Consiglio Nazionale delle Ricerche | ISPC ISTITUTO di SCIENZE del PATRIMONIO CULTURALE | INFN

X-ray methods for cultural heritage applications

Francesco Paolo Romano

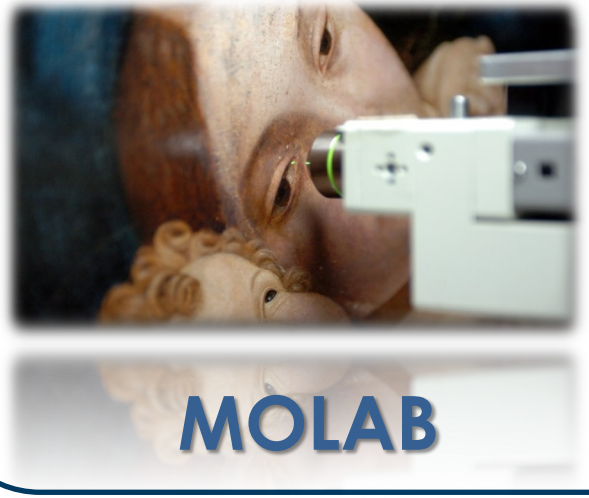
E-RIHS
EUROPEAN RESEARCH INFRASTRUCTURE FOR HERITAGE SCIENCE

XRAYLab, ISPC-CNR & LANDIS, LNS-INFN

Developments of advanced X-ray methods for the non-invasive investigation of tangible cultural heritage

- MA-XRF /uXRF (mobile)
- MA-XRPD (mobile)
- Confocal XRF (mobile)
- TXRF/GIXRF (mobile)
- XANES/EXAFS (lab.)
- PIXE (lab.)
- PAA (lab.)

E-RIHS: European Research Infrastructure on Heritage Science



Access to advanced portable equipment and related competences, for in-situ non-destructive measurements on artworks.

E-RIHS
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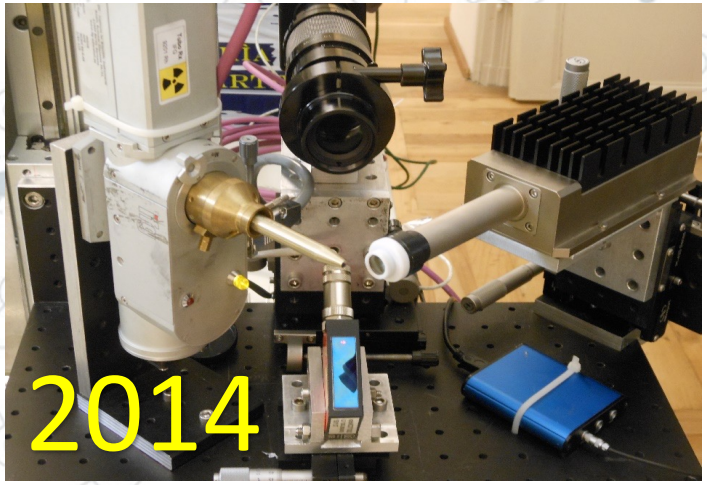
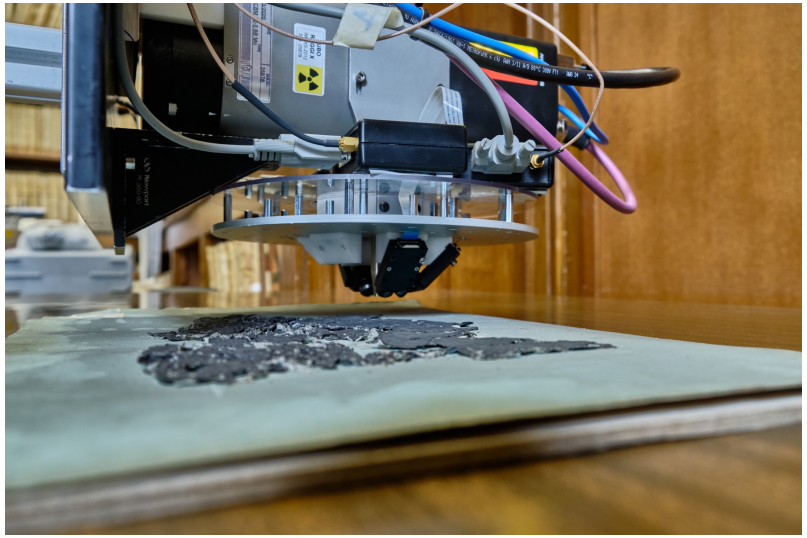
MA-XRF developments at XRAYLab in Catania



NO real time technology
step by step scanning
1 -SDD detector

Real time technology & imaging
continuous scanning at 100mm/s
2 -SDD detectors with TLIST

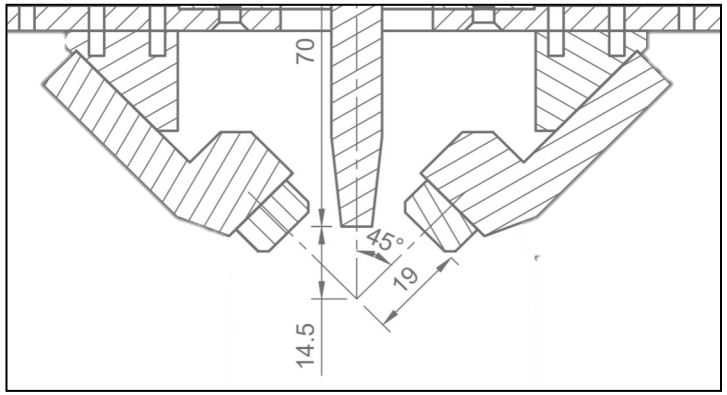
Real time technology & imgaing
Rotational continuous scanning
2-SDD detectors with TLIST



2021

Real time technology and imaging
continuous scanning at 150 mm/s
6-SDD detectors with fast-mapping

Spectrometric head



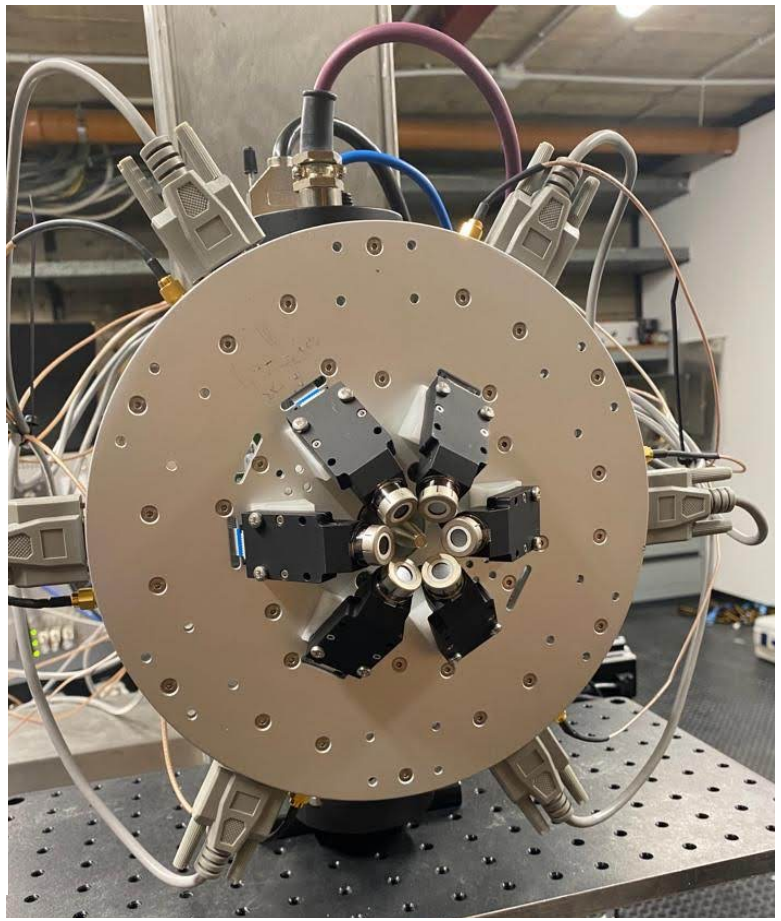
pped x-ray mm-lens detector composed of 6-SDDs

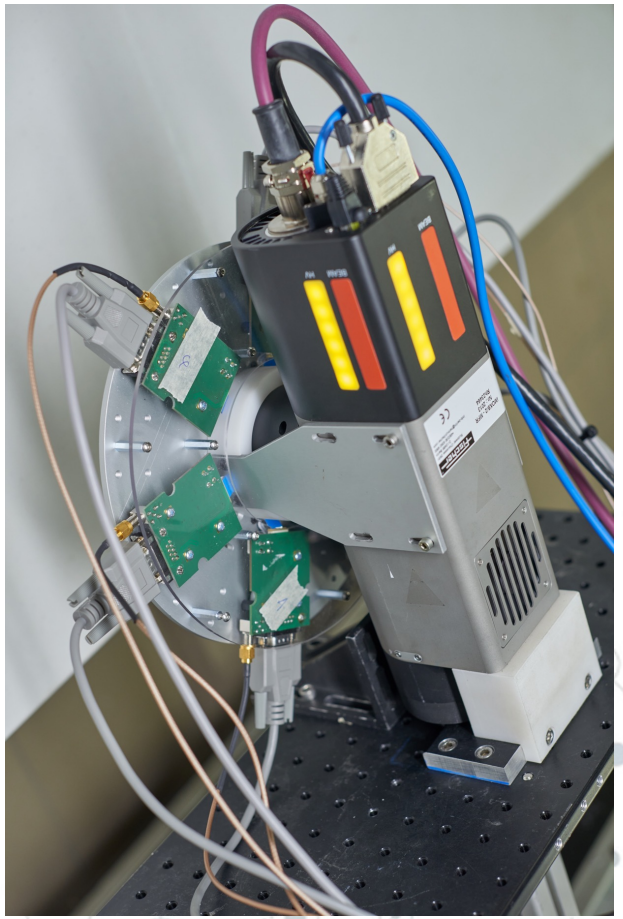
m at operated in parallel arranged in an 3D

annular compact geometry

E, keV	3-5	5-7.5	7.5-10	10-15	15-20	20-25	25-30
Focus size, µm	43	37	33	37	45	50	55
Intensity Gain	3810	3330	12000	13500	10480	5216	550

