The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

SMR/1843-10

X-Ray Emission Techniques for Forensic Applications

28 May - 1 June, 2007

Role of non-destructive analysis in better documentation of cultural heritage artefacts in support of combating illicit trafficking

Nikolla Civici
Institute of Nuclear Physics
Tirana, Albania

Strada Costiera 11, 34014 Trieste, Italy - Tel. +39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it, www.ictp.it

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Nikolla Civici
Institute of Nuclear Physics
P.O.Box 85, Tirana, Albania
E-mail: ncivici@yahoo.com

Department of Instrumental Analytical Methods
X-ray Fluorescence Laboratory

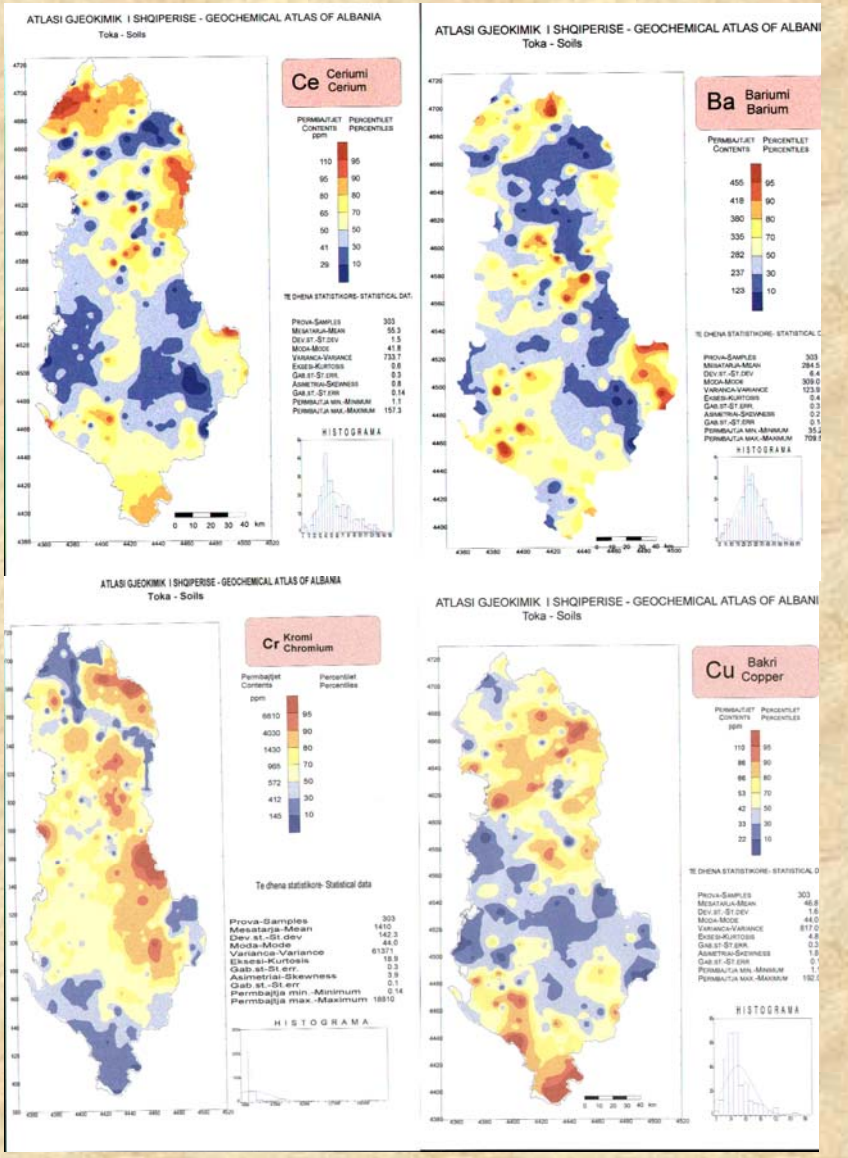
- Staff - two researchers and
  – one technician
- Equipments
  - Tube excited EDXRF system
  - TXRF system
  - Radioisotope excited EDXRF system
  - Field portable EDXRF system

FPXRF system

- **Measuring head**:
  - Si-PIN X-ray detector (mod. XR-100CR)
  - Radioactive disc sources Cd-109 (740 MBq) and Am-241 (370 MBq)
  - Low power X-ray tube
- **Spectrum acquisition**:
  - HV power supply and spectroscopy amplifier (mod. PX2CR)
  - Pocket MCA 8000A
  - Special software that works on a palmtop computer HP 200LX or on a laptop

EDXRF Laboratory – Aplications
1. Geology and geochemistry

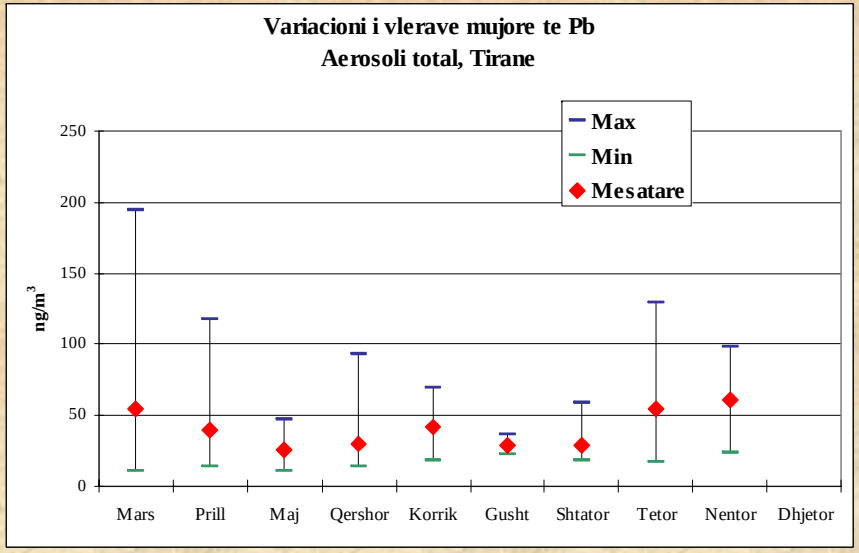
- Multielemental analyses of rocks, soils, sediments and mineral ores
- Project for the preparation of geochemical map of Albania
  - 25 – 30 elements were determined in 1500 soil and sediment samples
- **N. Civici, R. Van Grieken** *"Energy dispersive X-ray fluorescence analysis in geochemical mapping"*, **X-ray Spectrometry, Vol. 26, 147-152, (1997).**

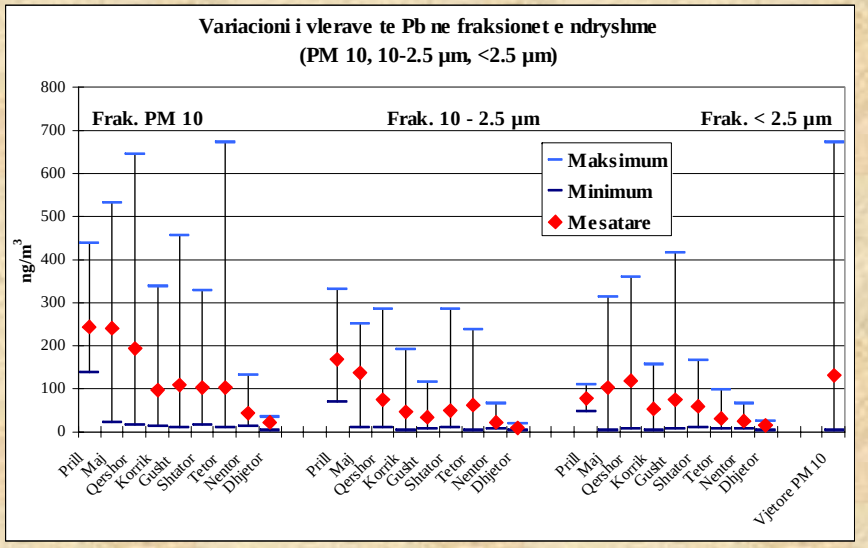


EDXRF Laboratory – Aplications
2. Air pollution monitoring

- Determination of toxic elements (Cr, Mn, Ni, Pb, etc.) in suspended particulate matter

- **N. Civici** *"Determination of elemental concentrations in atmospheric aerosol in Tirana by EDXRF spectrometry"*, **Albanian Journal of Natural and Technical Sciences, No. 11, 65, (2001)**

