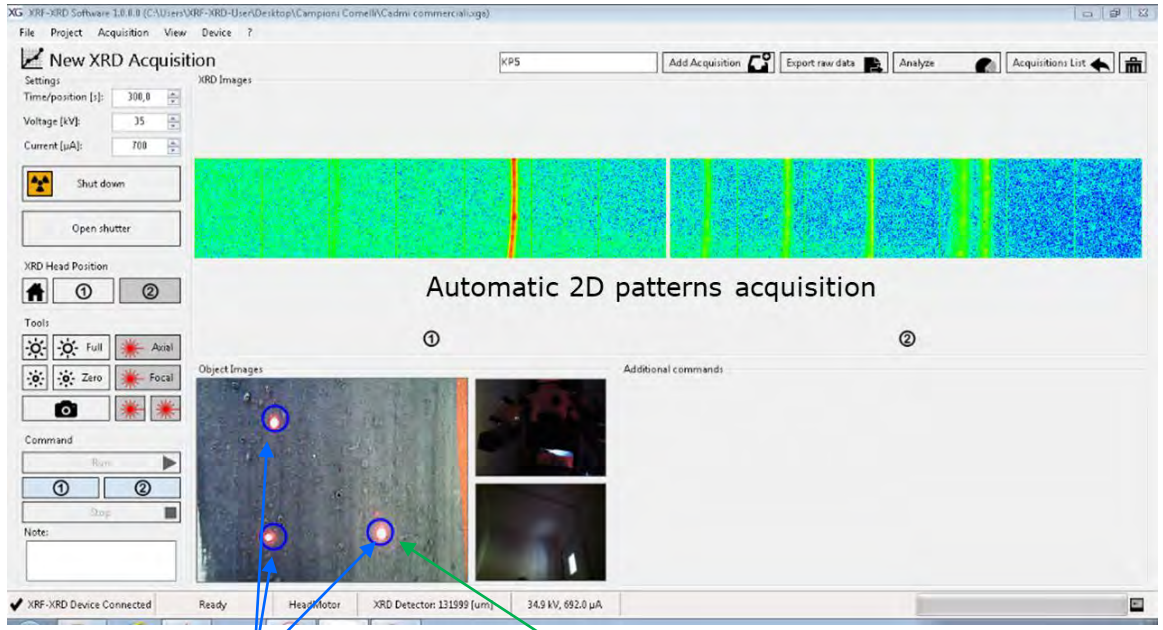
XRF Acquisition Panel



Live microscope camera on area of analysis

Possibility to add up to 2 external cameras

XRD Acquisition Panel



Alignment and focusing system based 4 LASERs

Point of analysis

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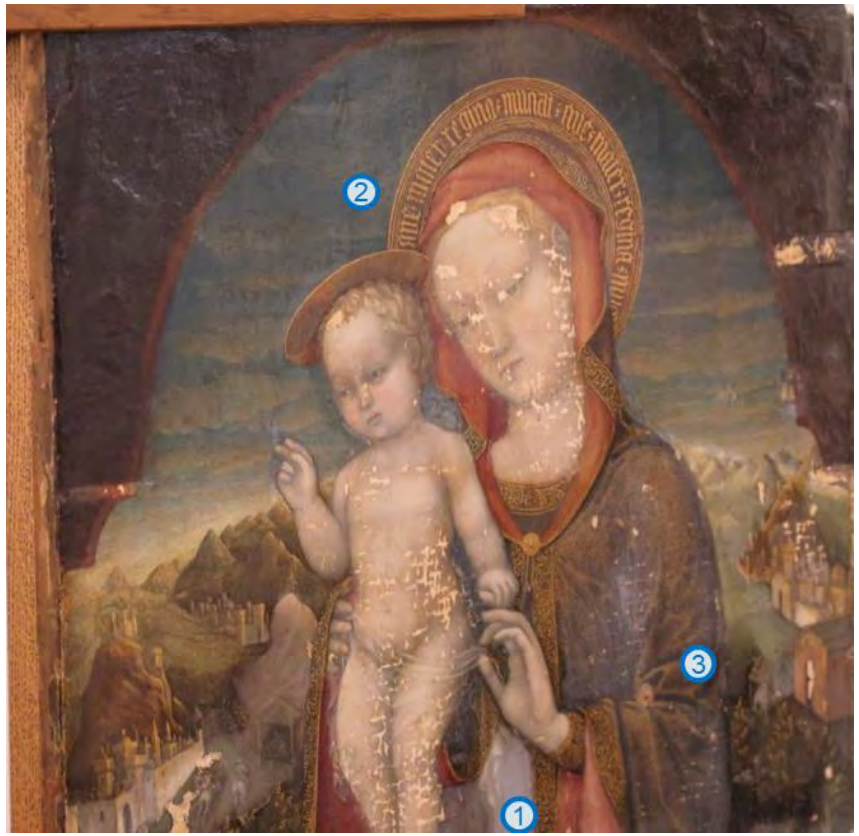
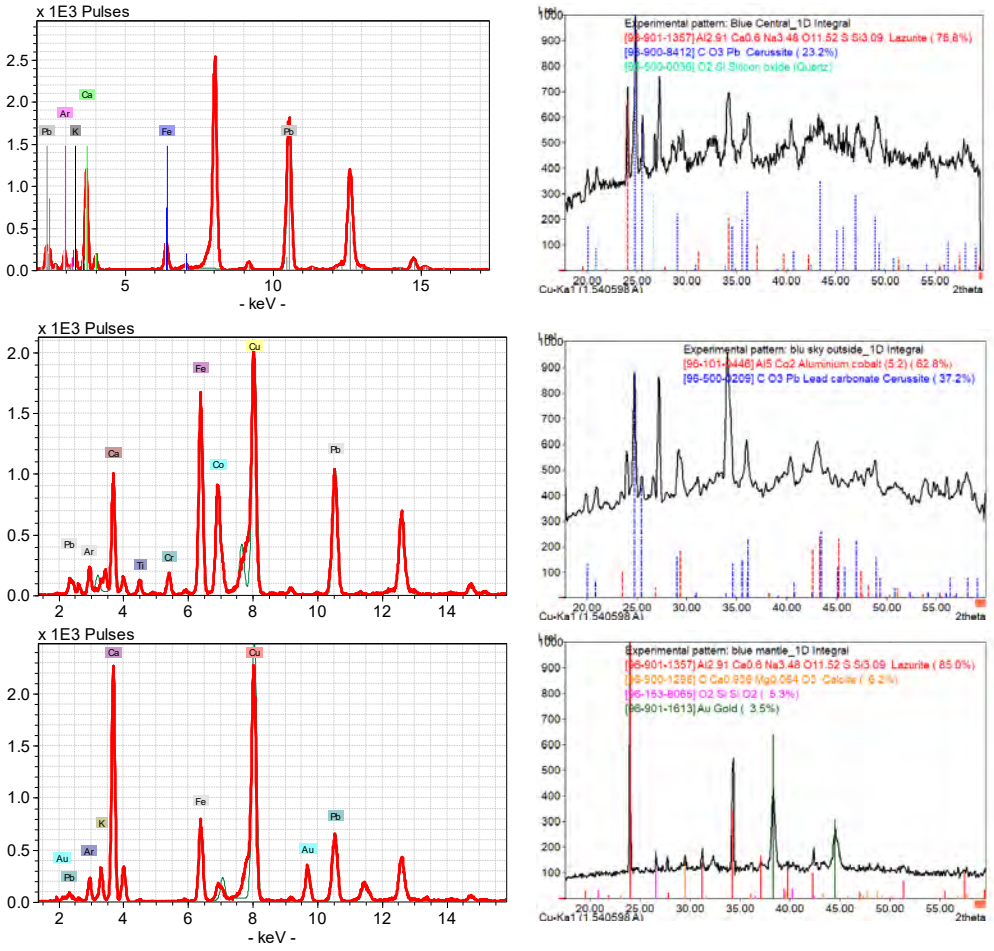
HYDRA – Portable XRF-XRD



Measurements on “Madonna dell’Umiltà adorata da un principe della casata estense”, Jacopo Bellini, Louvre, Parigi

Courtesy of C2RMF



Point 1:

- Lazurite
- Cerussite
- Quartz

Point 2:

- Aluminum cobalt
- Cerussite

Point 3:

