ENAA, XRF, Digital Radiography, FT IR and Raman Spectroscopy Investigation of Nine Russian and Romanian Icons from XVIII –XIXth Century

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In the Byzantine Empire, the word ικονοσ (image in Greek) referred to any representation of Jesus Christ Virgin Mary, saints or events.

Today the term is used for paintings, fresco, stained glass, sculptures or mosaics.

There where two main tendencies in the evolution period of the religious art:

-the Hellenistic one representing the Greek spirit of Syrian origin from Jerusalem

-the Byzantine one, arbitrarily used to define the Orthodox art

Throughout centuries the icons have been painted on various materials such as wall, canvas, leather,papyrus, paper and wood were the usual supports.

As far as wood is concerned, oak is the best option for a panel, but other essences such as lime, pine or white poplar were currently used

The paint layer is coated with varnish made of vegetable resin to protect the colours against physical and chemical factors as well as to make them more vivid

Both in Russia and Romania, the Icon Art has its roots in Byzantine tradition transmitted by the local disciples of the Byzantine painters, who worked together or imitated the icons brought from that area.

Tempera on wood became the dominant technique.

The pigments used were of local origin, most of Them of mineral source such as lead white, cinnabar, orpiment, minium or ocher, but in few cases exotic mineral pigments such malachite, azurite or lapis-lazuli were used too.

With the development of chemistry following the Industrial revolution, and beginning with the second half of the XVIIIth century, new artificial pigments were discovered, produced at an industrial scale and used in painting.

It is the case of Prussian blue : $Fe_4[Fe(CN)_6]_3 \cdot x\,H_2O$ (1708), Viridian: $Cr_2O_3 \cdot nH_2O$ (1856), Cadmium yellow: CdS (1840) Zinc white: ZnO (1850), Titanium white: TiO_2 (1921), etc.

The trade with India brought the natural Indigo, later industrialy synthesized in 1897, allowing to use more frequently the blue colour, extremely rare and expensive in the Mid-Age.

With the exception of lapis-lazuli (lazurite), Prussian blue and Indigo, all other pigments used from antiquity to modern era are mineral oxides and salts of heavy metals such as Cr, Fe, Co, Cu, Zn, As, Hg or Pb, elements which could be well evidenced by Instrumental Neutron Activation Analysis (INAA) of X-rays Fluorescence (XRF).

The two methods are complementary to each other as XRF is completely noninvasive but has a limited sensitivity and accuracy while INAA has a significant higher precision but needs some fragments to be removed from the painting layer.

The systematic investigation, by using the actual most sensitive techniques of any kind paintings including icons has not only a scientific significance but also represents excellent tools in establishing the origin, the age or the conservation status, and in the first place the authenticity as toady, the art works market was estimated in 2015 to 50 billons dollars, and its value is continuously growing.

Not only the INAA or XRF are intensively used, but also other noninvasive techniques such as such Digital Radiography (DR) and Computed Tomography, Fourier Transform Infrared (FTIR)and Raman spectroscopy (FTR), or Multispectral imaging.

Under these circumstances, we have investigated nine orthodox icons belonging to three monastic Institutors of Romania:

Antim Monastery of Bucharest,

One –wood Monastery of Valcea county
An orthodox church from Sibiu.

For a comparative study regarding not only the style but also the materials as well as the conservation status, we have used in tandem more techniques such as DR, UV fluorescence, XRF, Epithermal Neutron Activation Analysis (ENAA), as

well as FT-IR and FT-R spectroscopy.

A great diversity of motifs, but all have a lot of common treats such as color palette or Byzantine style, excepting the Sibiu one which shows a Western European

influence

R1: St. Nicholas
R2: Christ entering Jerusalem

L1: St. Basil the Great
L2: St. John Baptist
L3: Mater Dolorosa

V: Holy Trinity (Walachia)

P1: Popular icon in four fields
P2: Popular icon in four fields

S: Holy Trinity (Transylvania)

A complex investigation concerns wooden panel, ground and especially painting layer, each of them having specific methods.

In the case of wooden panel, DR and SEM give the most pertinent information while for ground and painting layers XRF, ENAA, FT-IR and Raman spectroscopy are the most appropriate one.

XRF , ENAA and FT Raman spectroscopy allow to identify the pigments as excepting the indigo, all ancient pigments consisted of various minerals and rocks while FTIR gives the most pertinent information regarding organic binders (egg yolk and linseed oil)

XRF analysis performed noninvasive byX-MET 3000 TXR+™ portable XRF spectrometer provided with a 40 kV Rh anode and a PIN silicon diode detector cooled by Peltier effec

DR were obtaine by a SwissRay DDR Multi-Digital Radiographic System CPI GEN-X-4000™ machine, DICOM images converted into bitmap tif files by ImageJ and processed by CorelPhotoPaint™.