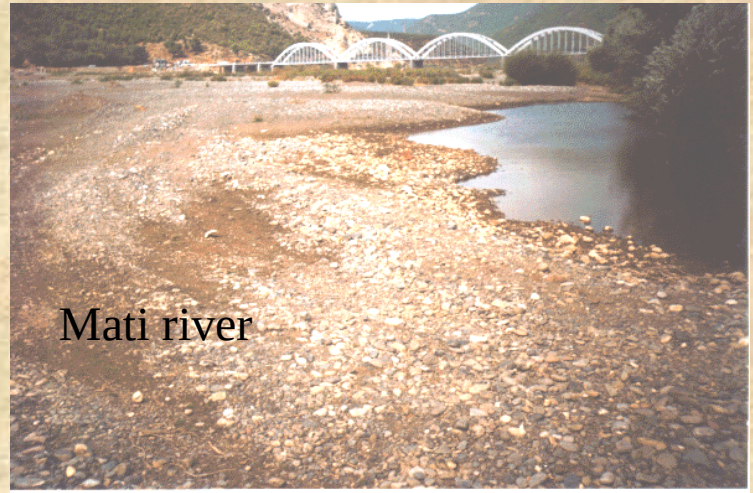




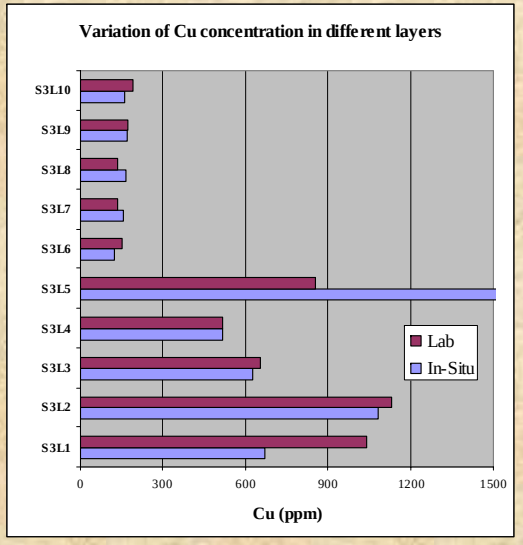
EDXRF Laboratory – Applications

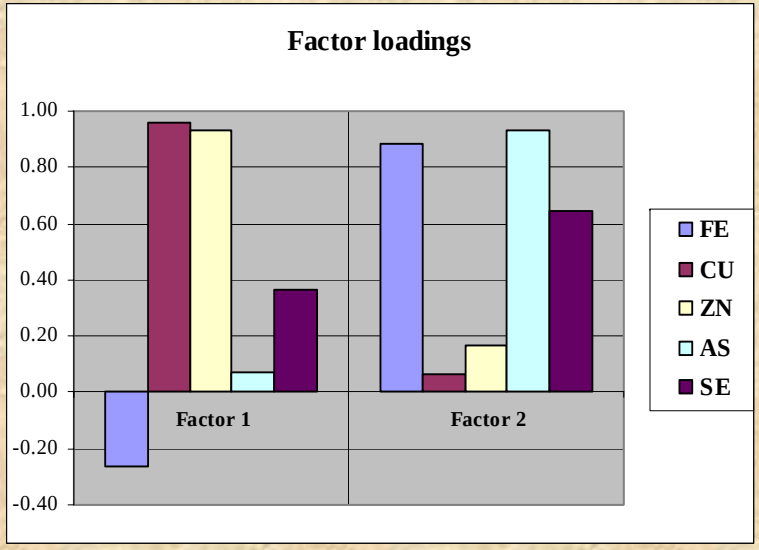
3. Assessment of pollution in over bank sediments

CRP “In situ application of XRF techniques”



- High values of Cu, Zn, Fe, As and Se were found in the polluted layers
- Pollution sources
  - Copper metallurgy (Cu, Zn)
  - Copper mining and ore processing industries (Fe, As and Se, pyrites)



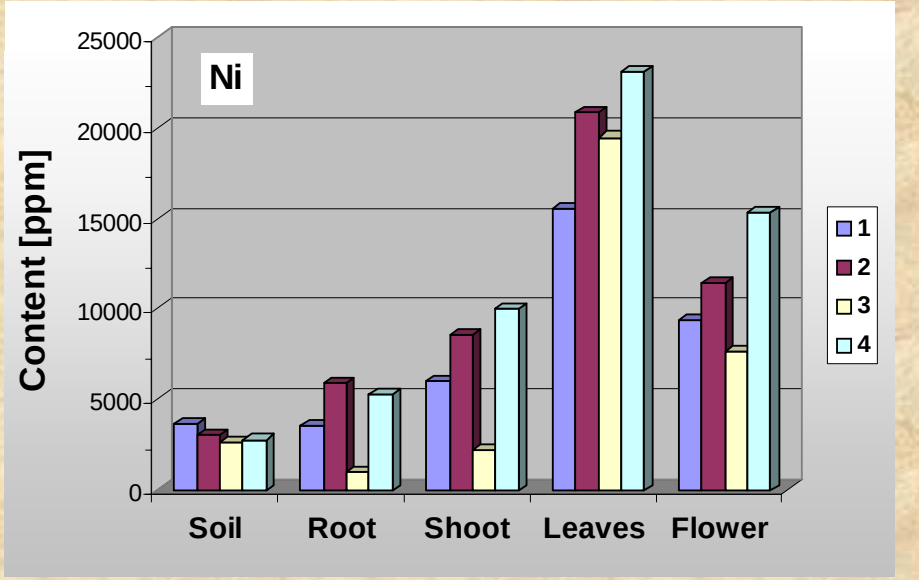


EDXRF Laboratory – Applications
4. Evaluation of hyperaccumulator plant species grown in metalliferous sites in Albania

***Alyssum Bornmuellera Thlaspi* (*Alyssum murale*)**

- **Grows in areas covered with serpentine soil**
- **It is a model system for understanding metal hyper-accumulation (Ni)**

The photosynthetic activity shows an inverse relationship to Ni content in plant.



Proficiency test – IAG GEOPT20

EDXRF, IFB (U 66)			OPY-1, Ultramafic rock		
	Reported values X	St. Dev	**Assigned values Xa**	**Target Precision Ha**	**Z - score Z=[X-Xa]/Ha**
CaO	**7.62**	0.130	**7.8**	0.115	**-0.79**
TiO2	**0.38**	0.020	**0.38**	0.009	**-0.16**
MnO	**0.167**	0.0113	**0.18**	0.005	**-1.29**
Fe2O3	**11.72**	0.160	**11.84**	0.163	**-0.37**
Cr	**2740**	88.0	**2420.74**	59.93	**2.66**
Ni	**915**	4.3	**870.62**	25.141	**0.88**
Cu	**51**	8.9	**43.65**	1.978	**1.86**
Zn	**63**	5.2	**61.81**	2.658	**0.22**
Sr	**14**	1.3	**15.99**	0.843	**-1.18**