- Lazurite
- Calcite
- Gold

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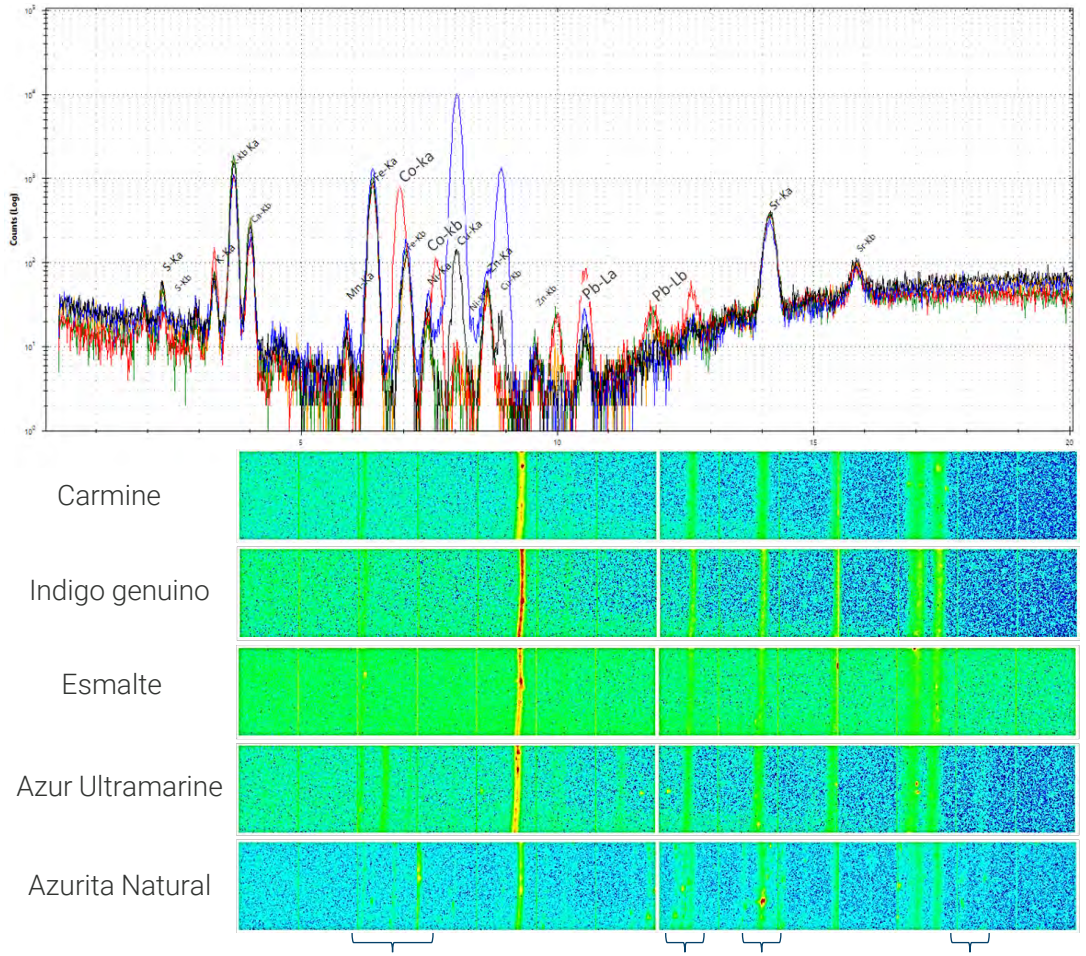
HYDRA – Portable XRF-XRD

Courtesy of Auxiliadora Gomez-Moron, Universidad Pablo de Olavide Sevilla



- Comparison of different pigment XRF spectra
- Identification of preparation layers
- Comparison of 2D diffractograms for different acquisitions
- Identification of common and different diffraction patterns

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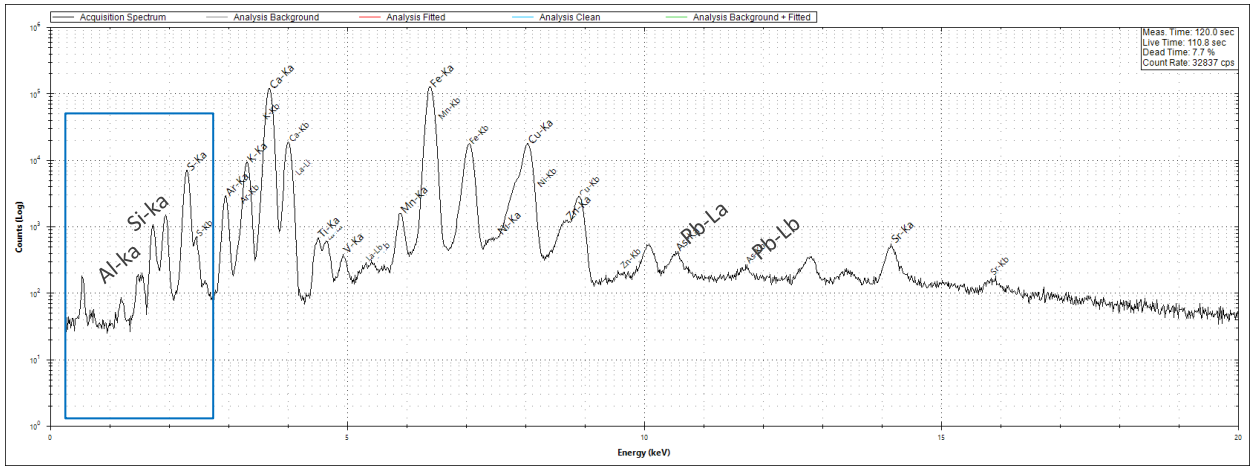
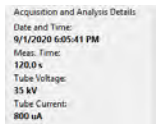
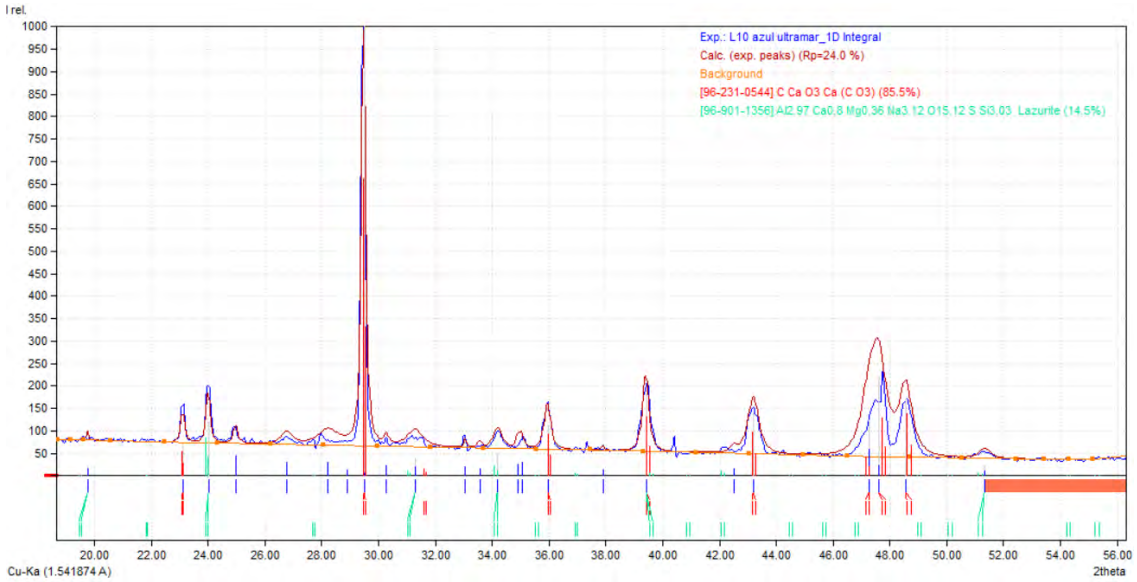
HYDRA – Portable XRF-XRD

- The case of ultramarine blue







Thanks to **the selectable filtering options**, Hydra has outstanding performances at **low energies (<2keV)** in air.

Aluminum [Al-ka] and Silicon [Si-ka] were successfully detected.

Courtesy of Auxiliadora Gomez-Moron, Universidad Pablo de Olavide Sevilla

By setting the constraints on the presence of Aluminum, Silicon and Sulfur first and on the presence of Calcium after, it was possible to identify the presence of **Calcite** and **Lazurite (** (used typically for ultramarine blue)

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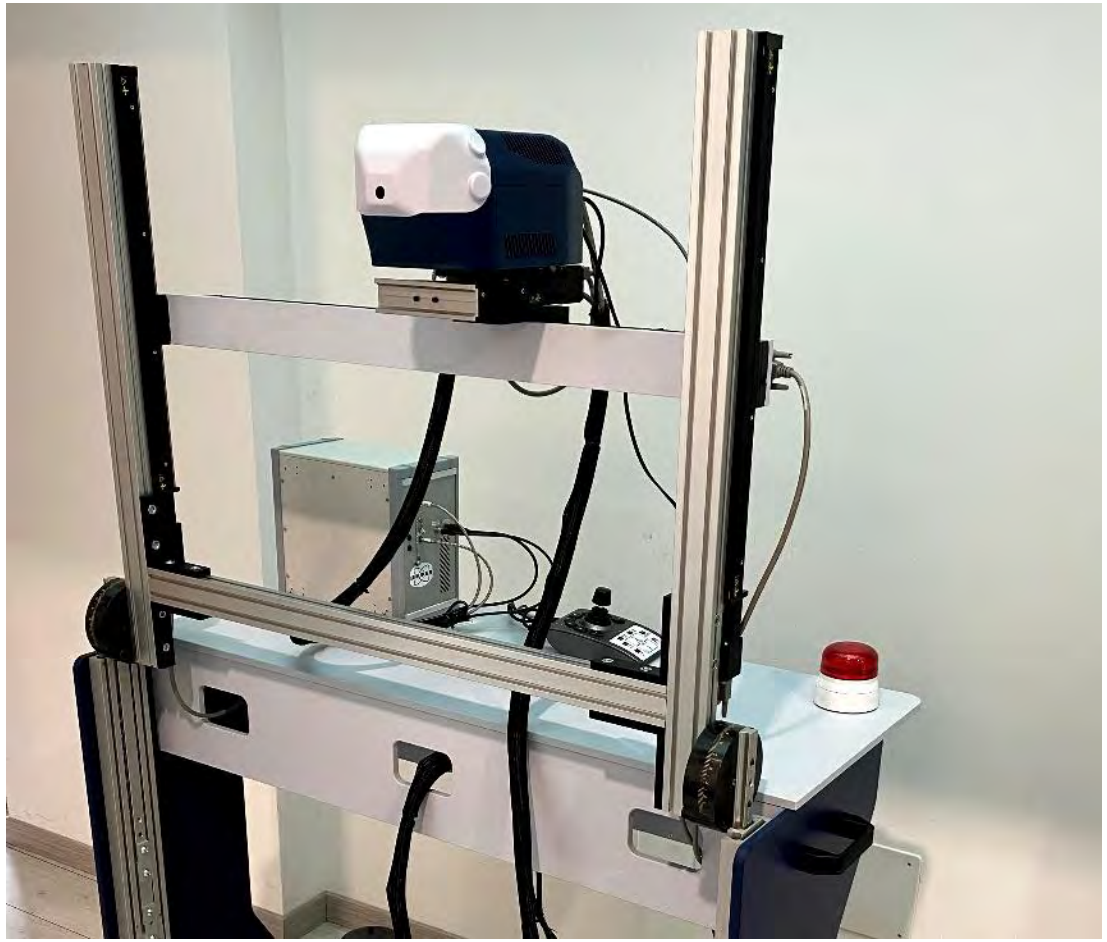
IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER



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

XRF

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

Reflectance Spectroscopy

- Excitation: Halogen Lamp
- Detection: two spectrometers covering **380 nm** to **2500 nm**

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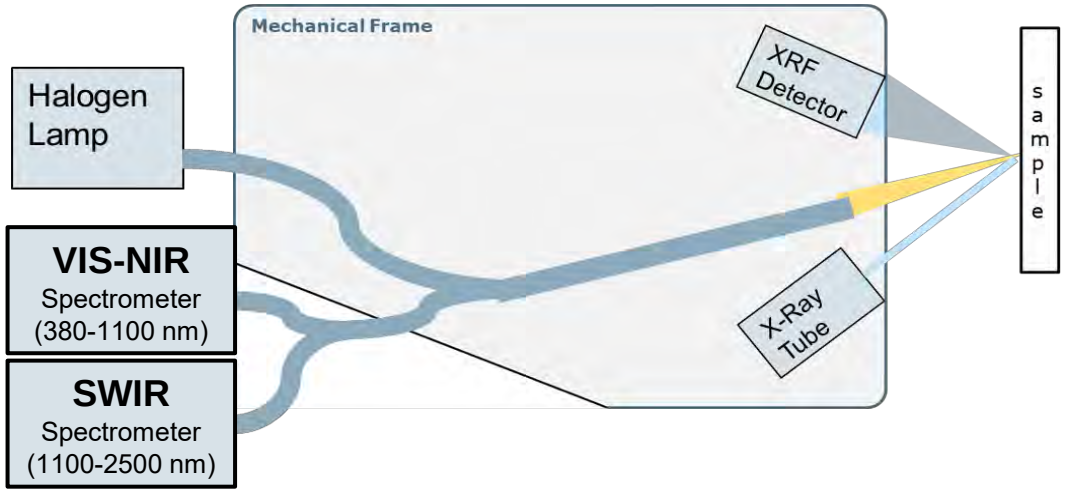
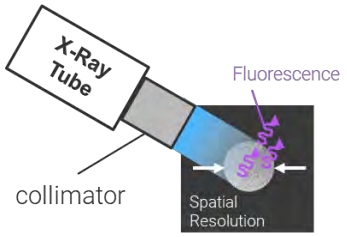
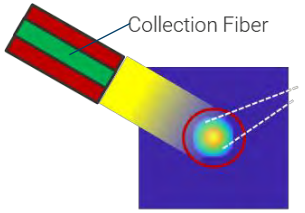
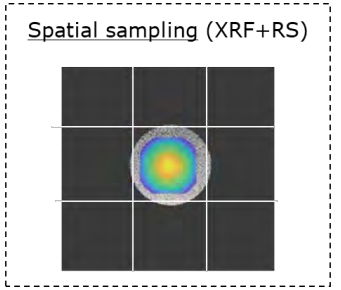
IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER

- XRF and Reflectance Spectroscopy excitation and detection are integrated in a compact detection head:









- X-ray fluorescence optimal geometrical setup
- Coaxial VIS-NIR-SWIR excitation and detection
- Perfectly registered XRF and RS spot of analysis

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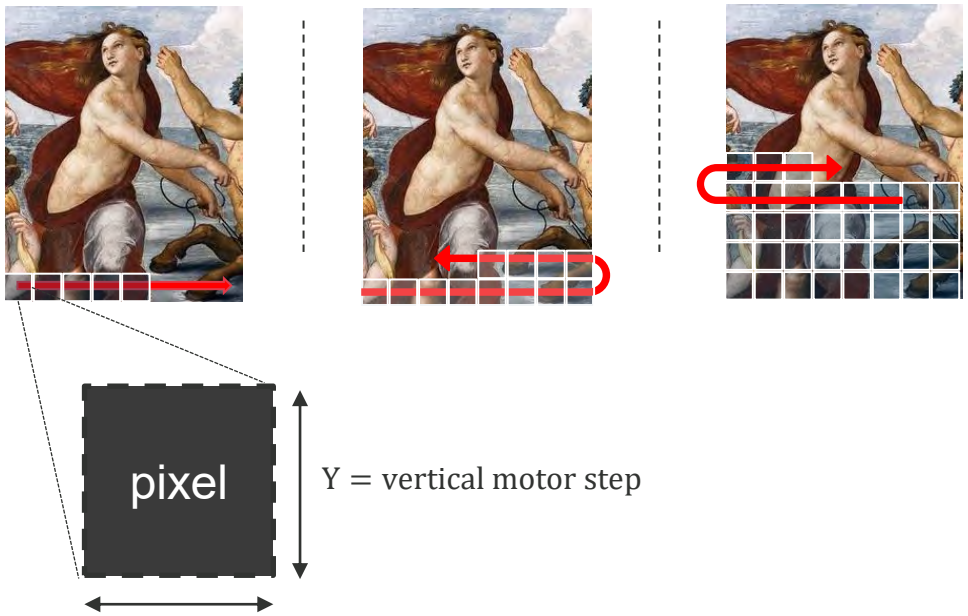
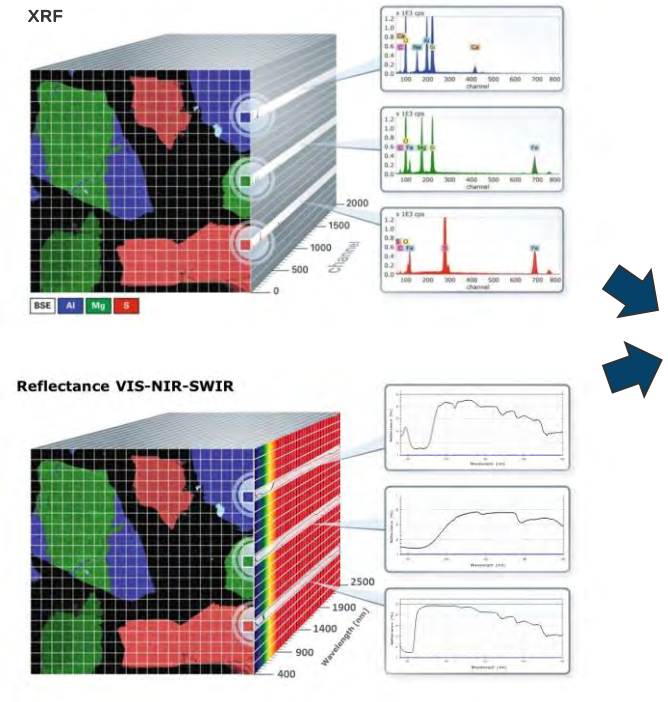
IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER

- Hyperspectral scanning and data output:

