

# **Analysis of inorganic pigments by Nuclear Microprobe: The case of the paintings by the Master HGG**

---

**Stjepko Fazinić, Željko Pastuović, Milko Jakšić  
Rudjer Bošković Institute, Zagreb, Croatia**

**Mario Braun, Dragica Krstić, Domagoj Mudronja  
Croatian Conservation Institute, Zagreb, Croatia**



## Layout of the presentation:

---

- General about the RBI involvement in the field of protection of cultural heritage
- Few examples of the work done by RBI related to cultural heritage in cooperation with museums, conservators or art historians
- More detailed description of the current collaborative work related to identification of pigments in paintings



## Layout of the presentation:

---

- General about the RBI involvement in the field of protection of cultural heritage
- Few examples of the work done by RBI related to cultural heritage in cooperation with museums, conservators or art historians
- More detailed description of the current collaborative work related to identification of pigments in paintings



## **RBI Laboratories involved in activities related to the protection of cultural heritage objects:**

---

- I. Laboratory for Ion Beam Interactions
- II. Radiocarbon and Tritium Laboratory
- III. Radiation Chemistry and Dosimetry Laboratory

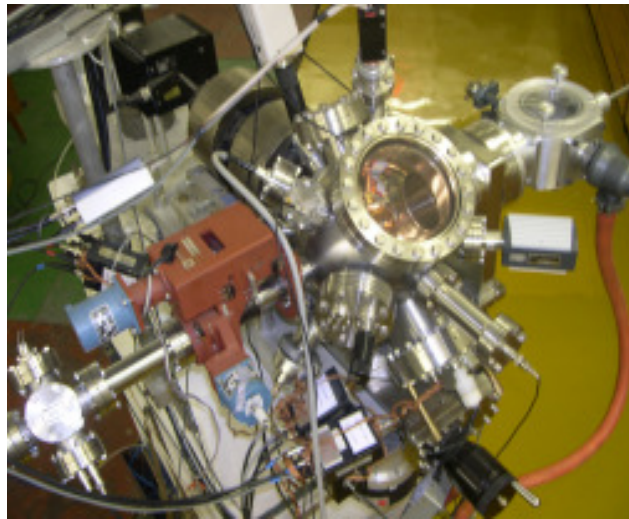


# Laboratory for Ion Beam Interactions

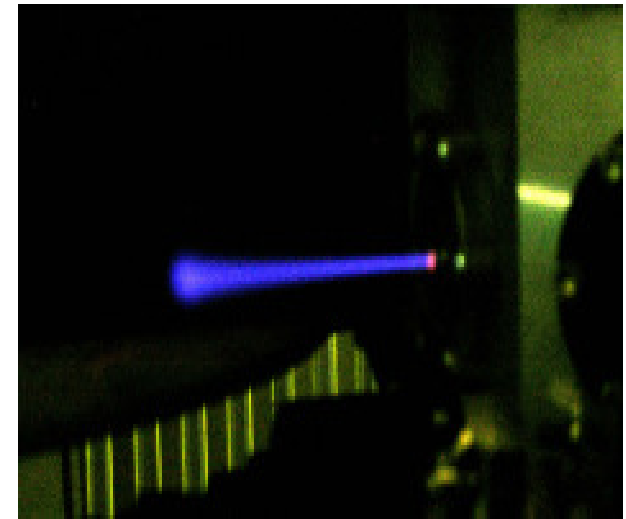
## Analytical capabilities



Broad beam analysis  
in vacuum  
Sample size:  
several mm



Microbeam analysis  
in vacuum  
Sample size:  
down to  $\mu\text{m}$  size



Broad beam analysis  
in air  
under construction



## Laboratory for Measurements of Low-level Radioactivity

---



*Plan for the next 1-3 years period:*

**Introduction of sample preparation method for AMS dating**

**Radiocarbon dating:**

**Gas proportional counting technique** - since 1968

**Liquid scintillation counting technique** - since 2003



# Radiation Chemistry and Dosimetry Laboratory

Technique: gamma  
irradiation

Application examples:

desinsection  
wooden objects, textiles

decontamination  
wooden objects, paper,  
leather





## Layout of the presentation:

---

- General about the RBI involvement in the field of protection of cultural heritage
- Few examples of the work done by RBI related to cultural heritage in cooperation with museums, conservators or art historians
- More detailed description of the current collaborative work related to identification of pigments in paintings





## Collaborations:

### within Croatia:

- Croatian Conservation Institute
- Antropology Institute
- Regional Conservation workshops
- Several individual museum workshops
- Restauration Department, Academy of Visual Arts
- Faculty of Forestry

### •International

- IAEA
  - National TC project
  - Regional TC Project RER/1/006
  - CRP on the use of NATs for authenticity of art objects
- China
- Italy