FT-IR and Raman spectra were recorded contacless by a Bruker VERTEX 70™ spectrometer provided with a NIR 1064 nm Nd;YAG laser and a HPGe detector cooled by liquid nitrogen.

ENAA were performed at the Frank Neutron Physics laboratory IBR 2 reactor by means of both short and long time activation.

DR

DR gives the first informations on pigments, state of conservation or on previous restorations or repaintings.

Mater Dolorosa, Lipovans, (Norh Dodrogea) XIXth century

Popular Icon, Walachia, second half of the XIXth century

Lead white ($2PbCO_3 \cdot Pb(OH)_2$) minium ($Pb^{2+}2Pb^{4+}O_4$) and cinnabar (HgS) are the most opaque

DR

DR gives the first informations on pigments, state of conservation or on previous restorations or repaintings.

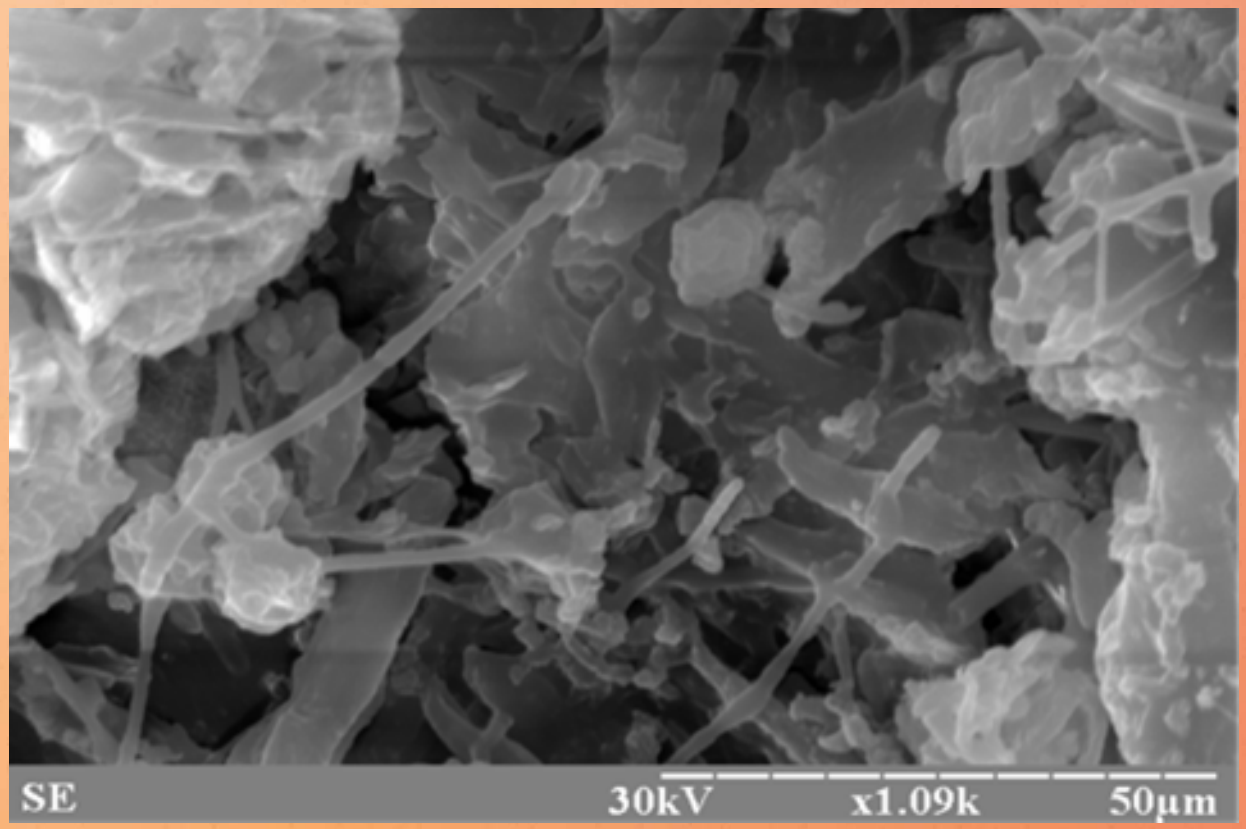
St. Nicholas, Russia, end of XIXth century

Holy Trinity, Transylvania, second half of the XIXth century

Lead white ($2PbCO_3 \cdot Pb(OH)_2$) minium ($Pb^{2+}2Pb^{4+}O_4$) and cinnabar (HgS) are the most opaque

SEM

If the visual inspection shows significant degrada-tions of the wooden plate, SEM can elucidate the cause



Fungus attack on degradated wooden plate.
Image obtained at the Geological Institute of Romania