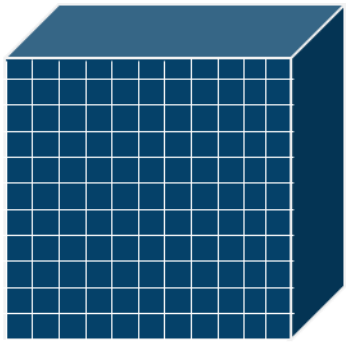
Whisk broom scanning



Data output



Hyperspectral Data Cube



XRF+VIS-NIR+SWIR consistent information for each pixel

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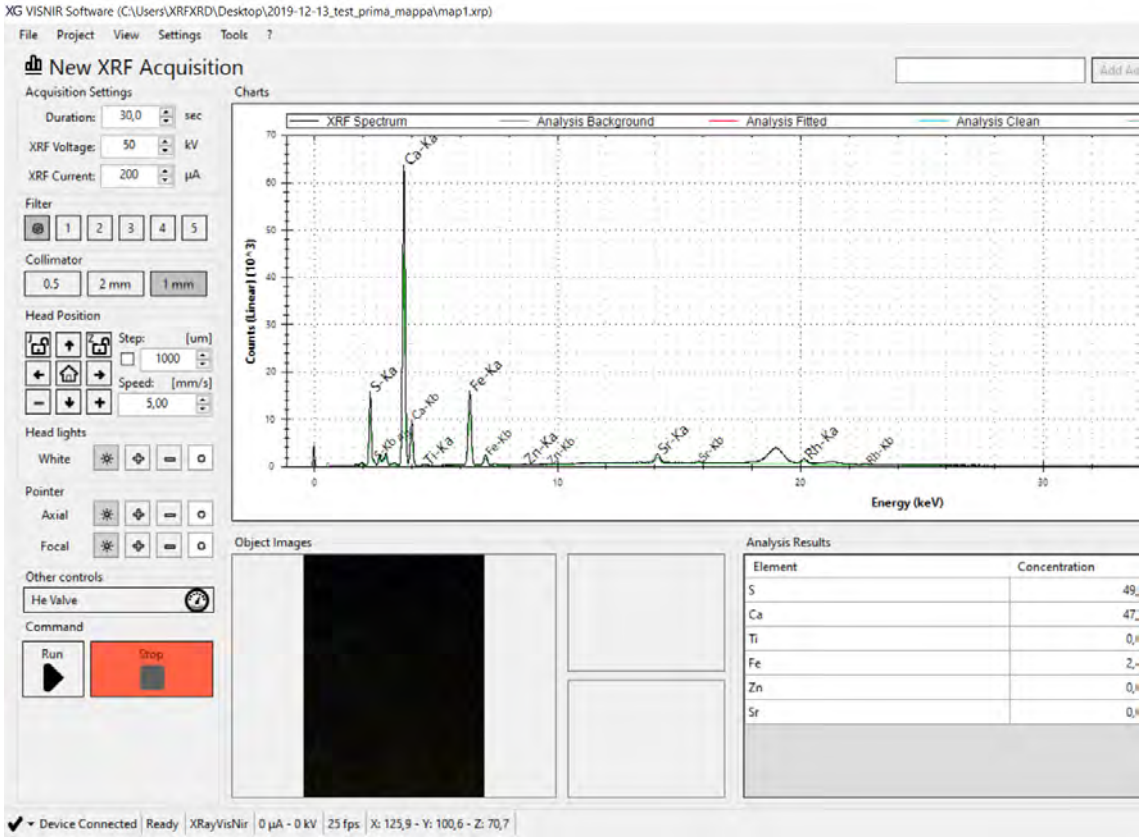
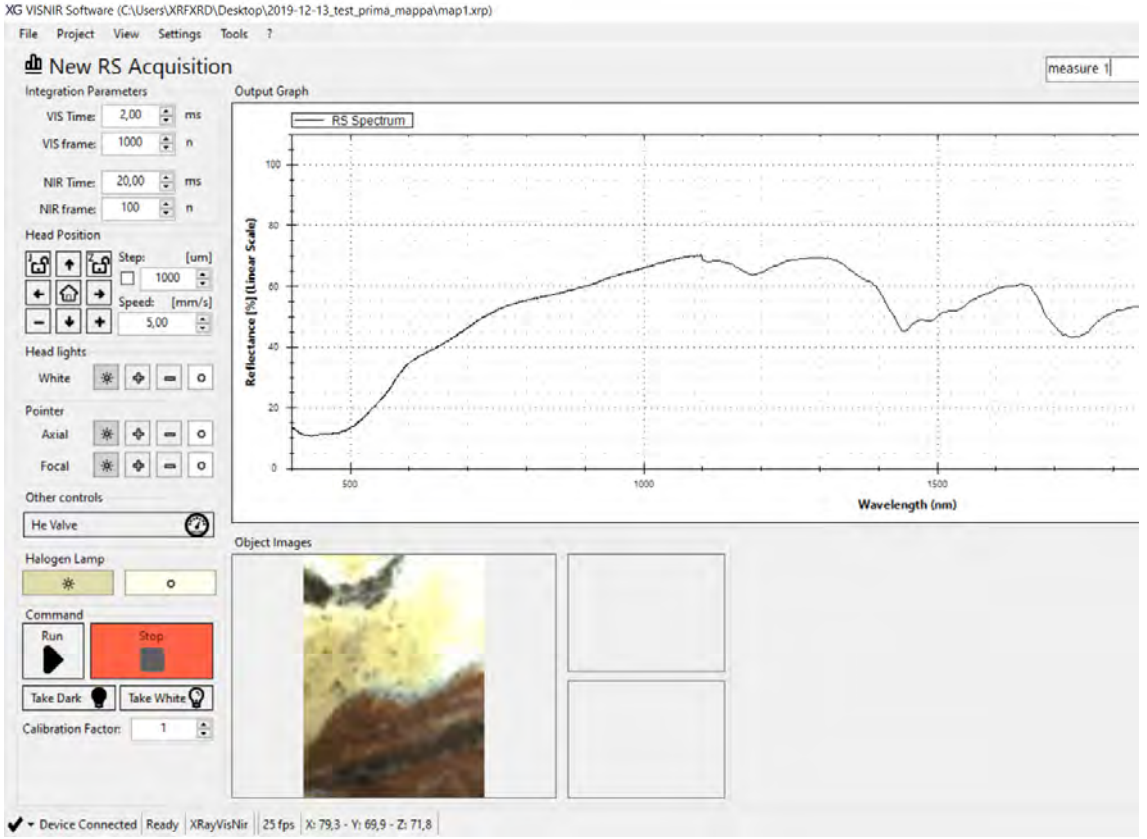
IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER

- IRIS Acquisition Software overview

XRF Acquisition Panel



Reflectance Spectroscopy Acquisition Panel



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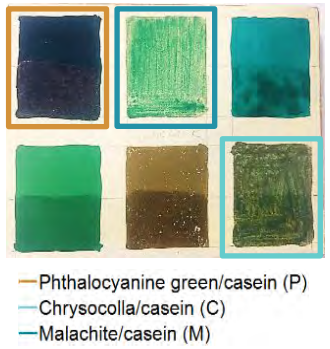
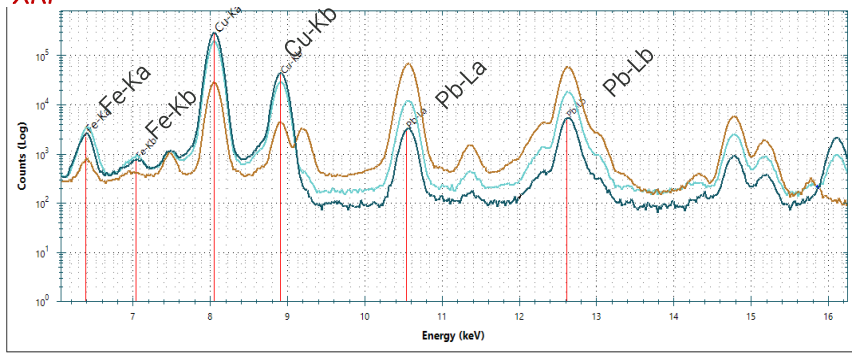
IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER

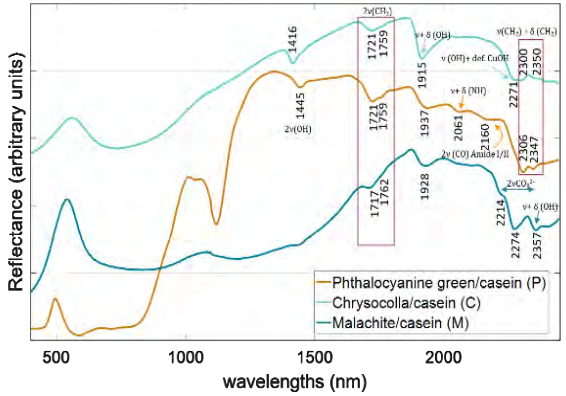
- Examples of elaboration and analysis enabled by the VIS-NIR-SWIR acquisition