- Hodoscope
- Some of the detector electronics integrated in the hodoscope





6 SDDs (VIAMP layout):

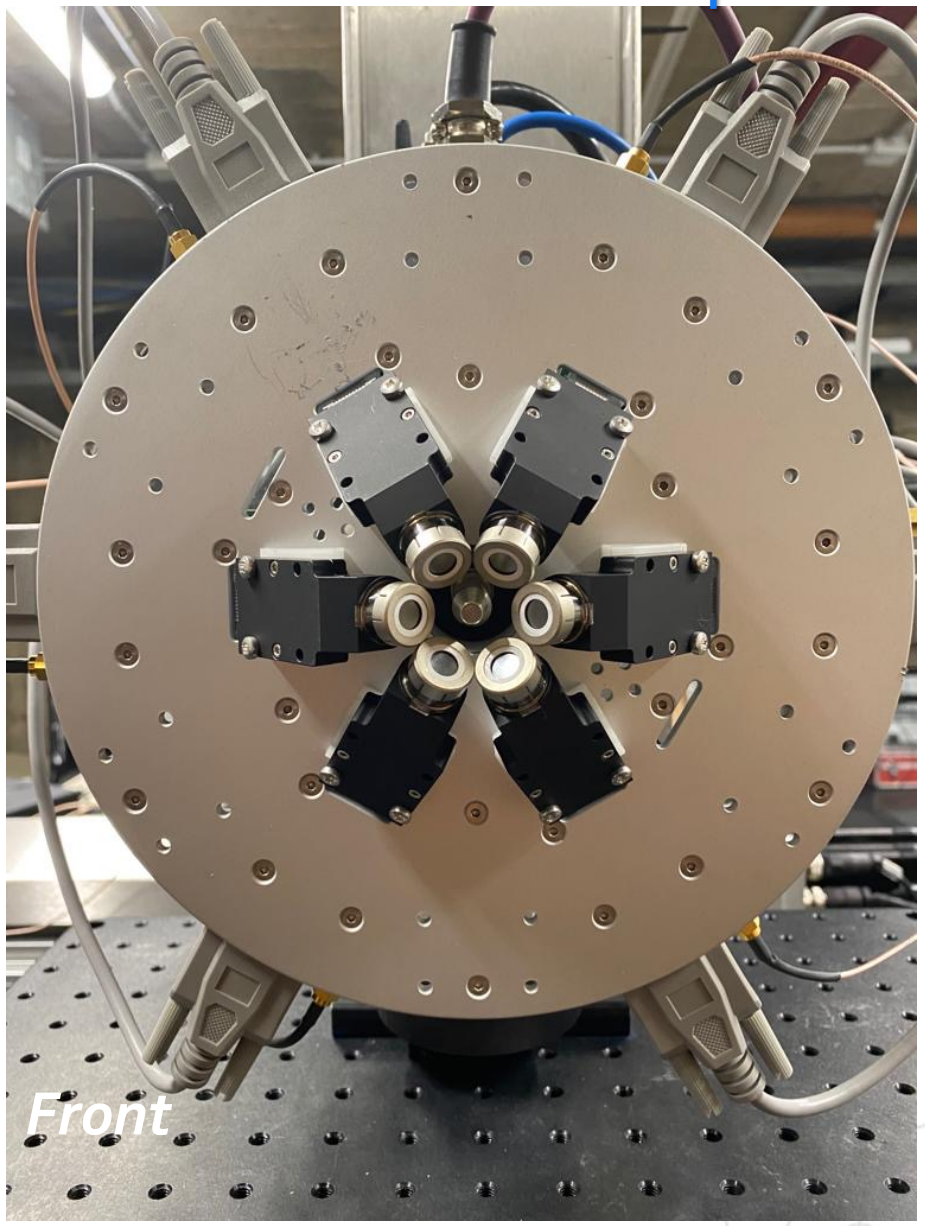
- 50mm² collimated to 40mm² for a total active area of 240mm²
- 125 eV @ Mn-Kα energy resolution
- 90-45deg measurement geometry

Spectrometric head

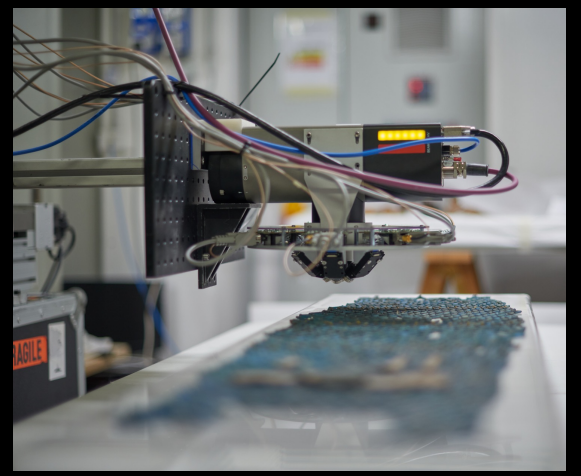
Advantages:

- **maximizing** the measured vs. input count rate while **minimizing the dead time** with respect to a single detector setup under a beam intensity (about) x6 higher;
- **increasing** sensitivity and LoD;
- **controlling** surface topology of samples

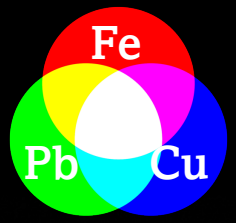
6 SDDs hodoscope

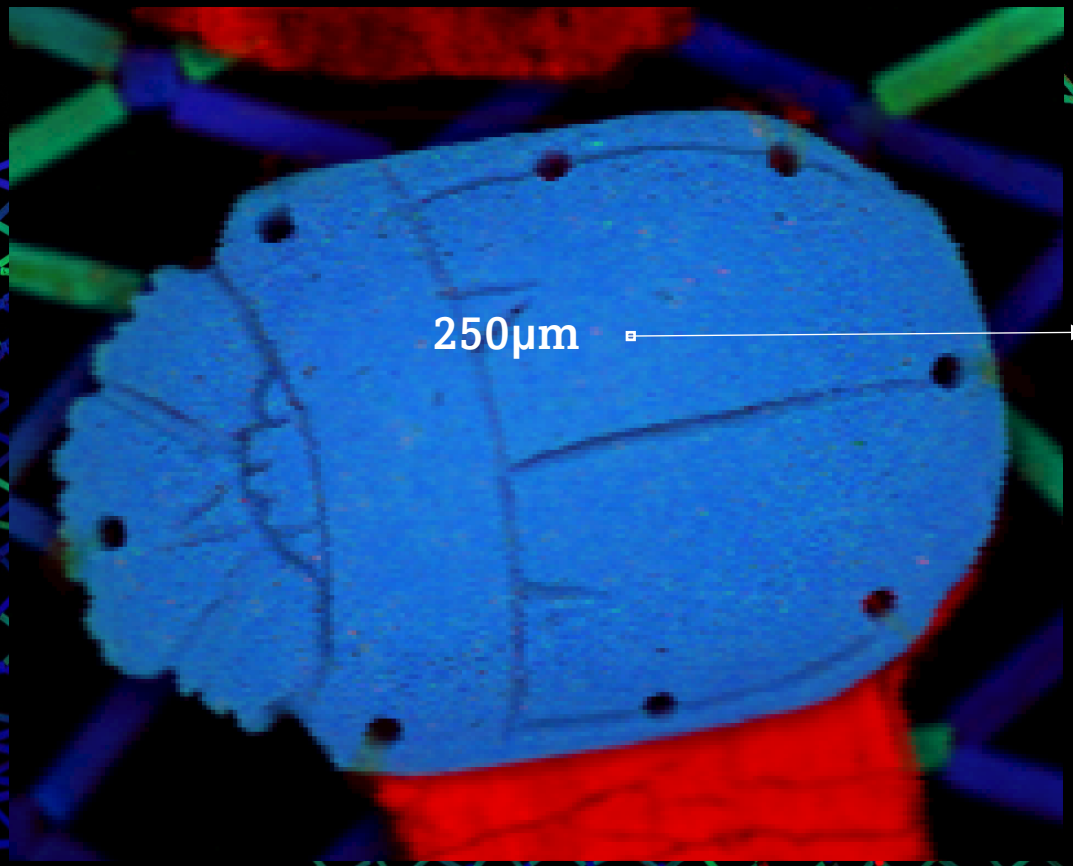


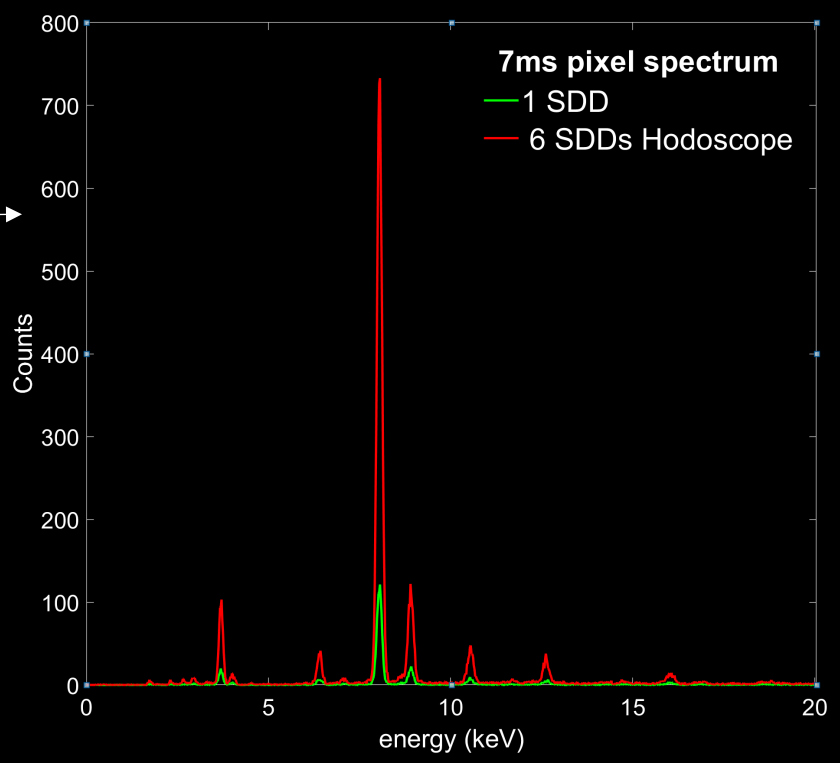
The 3D detector array allows us to increase the throughput of the fluorescence radiation ensuring enough statistics for pixel XRF spectra at short dwell-time