XRF

St. Nicholas (Russia) XIXth century

Vermeil

Ochre

Ochre + lead white

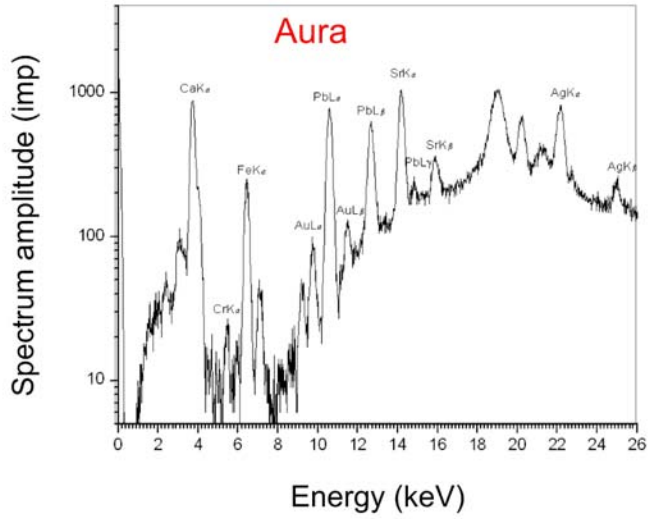
Azurite + lead white + Au + Ag

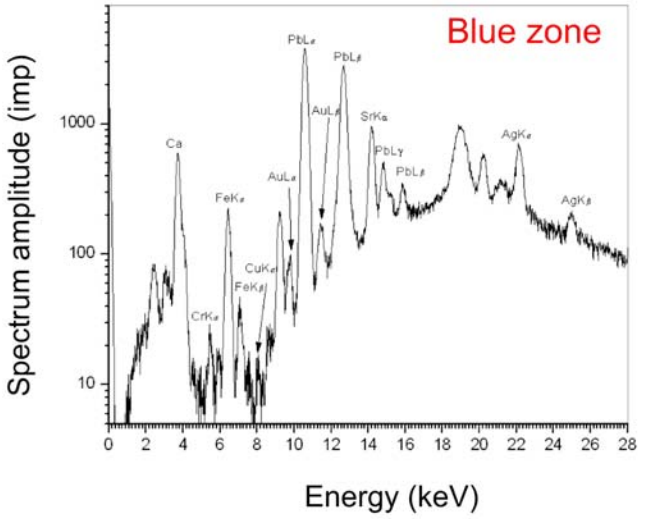
Lead white