# CROATIAN CONSERVATION INSTITUTE

- **Central conservation & restoration institute under jurisdiction of the Ministry of Culture**



- **Architectural monuments**
  - ☐ Wall painting
  - ☐ Stucco decoration
  - ☐ Mosaics
  - ☐ Stone sculpture
- **Mobile art**
  - ☐ Paintings on different support
  - ☐ Wooden polychrome sculpture & objects
  - ☐ Metal objects
  - ☐ Textile objects
  - ☐ Paper objects
  - ☐ Archeological objects /ceramics & metal
  - ☐ Furniture
- **Documentation and laboratories**
- **Underwater archeology department**
- **Regional workshops**
  - ☐ Osijek
  - ☐ Ludbreg
  - ☐ Istra ( Juršići-Vodnjan)
  - ☐ Split
  - ☐ Dubrovnik



# Examples of the work done and current work in collaboration with the Croatian Conservation Institute

- Analysis of pigments for the Račić-Kraljević project
- Analysis of Apoximenos Statue
- Restoration of the portal of the St. Marco church in Zagreb
- Analysis of pigments for the Hans Georg Geiger project

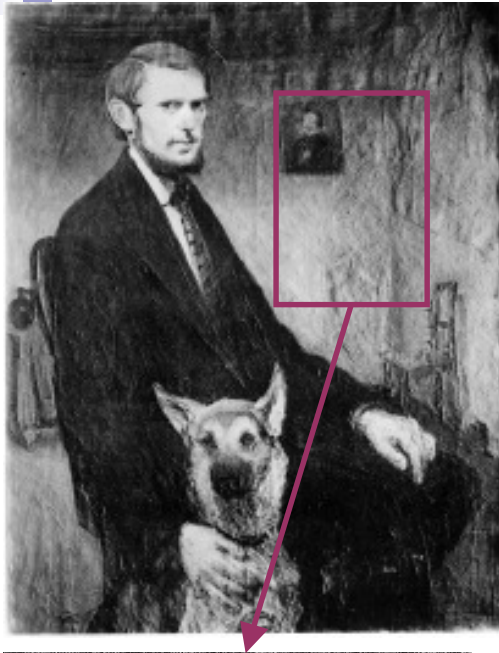


## Project Račić-Kraljević

First sistematic scientific investigations of paintings by CCI done in 1986.