Proficiency test – IAEA
Ancient Chinese clay

Laboratory Code 26

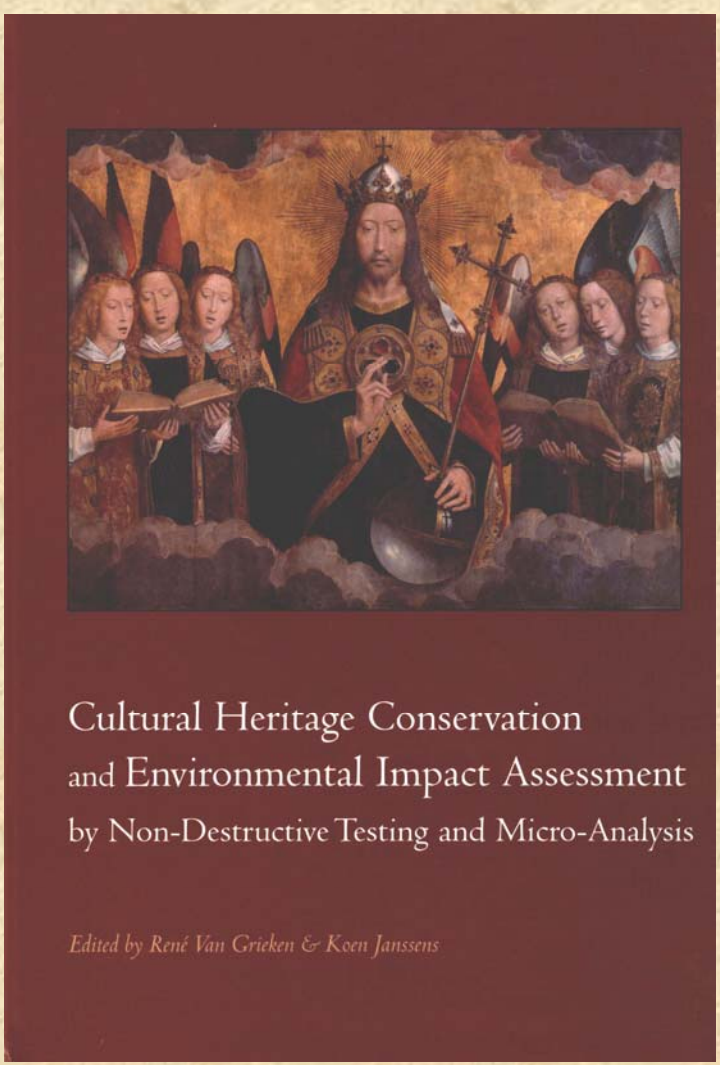
Method: ED-XRF

Analyte	Unit	IAEA		Laboratory results			R. bias	Z-score	U-Test	Lab./IAEA	Acceptance criteria					Final score
		Target value	Target Uncertainty	Reported value	Uncertainty	[%]	%				Trueness A1	Trueness A2	Trueness Score	Precision P	Precision Score	
CaO	[%]	0.62	0.05	0.59	0.08	13.56	-4.84	-0.48	-0.32	0.95	0.03	0.24	A	15.78	A	A
Fe_2O_3	[%]	2.7	0.1	2.91	0.18	6.19	7.78	0.78	1.02	1.08	0.21	0.53	A	7.21	A	A
K_2O	[%]	2.3	0.2	2.27	0.16	7.05	-1.30	-0.13	-0.12	0.99	0.03	0.66	A	11.19	A	A
MnO	[%]	0.026	0.001	0.03	0.003	10.87	6.15	0.62	0.51	1.06	0.00	0.01	A	11.53	A	A
TiO_2	[%]	0.95	0.04	0.90	0.08	8.89	-5.26	-0.53	-0.56	0.95	0.05	0.23	A	9.84	A	A
Ba	[mg/kg]	371	51	421.00	9.5	2.26	13.48	1.35	0.96	1.13	50.00	133.84	A	13.93	A	A
Ce	[mg/kg]	118	18	140.00	8.3	5.93	18.64	1.86	1.11	1.19	22.00	51.14	A	16.37	A	A
Ga	[mg/kg]	34	5.8	34.00	5	14.71	0.00	0.00	0.00	1.00	0.00	19.76	A	22.52	A	A
La	[mg/kg]	68.8	5.4	75.00	10.2	13.60	9.01	0.90	0.54	1.09	6.20	29.78	A	15.7	A	A
Nd	[mg/kg]	51.9	7.2	53.00	8.2	15.47	2.12	0.21	0.10	1.02	1.10	28.15	A	20.78	A	A
Pb	[mg/kg]	36.5	5	36.00	3.5	9.72	-1.37	-0.14	-0.08	0.99	0.50	15.75	A	16.8	A	A
Rb	[mg/kg]	113	18	120.00	9.1	7.58	6.19	0.62	0.35	1.06	7.00	52.04	A	17.64	A	A
Sr	[mg/kg]	103	16	107.00	8.2	7.66	3.88	0.39	0.22	1.04	4.00	46.39	A	17.32	A	A
Y	[mg/kg]	37.2	4.8	42.00	3.8	9.05	12.90	1.29	0.78	1.13	4.80	15.79	A	15.76	A	A
Zn	[mg/kg]	58.5	6.6	58.00	8.5	14.66	-0.85	-0.09	-0.05	0.99	0.50	27.76	A	18.49	A	A
Zr	[mg/kg]	337	42	303.00	35	11.55	-10.09	-1.01	-0.62	0.90	34.00	141.05	A	16.99	A	A

Objectives of cultural heritage studies

1. **Fundamental interest in materials and methods of artist**
   - **Provenance**
   - **Dating**
   - **Authenticity**
2. **Questions concerning restoration and conservation**
3. **Documentation**

"Art 2002"



7th International Conference on

"Non-destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage"

2 – 6 June 2002

University of Antwerp, Belgium

Many contributions included X-rays

Of all contributions at this conference, 115 used analysis techniques (others were on strategy, education, etc).

Of these 115:

-63 used X-rays, namely:

- **32 XRF**
- **23 SEM/EMPA**
- **13 PIXE**
- **11 XRD**
- **5 XAS**
- **4 TXRF**
- **4 X-ray microtomography**

-28 used IR

-14 used Raman spectrometry

-12 used visible light (and reflectometry)

-6 used GC-MS

-2 used each of NAA, SIMS, ICP-AES/MS, NMR, IC

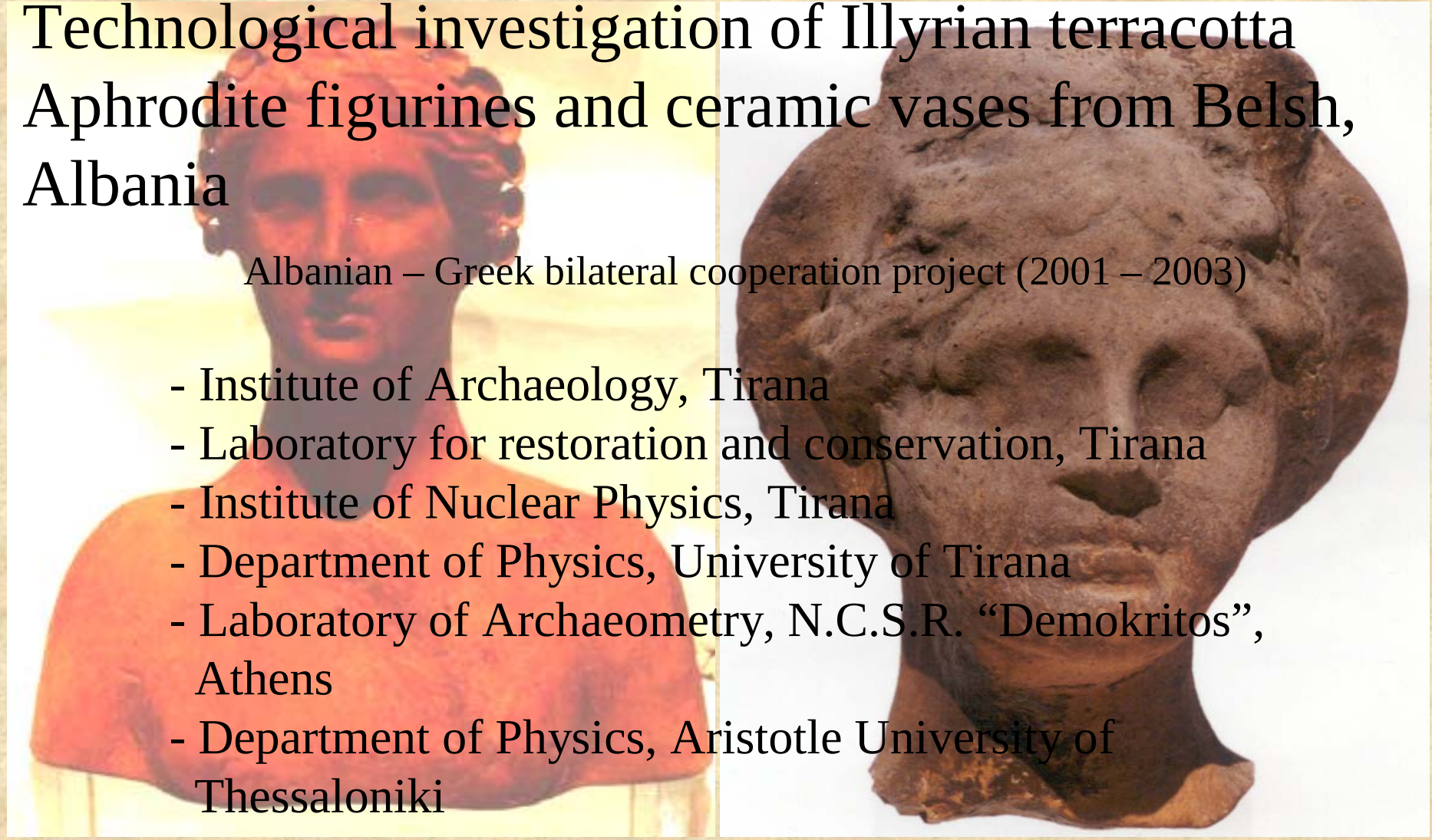
Features of XRF

- Non-destructive analysis (e.g., museum samples, works of art, archaeological samples)
- Simplicity, speed of operation, flexible requirements for sample preparation
- Immediate analytical results (important for interactive measurement programmes, e.g., study of art objects)
- Not so expensive

Study of Cultural Heritage Artifacts - 1

Technological investigation of Illyrian terracotta Aphrodite figurines and ceramic vases from Belsh, Albania

Albanian – Greek bilateral cooperation project (2001 – 2003)



- Institute of Archaeology, Tirana
- Laboratory for restoration and conservation, Tirana
- Institute of Nuclear Physics, Tirana
- Department of Physics, University of Tirana
- Laboratory of Archaeometry, N.C.S.R. “Demokritos”, Athens
- Department of Physics, Aristotle University of Thessaloniki

Study of Cultural Heritage Artifacts - 2

- Investigation of the composition and technology of silver coins from Kreshpan hoard (III-rd cent. B.C.)
  - » Albanian – Greek bilateral cooperation project (2004-2005)
  - Institute of Archaeology
  - Laboratory for restoration and conservation
  - Institute of Nuclear Physics (EDXRF)
  - Department of Physics, University of Tirana
  - Department of Physics, Aristotle University of Thessaloniki

Study of Cultural Heritage Artifacts – 3
Identification of materials and techniques in wall paintings.

