

# Analisi Fisiche sui Beni Culturali ed Archeologici

Francesco Paolo Romano

*IBAM-CNR & LNS-INFN, Catania*



# Archeometria: la scienza che affianca l'Archeologia

Chi trova un reperto archeologico o chi studia un'opera d'arte si pone sempre delle domande riguardanti i **materiali che lo compongono**, la loro **provenienza** e le **tecniche di fabbricazione**

Le risposte a queste domande vengono dall'**Archeometria**, una disciplina che comprende un insieme di metodi di indagine (biologia, chimica, fisica, geologia, etc.) che permette di acquisire **informazioni sul reperto**, sull'ambiente **storico** di origine e sul suo **stato di conservazione**



# LANDIS laboratory at the LNS-INFN



LANDIS (Laboratory of non destructive analysis) operates at INFN-LNS since 1996.

The research activity is focused on development of novel XRS and IBAM techniques and analytical methods for nondestructive investigation of Cultural Heritage and Archeological materials.

LANDIS Group:

F.P. Romano, CNR

F. Rizzo, INFN

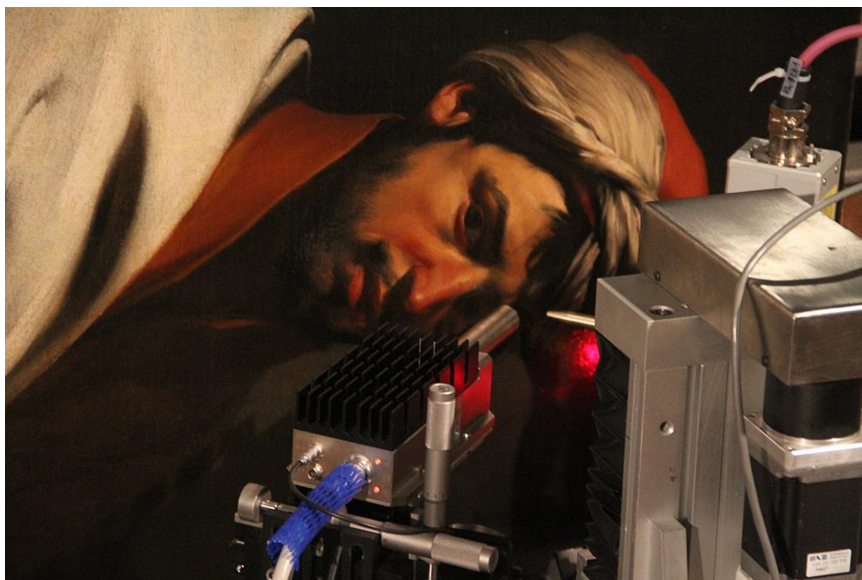
L. Pappalardo, CNR

C. Caliri, INFN



# Mobile instrumentation developed at LANDIS

- **Portable** XRF and micro XRF
- **Mobile** scanning micro-XRF, Macro-XRF and confocal-XRF
- **Portable** alpha-PIXE
- **Portable** X-ray diffraction





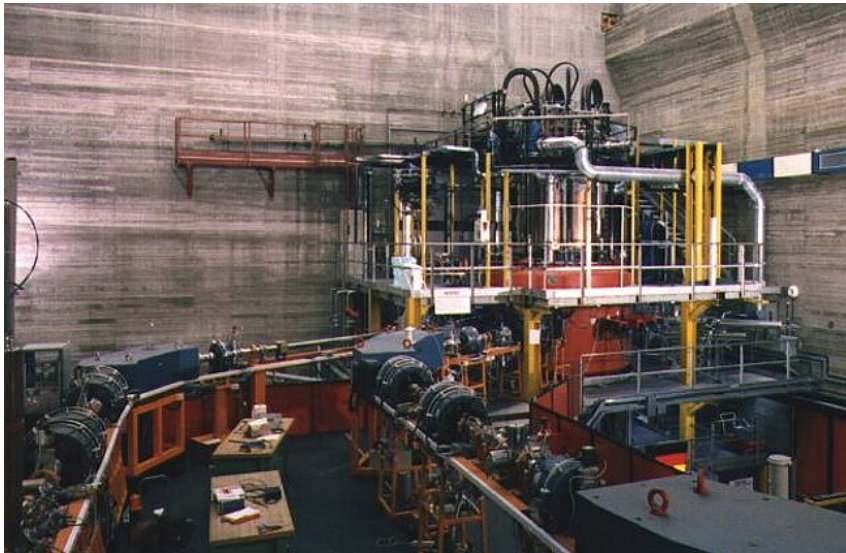
# Proton based analytical techniques



**TANDEM** → Protons in the range 3 -25 MeV in air

Deep Proton Activation analysis (20 MeV)

Full Field Micro PIXE imaging (3 MeV)



**CS** → Protons up to 80 MeV extracted in air

Prompt Gamma Analysis and High Energy Proton Activation (in progress)

# La scoperta dei raggi X

Un momento importante nella storia dell'Archeometria è dato dalla scoperta dei raggi X nel 1895



Radiografia della mano sinistra della moglie di Roentgen

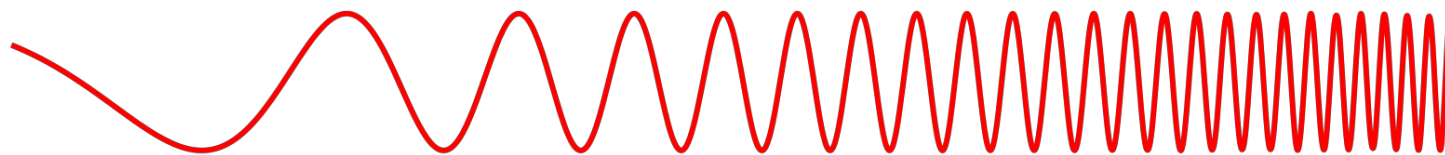
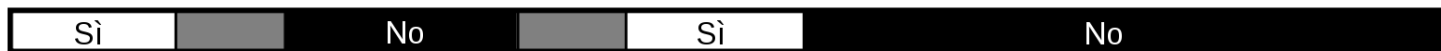
Röntgen stava studiando gli effetti del passaggio di corrente elettrica in un tubo contenente un gas.

Un foglio coperto di sali di bario e platino nelle vicinanze del tubo diventò fluorescente

Röntgen spiegò il fenomeno con una forma sconosciuta di raggi emessi dal tubo. Li chiamò raggi X in attesa di capire cosa fossero.

# La scoperta dei raggi X

Penetra l'atmosfera terrestre?