Lateral resolution 250µm
7ms dwell-time
5.5 Mega pixels







Sensitivity and LoD

The 6 SDD hodoscope allows a steep improvement of the overall sensitivity

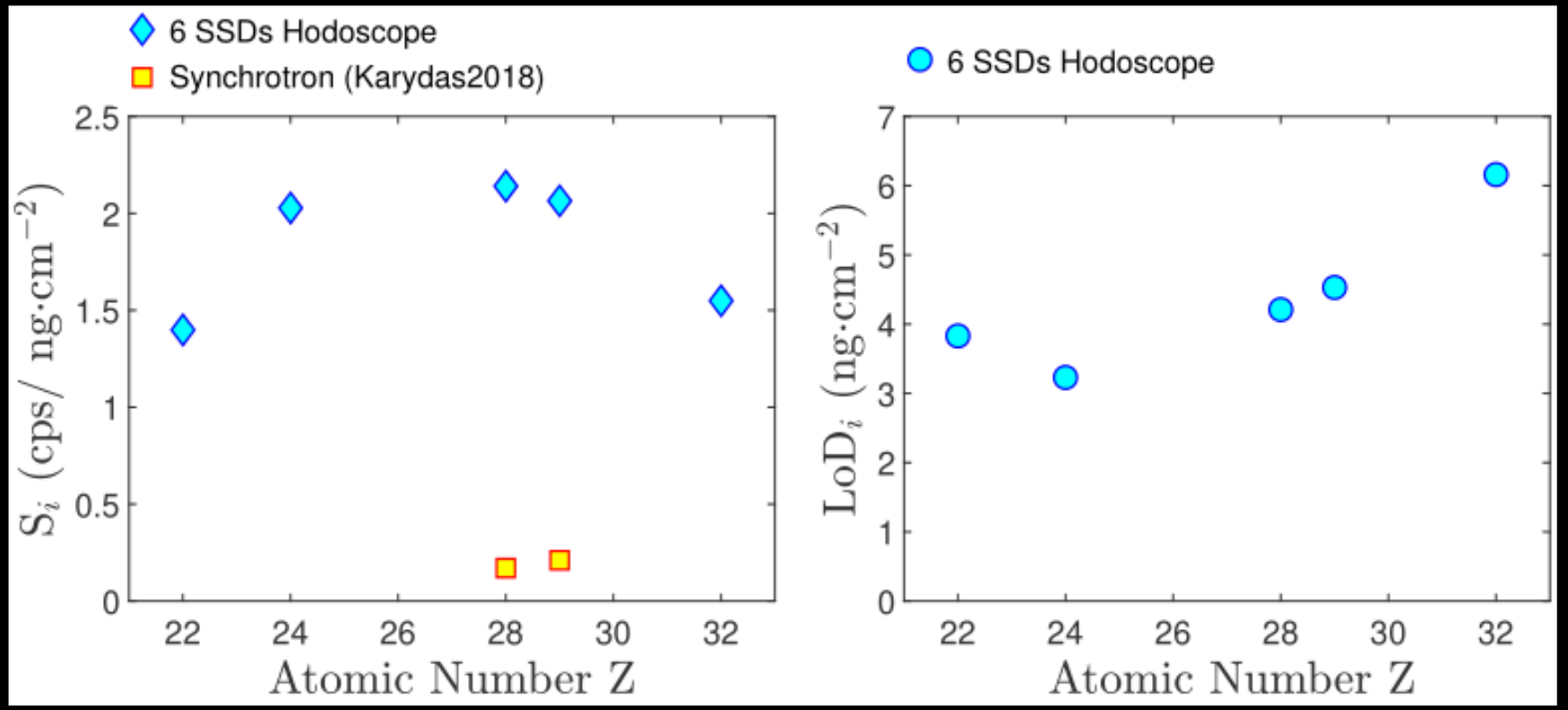
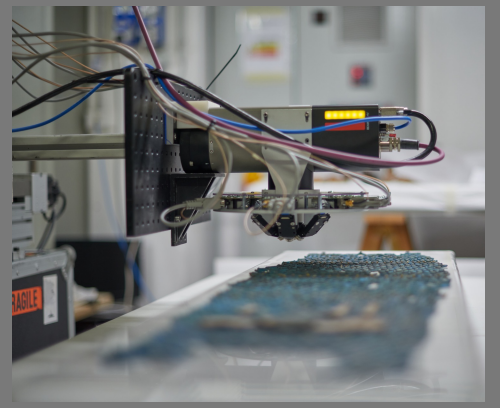
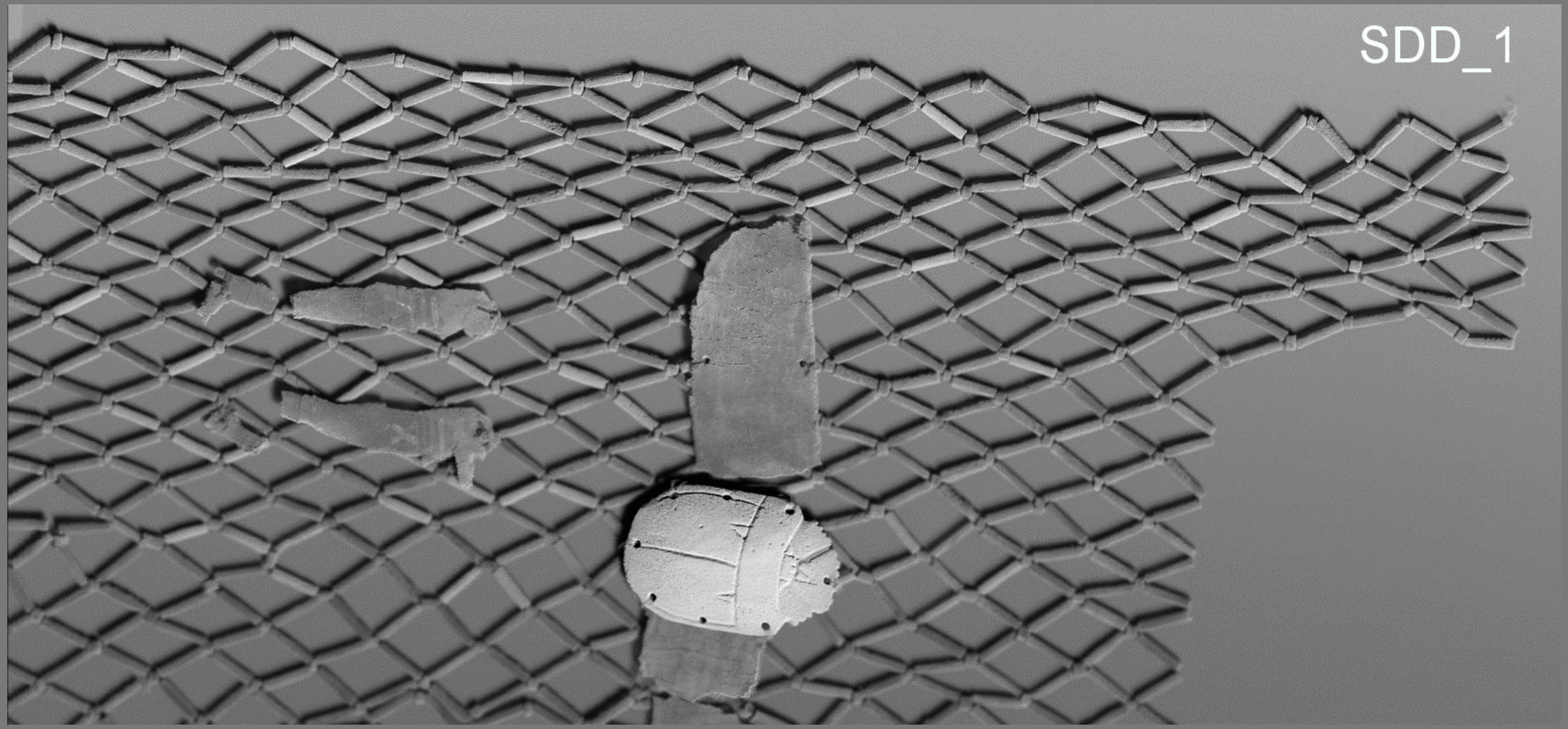


Figure of merit of the upgraded system in comparison with a typical single-detector set-up available in a synchrotron facility
(Karydas, et al. Journal of Synchrotron Radiation 25.1 (2018): 189-203)

By using Micromatter™ reference single metal evaporation (50μg/cm²)
(live time 300 sec at 50kV and 600μA)

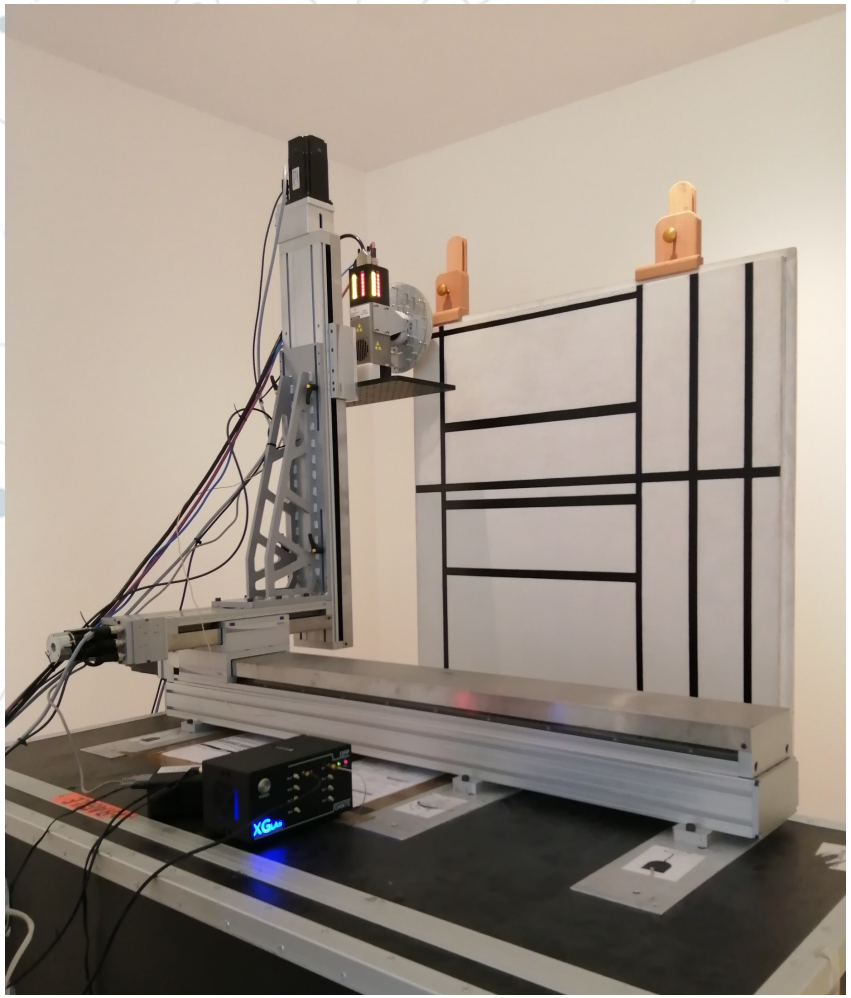
Possibility analyze one single detector per time and to correct the elemental distribution images for the surface topology of the art object



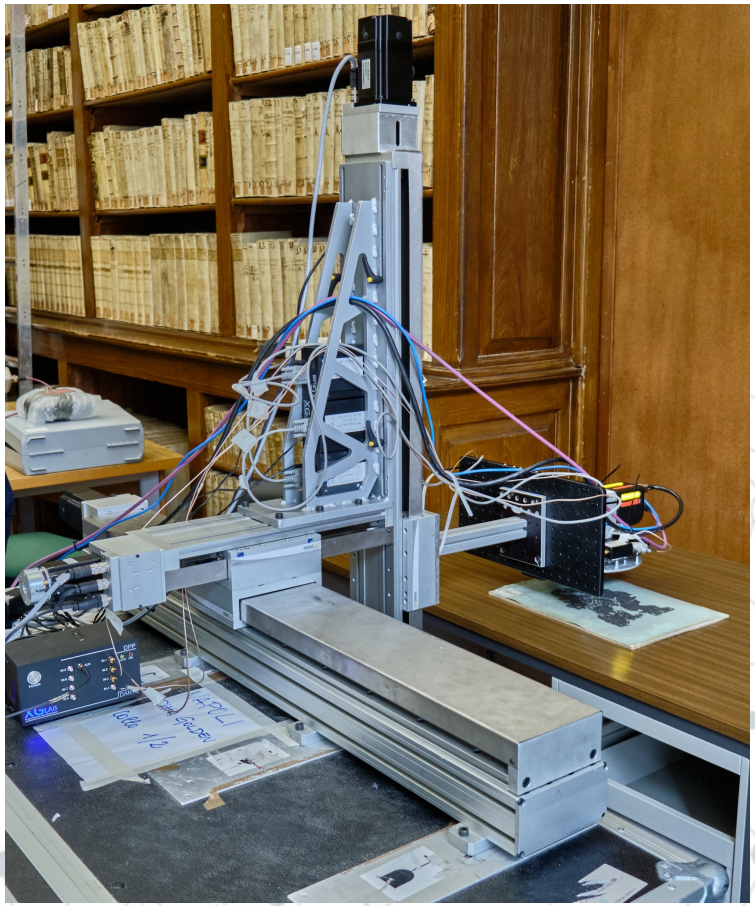


Mechatronics

- Scanning area: **120×90×20cm³**
- **MCA**, **fast-mapping and TLIST** acquisition capabilities
- Max. scanning speed **150mm/sec** (e.g., 5ms dwell-time for 1mm pixel size)
- Laser sensor for **dynamic correction** of the focus distance
- **Vertical/Horizontal** configuration