- X-Rays
- UVF
- IRR
- IRF
- Cross Sections Chemical Analysis
- XRF





X rays define a new  
picture below

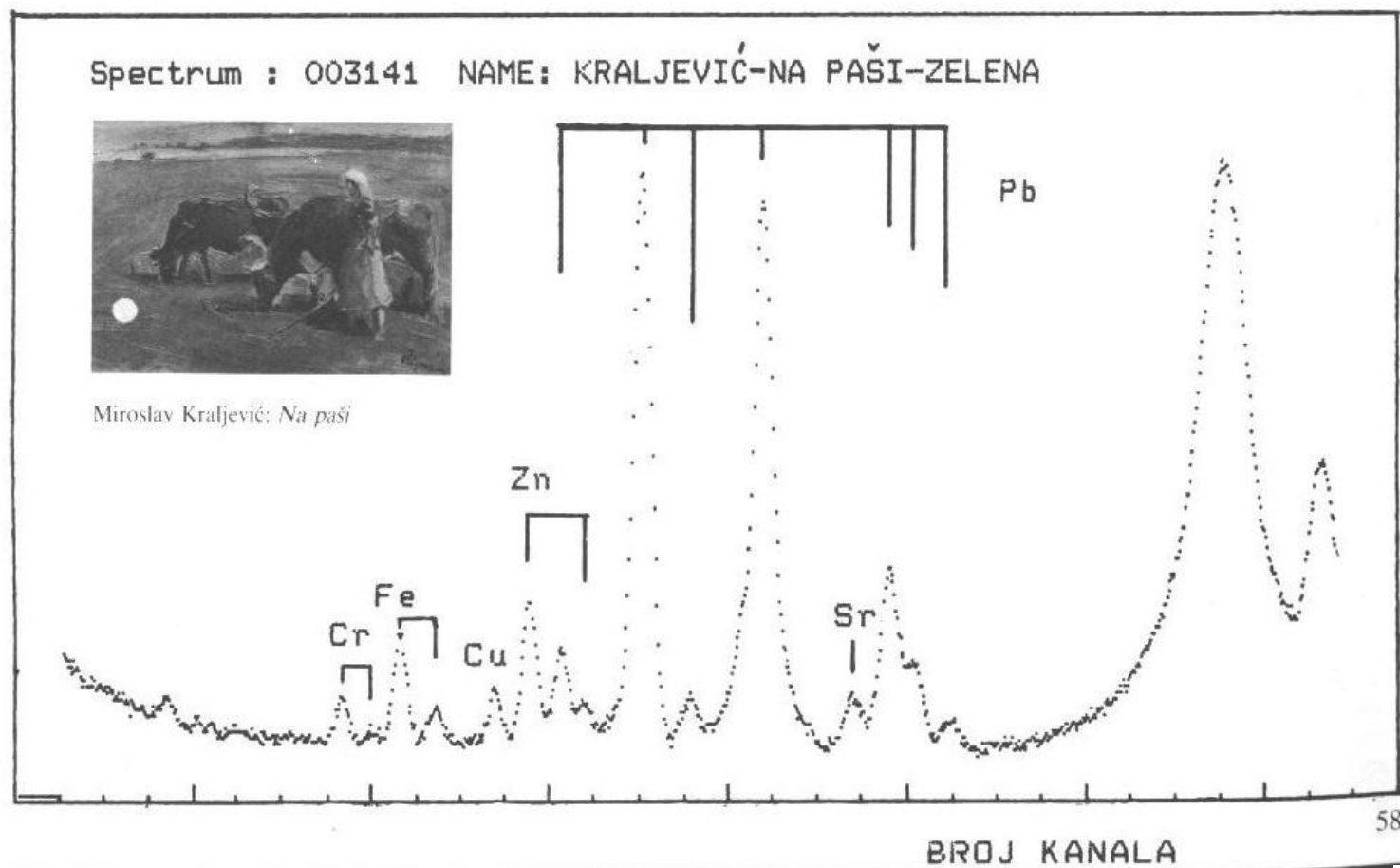


IRR defines black  
pigments



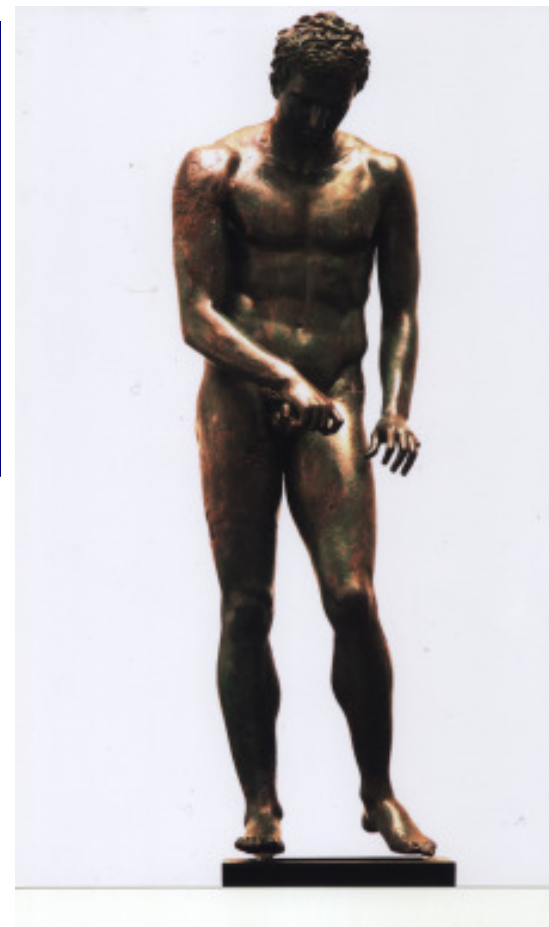


## Pigments analyzed by XRF at the RBI



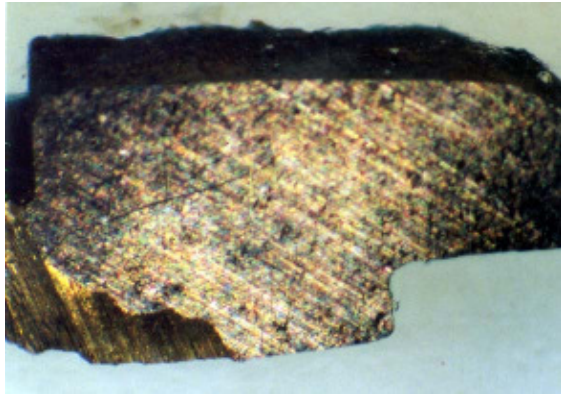
## Bronze sculpture – Apoximenos

- Sculpture -2200 years in sea
- Analyses of state, construction, molding, organic material in sculpture
- X-ray
- PIXE, microprobe