Tipo di radiazione  
Lunghezza d'onda (m)

**Radio**

$10^3$

**Microonde**

$10^{-2}$

**Infrarosso**

$10^{-5}$

**Visibile**

$0.5 \times 10^{-6}$

**Ultravioletto**

$10^{-8}$

**Raggi X**

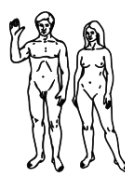
$10^{-10}$

**Raggi Gamma**

$10^{-12}$



Edifici



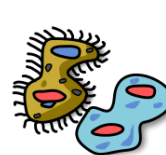
Esseri umani



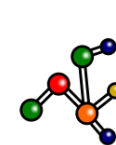
Farfalle



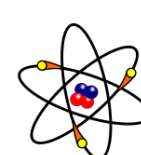
Punta di un ago



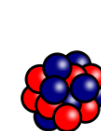
Protozoi



Molecole



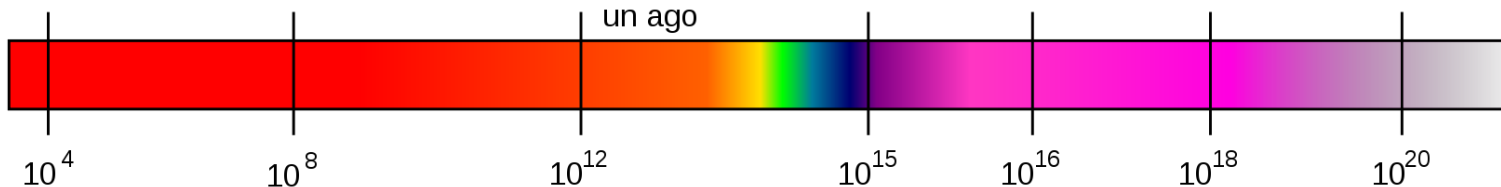
Atomi



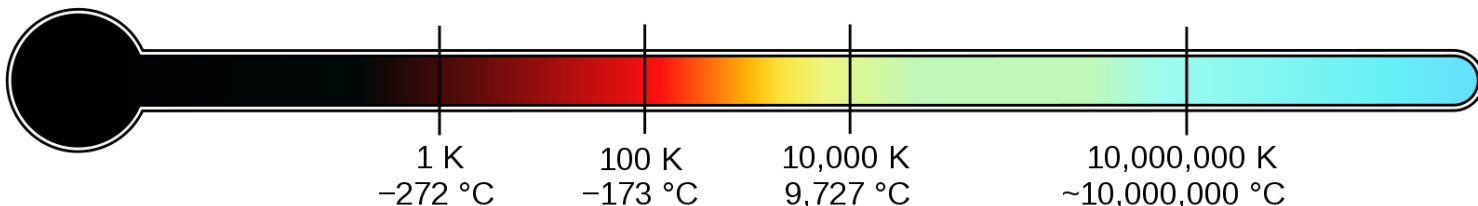
Nuclei atomici

Scala approssimativa della lunghezza d'onda

Frequenza (Hz)

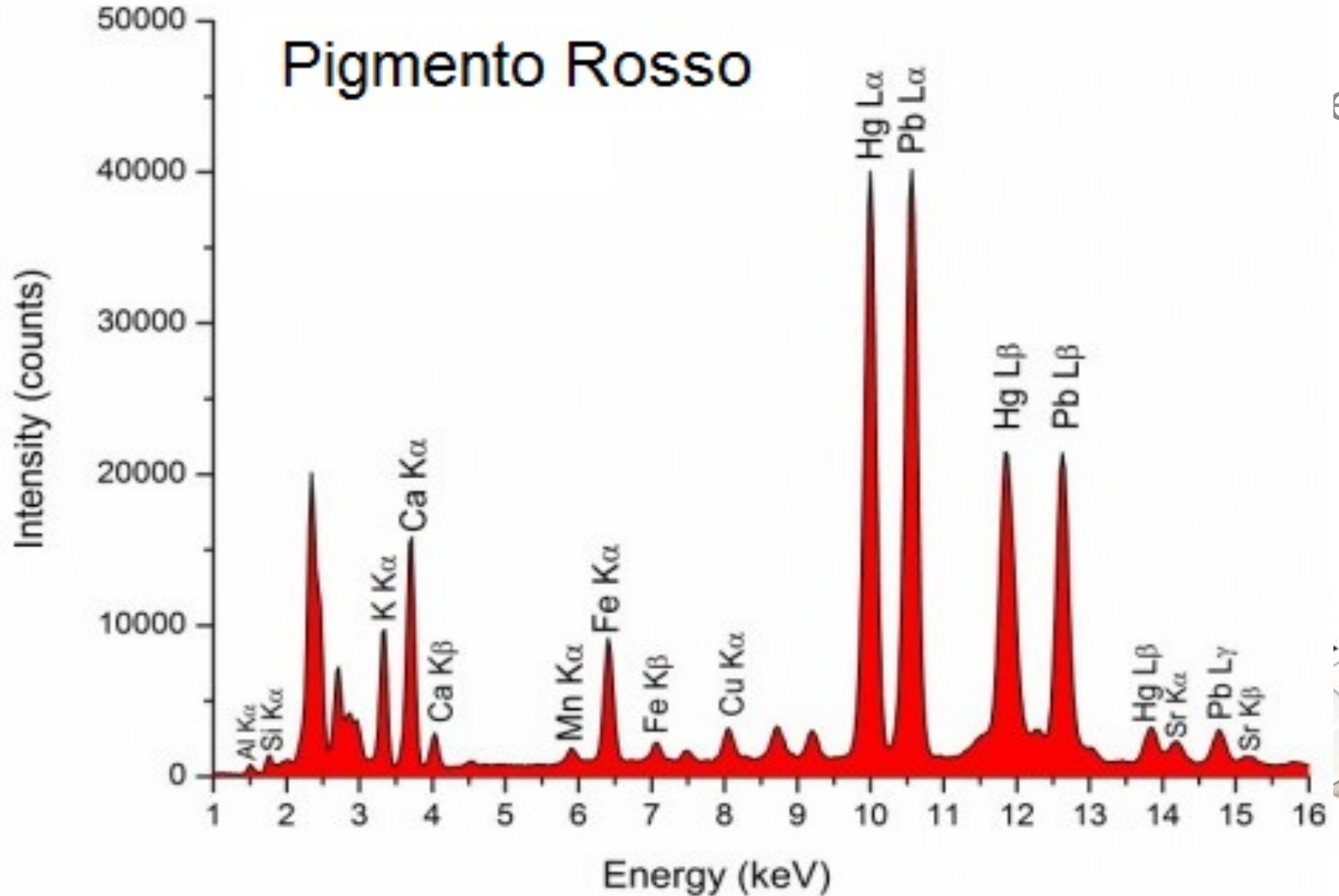


Temperatura degli oggetti alla quale questa radiazione è la più intensa lunghezza d'onda emessa