- **“Saint Trinity” church, Berat**
  - 14th century, Byzantine, painter - anonymous
- **“Saint Theodore” church, Berat**
  - 16th cent., painter – Onufri
- **“Saint Nikollas” church, Shelcan, Elbasan**
  - 16th cent., painter – Onufri
- **“Saint Paraskevi” church, Valsh, Elbasan**
  - 16th cent., painter – Onufri
- **“Saint Athanas” church, Voskopoje, Korce**
  - 18th cent., painters – Zografi brothers
- **“40 Saints” church, Saranda**
  - 5th – 6th cent., painter – anonymous
- **Two mosques in Berati**
  - 18 – 19th cent., painter - anonymous

The center for the recording and documentation of cultural heritage artifacts

- Electronic database that contain every know detail of the artifact
  - Name, author, size, period, place,…….,photo
- They are trying to include in the database the artifacts possessed by the privates
- They try to control the movement of all these artifacts by giving permissions and on the other hand the database has been made available to the border police.

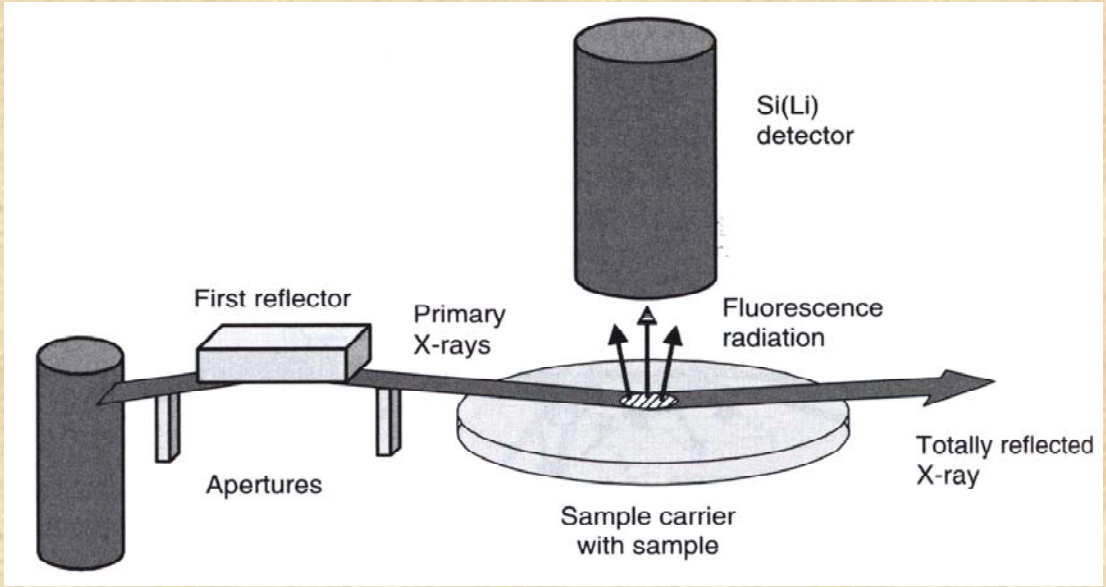
Our proposal

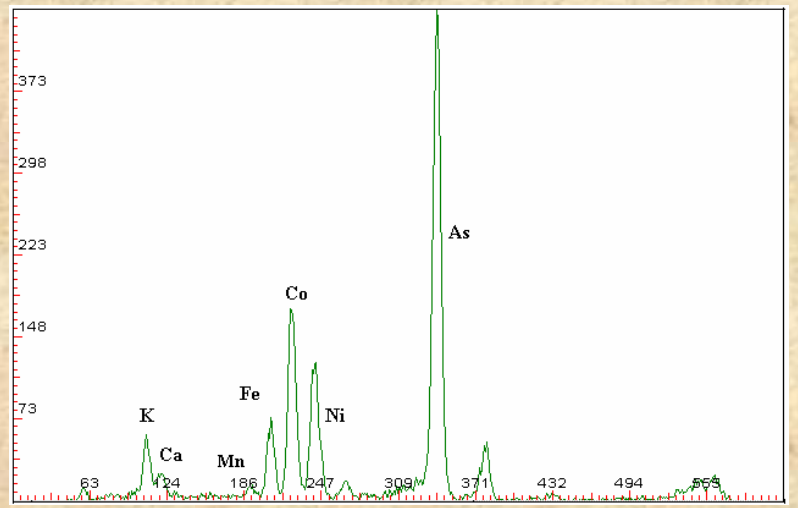
- To add to the database some details about the materials and techniques used for the production of some important artifacts (icons, etc.).
- This can prevent the return of a perfect copy of the original.

Identification of inorganic pigments used in 14^{th} to 19^{th} century icons using TXRF.

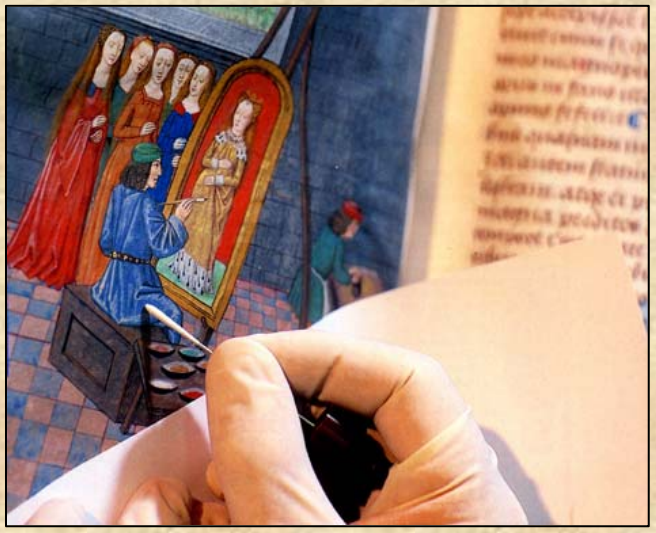
- The objective of this study was to obtain detailed data that can be useful:
  - For restoration and conservation purposes
  - Will allow the reconstruction of the palette of different old painters.
  - Documentation

TXRF Spectrometer – Working principle





Total reflection of primary beam =
no penetration in support =
no background = extremely good sensitivity =
micro-sample



Pigment Identification by XRF

- The number of materials used as pigments is not very large and their composition is very well known.
- Any pigment can be characterized by 1-5 major elements, which can be regarded as key elements.
- The application of XRF techniques for the identification of pigments is based on the identification and measurement in the spectrum of one or a few key elements for each individual pigment.
- In most of the cases this way of identification, i. e. the combination of the pigment's colour with the detected key elements, can lead to good results.

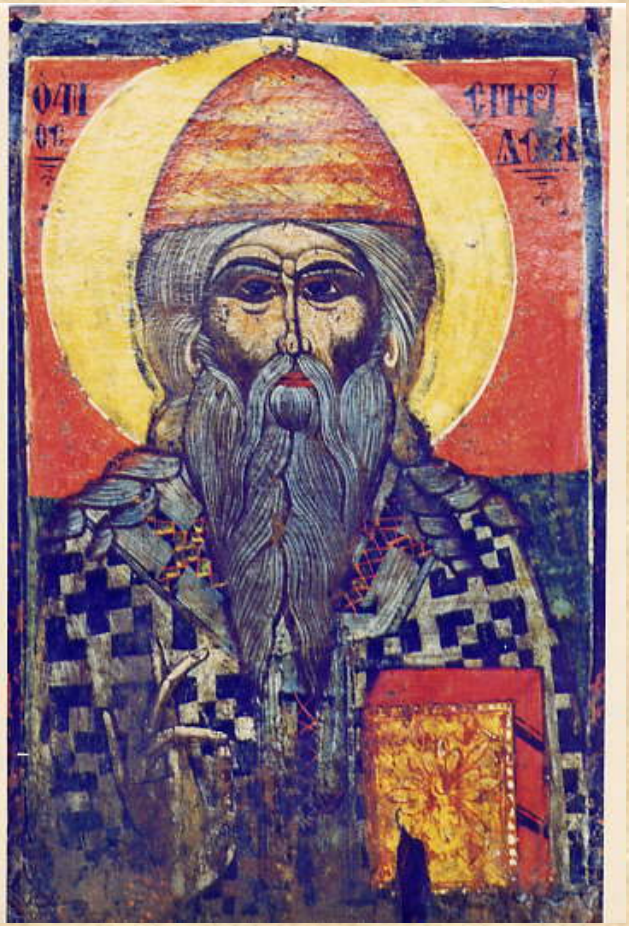
Inorganic pigments and the key elements that can be used for their identification based on x-ray techniques