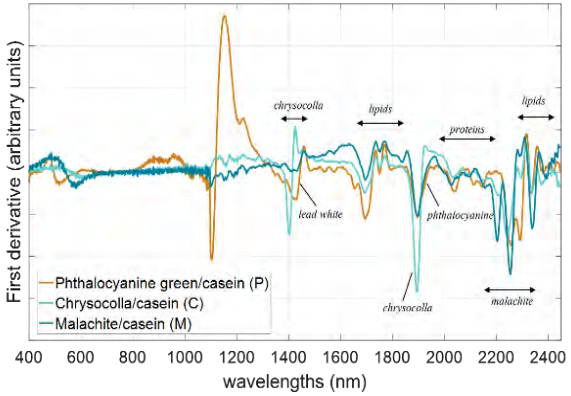


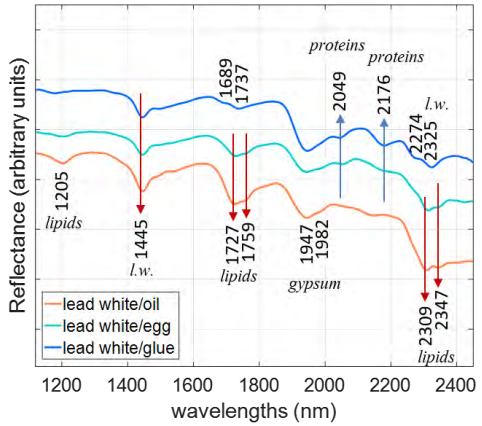
XRF

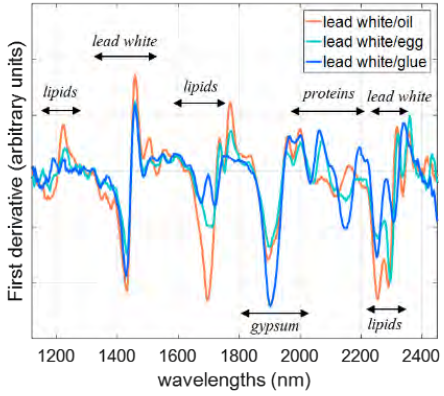


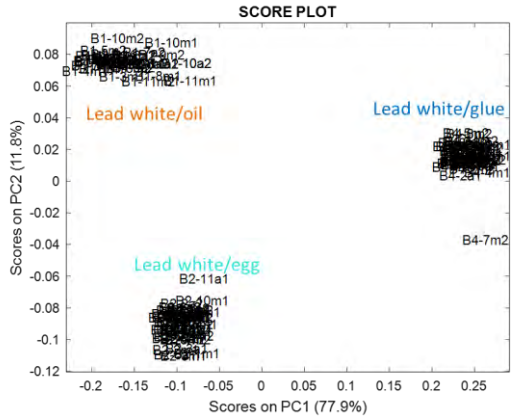
Reflectance











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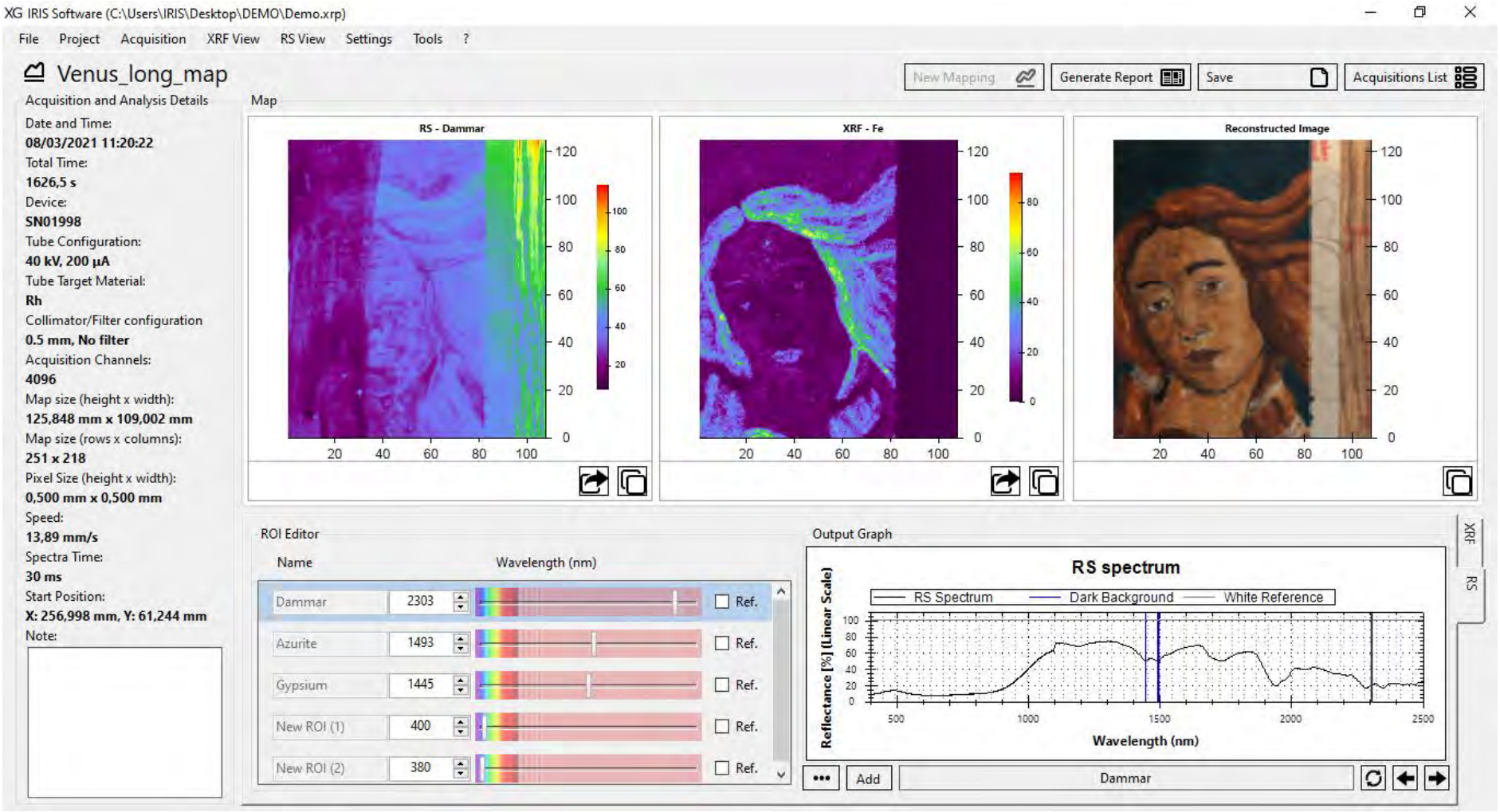
IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER



Work developed in collaboration with the Microchemistry and Microscopy Art Diagnostic Laboratory (M2ADL), Department of Chemistry "Giacomo Ciamician – University of Bologna

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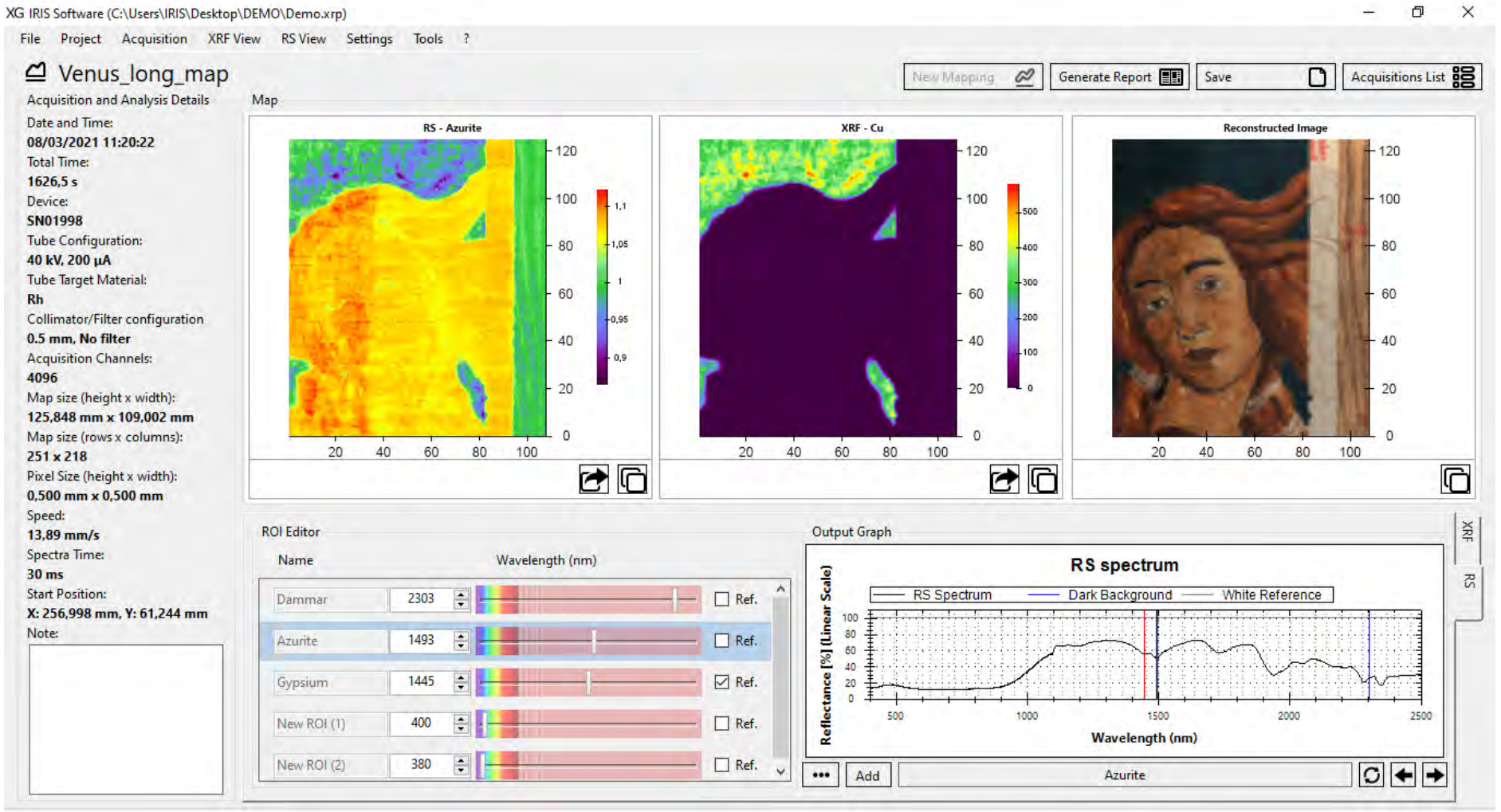
IRIS – XRF/VIS-NIR-SWIR HYPERSPECTRAL SCANNER



Work developed in collaboration with the Microchemistry and Microscopy Art Diagnostic Laboratory (M2ADL), Department of Chemistry "Giacomo Ciamician – University of Bologna

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Strumentazione portatile e archeologia da campo

sfide tecniche e prospettive di ricerca

CLAUDIA SCIUTO DIPARTIMENTO DI CIVILTÀ E FORME DEL SAPERE, UNIVERSITÀ DI PISA
SIMONA RANERI ICCOM-CNR, PISA

LAD-Laboratorio di Archeometria e Diagnostica

- Sviluppo di protocolli non distruttivi per l'analisi in situ e in laboratorio
- Raccolta e condivisione di reference data
- Data sharing, repositories e open data archeometrici

Attività e ricerche archeologiche sul campo

Italia, Francia, Grecia, Turchia, Egitto, Iran, Oman

La rivoluzione dell’archeometria da campo

VERSO UN CAMBIO DI PARADIGMA?