# La Fluorescenza X: un mezzo per studiare i materiali antichi

S  
ir  
n



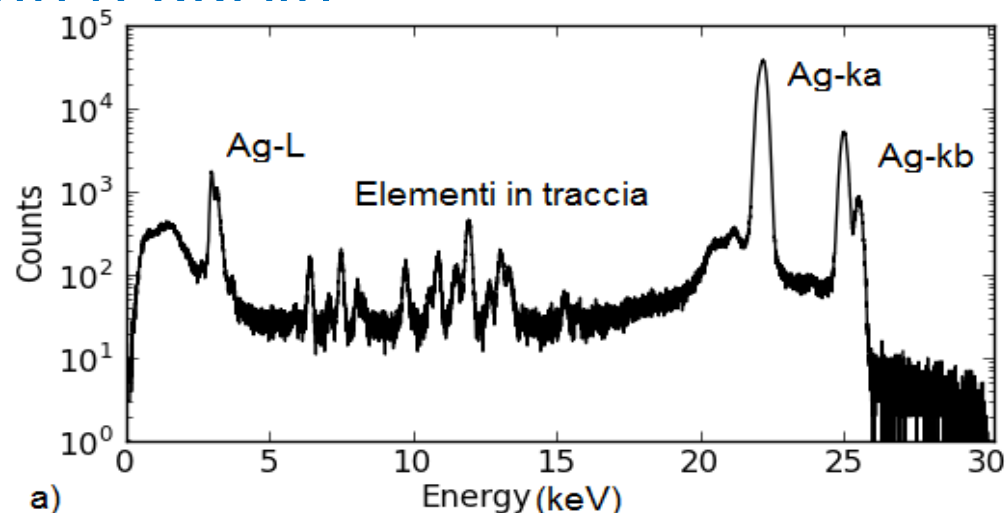
ei



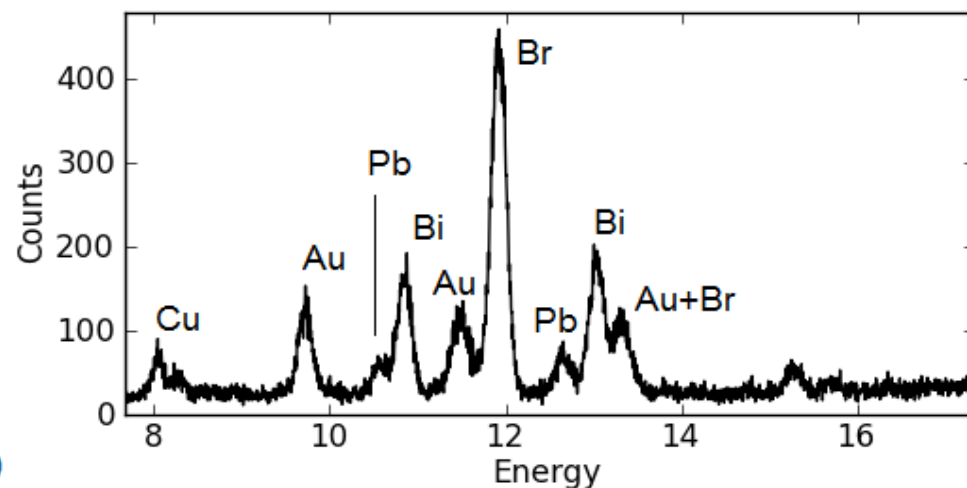
# La Fluorescenza X: un mezzo per studiare i materiali antichi

Soddisfa alcuni importanti requisiti:

- Non-distruttiva
- Semplice e veloce
- multi-elementale
- Portatile
- Bassi DL ( $\sim \mu\text{gr/gr}$ )
- Quantitativa



a)



b)