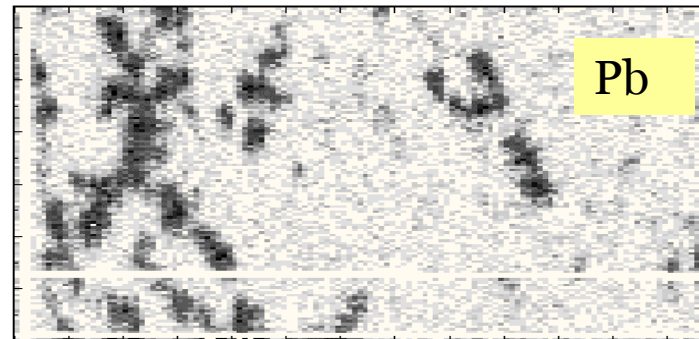
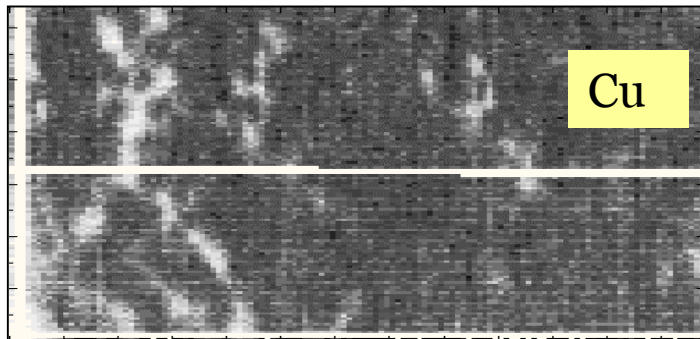




## Example: analysis of Apoximenos sculpture



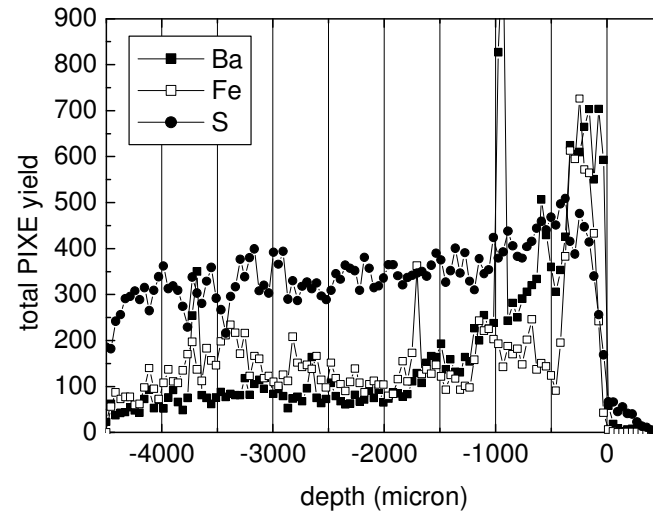
PIXE/RBS microprobe  
analysis:  
Elemental distribution!



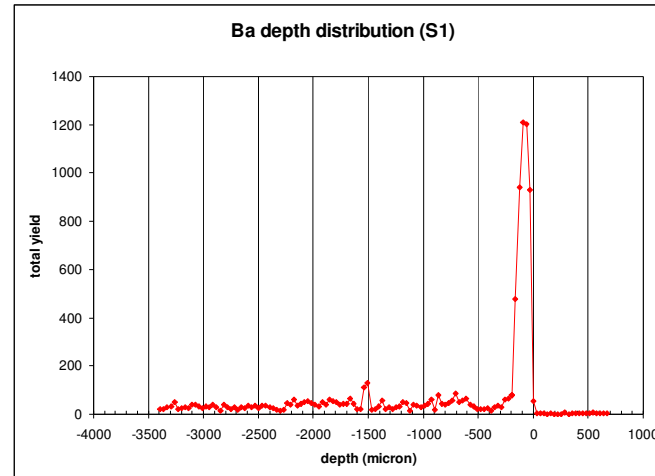
Cu is leached by seawater that explain increased concentration of Pb at the surface --> Sculpture is of Greek origin (+ C<sup>14</sup> dating of organic material)



## Example: Conservation of St. Marko church portal



Portal  
sample  
P1



Sandstone  
sample  
treated in  
laboratory

Florentine method of cleaning and consolidation by soaking the stone in ammonium carbonate and barium hydroxide



## Layout of the presentation:

---

- General about the RBI analytical capabilities to work in the field of protection of cultural heritage
- Examples of the work done by RBI related to cultural heritage in cooperation with museums, conservators or art historians
- More detailed description of the current collaborative work related to identification of pigments in paintings



## Paintings of Hans Georg Geiger (HGG)



Ruđer Bošković Institute, Zagreb, Croatia





# Analysis of Master HGG paintings

---

- ***17th century cultural heritage in Croatia minimal***
- ***Hans Georg Geiger***
  - ***was living and working between 1641 and 1680 in Slovenia and Croatia (Austrian Monarchy)***
  - ***He left 32 paintings (half in Croatia)***
  - ***Most of his preserved works had not been signed***
  - ***Almost all paintings in churches***