Green	**Basic copper sulfate**	**$Cu_x(SO_4)_y(OH)_z$**	**Cu**
	Chromium oxide	**Cr_2O_3**	**Cr**
	Chrysocolla	**$CuSiO_3.nH_2O$**	**Cu**
	Cobalt Green	**$CoO.5ZnO$**	**Co, Zn**
	Emerald Green	**$Cu(CH_3COO)_2.3Cu(AsO_2)_2$**	**Cu, As**
	Guignent Green	**$Cr_2O_3.nH_2O + H_3BO_3$**	**Cr**
	Malachite	**$CuCO_3.Cu(OH)_2$**	**Cu**
	Verdigris	**$Cu(CH_3COO)_2.nCu(OH)_2$**	**Cu**
Blue	**Azurite**	**$2CuCO_3.Cu(OH)_2$**	**Cu**
	Cerulean Blue	**$CoO.SnO_2$**	**Co, Sn**
	Cobalt Blue	**$CoO.Al_2O_3$**	**Co, Al**
	Cobalt Violet	**$Co_3(PO_4)_2$**	**Co**
	Egyptian Blue	**$CaO.CuO.4SiO_2$**	**Ca, Cu, Si**
	Manganese Blue	**$BaSO_4.Ba_3(MnO_4)_2$**	**Ba, Mn**
	Prussian Blue	**$Fe_4[Fe(CN)_6]_3$**	**Fe**
	Smalt	**Co-glass (K_2O,SiO_2,CoO)**	**Si, K, Co**
	Ultramarine	**$Na_{8\text{-}10}Al_6Si_6O_{24}S_{2\text{-}4}$**	**Si, Al, Na, S**
Black	**Antimony Black**	**Sb_2O_3**	**Sb**
	Black iron oxide	**$FeO.Fe_2O_3$**	**Fe**
	Carbon/charcoal black	**C (95%)**	**- (K)**
	Cobalt Black	**CoO**	**Co**
	Ivory Black	**$C + Ca_3(PO_4)_2$**	**P, Ca**
	Manganese oxide	**$MnO + Mn_2O_3$**	**Mn**

XRF Disadvantages

- Low sensitivity for low Z elements.
- Can not be directly identified:
  - Organic pigments, charcoal and ultramarine(?).
  - A few inorganic pigments having same colour and the same detectable key element but different molecular composition, like malachite and verdigris (Cu).
- It is a good practice to combine XRF with other techniques

13-14th century icons – anonymous painters

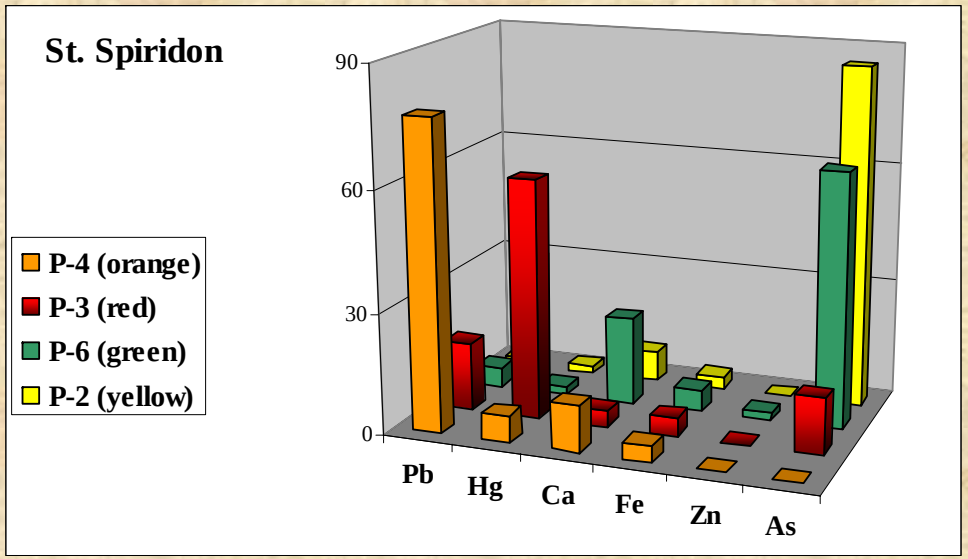


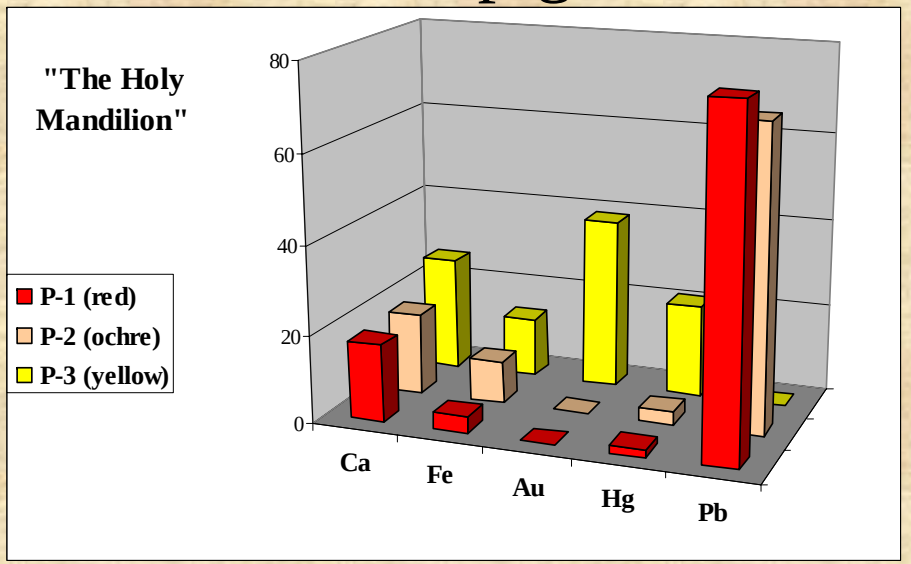
"Saint Spiridon"

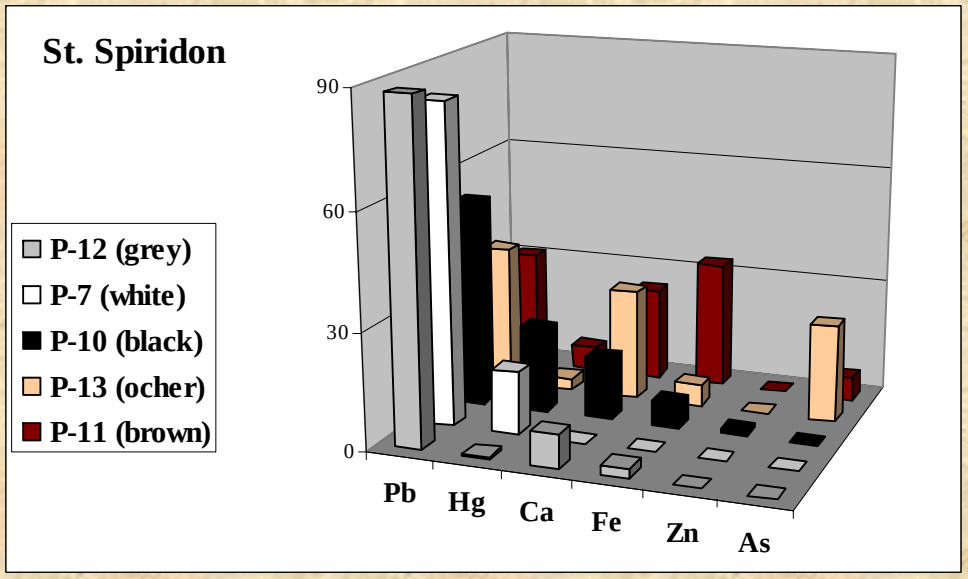
"The Holy Mandilion"