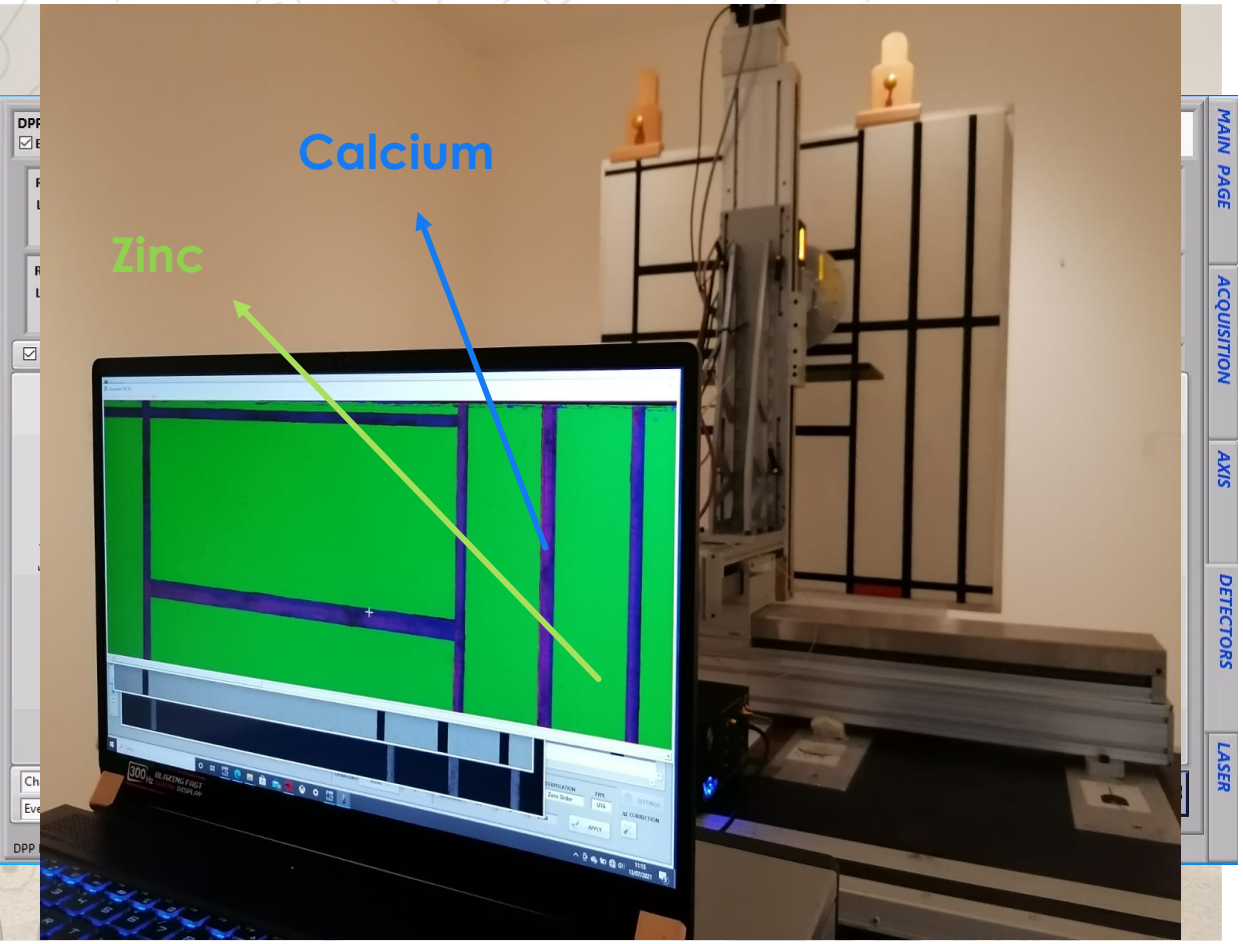


The new scanner in use for the MOLAB @ Peggy Guggenheim Museum in Venice for a painting by Mondrian



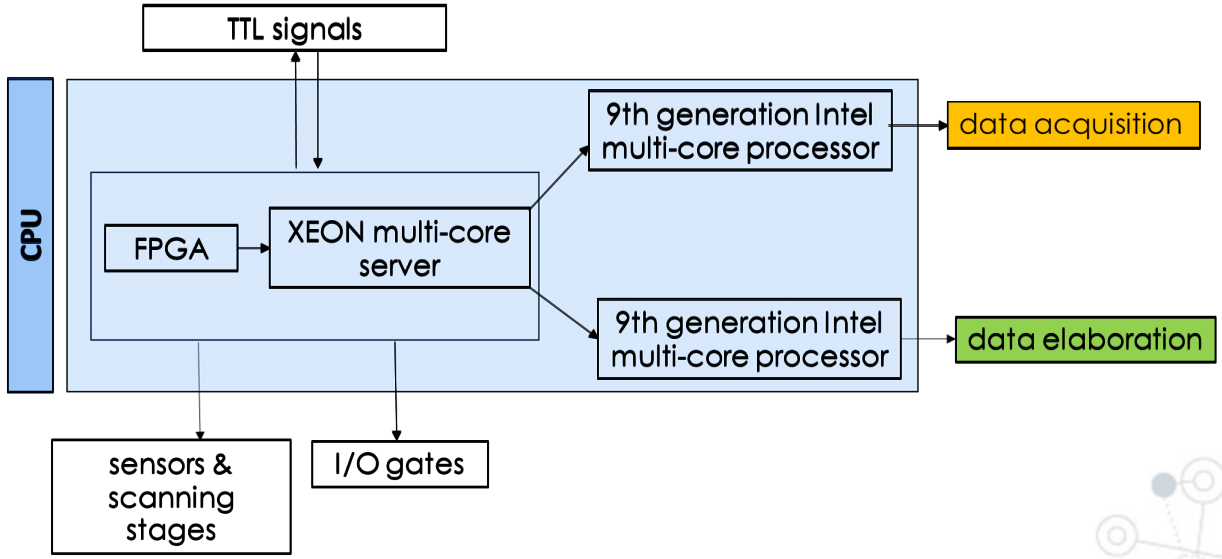
The new scanner in horizontal configuration in use @ the Biblioteca Nazionale in Naples for Herculaneum papyri

Mechatronics



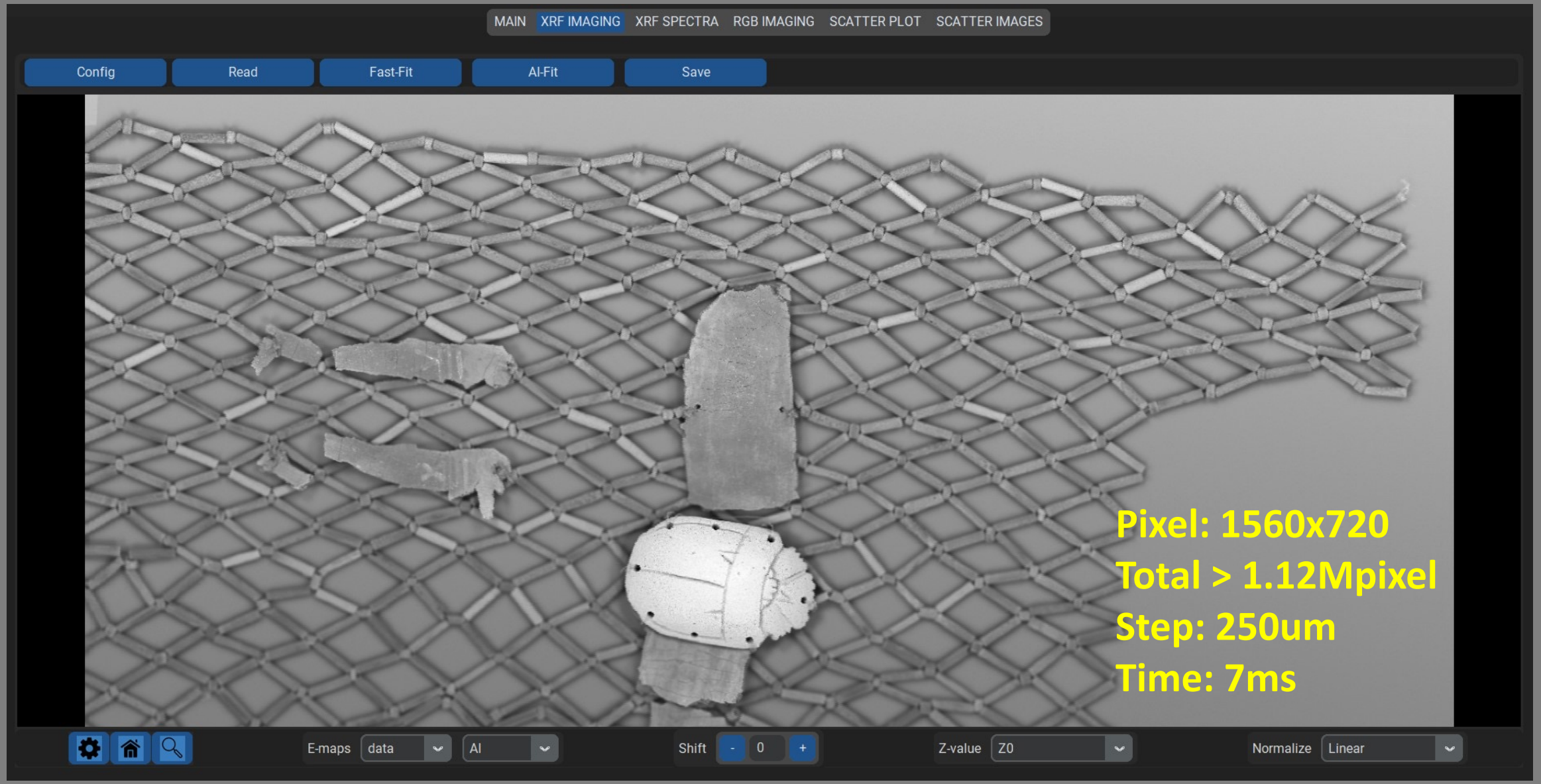
The new scanner in use for the MOLAB
@ Peggy Guggenheim Museum in Venice for
a painting by Mondrian

The **Control Processing Unit (CPU)** is developed in a **multi-node design** and programmed in a **real-time environment**



- All measurement parameters are entered and monitored by the users through an **interactive dashboard**
- XRF pixel spectra are **fitted in real-time** by using a fast-fitting (Pymca) or AI/ML models. Deconvoluted elemental distribution maps are available on the fly.

New dashboard for analysis (Real-time/Off-line): use of classical fast-fitting (PyMCA) or Artificial Intelligence



Advantages of the new MA-XRF system

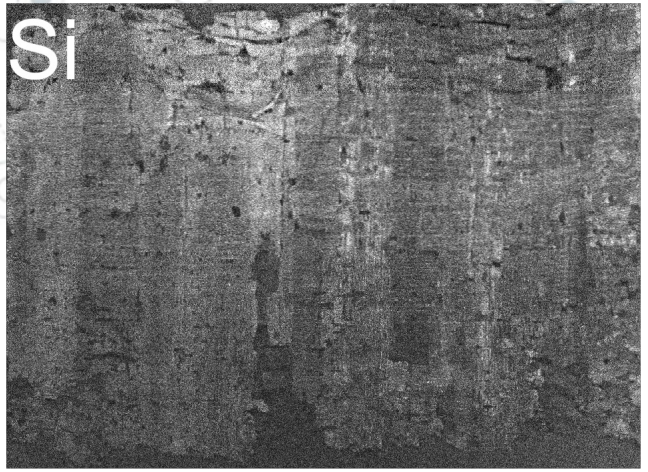
The 6 SDD hodoscope allows a steep improvement of the overall sensitivity

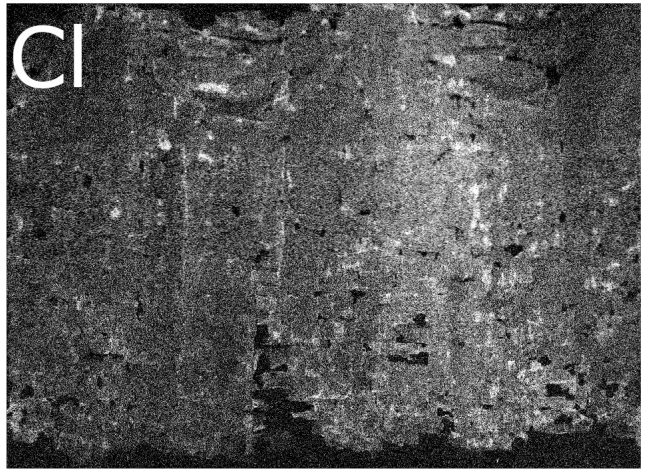
Herculaneum papyri at the Biblioteca Nazionale in Naples

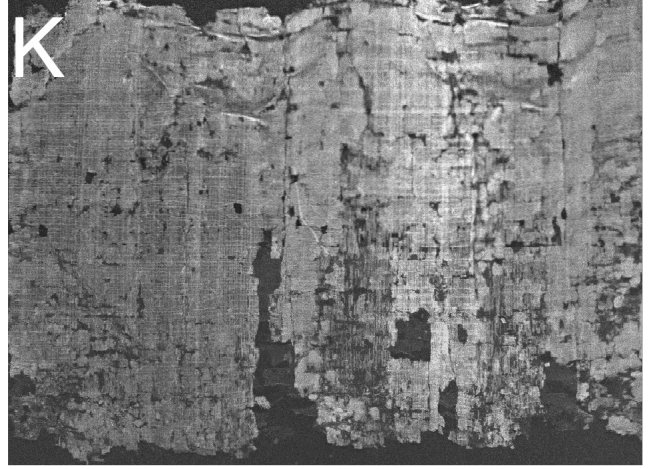
Have been detected for the first time in situ even very **small traces of metallic elements in degraded and brittle materials**, such as the **carbonized Herculaneum papyri!**