## Work in progress

- a) detail of the painting from the St. Mihael Ch., Gracani
- b) x-ray picture of the same detail
- c) IR of the other detail of the same painting



# Analysis of Master HGG paintings

---

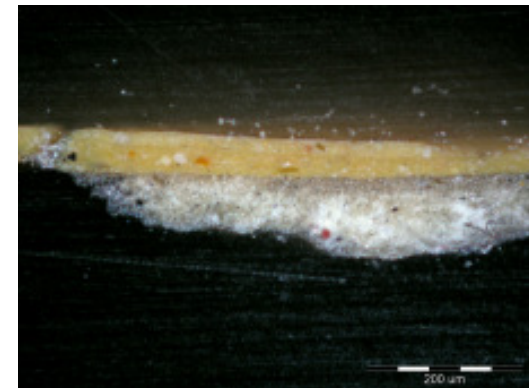
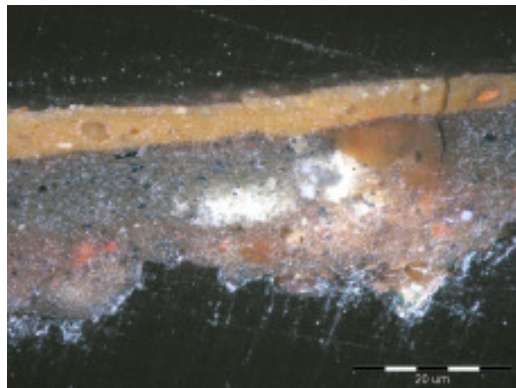
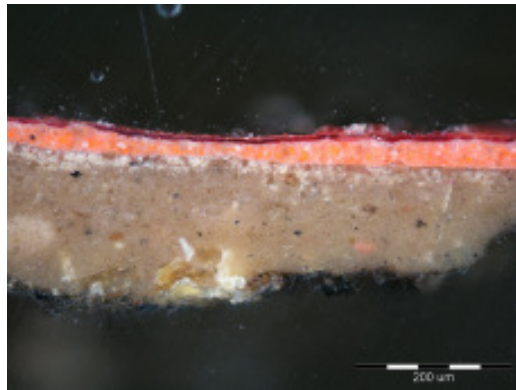
- We started to be involved at the end of 2004
- CCI prepared about 100 micro-samples
  - CCI performed X-Ray, UV, IR analysis
  - RBI - measurements in progress
    - About 30 samples measured so far
    - Analysis of spectra done
    - Pigments identified