# Storia dell'arte

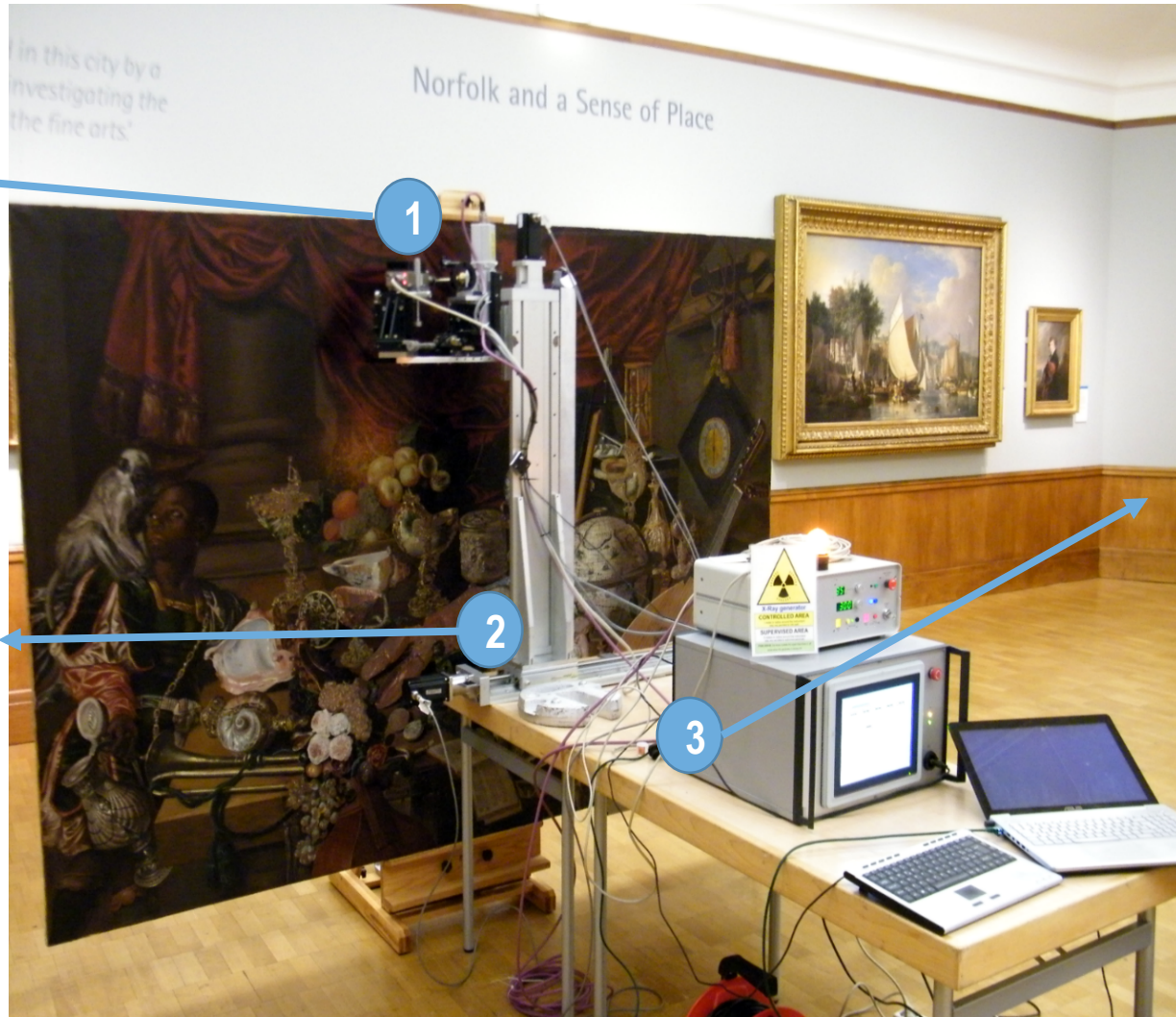




# Mobile scanning MA-XRF system: Main components

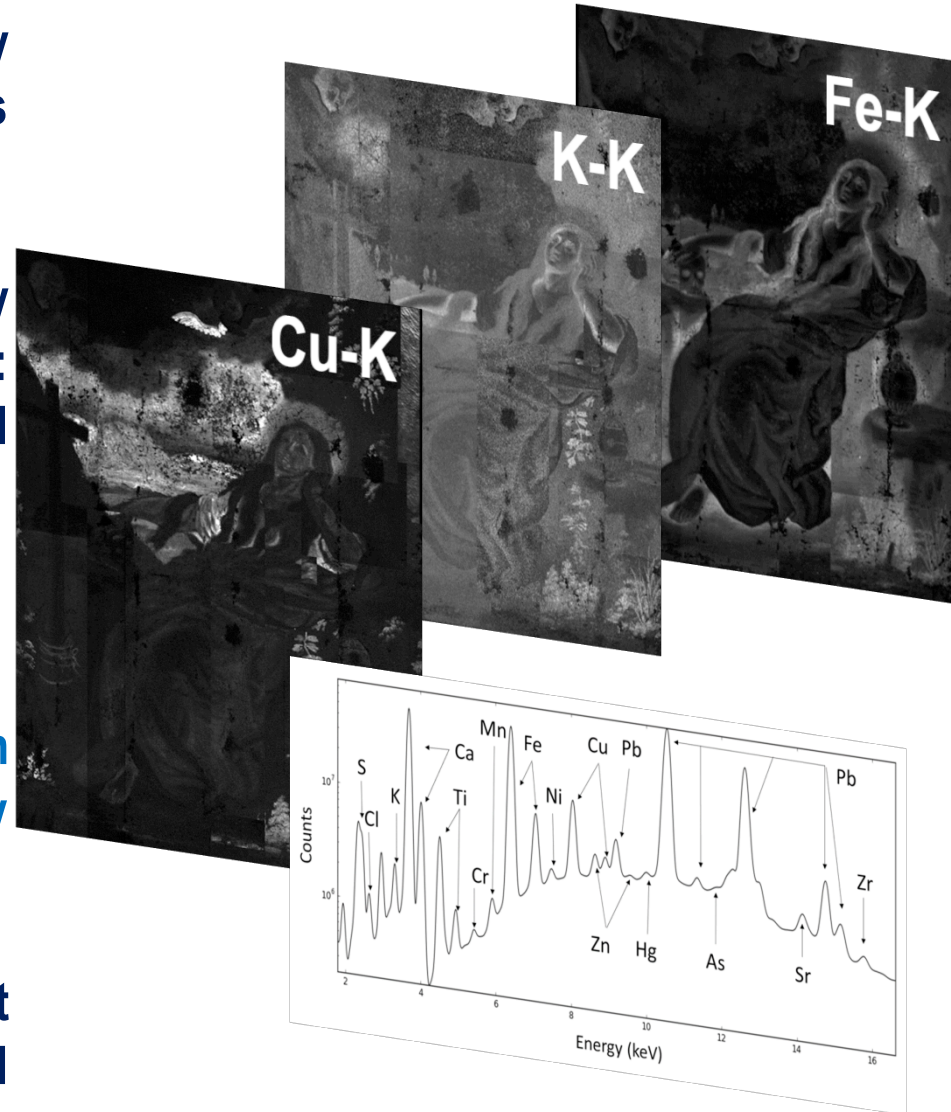
X-ray spectrometer  
(measuring head)

XYZ  
custom-  
designed  
long-range  
linear axis



# XRF *imaging* technique

1. Easier Identification of the pigments by observing the chemical elements distribution and their correlations.
2. Visualization of the changes made by the artist during the painting process: hidden sub-layered figures called *pentimenti*.
3. latest restorations treatments.
4. information concerning the conservation state of artworks and authenticity (anachronistic pigments presence)
5. Maps are easily interpreted by art historical scholars, archaeologists and conservators







*Dimensions: 50x40 cm*

*Scanning speed 20 mm/sec*

*Pixel 100  $\mu$ m – dwell time 5 ms*

*Time 22 h.*

*1 pixel*

**Ti**



Fe-Mn-Ti



Pb-Hg





Fast scanning: Matthias Stomer (Mocking of Christ, 1640 ca., 210x154 cm<sup>2</sup>)



Scanning speed @ 100 mm/sec

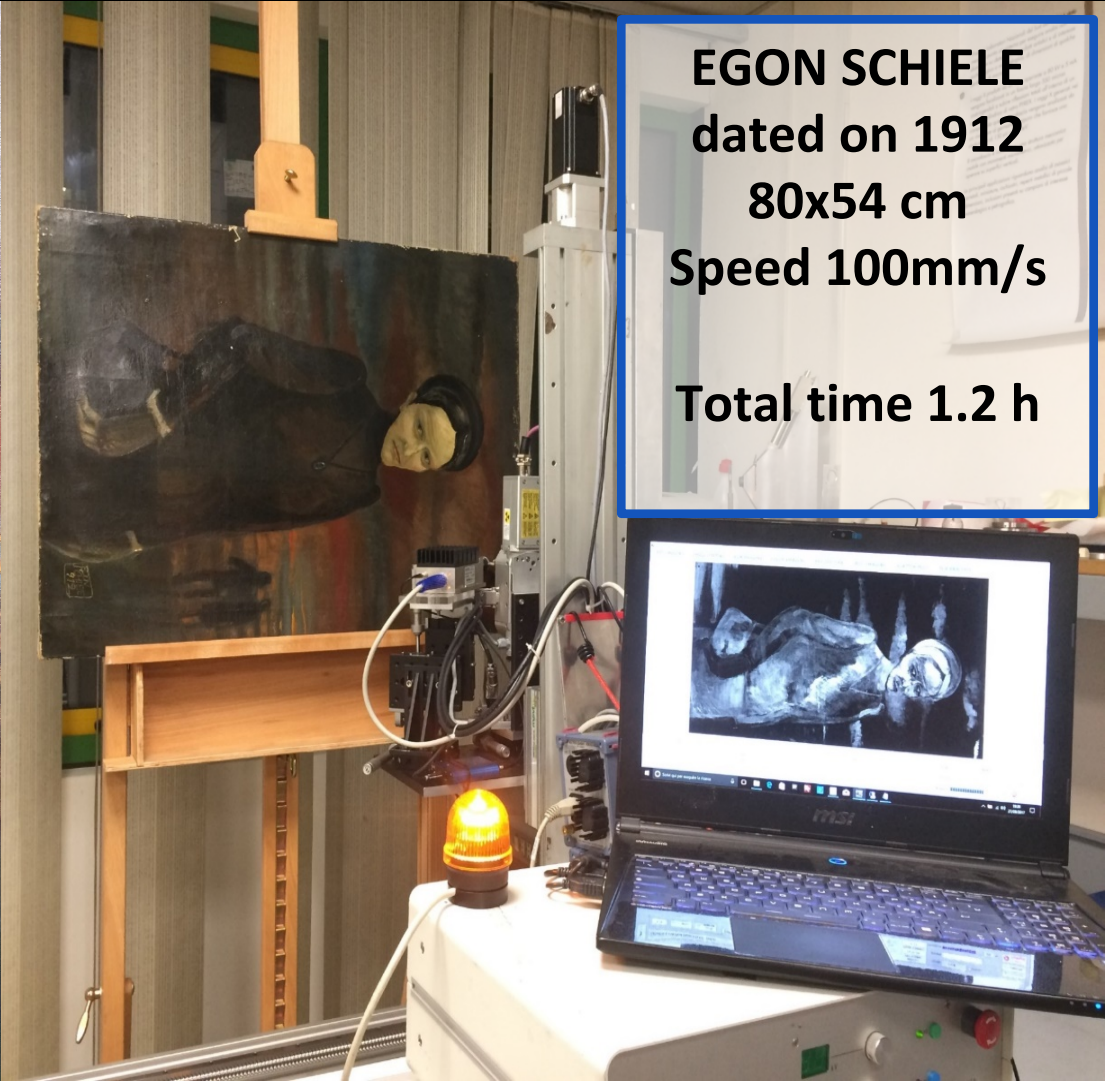
Elemental maps elaborated with 1 mm pixel size (equivalent to 10 ms dwell time)