TXRF results

Relative element distribution in different pigments





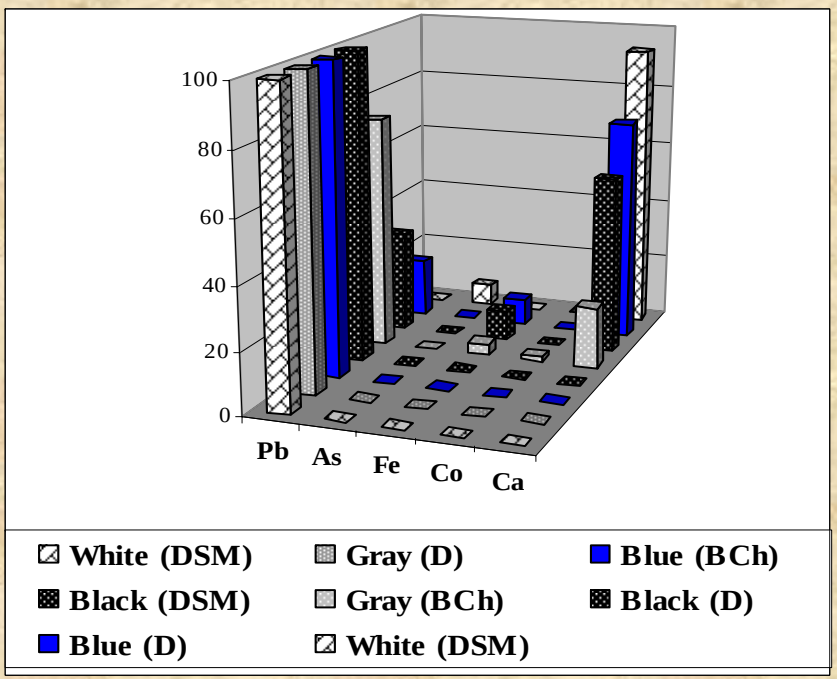


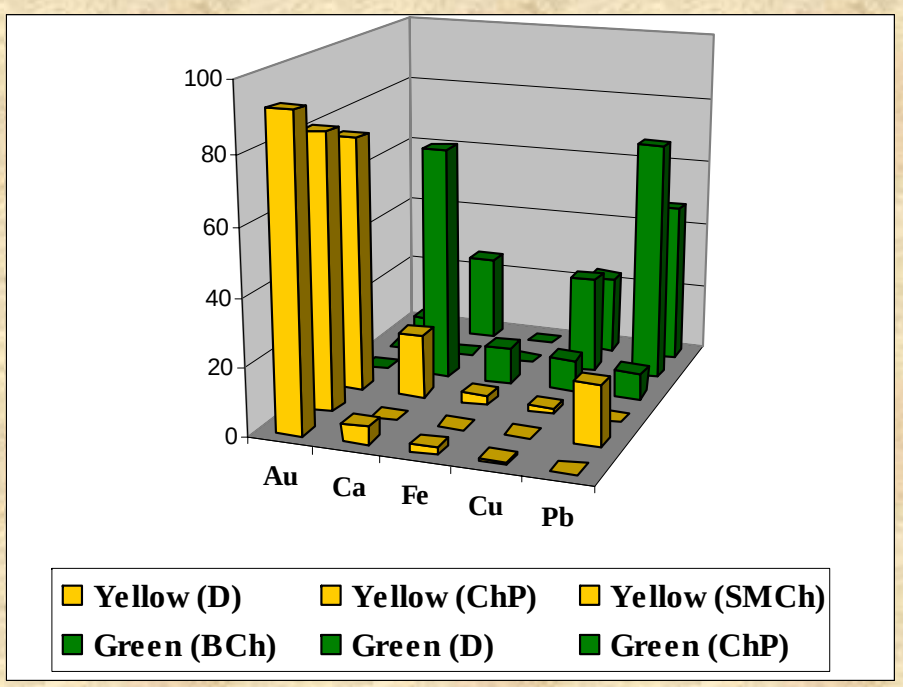
Identified pigments:

White – White lead (Pb)
Yellow – Orpiment (As)
Green – Orpiment (As) + Indigo
Red – Vermilion (Hg)
Red lead (Pb)
Red ochre (Fe)
Black – probably Carbon
Grey, Ochre and brown – mixtures

Icons painted by Onufri Qiprioti – 16-17th cent.

TXRF results





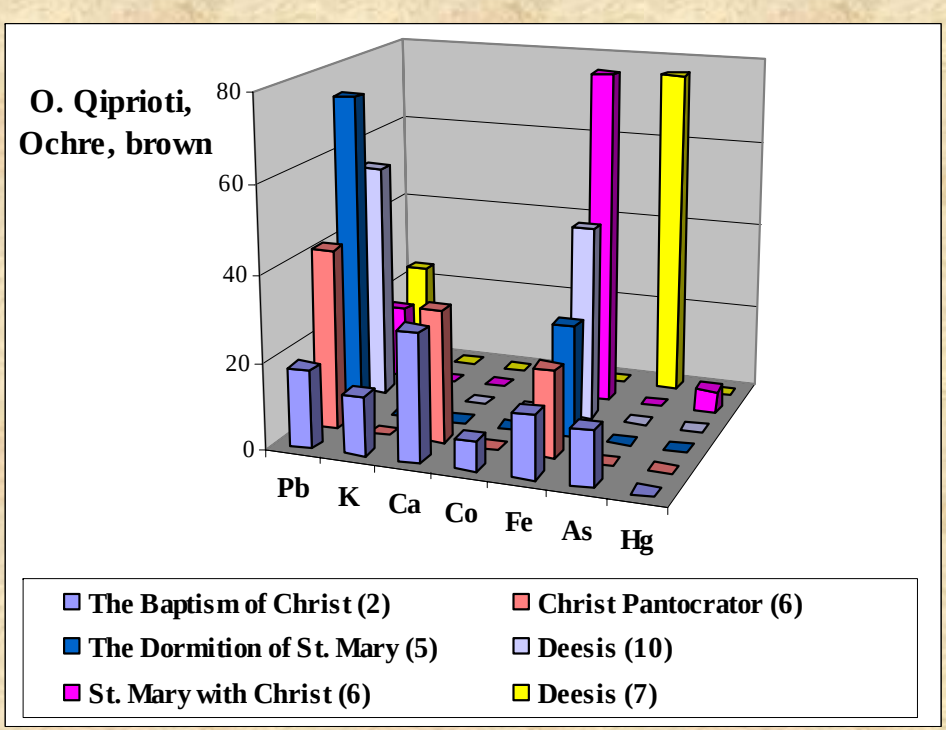
- White – Lead white (Pb)
    - Calcium white (Ca)
- Black – Probably Charcoal
- Blue – Probably Indigo or Ultramarine
    - Smalt (K, Co)

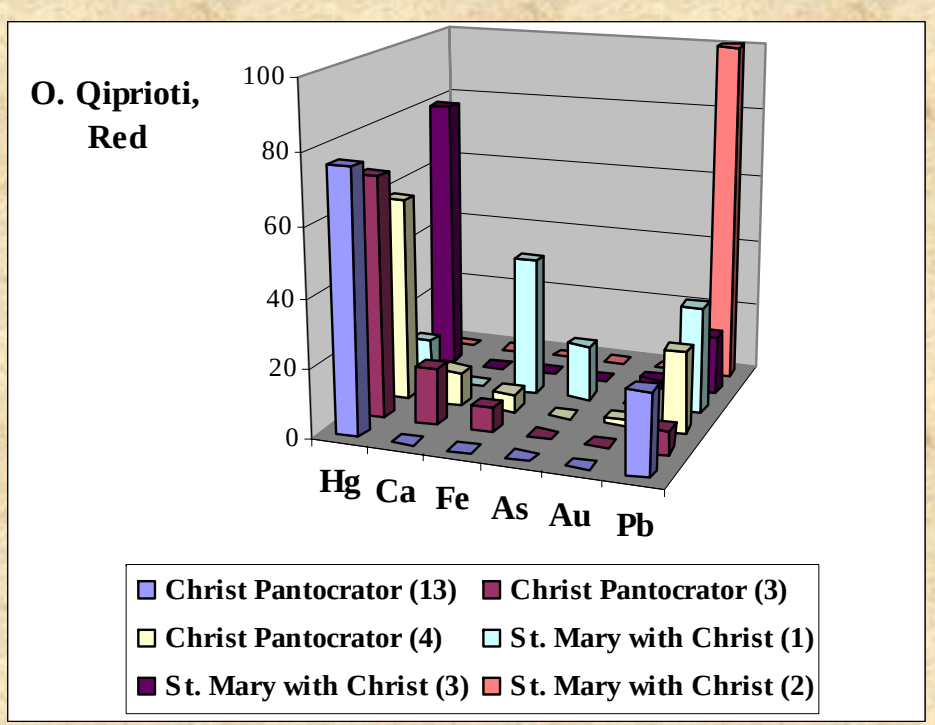
Yellow – Gold (Au)

- Orpiment (As)

Green – Malachite or Verdigris (Cu)