Material biographies come
indicatori ambientali, sociali e tecnologici

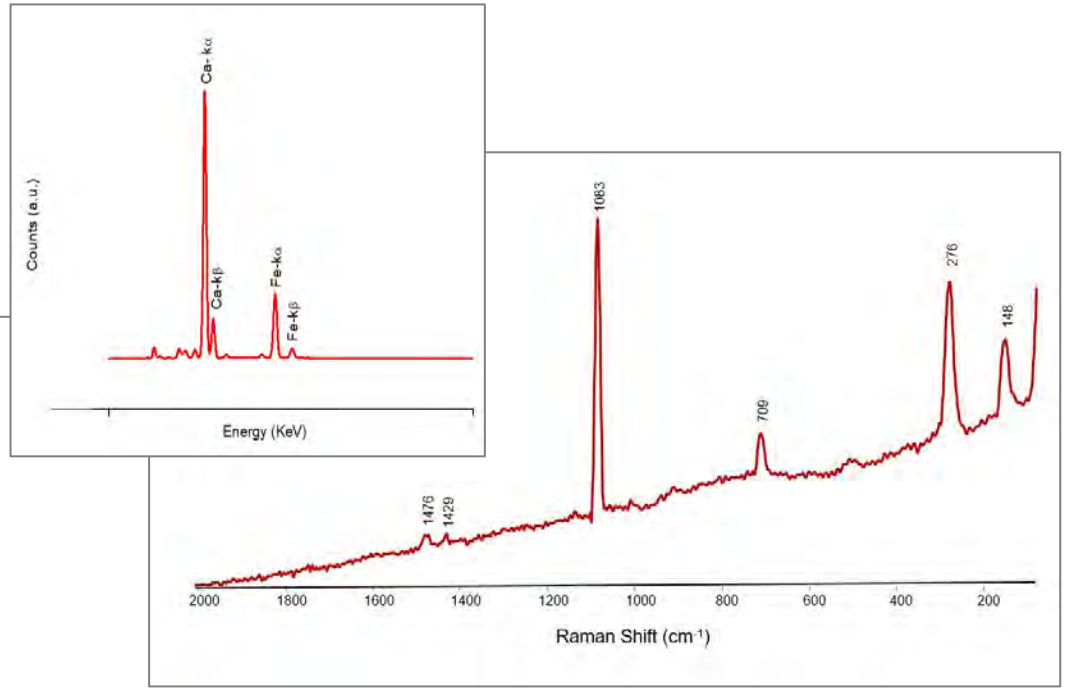
‘The apparent ‘‘discipline’’ of archaeology thus appears very undisciplined’

Hodder I. 1999 The Archaeological Process: An Introduction, p. 19

Archeometria “da campo”: challenges

Contesti e problematiche:

- posizionamento della strumentazione
- caratteristiche dei target
- condizioni ambientali
- superfici non “pulite”



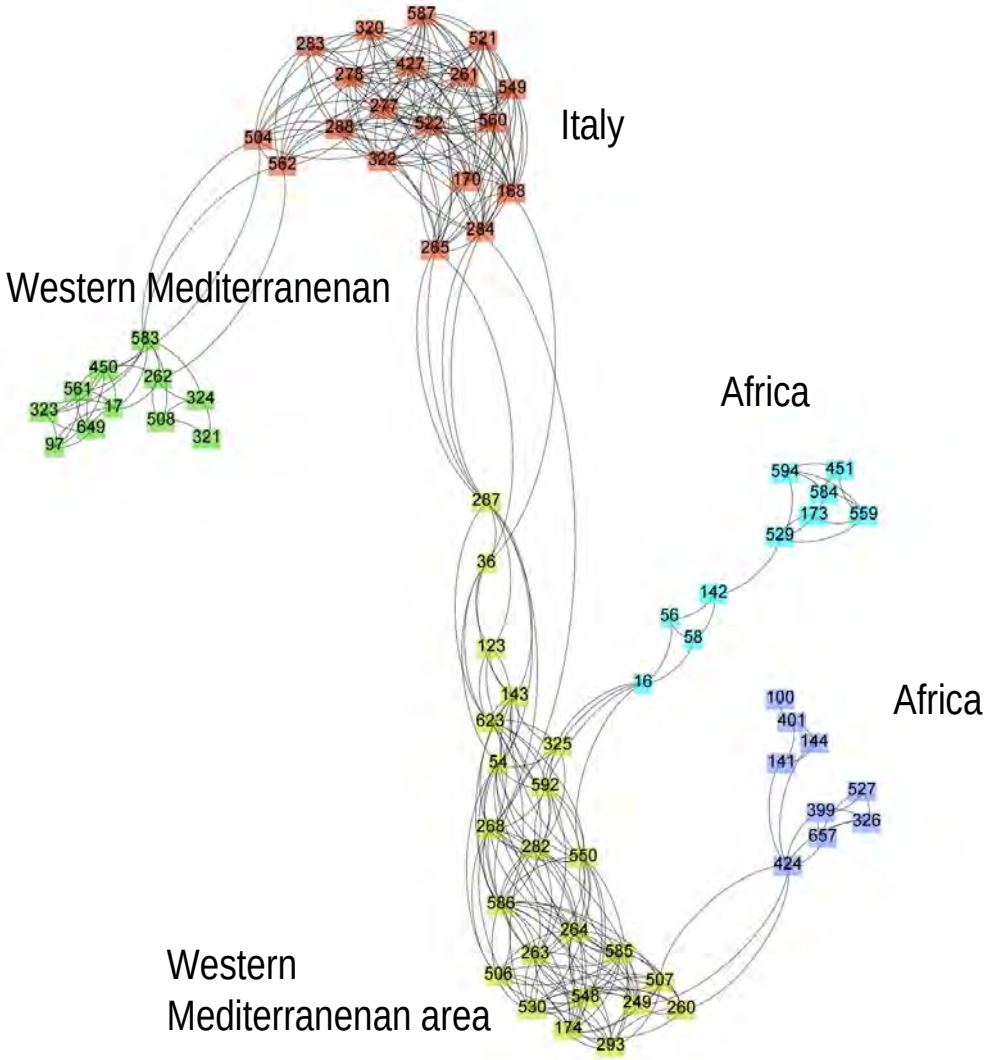
Ricostruzione di cantieri in grandi strutture (Villa Tardo Romana *dei Vetti*, Capraia-Limite sull'Arno, Firenze)

Provenienza delle materie prime per interpretare rapporti tra maestranze e modelli architettonici

- confidential -

Ricostruzione di cantieri in grandi strutture (Villa Tardo Romana *dei Vetti*, Capraia-Limite sull'Arno, Firenze)

Murature affrescate frammentarie. ricostruzione del "puzzle" per lettura delle iconografie



Classificazione provenienza *anfore da trasporto*

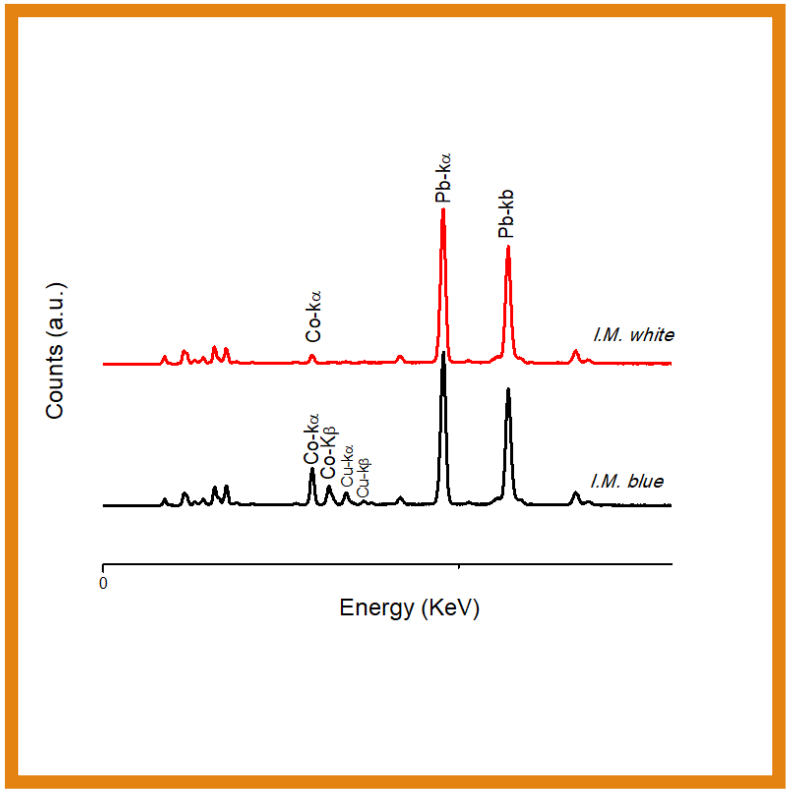
(Acropoli di Volterra)