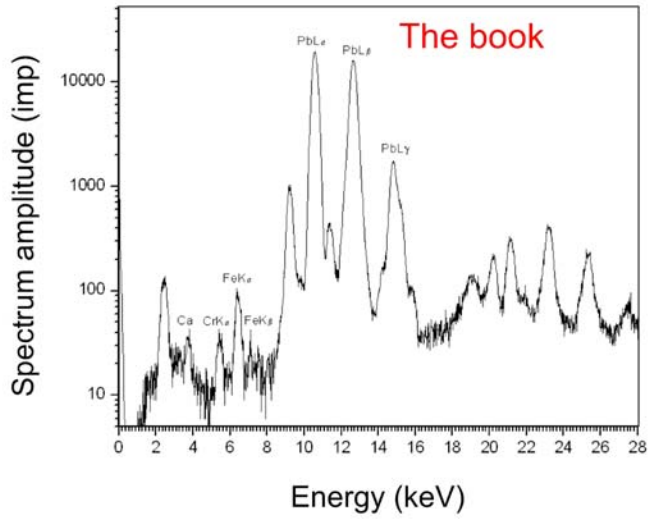
Ochre + chrome yellow + lead white

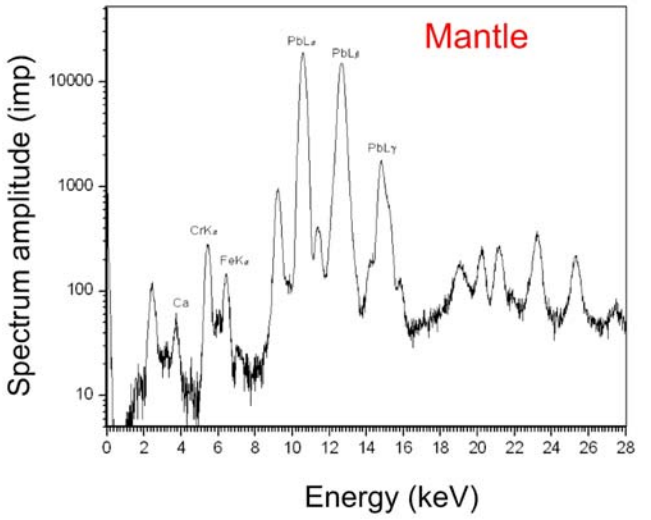
XRF

St. Nicholas (Russia) XIXth century



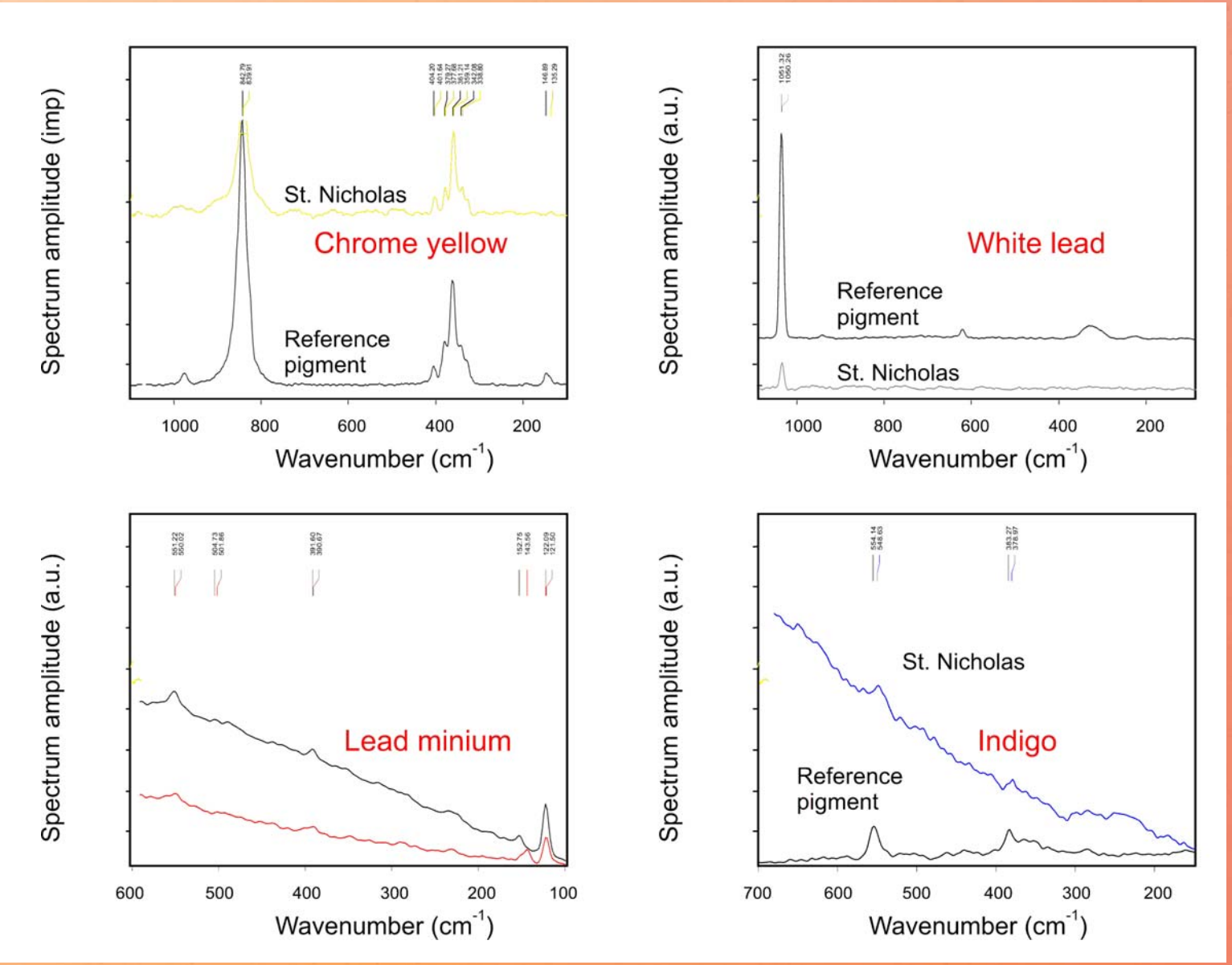