TXRF results





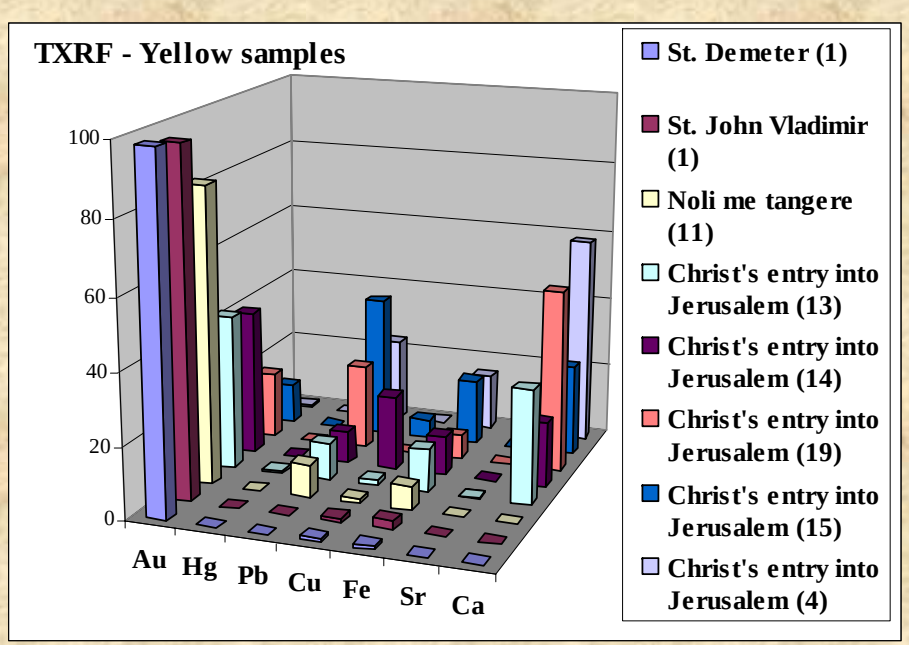
- Red – Vermilion (Hg), Red lead (Pb), Red ochre
- Ochre and brown – Mixtures of red or yellow ochre (Fe) with lead or calcium white, orpiment and black in some cases

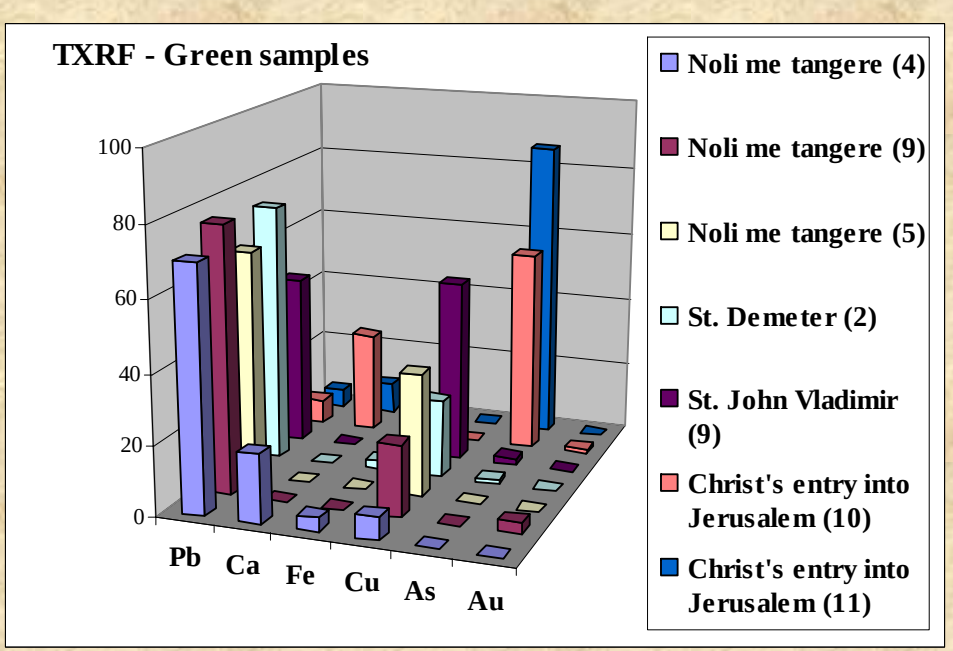
Summary of the main pigments

	Deisis	**Christ Pantocrator**	**Saint Mary with Christ**	**The Baptism of Christ**	**The Dormition of Saint Mary**
White	Lead white	Lead white Calcium white	Lead white		Lead white Calcium white
Black	Charcoal or bone black	Charcoal or bone black	Charcoal or bone black		Charcoal
Blue	Indigo Ultramarine (?)	Indigo		Indigo	Indigo
Yellow	Gold	Gold Orpiment	Gold	Gold	Gold Orpiment
Green	malachite or verdigris	malachite or verdigris		malachite or verdigris	malachite or verdigris
Red	vermilion red lead	vermilion	vermilion red lead red ochre	vermilion red lead	vermilion red lead red ochre
Ochre and Brown	Yellow or red ochre + orpiment + Ca white	Yellow or red ochre + orpiment + Pb white	Yellow or red ochre + Pb white + vermilion	Yellow or red ochre + orpiment + Ca white	Yellow or red ochre + Ca white + red Pb

Icons painted by Constantin Ieromonachu, 17 - 18th cent.

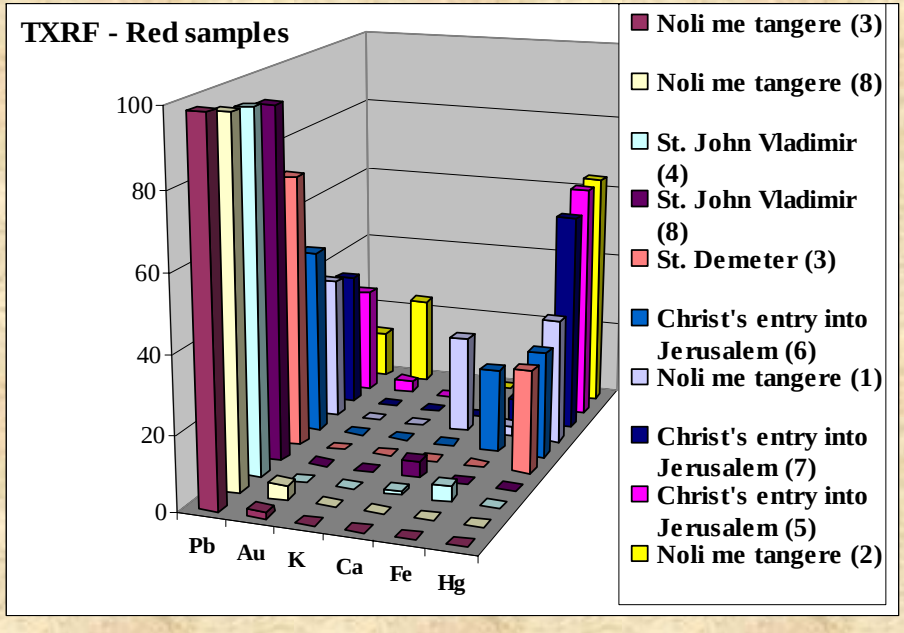
TXRF results

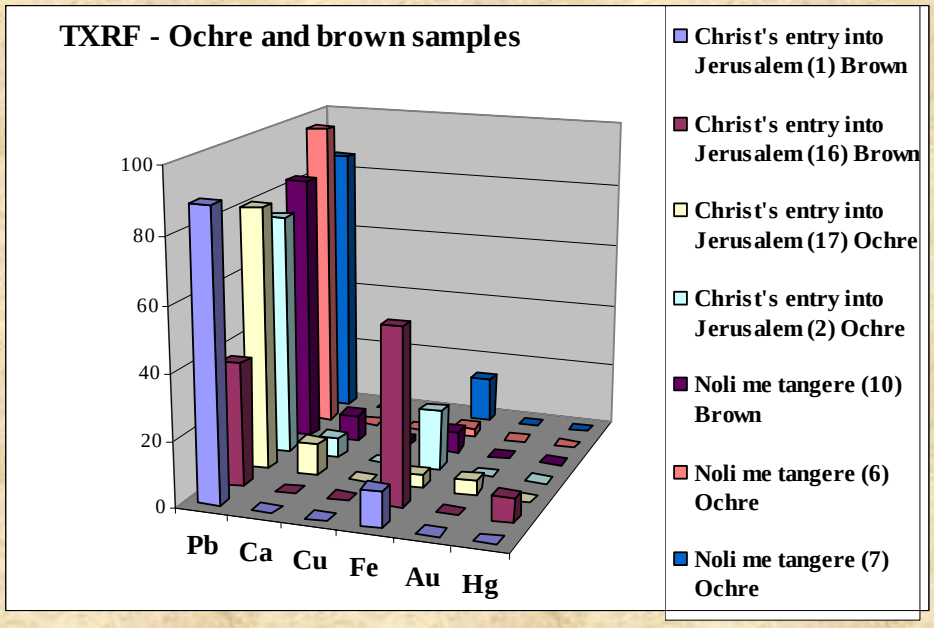




- Yellow – Gold (Au)
  - Yellow ochre (Fe)
- Green - Malachite or Verdigris (Cu)
  - Orpiment (As) + Indigo