**Pixels: 3.2 Mega; Scanning time 9,5 h (including a full fitting of pixel spectra)**

Pb-L







**EGON SCHIELE**  
**dated on 1912**  
**80x54 cm**  
**Speed 100mm/s**  
**Total time 1.2 h**





Ca



Pb



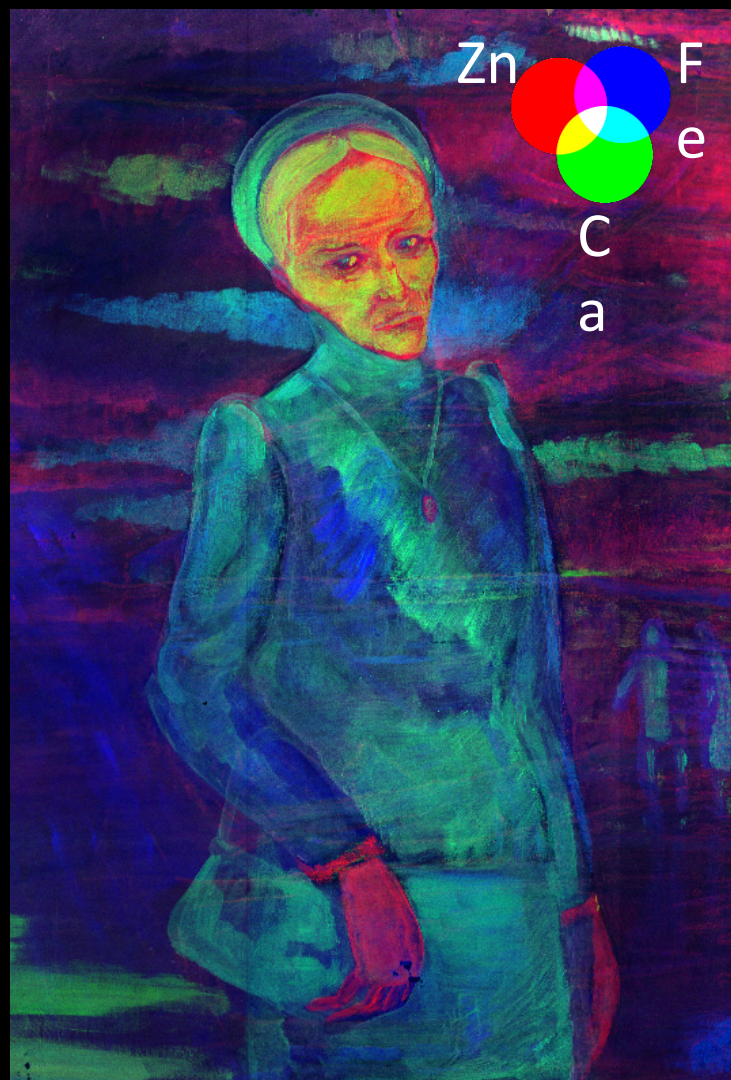
Zn



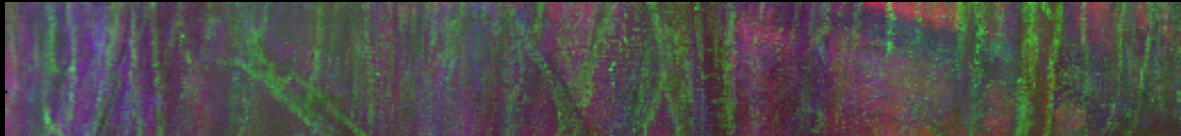
Fe



Ba







SCHIELE  
MAY 07





# Combining MA-XRF and micro-XRF elemental maps



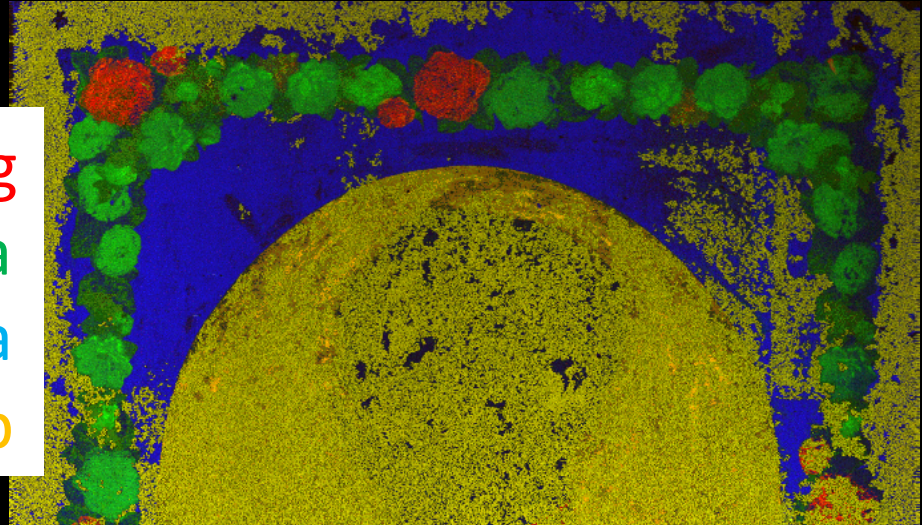
- A portrait of Vittorio Emanuele II dating around 1860/70
- The pictorial layer is decorated with glassy spheres of sub-millimeter dimensions
- A strong degradation is visible as parts of the painting suffers a detachment
- Elemental maps were used for addressing its restoration