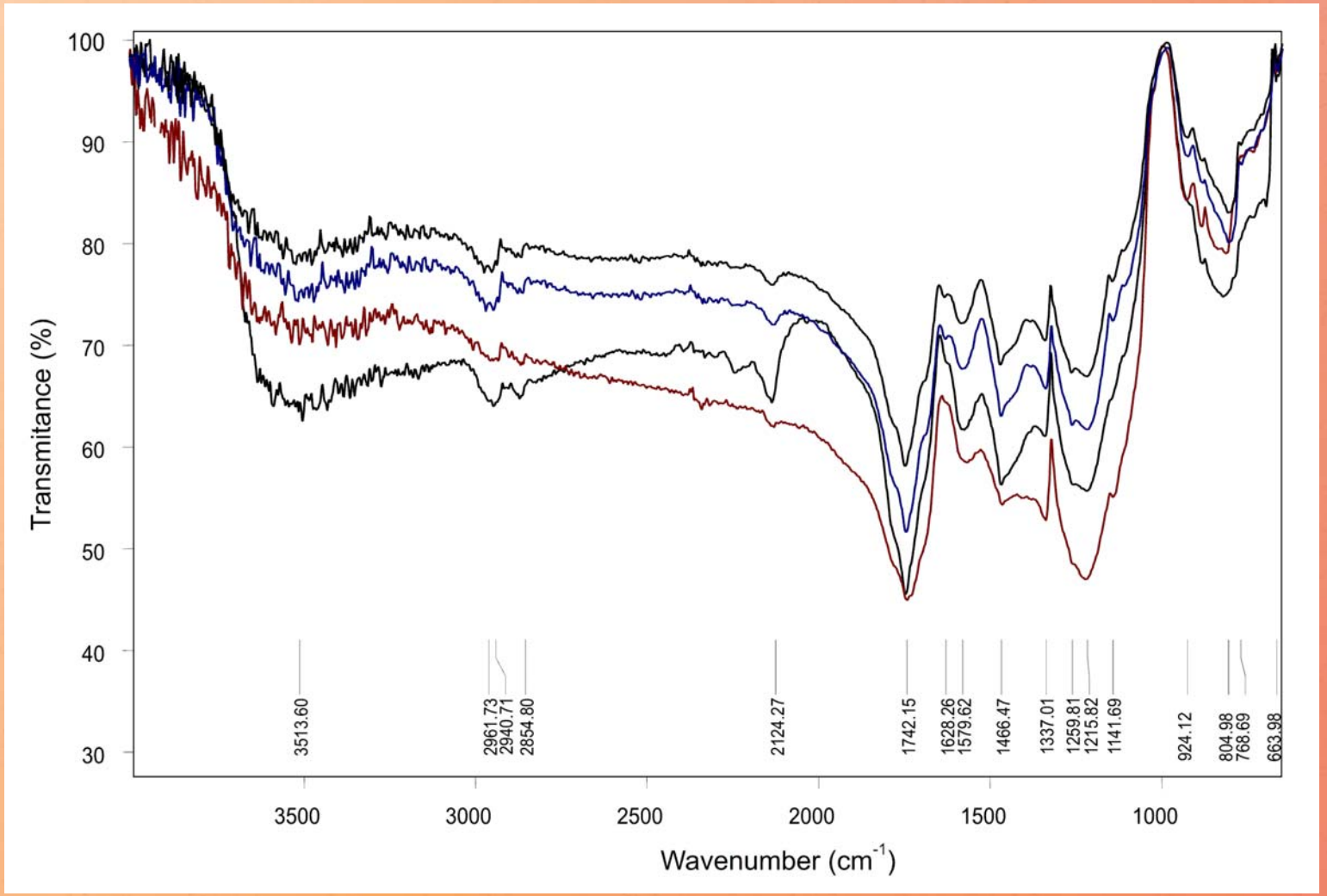
FT Raman

St. Nicholas (Russia) XIXth century



FT IR

St. Nicholas (Russia) XIXth century



XRF

Holy Trinity (Transylvania)
XIXth cenury (second half)