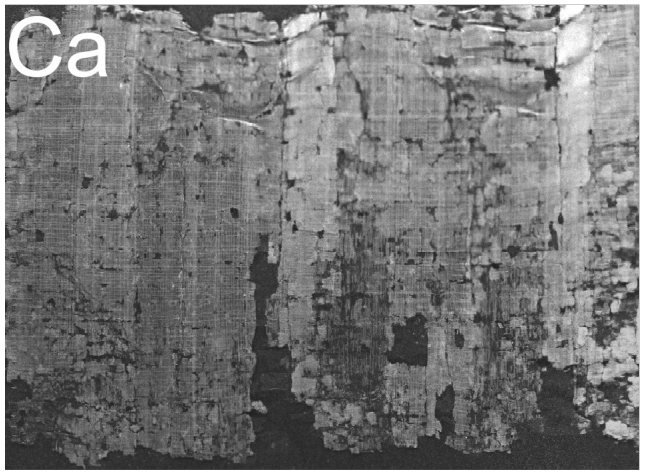
PHerc. 1420, cornice 2

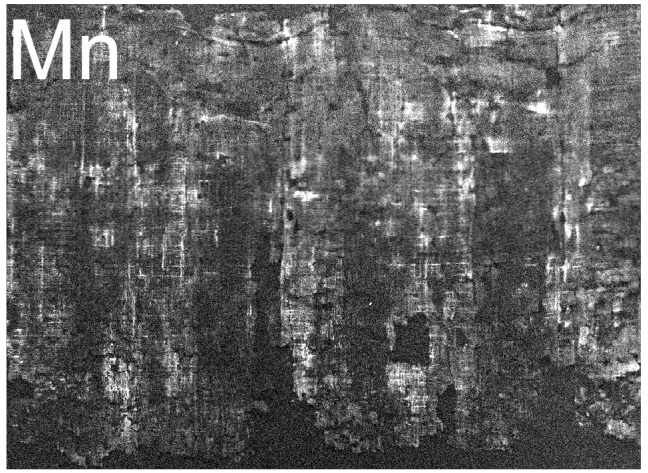
Scanning step 250um
Dwell time 10ms

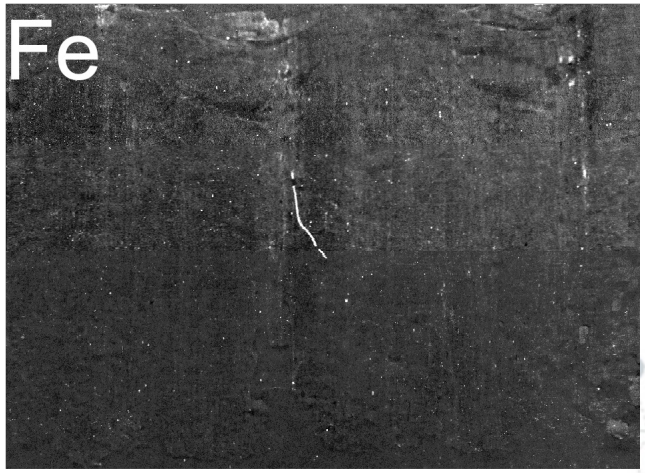


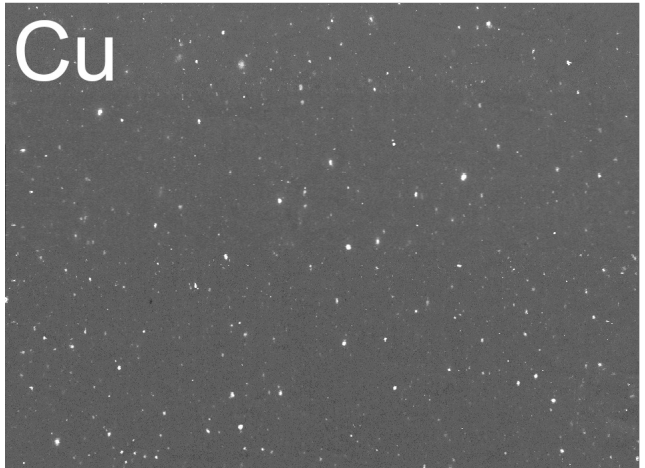


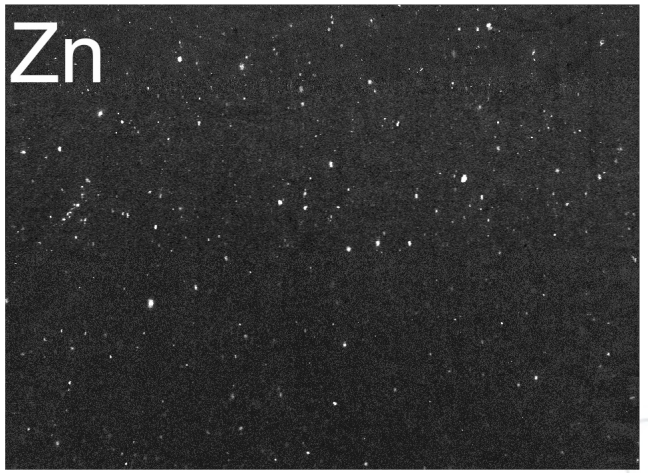


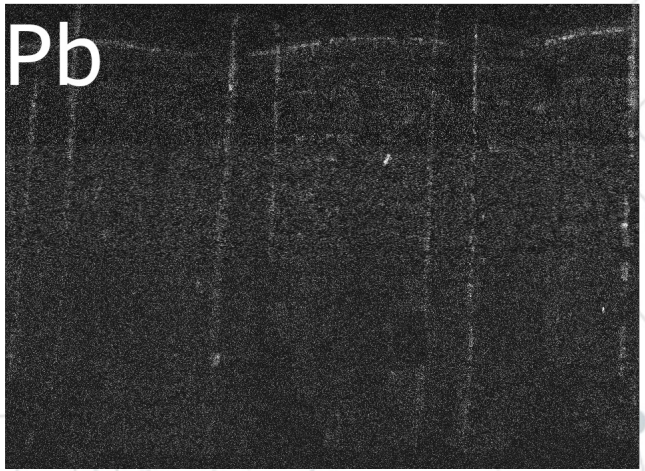


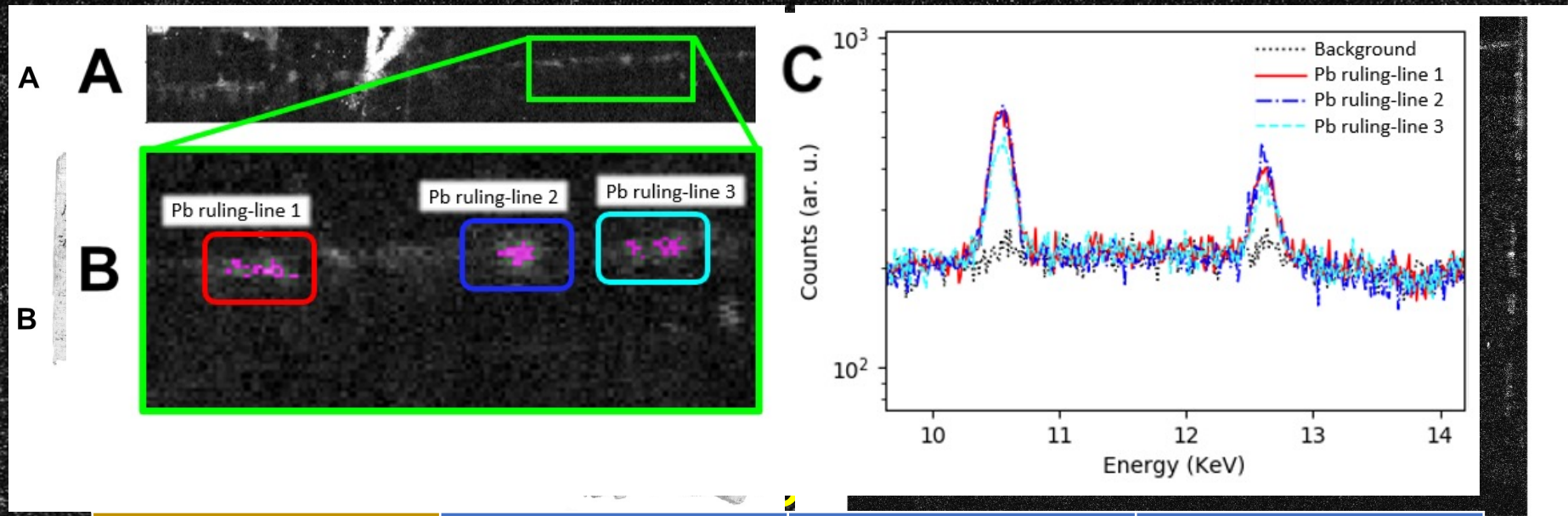












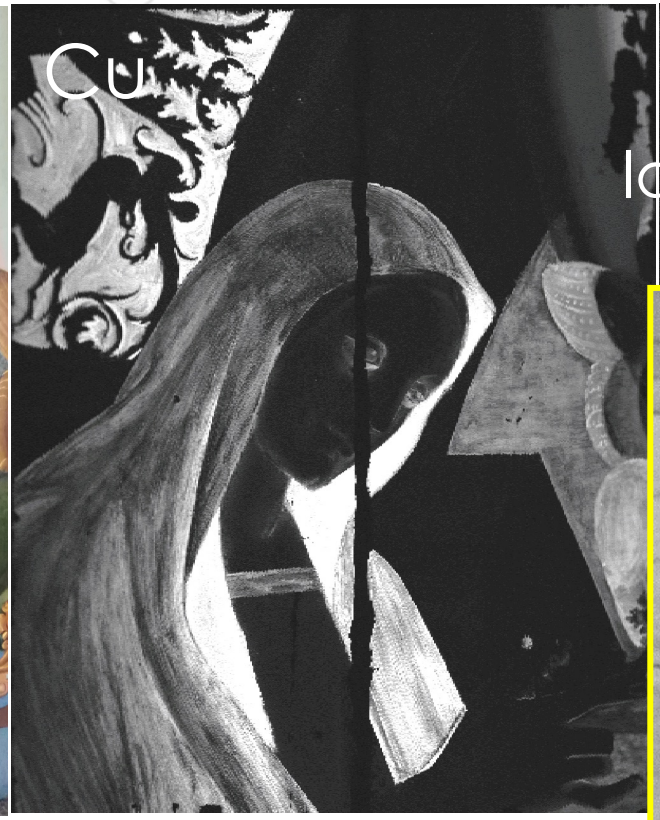
Papyrus	Location	Pb areal density ($\mu g \cdot cm^{-2}$)	Pb per pixel (ng)
PHerc. 1018	Pb ruling-line 1	63	7.9
	Pb ruling-line 2	66	8.2
	Pb ruling-line 3	45	5.7
	background	6	0.8
PHerc. 164	Pb ruling-line 1	67	8.4
	Pb ruling-line 2	68	8.4
	Pb ruling-line 3	74	9.2
	background	8	1
Average value	**Pb on the ruling lines**	**64**	**8.0**
	Pb on the background	**7**	**0.9**