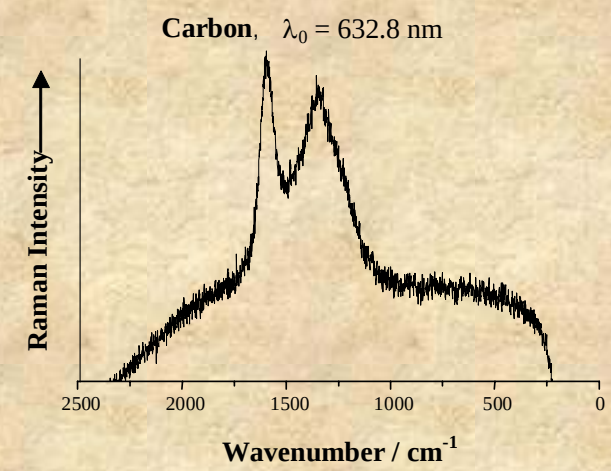
TXRF results

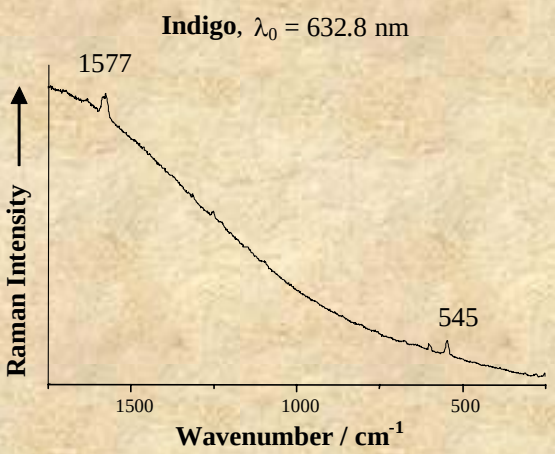


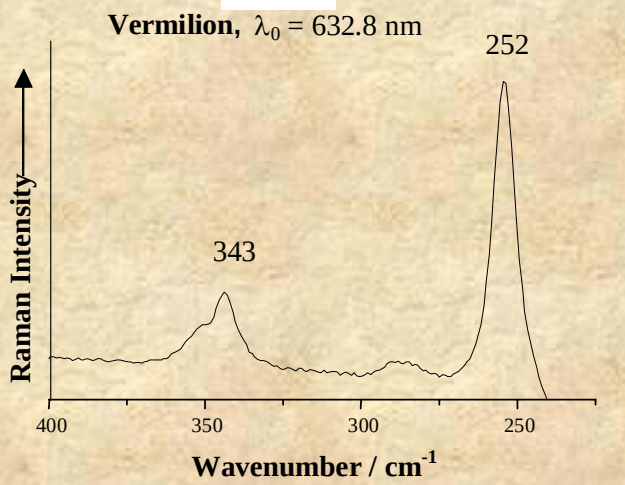


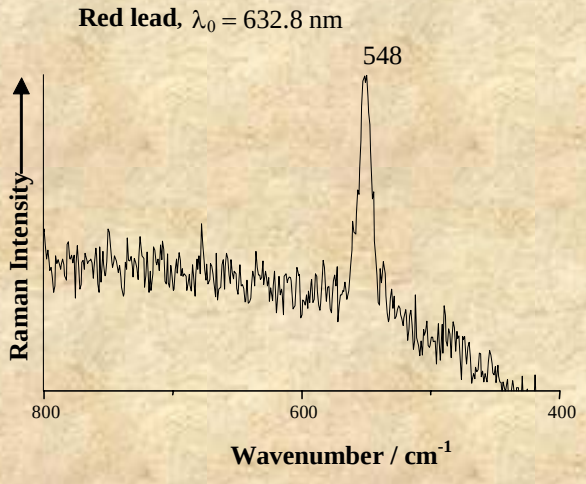
- Red – Vermilion (Hg), red Laed (Pb)
- Ochre and brown – Yellow or red ochre (Fe) + white lead (Pb) + Carbon

Raman microscopy spectra









Summary of the main pigments

Colour	St. Joan Vladimir	Noli me tangere	St. Demetrius	Christ's entry into Jerusalem
White			White Pb	
Black				Charcoal
Gray	White Pb + charcoal	White Pb + charcoal	White Pb + charcoal	White Pb + charcoal
Blue			White Pb + Indigo	
Yellow	Au	Au	Au	Au + yellow ochre + white Ca or Pb
Ochre and brown		Red ochre + white Pb		Red ochre + white Pb
Red	Red Pb	Red Pb, Vermilion + white Pb	Red Pb, Vermilion	Vermilion, Red Pb
Green	Malachite or verdigris	Malachite or verdigris	Malachite or verdigris	Oripiment+Indigo

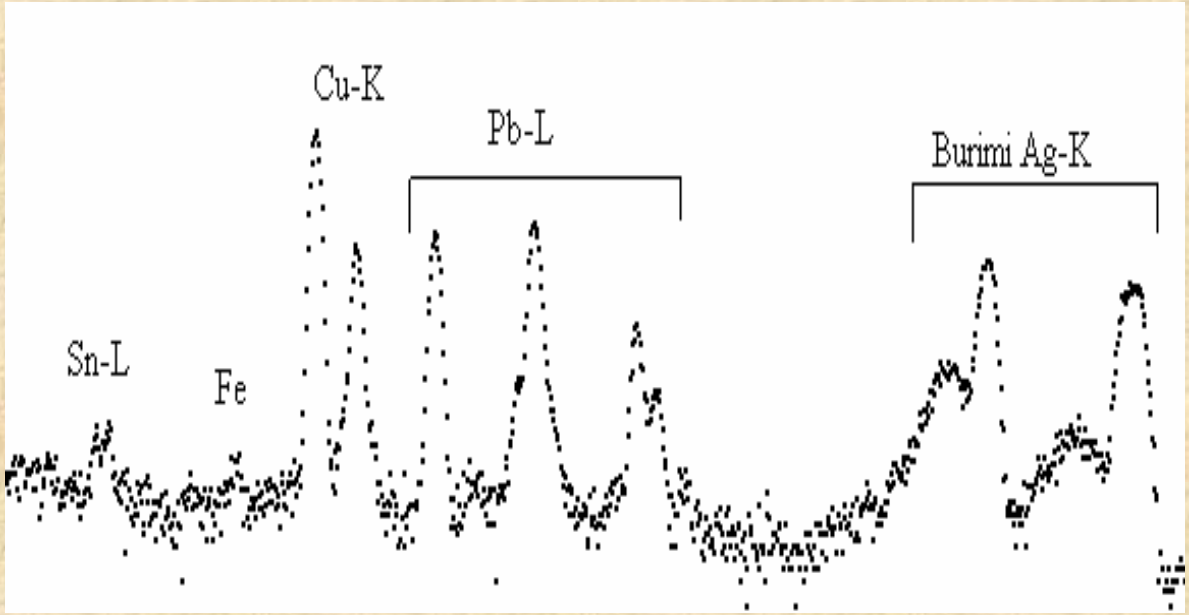
Conclusions

- The painters' palette was composed of:
  - white lead, calcium white
  - gold, orpiment, yellow ochre
  - vermilion, red lead, red ochre
  - malachite or verdigris
  - smalt, indigo
  - Charcoal or black bone
- Small differences were observed between the painters of different periods and icons attributed to the same painter as well.
- The identified pigment types and their limited number show that the painters had followed the Byzantine painting tradition.
- The fact that we have not found industrial pigments, introduced mainly during the 19th century, can be an indication that no recent interventions were made on the icons.

Publications

- **N. Civici, O. Demko, R. J. H. Clark,** "*Identification of pigments used on late 17th century Albanian icons by Total reflection X-ray fluorescence and Raman microscopy*", **Journal of Cultural Heritage, 6, 157-164, 2005**
- **N. Civici** "*Non-destructive identification of inorganic pigments used in 16 – 17th century Albanian icons by total reflection x-ray fluorescence analysis*", **Journal of Cultural Heritage, 7, 4, 339-343, 2006**

Hermes or Mercury?



- Composition:

Cu - 52,7 %
Sn - 36 %
Pb - 12.9 %
Zn - 0,3 %
Fe - 0,1 %

→ Greek bronze

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- **Prof. As. Konstantin Paraskevopoulos**, Department of Physics, “Aristotle”University of Thessaloniki
- **Prof. As. Stathis Polichroniadis**, Department of Physics, “Aristotle”University of Thessaloniki

Thank you
for your attention