Vermeil

Ochre

Ochre + lead white

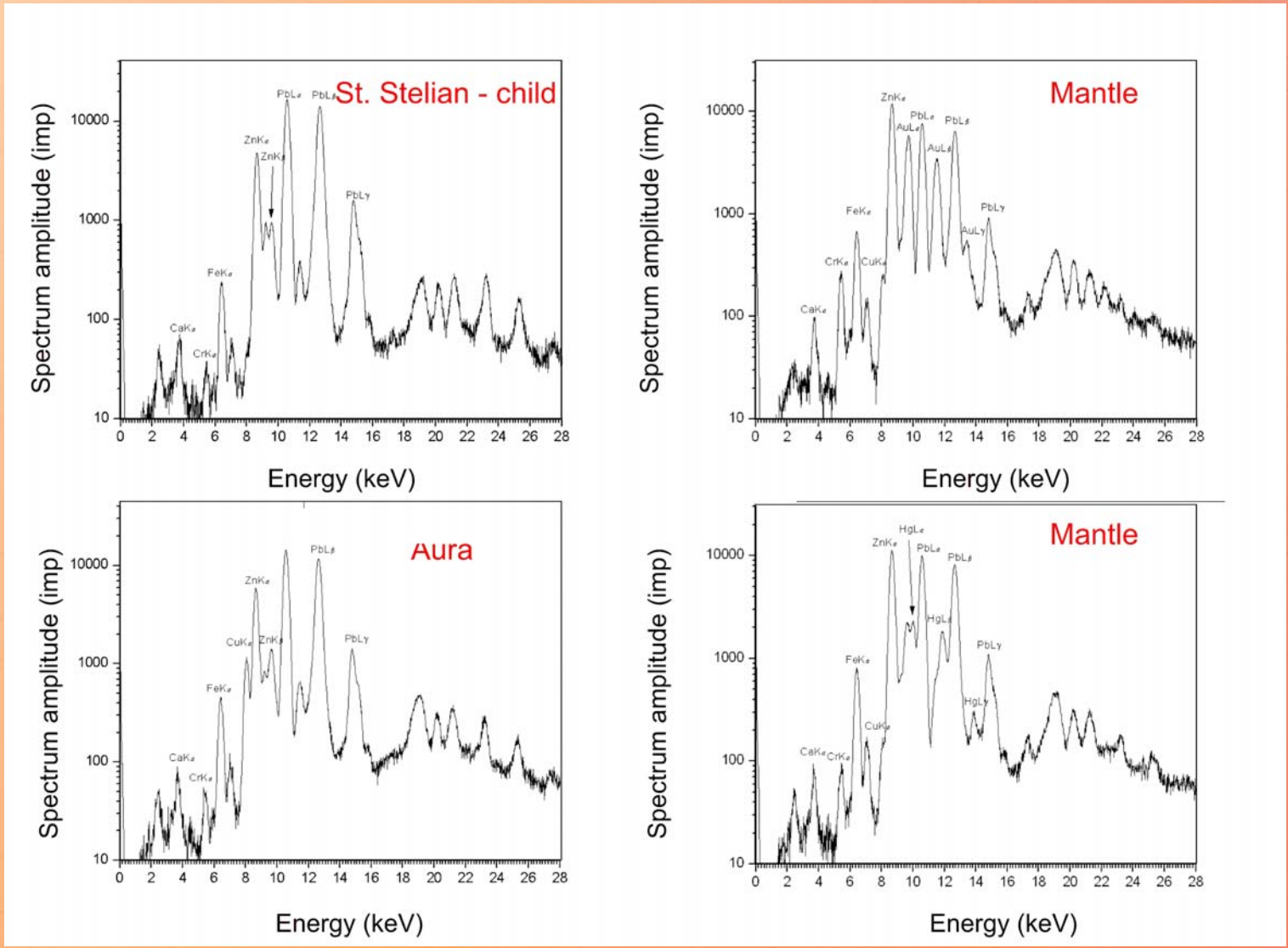
Azurite + lead white + Au + Ag

Lead white

Ochre + chrome yellow + lead white

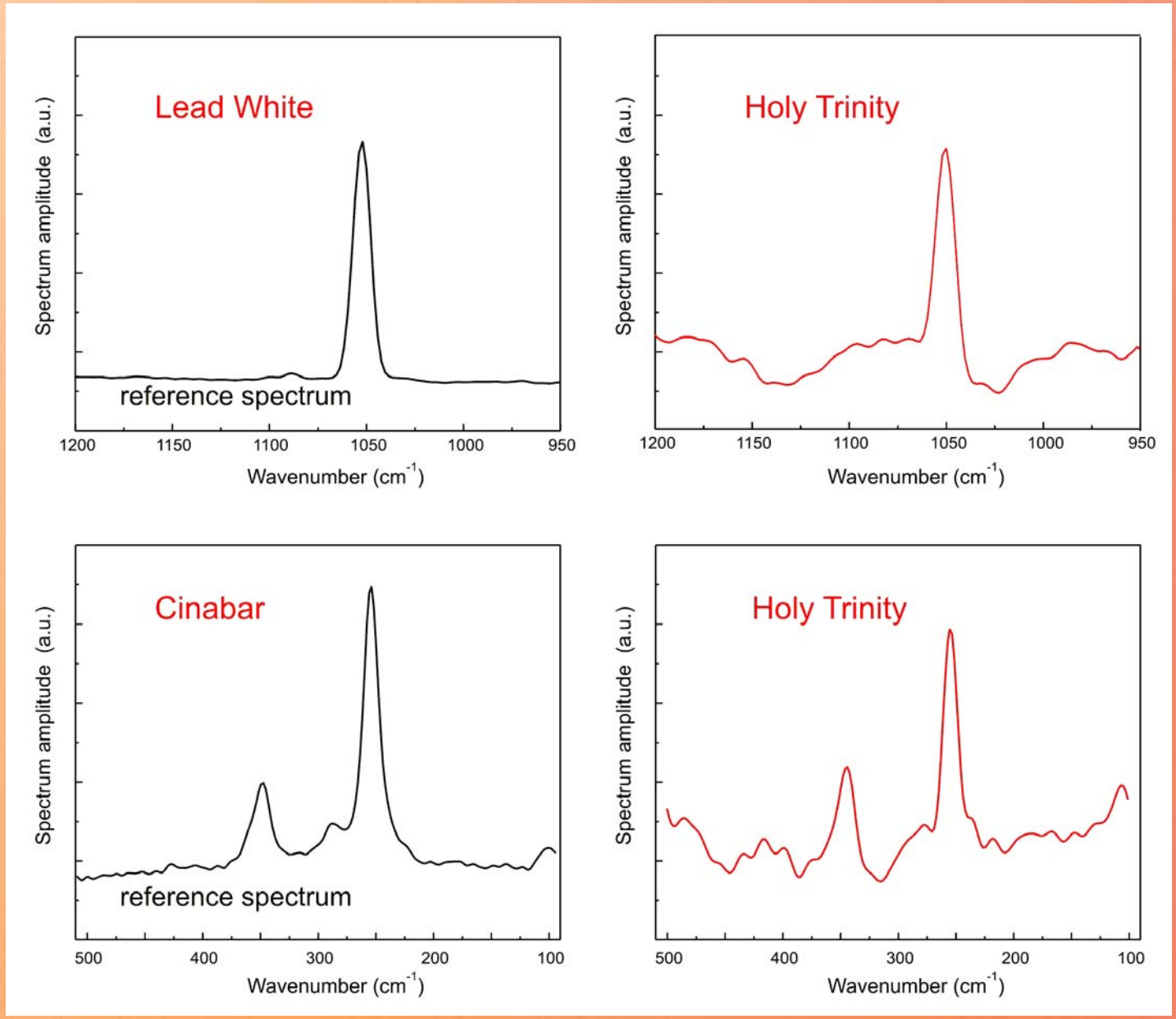
XRF

Holy Trinity (Transylvania)