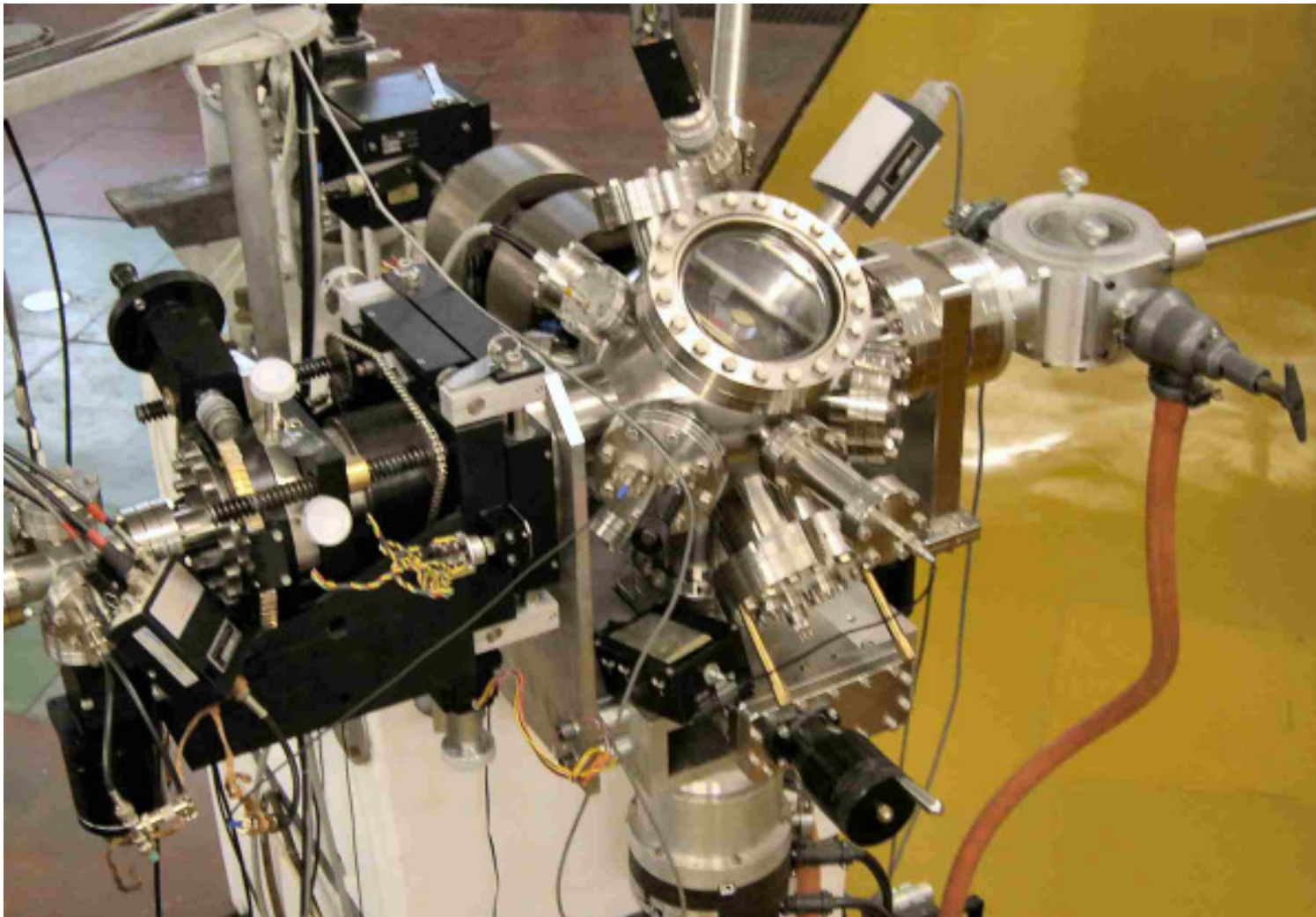


# Work in progress

## micro-samples are the same as for OM techniques

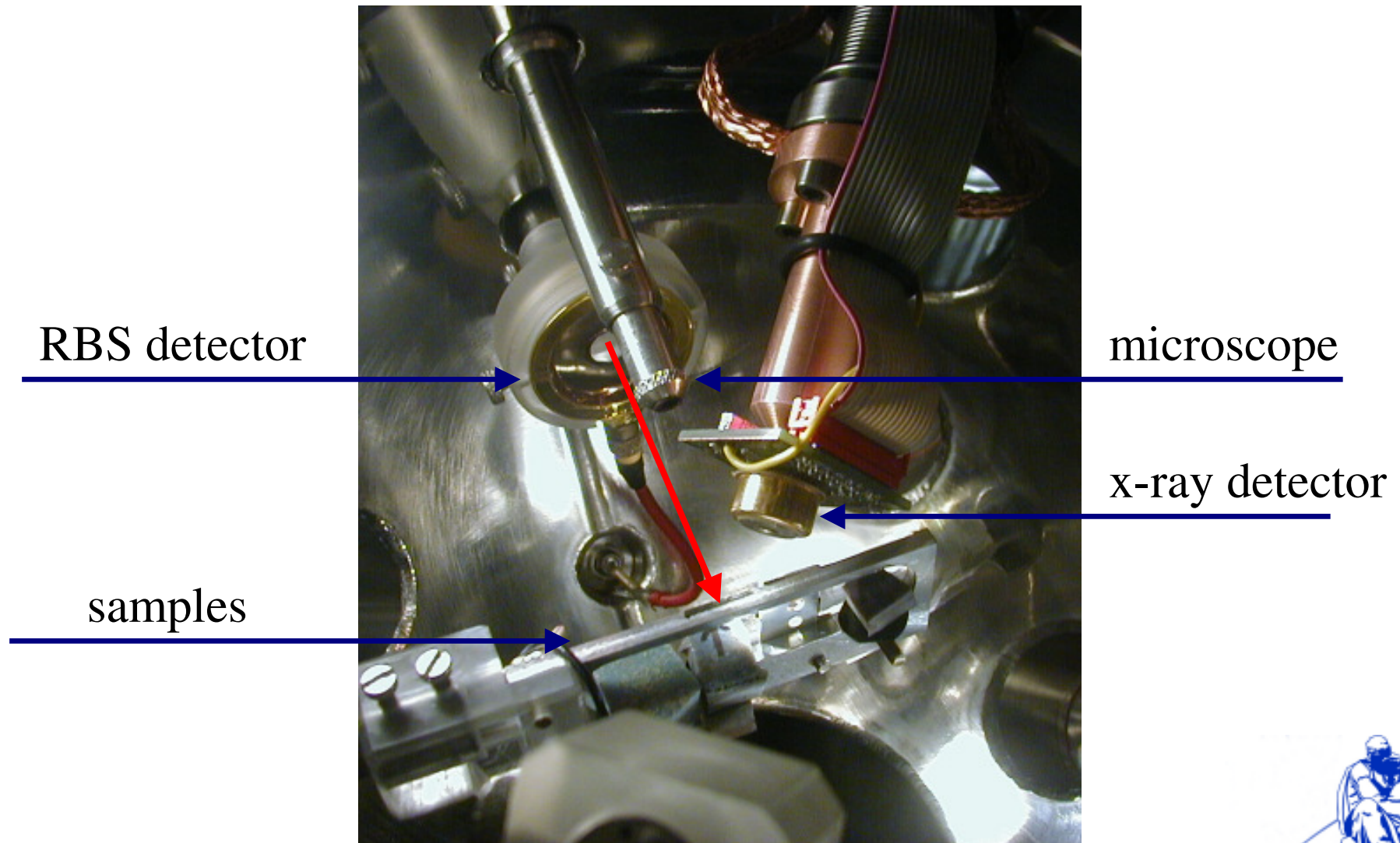