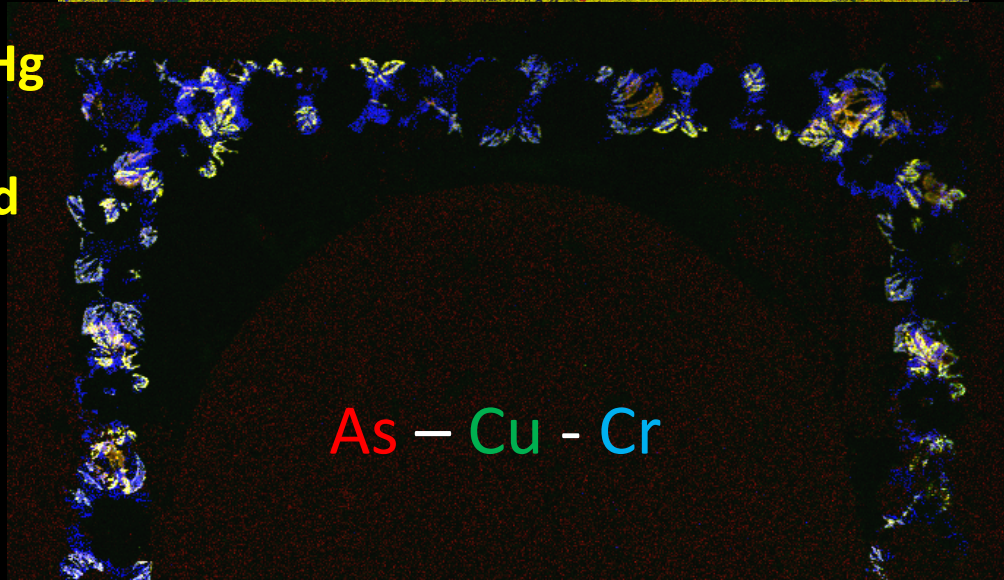
# MA-XRF scanning



Hg  
Ca  
Ba  
Pb



- **Red and Green are composed by Hg**  
Green decorative pattern is not visible in the painting due to its light color
- **White background is characterized by Ba**  
It is composed of Cr, Cu and As
- **The glassy spheres are composed by Pb**  
Spatial correlation of As and Cu suggest the use of Emerald Green in combination with Chromium oxides (Viridian green?)





# Micro-XRF scanning

2x2 cm,  
1 mm/sec  
50 um pixel  
50 ms dwell time  
2h scanning time

Pb



K



Ca



Hg





# Archeologia





# Black gloss in Attic pottery and imitation products



The Attic manufacturing technique was successfully imitated in Italy → use of same materials and technique?

Composition:

Fine suspension of illitic clays enriched in Fe and K

Firing cycle:

Oxydizing-Reducing-Oxidixing

$T = 800-950\text{ }^{\circ}\text{C} / \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$

Integration of portable

Techniques: PIXE, XRF, XRD and Scanning u-XRF

Synchrotron Radiation: GI-XANES (Fe oxidation state in black gloss), GI-XRF and Angula Scansion (Trace elements in black Gloss)

# Attic and imitations artworks in Sicily



(410-390 B.C.)



(370-360 B.C.)



IV cent. B.C.



IV cent. B.C.



(330-310 B.C.)



IV cent. B.C.



IV sec. B.C.



IV cent. B.C.



(430-420 B.C.)

# Quantitative data on Attic pottery

	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	Fe <sub>tot</sub>
ATT-1	1.9	31.7	46.8	4.1	0.9	13.5
ATT-2	1.8	31	46.7	5.5	0.3	13.1
ATT-3	2.2	29.8	43.4	6.1	0.9	15.4
ATT-4	1.9	29.2	45.6	4.7	0.6	15.3
ATT-5	1.9	30.9	45.3	6.5	-	14.8
ATT-6	1.6	32.4	45.8	3	0.3	15.5
<b>ATT-7(*)</b>	<b>2 (1.5)</b>	<b>29 (2)</b>	<b>42 (2)</b>	<b>3.3 (0.2)</b>	<b>0.45 (0.2)</b>	<b>13.1 (1)</b>

Data from Maniatis et al., 1993, Archaeometry 35, 23-24.

(\*)  $\alpha$ -PIXE data



# $\alpha$ -PIXE data on Attic and doubtful artworks

	N. Inv.	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>2</sub>	ClO	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Fetot
Liber31	9421	2.52	30.52	41.8	0.61	0.44	4.76	1.56	0.52	15.23
Liber30	9418	2.1	25.7	43.94	1.01	0.5	5.3	1.8	0.66	16.3
Liber33	097	3.57	28.58	45.01	0.69	0.41	4.98	2	0.74	12.78
Liber36	05-016	2.55	31.99	41.71	0.64	0.84	4.55	2.16	0.57	12.09
Liber38	9402	2.13	30.38	42.77	1.01	0.4	4.44	2.29	0	13.57
Liber34	11829	1.93	28.41	41.28	1.65	0.59	5.08	2.88	0.17	15.67
Liber26	9419	1.8	28.9	43.19	1.81	0.49	4.06	3.96	0.44	12.21
Liber35	9420	2.92	31.69	35.57	0.97	2.5	4	4.1	0.67	16.46
Liber32	9422	1.71	25.48	39.25	4.73	1.04	4.82	4.25	0.37	15.35
Liber27	9404	2.35	27.46	46.64	1.29	0.54	4.77	4.77	0.45	13.58

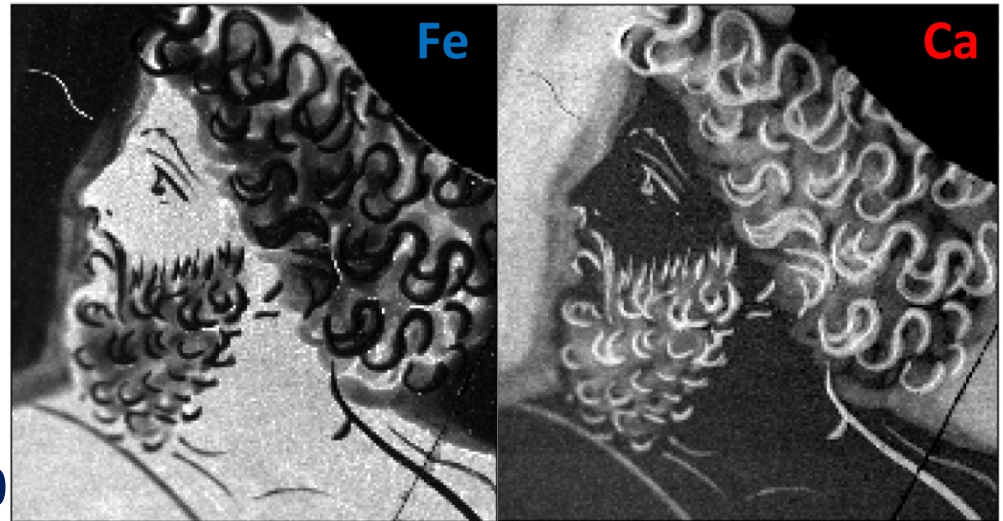
A first attribution can be performed based on the Ca content.