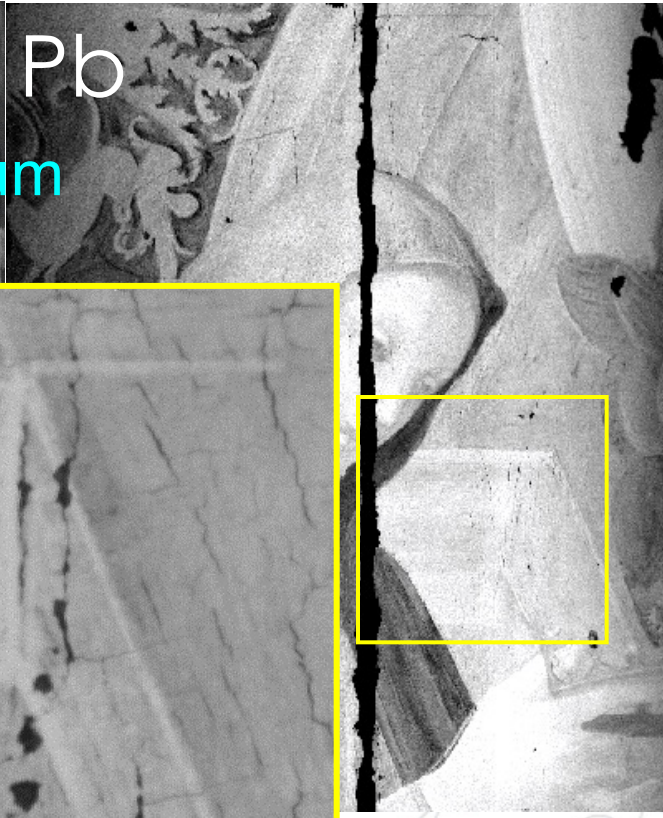
calcium distribution

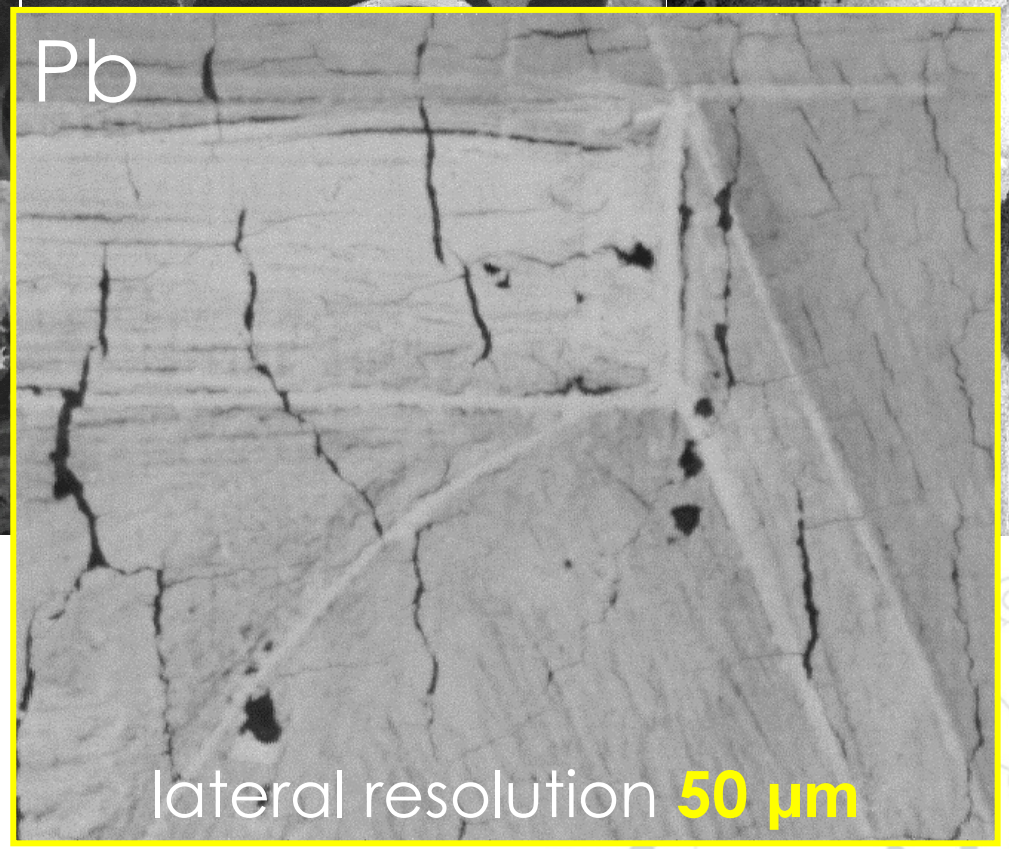
Papyrus structure and conservation state

Additionally, metals (Fe, Zn, Cu, etc.) are heterogeneously distributed on the surface

MA-XRF mapping : benefit of high resolution



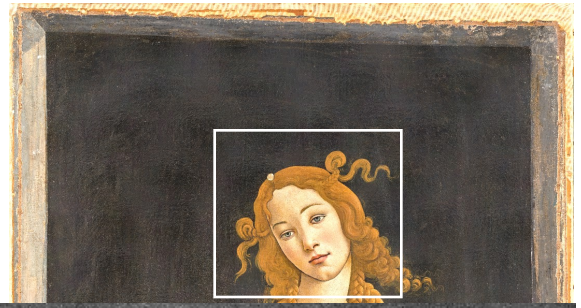


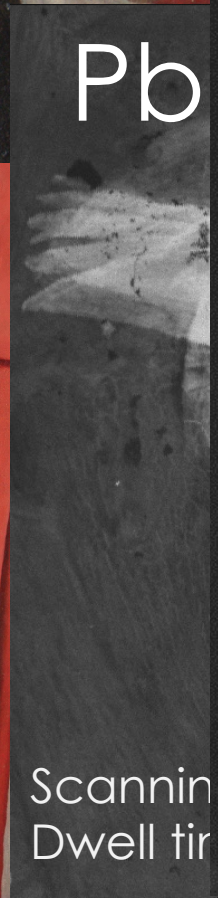


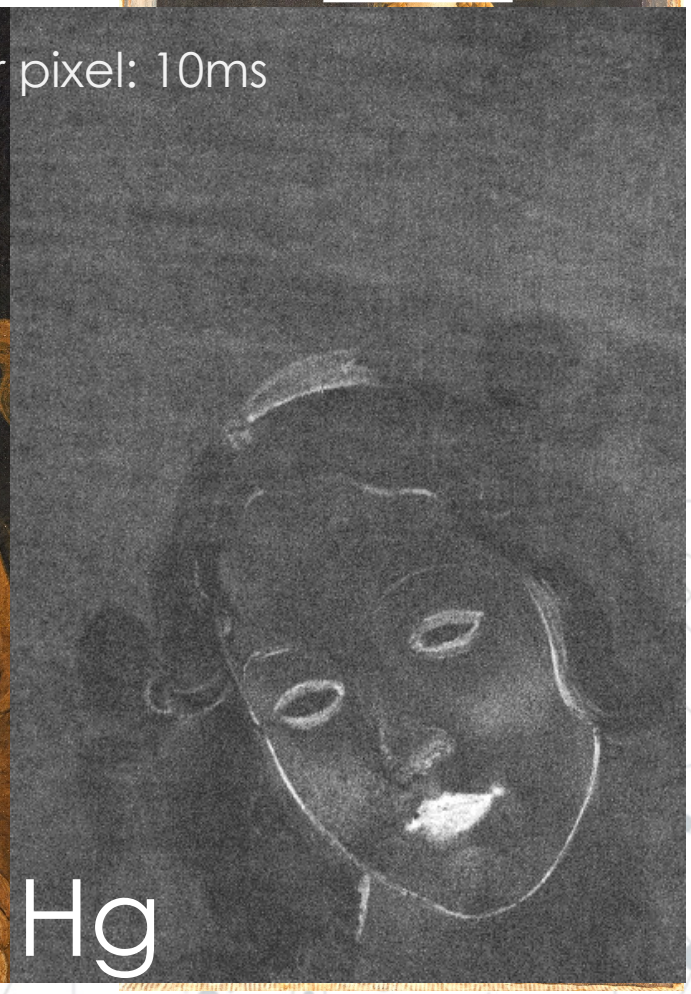
Vergine by Raffaello (1500-01, 51 x 41 cm^2)
at the Museo di Capodimonte in Napoli

MA-XRF mapping : benefit in the creative process

Ritratto del cardinale
by Raffaello
at the Museo di
Capodimonte in Napoli







High resolution 1D/3D confocal XRF

EXPERIMENTAL SET-UP

- Mo/Rh anode X-ray source (30W) focused by micro-lens (7μm @ Rh-K)
- SDD1 for micro-XRF (FWHM 130eV @5.9keV)
- SDD2 + micro-lens (10μm @ Rh-K) for confocal XRF
- DXP operated in TLIST/Mapping for continuous scanning
- Long range microscope (optical resolution 2.2μm)
- XYZ travel range system (50x50x20 cm^3)

X-ray source

PARAMETERS OF FOCUS

E, keV	3-5	5-7.5	7.5-10	10-15	15-20	20-25	25-30
Focus size *, μm	13	13	13	11	8	7	7
Intensity gain**	3677	6416	9693	7223	4667	1303	219