## Analysis of micro-samples was done at the RBI nuclear microbeam setup

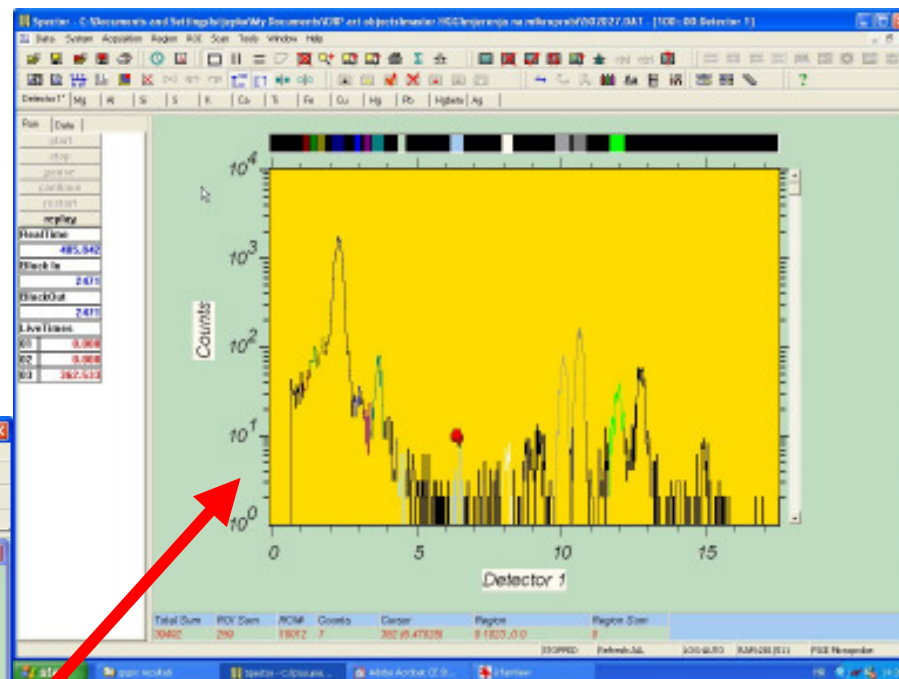
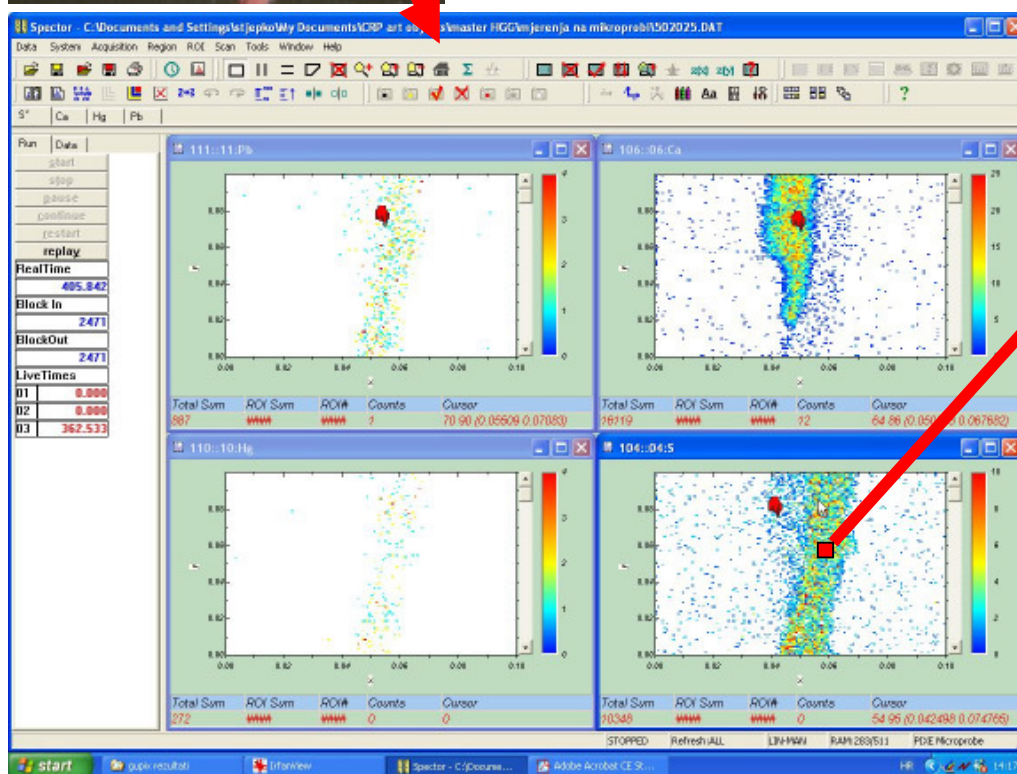
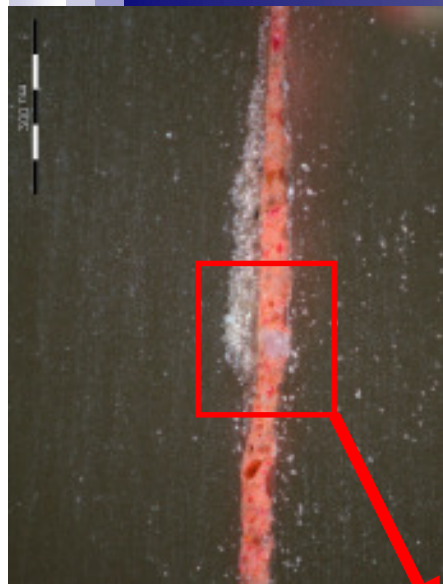