XIXth cenury (second half)



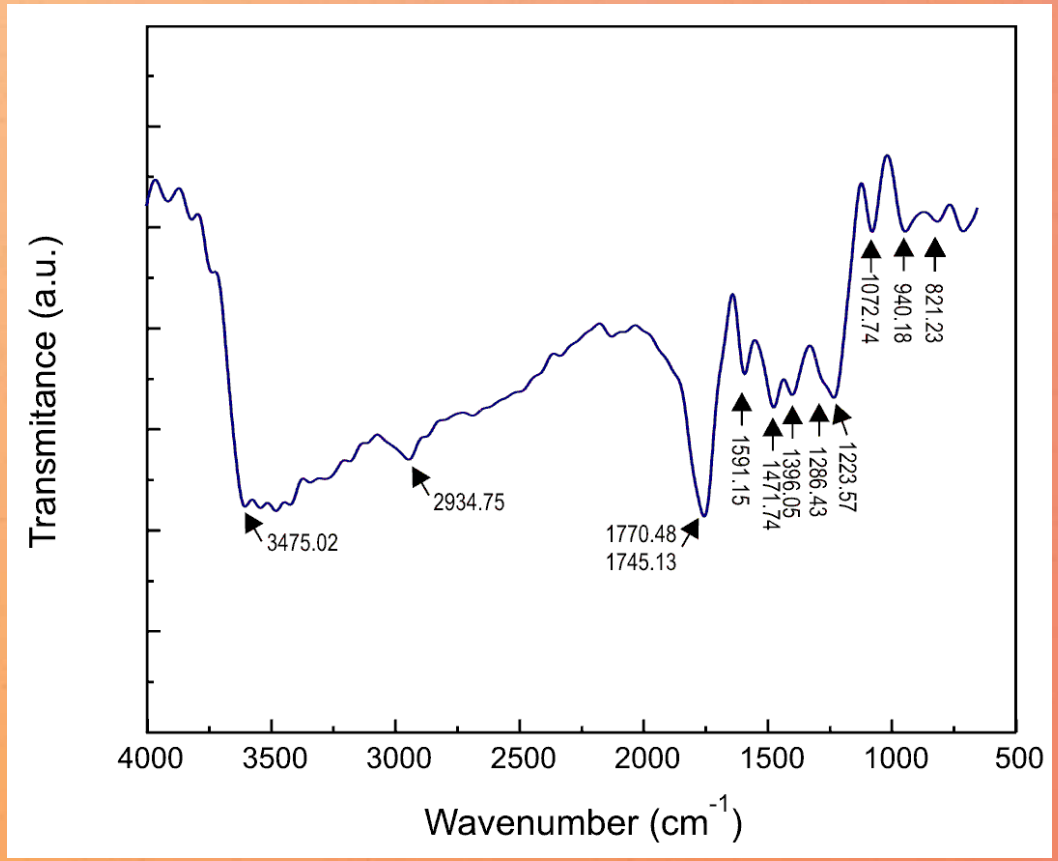
FT Raman

Holy Trinity (Transylvania)
XIXth cenury (second half)



FT IR

Holy Trinity (Transylvania)
XIXth cenury (second half)