# Scanning $\mu$ XRF

- Image : 173 × 184 pixels
- Step-size: 150  $\mu$ m
- Step-time: 1 sec



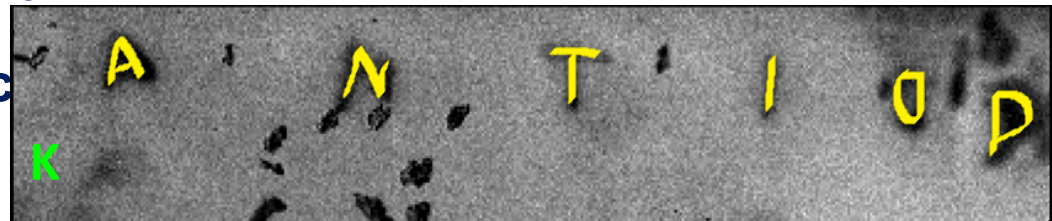
*Apulo (440-410 b.C.)*



- Image : 420 × 80 pixels
- Step-size: 100  $\mu$ m
- Step-time: 1 sec



*Attic Sample 425-400 b.C.*





IAEA  
International Atomic Energy Agency

# XANES: Attic Black Gloss (BG)

## X-ray Absorption Near Edge Spectroscopy



The pre-edge structure in the K-edge of Iron XANES spectra is sensitive to the Fe oxidation states

Can be useful for discriminating the 3-stages firing (ORO) process in different workshops in different geographic areas

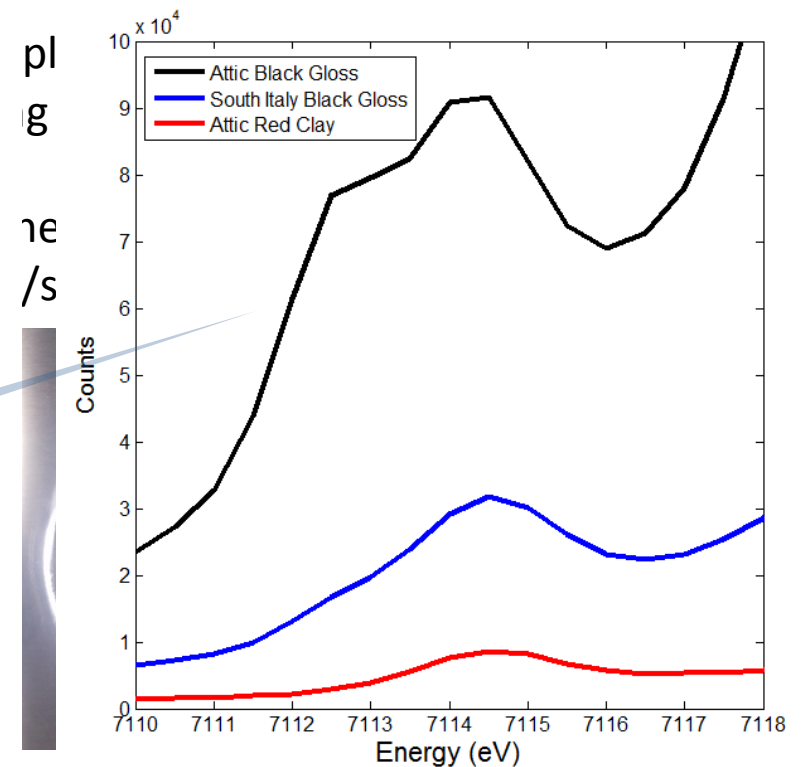
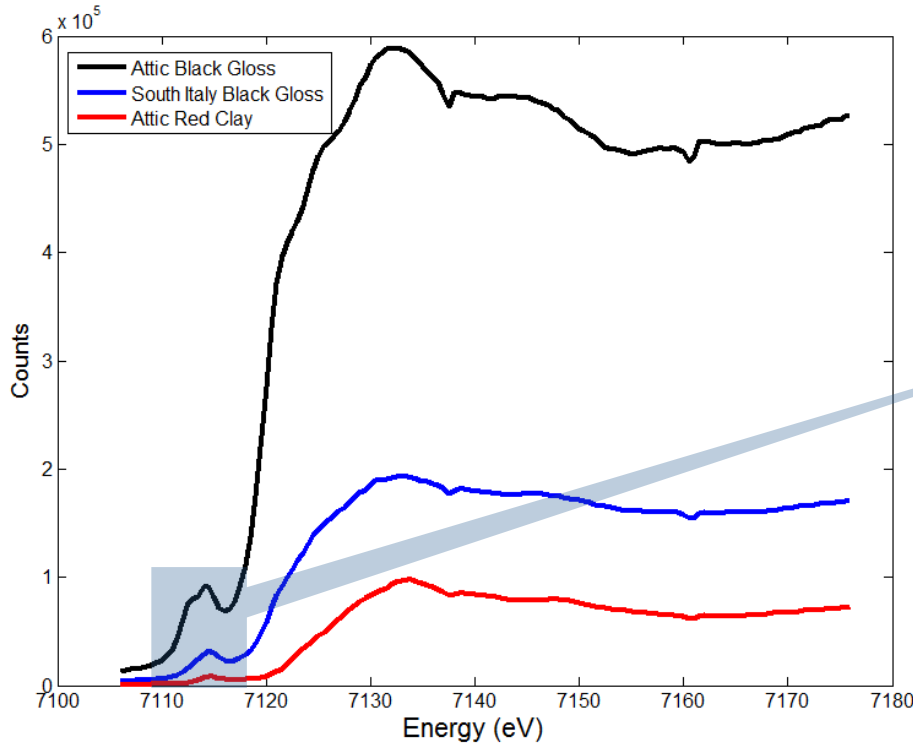
### IAEA - XRF endstation station