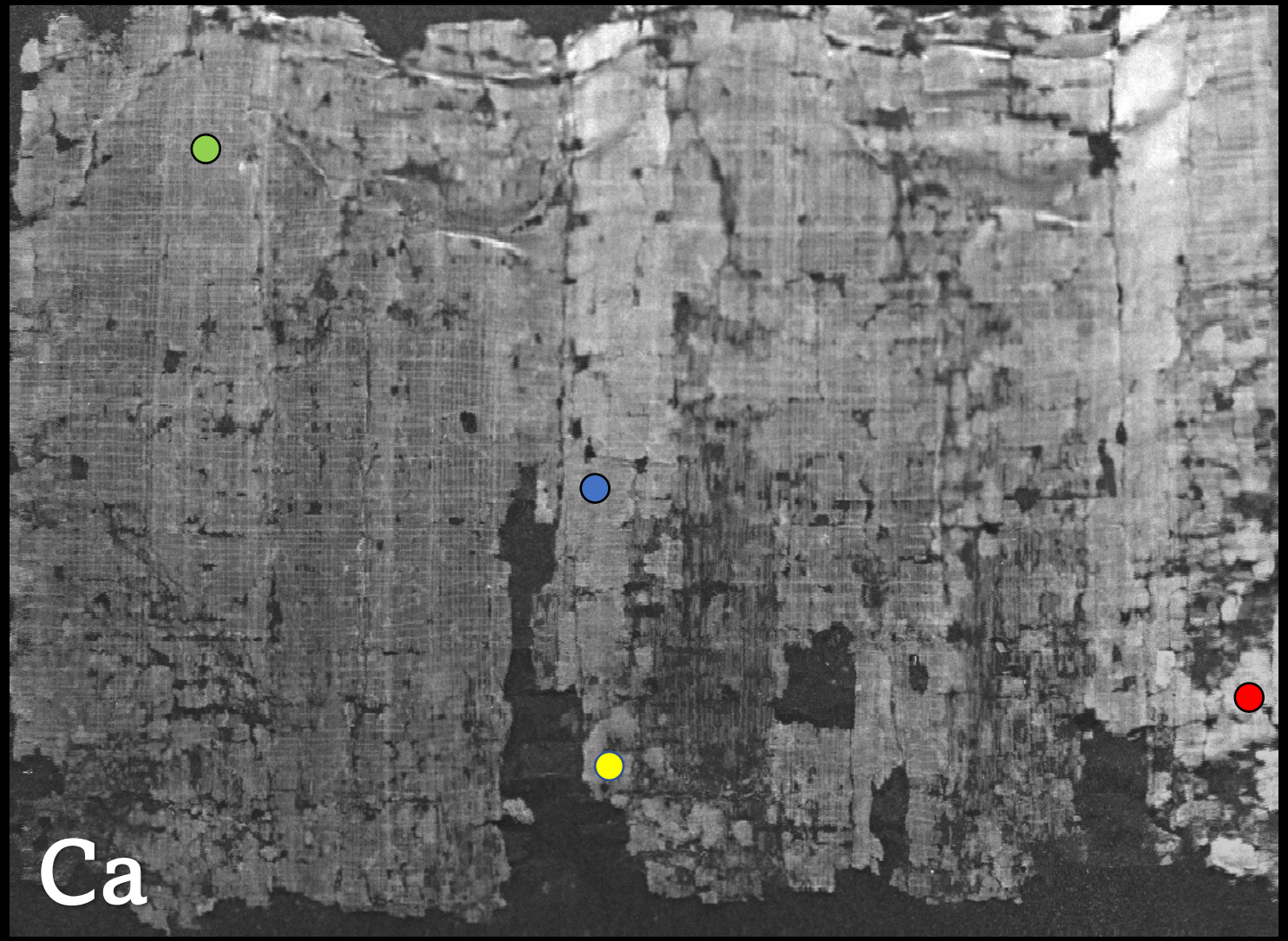
Detector

PARAMETERS OF FOCUS

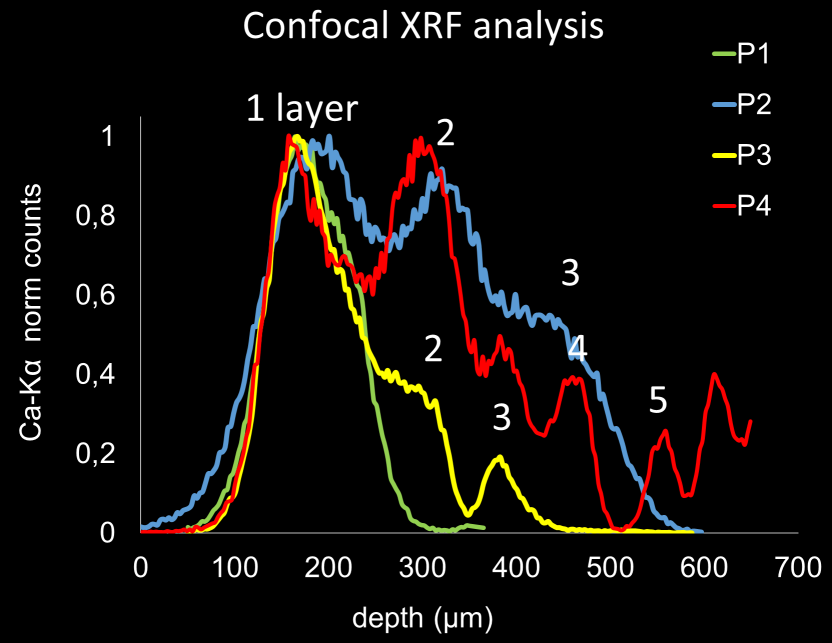
E, keV	3-5	5-7.5	7.5-10	10-15	15-20	20-25	25-30
Focus size *, μm	18	19	17	14	11	10	10
Intensity gain**	3276	6336	7102	5257	2835	1130	135

1D CXRF on carbonized Herculaneum papyri

Ca map from MA-XRF shows structure and conservation state after the mechanical unrolling



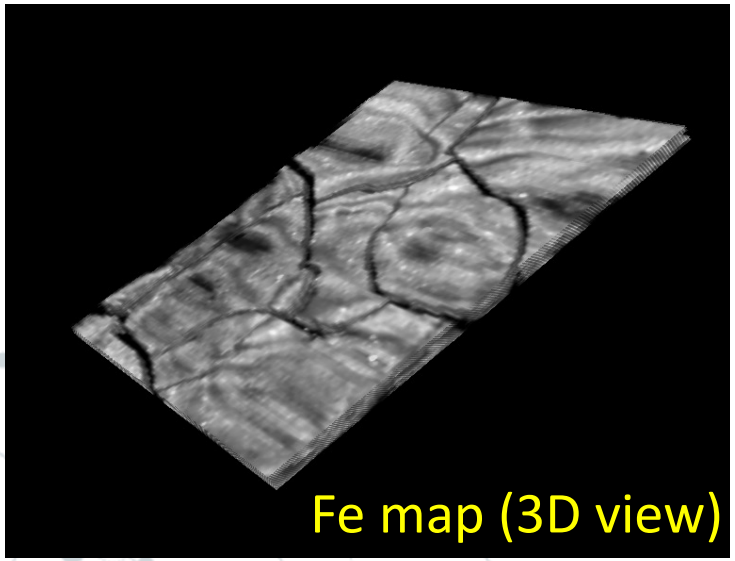
Ca-Kα fluorescence signal along the stratigraphy for the identification of overlaid/underlaid layers

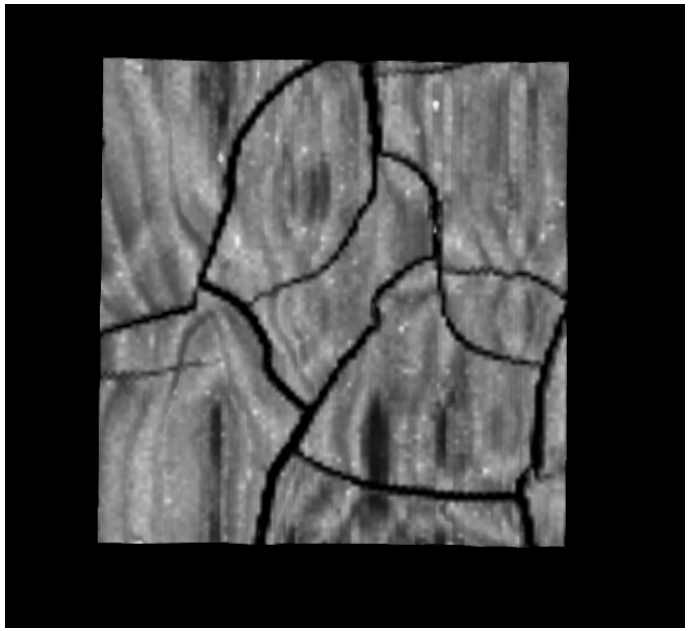


3D CXRF for evidencing delamination process in paint layers

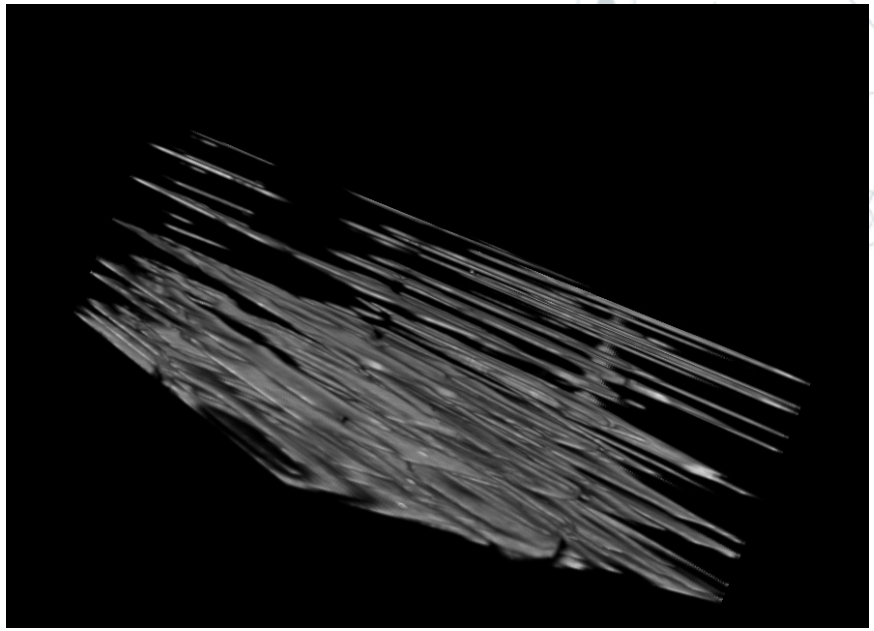
High resolution 3D confocal XRF

- Source 50kV & 600μA
- Scanning step XY: 50μm
- Scanning step Z: 3μm
- Dwell-time per pixel: 500ms
- Scanning area: 5mmx5mmx200μm
- GPU Rendering of 3 models (cubic)



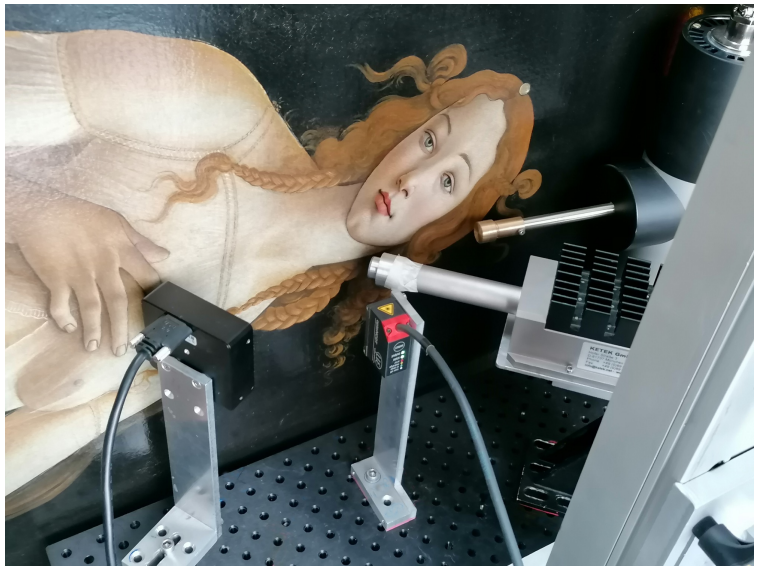


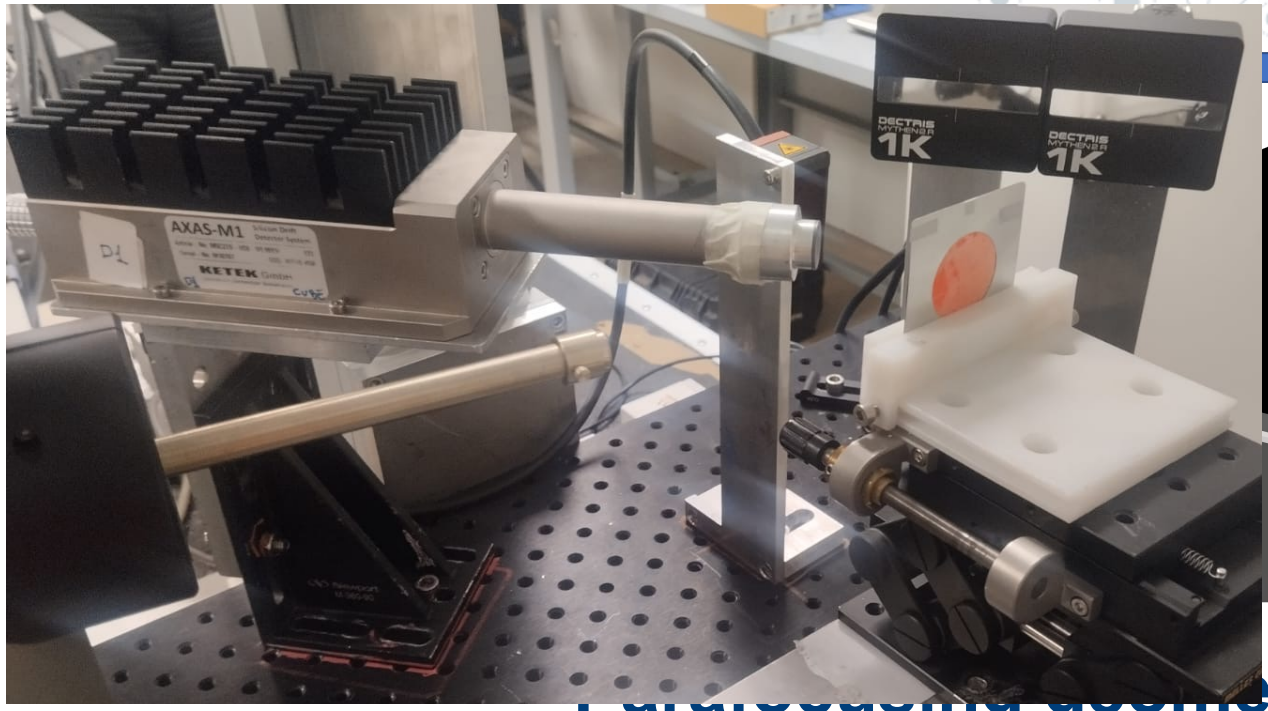
Fe map (XY view)