ENAA

19 fragments of colour, ground and pieces of wood of 8 icons

	Na (%)	Mg (%)	Cl (%)	K (%)	Ca (%)	Ti (%)	Fe (%)	Zn	As	Sr	Sb	Ba	Au	Hg
L_3: Mater Dolorosa: ochre	0.06	0.25	0.4	--	26.1	0.02	0.4	36	14	2250	40	123	--	--
R_2: Christ entering Jerusalem: yellow foil	0.04	0.12	0.58	0.2	41.5	--	0.2	64	1	1090	--	--	4	--
R_2: Christ entering Jerusalem: ochre	0.08	0	0.81	0	38.5	--	0.1	57	5	954	2	223	1	--
R_2: Christ entering Jerusalem: vestment	0.08	0.16	0.58	0.1	4.6	--	--	187	4	206	2	105	3	--
R_2: Christ entering Jerusalem: wood	0.13	0.19	0.7	0.1	1.1	0.02	0.7	107	3	77	--	56	2	--
L_1: St. John Baptist: white colour	0.09	0.16	0.11	0.1	21.2	0.01	0.2	66	7	522	11	42	1	--
L_1: St. John Baptist: ground	0.17	1.14	0.05	0.3	7.6	0.12	4.5	395	27	378	4	507	8	--
P_1: Popular: red colour	0.1	0.14	0.19	0.2	22.3	--	0.4	115	87	1270	2	324	--	104
P_1: Popular: red colour	0.11	0.11	0.09	0.4	20.2	--	--	--	50	502	--	--	7	985
P_1: Popular: white-yellowish colour	0.16	0.17	0.1	2.4	23.1	--	--	--	134	--	--	--	27	30
R_1: St. Nicholas: manuscript	0.8	0.2	0.85	--	14	--	0.4	78	6	393	2	106	--	--
R_1: St. Nicholas: bolus	0.17	0.21	1.13	--	30	--	0	62	12	733	23	--	--	--
R_1: St. Nicholas: piece of wood	0.06	0.06	0.29	0.1	0.5	--	0.2	1	19	5	37	--	--	--
L_1: St. Basil the Great: piece of wood	0.02	0	0.08	--	0.1	--	--	--	10	2	--	--	27	--
V: Holy Trinity: piece of wood + colour	0.16	0.13	0.08	--	25.9	--	--	--	31	4850	1240	135	212	1
V: Holy Trinity: piece of reverse wood	0.19	0.15	0.24	0.2	13.5	--	0.3	1	56	13	603	--	84	--
V: Holy Trinity: piece of reverse ground	0.21	0.1	0.07	1.1	27.7	--	--	--	30	7210	1640	189	117	1
S: Holy Trinity: piece of reverse ground	0.14	0.07	0.15	0.2	3.4	--	0.4	1	25	23	179	--	146	--
S: Holy Trinity: piece of reverse ground	0.03	0	4.11	--	0.3	--	--	9	40	8	24	--	21	--

ENAA

19 fragments of colour, ground and pieces of wood of 8 icons

	Na	Mg	Cl	K	Ca	Ti	Fe	Zn	As	Br	Sr	Sb	Ba	Au
Mg	0.058													
Cl	-0.054	-0.127												
K	0.431	-0.034	-0.366											
Ca	0.003	-0.182	-0.204	0.337										
Ti	0.783	0.999	-0.566	1.000	-0.361									
Fe	0.033	0.987	-0.374	0.822	-0.295	0.997								
Zn	0.072	0.900	-0.130	-0.074	-0.166	0.981	0.964							
As	0.084	-0.150	-0.186	0.314	0.266	0.915	0.141	-0.200						
Br	0.132	-0.275	0.260	0.518	0.333	-0.556	-0.345	-0.133	-0.218					
Sr	-0.097	-0.095	-0.307	0.669	0.724	-0.262	-0.175	-0.231	0.457	-0.070				
Sb	0.068	-0.138	-0.199	0.936	0.337	-0.331	-0.018	-0.218	0.981	-0.226	0.565			
Ba	0.019	0.785	-0.325	0.041	0.249	0.992	0.791	0.734	0.023	-0.072	0.154	0.017		
Au	-0.020	0.168	-0.202	0.876	0.136	0.978	0.860	0.867	-0.087	0.261	-0.129	-0.105	0.704	
Hg	-0.075	-0.113	-0.150	-0.006	0.069	-0.021	-0.095	0.075	-0.097	-0.083	-0.024	-0.120	0.396	0.174

Concluding Remarks

More analytical techniques were used to investigate nine orthodox icons from Russia, Northern Dobrogea, Transylvania and Walachia, painted between the end of XVIIIth and second half of the XIXth century.

Digital radiography, X-rays Fluorescence, Fourie-transform IR and Raman spectroscopy as well as Epithermal Neutron Activation Analysis evidenced a multitude of details such as mechanical defects, former interventions an restorations, as well as the nature of pigments and binders.

It was proved, that, despite stylistic diversity and locations, all icons were painted by using relatively similar materials, which in fact reflects significant cultural and religious contacts.

Thank You for Attention

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Спасибо за внимание