1) Silicon Drift Detector 30 mm<sup>2</sup>

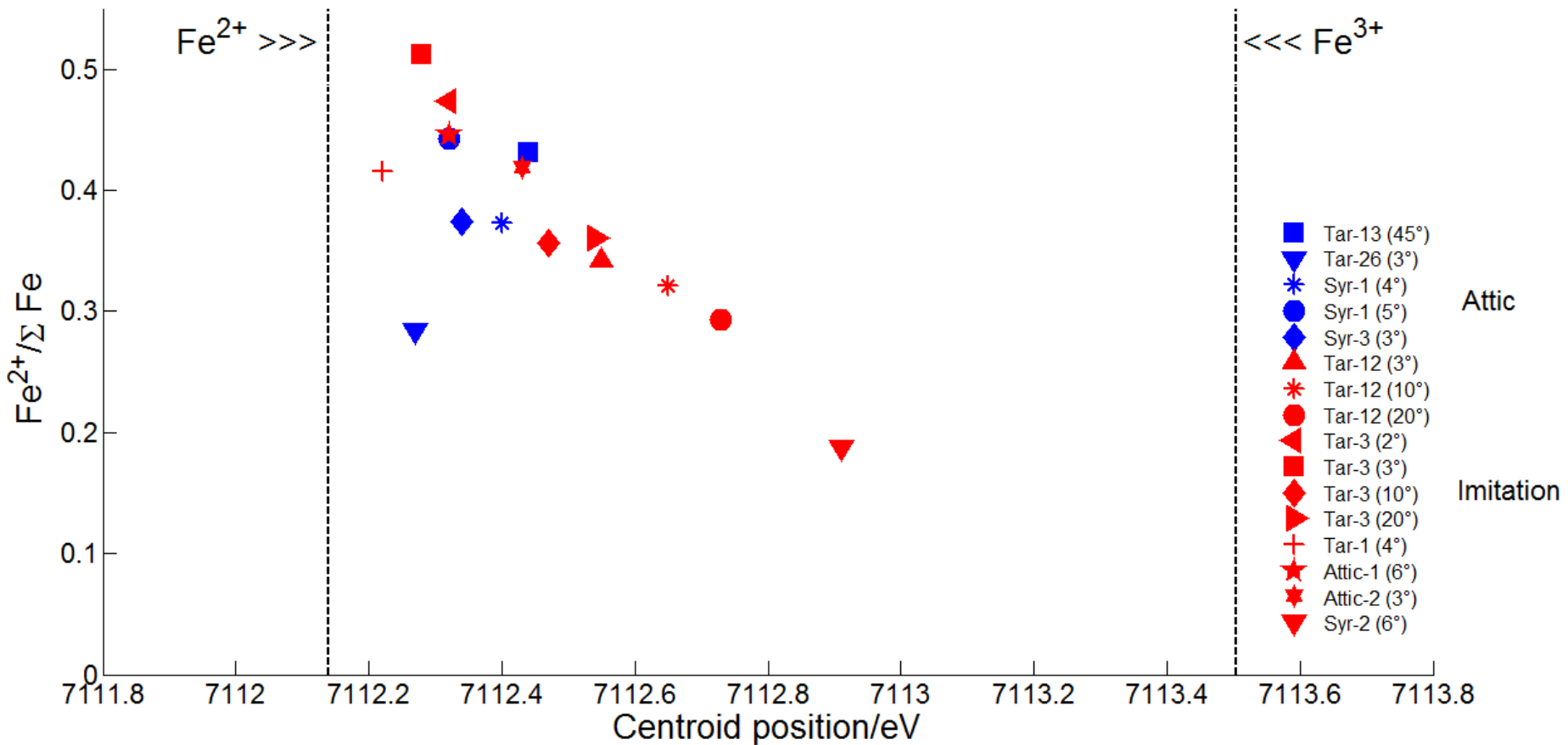
<133 eV @Mn-Ka, 75 eV @C-Ka

Pre-peak Fe-K region

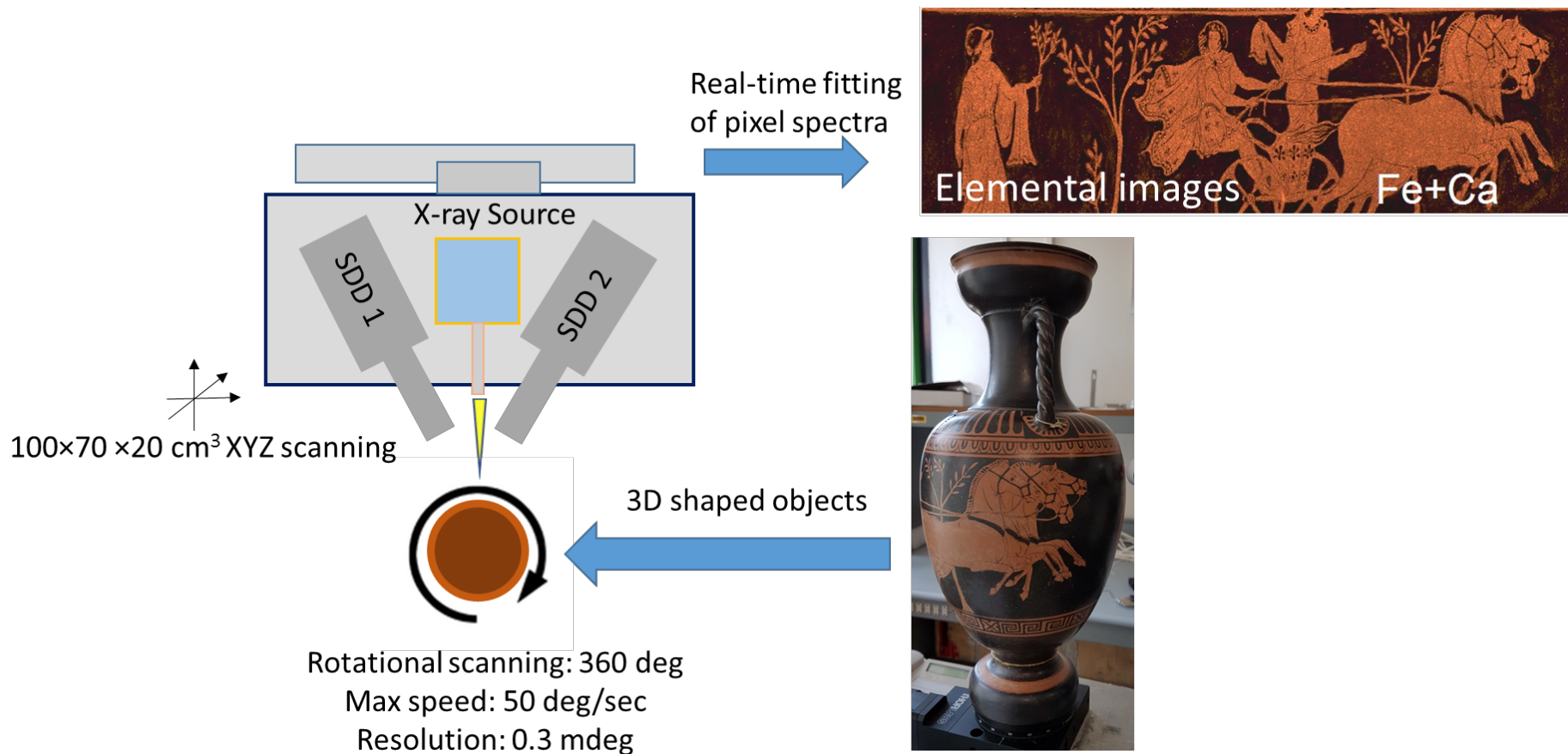


# XANES Results: Attic Black Gloss (BG)

Black Gloss



# LANDIS-X: Combining Rotational and Transational scanning









# Conclusioni

- I raggi X sono un valido mezzo per investigare la natura chimico-fisica dei materiali antichi
- Possono essere utilizzati in diverse configurazioni al fine di studiare sia la composizione chimica (Fluorescenza X) che quella mineralogica (Diffrazione)
- Le nuove tecniche di Imaging (Scansione e Full Field) consentono di ottenere informazioni con grande risoluzione spaziale e facilmente leggibili anche ai non addetti
- Le analisi sono non distruttive e spesso portatili
- I risultati sono utili in studi di provenienza, tecnologia di fabbricazione, autenticazioni