## Zoom inside the RBI nuclear microbeam scat. chamber



# Data acquisition and analysis



502027

Element	koncentracija u težinskim %	Greška u %
AlK	0.84	22.4
SiK	0.31	52.1
PK	0.60	34.6
SK	3.03	22.5
KK	0.21	54.1
CaK	2.19	7.5
CuK	0.22	32.6
HgLA	18.24	6.3
PbLA	52.83	3.7

**Red is Vermilion (HgS)**



# Analysis of Master HGG Paintings

## Identified pigments:

Painting	Time of origin	Sample	Yellow ochre	HgS	Alizarin Krapl.	Red ochre	Minium	Ultra marin	Smalt	Azurite	Cu resin	Green earth	C - soot	Ph white	Ag
St Anthony of Padua, <u>Klanjec</u>	1664	7967B 8172C 8174E	✓				✓						✓	✓	
St Leonard, <u>Klanjec</u>	~1670	8180D				✓								✓	
St Valentine - Ex Voto <u>Klanjec</u>	1675	7980A 8182C 8184E	✓					✓					✓	✓	
St Dionisius, <u>Zagreb</u>	1675/77	8186C 8189F		✓		✓	✓		✓					✓	
St Barbara, <u>Zagreb</u>	1665/67	8196B								✓					
St Yld, <u>Zagreb</u>	1665/67	8274F 8270B									✓	✓		✓	
St Apollonia, <u>Zagreb</u>	1665/67	7972A 8243D 8242C 7973B	✓ ✓ ✓			✓ ✓			✓					✓ ✓	
St Nicola, <u>Zagreb</u>	1665/67	7968A 7969B		✓		✓								✓ ✓	
St Michael, <u>Gračani</u>	~1677	8211G 8207C 8208D	✓ ✓	✓					✓		✓			✓ ✓	
St Sebastian - Ex Voto, <u>Zagreb</u>	1679	8278D 8279E		✓			✓		✓	✓				✓ ✓	
St Michael, <u>Yugrovec</u>	1680	8177D 8178E	✓	✓											
Good Father, <u>Yugrovec</u>	1680	8216D 8217E			✓	✓									✓
St Clara, <u>Varaždin</u>	~1680	8088A 8192D				✓ ✓								✓	





# Conclusions

---

*The nuclear microprobe in combination with PIXE and RBS analysis is valuable tool that can help in identification of pigments used by artists to make paintings.*

*Since the technique preserves the sample integrity, the same samples may be reused for complementary analysis by some other technique.*

*In this particular case, the technique has been successfully used in combination with OM to identify a number of pigments in 15 paintings.*

*Further analysis of the measured data, in combination with the data obtained by the other techniques will help to get the overall picture and understanding of the full Master HGG opus.*



# Thank you

---