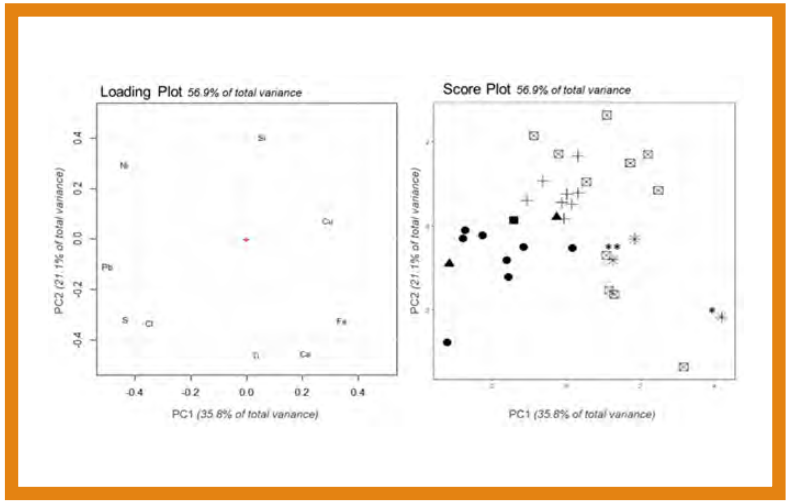
- screening per classificazione rapida di un gran numero di frammenti
- 3 misure per campione
- superficie: pulita, sezione ceramica, no superficie (slips o coatings)
- analisi qualitativa e <u>metodi statistici: Graph Clustering</u>

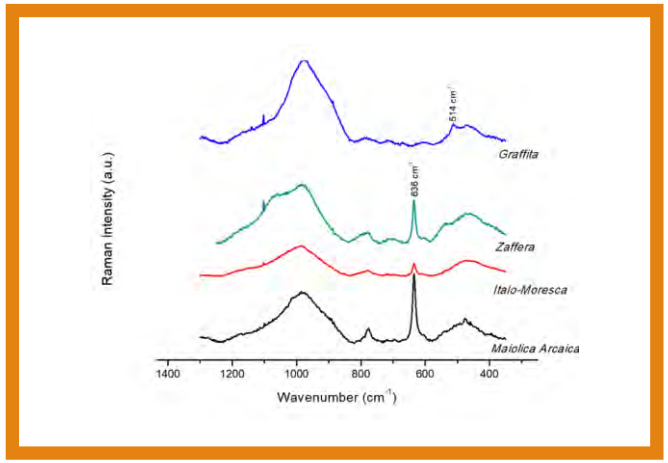
Confronto classificazione geochimica e tipologica:
75.35% attribuzione corretta
23.3% discrepanze: impasti grossolani, in alcuni casi tempers possono influenzare il dato

- confidential -

Classificazione vetrine, smalti e ingobbi da marker tecnologici



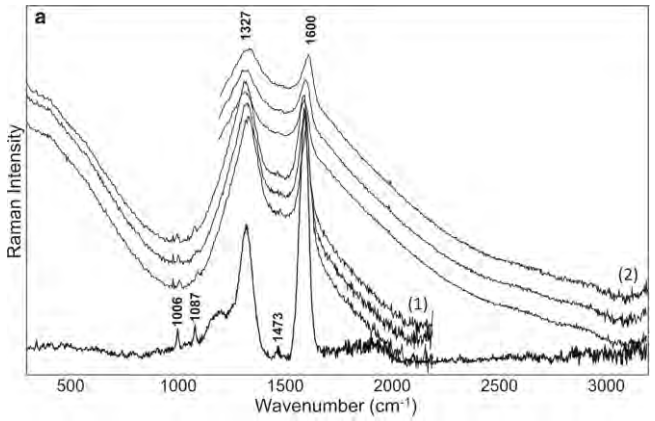




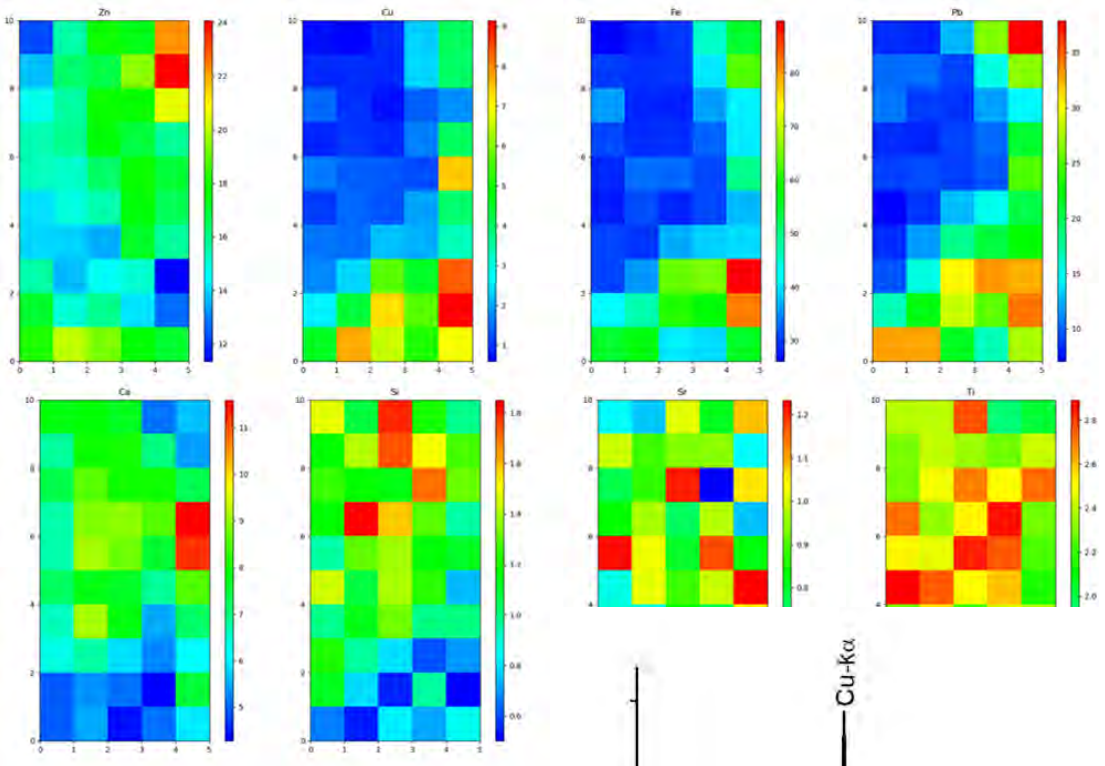
Tracce pittoriche

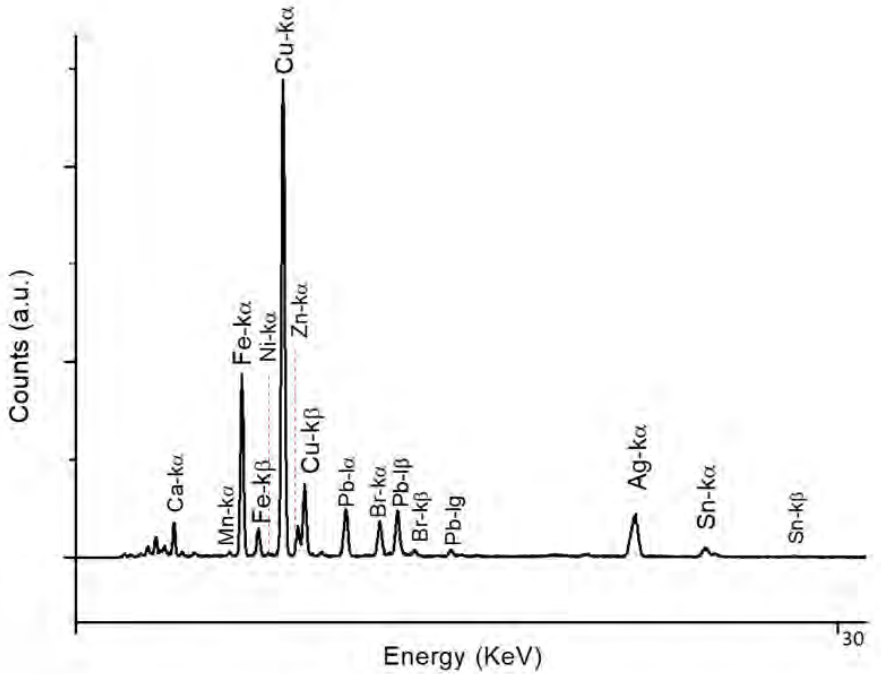
Materiali “organici” su substrato inorganico:

- XRF solo risultati su substrato (marmo)
- Raman utile per determinare natura dei pigmenti e eventuali patine/alterazioni
- Nota: The results retrieved from this handheld system should be handled with caution regarding spectral features and matrix details.