Fe scaled on Z
(Z scaling applied for evidencing intra layer structure)

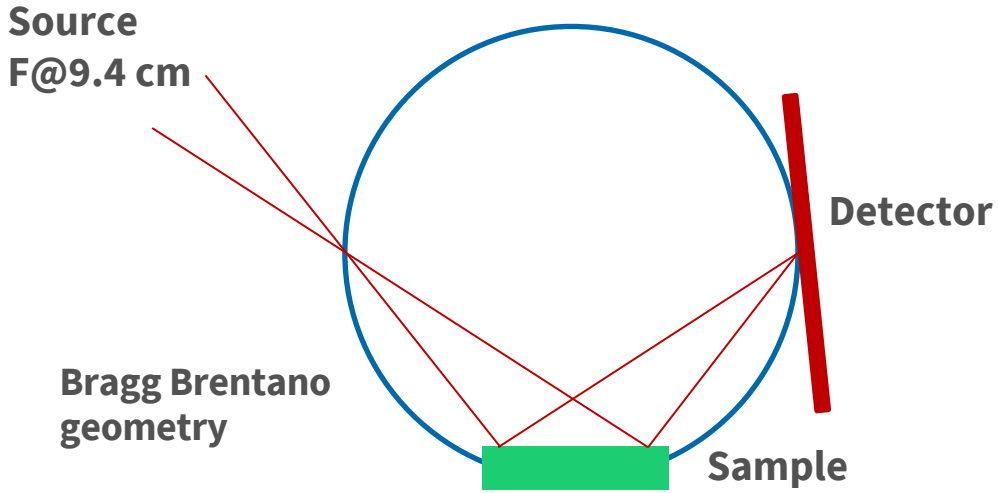
Mobile MA-XRPD for specific analysis of polycrystalline materials





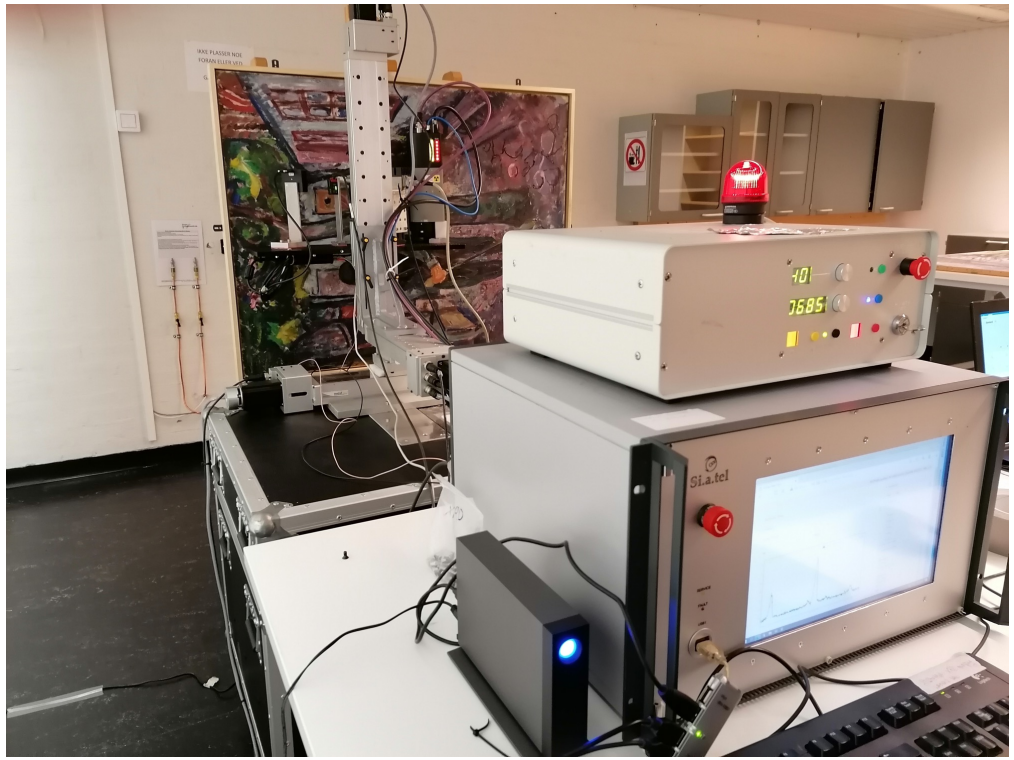
- **X-ray Source:** Cu-anode | Ni filter
- **X-ray Optic:** mini-lens 186μm | 109mrad div.
- **Collimation:** rectangular slit 0.6x10mm^2
- **XRD detector:** 1280 Si-strip, 50μmx8mm, hybrid photon-counting
- **XRF detector:** SDD (not visible in the schematic), 50mm^2 active-area
- **Laser sensor distance:** correct sample-source distance dynamically during scanning to have same focus for all pixels

Parafocusing geometry



FWHM (2θ) 0.2-0.25deg

Instrumental set-up



Scanning parameters (typical):

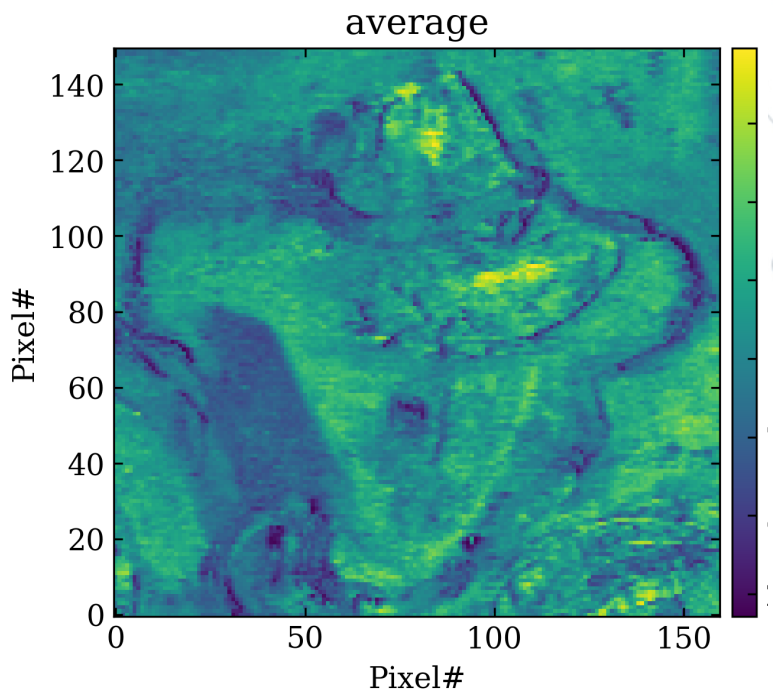
- Step mode
- 1mm pixel-size
- 3s dwell-time
- Angular range: 28deg 2θ

During scanning painting is in a fixed position. The XRD/XRF measurement-head is moved in front to cover the area under investigation

Scanning capabilities: XYZ linear motorized, with travel range of 50x50x20 cm^3, ± 50 cm mechanical adjustment on the vertical axis is possible facilitating the alignment on painting of large dimensions

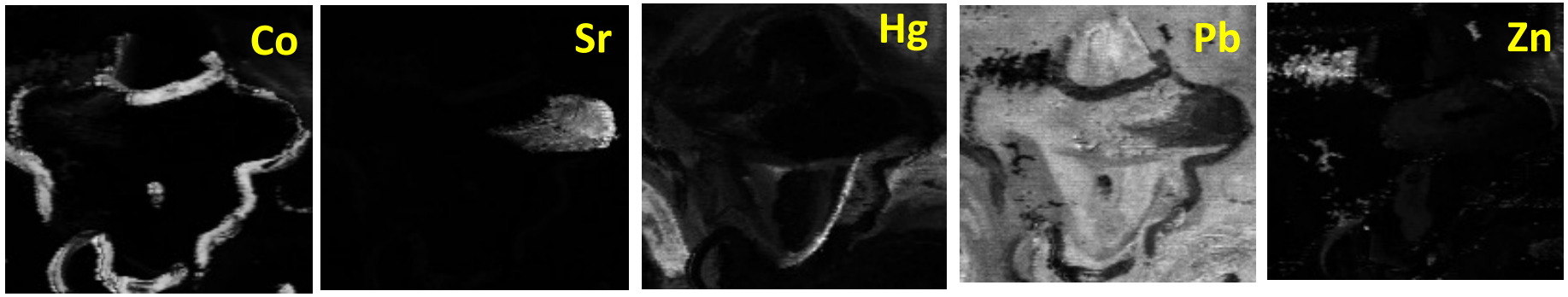
CPU**:** Real-time programmed. It controls mechatronics, detectors and laser; it provides a TTL gate to synchronize XRD and XRF acquisition in the same spot; it acquire XRD patterns and XRF spectra

MA-XRF/MA-XRD on paintings

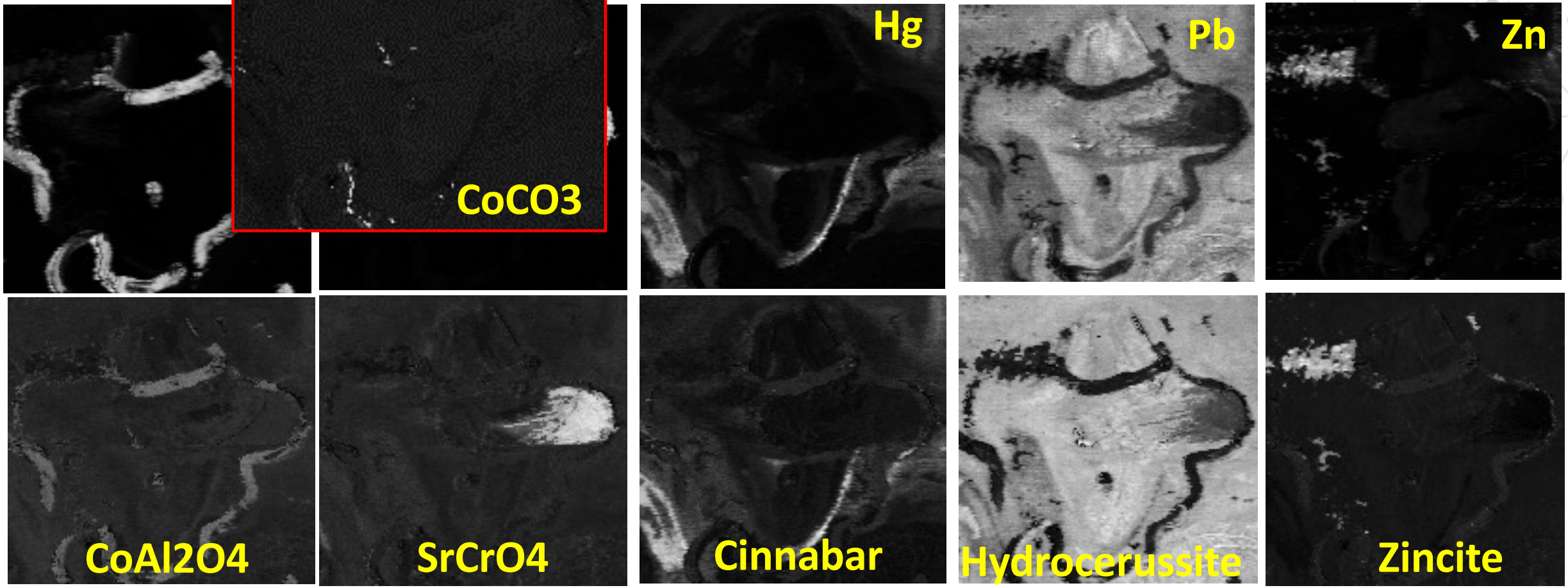


Area: 16cmx15cm
Step size : 1mm
Time/step : 3sec
Total n. pixel: 24k
Time: 20h

MA-XRF defines the phases to be included in the model



Specific p


CoCO3
Hg
Pb
Zn
CoAl2O4
SrCrO4
Cinnabar
Hydrocerussite
Zincite

Thanks!