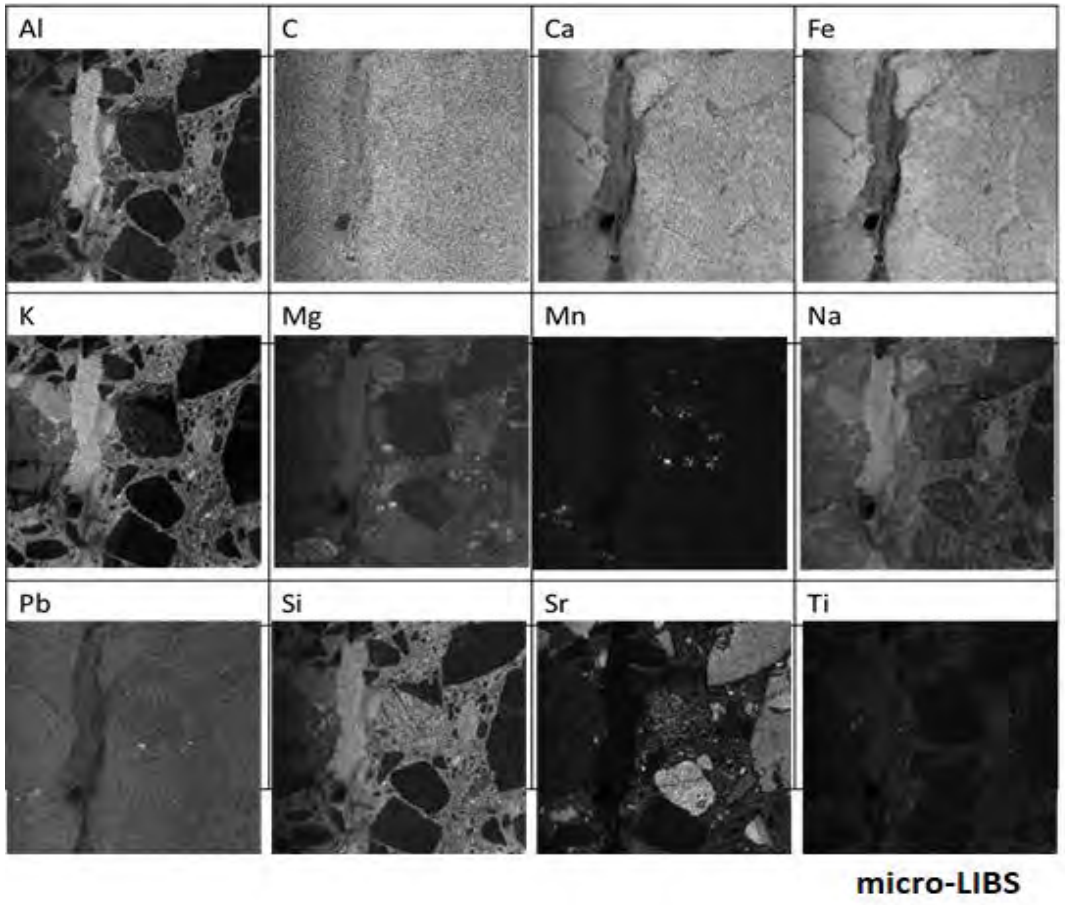
XRF mapping per l’archeologia

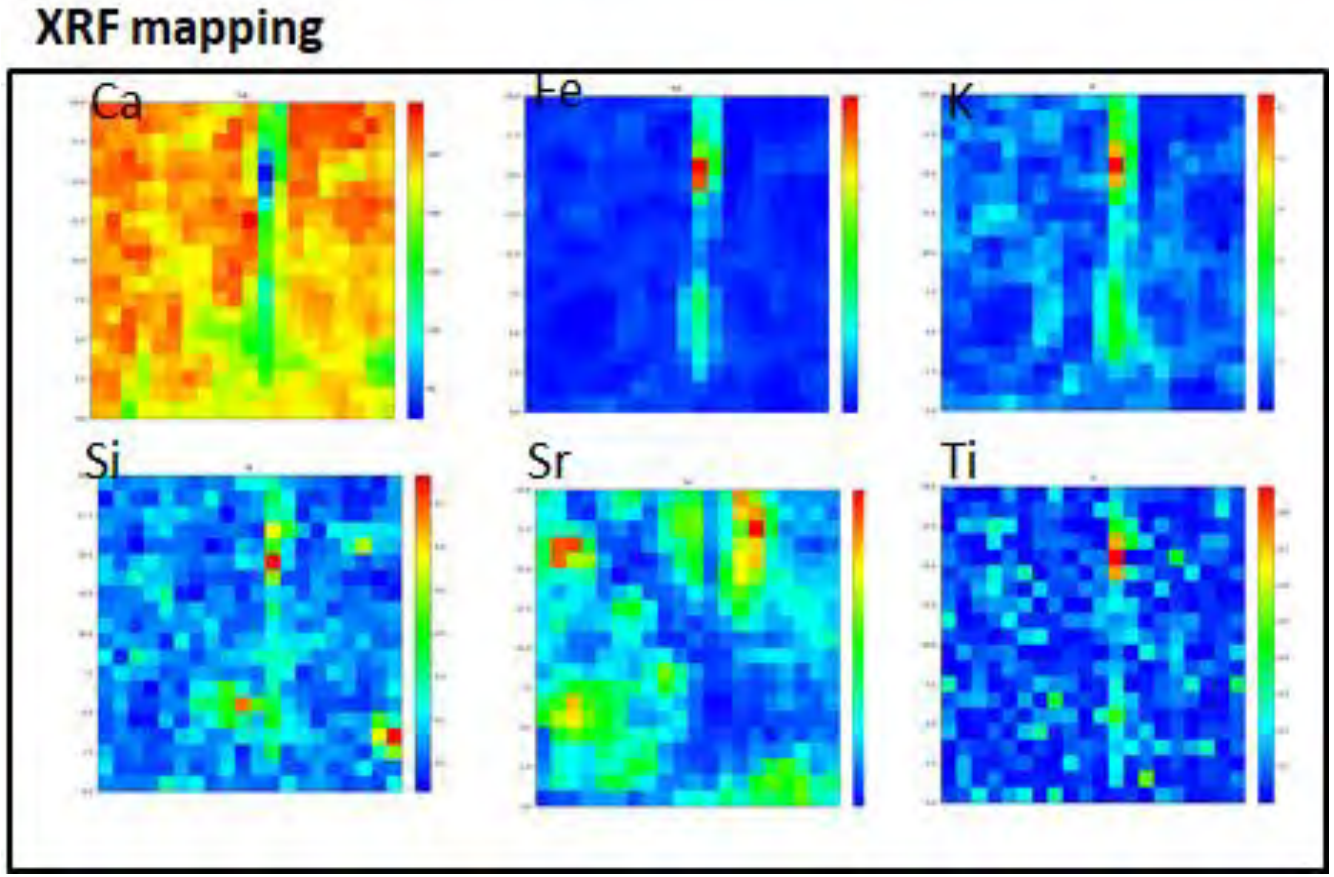


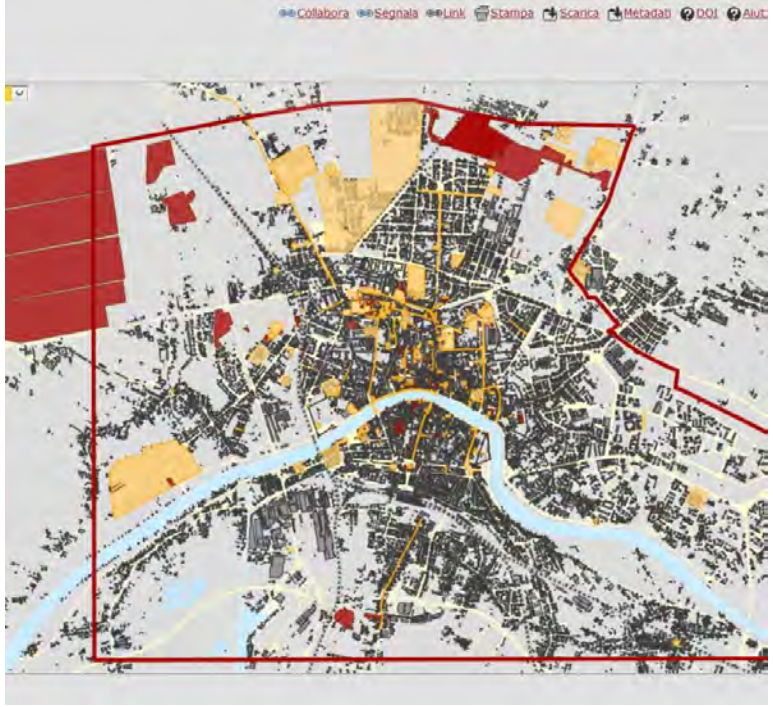


Microchemical mapping su geomateriali eterogenei: protocolli NDT e micro-distruttivi, data fusion

Mapping XRF e micro-LIBS





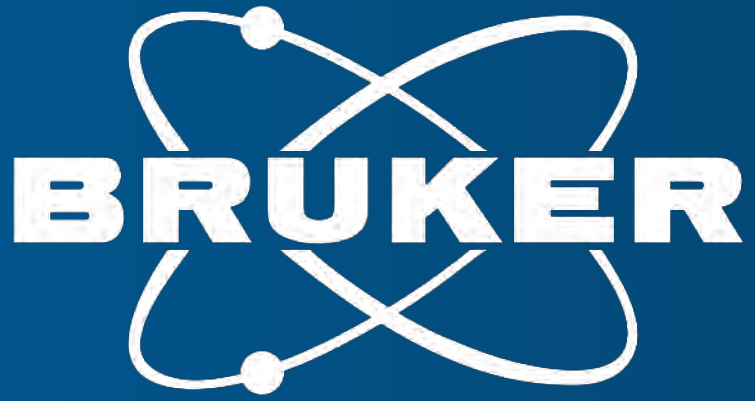


Repositories e open data archeometrici

Sharing is caring!

Rimaniamo in contatto:
claudia.sciuto@cfs.unipi.it
simona.raneri@pi.iccom.cnr.it

Thank you!



Innovation with Integrity