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 \textit{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 were 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 as 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: \( \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x \text{H}_2\text{O} \) (1708), Viridian: \( \text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O} \) (1856), Cadmium yellow: \( \text{CdS} \) (1840) Zinc white: \( \text{ZnO} \) (1850), Titanium white: \( \text{TiO}_2 \) (1921), etc.

The trade with India brought the natural Indigo, later industrially 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 billions 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 Institutes 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)

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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 by X-MET 3000 TXR+™ portable XRF spectrometer provided with a 40 kV Rh anode and a PIN silicon diode detector cooled by Peltier effect.

DR were obtained 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 contactless 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 gives the first informations on pigments, state of conservations or on previous restorations or repaintings.

Lead white \((2\text{PbCO}_3\cdot\text{Pb(OH)}_2)\) minium \((\text{Pb}^{2+}+2\text{Pb}^{4+}\text{O}_4)\) and cinnabar \((\text{HgS})\) are the most opaque.

Mater Dolorosa, Lipovans, (North Dobrogea) XIX\textsuperscript{th} century

Popular Icon, Walachia, second half of the XIX\textsuperscript{th} century
DR gives the first informations on pigments, state of conservations or previous restorations or repaintings.

St. Nicholas, Russia, end of XIXth century

Holy Trinity, Transylvania, second half of the XIXth century

Lead white \((2\text{PbCO}_3 \cdot \text{Pb(OH)}_2)\) minium \((\text{Pb}^2+2\text{Pb}^4+\text{O}_4)\) and cinnabar \((\text{HgS})\) are the most opaque
If the visual inspection shows significant degradations of the wooden plate, SEM can elucidate the cause.

Fungus attack on degradated wooden plate. Image obtained at the Geological Institute of Romania.
St. Nicholas (Russia) XIX\textsuperscript{th} century

- **XRF**
- **Vermeil**
- **Ochre**
- **Ochre + lead white**
- **Azurite + lead white + Au + Ag**
- **Lead white**
- **Ochre + chrome yellow + lead white**
XRF

St. Nicholas (Russia) XIXth century

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**Aura**

Spectrum amplitude (imp)

Energy (keV)

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**Blue zone**

Spectrum amplitude (imp)

Energy (keV)

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**The book**

Spectrum amplitude (imp)

Energy (keV)

---

**Mantle**

Spectrum amplitude (imp)

Energy (keV)
FT Raman

St. Nicholas (Russia) XIXth century

Chrome yellow

White lead

Lead minium

Indigo

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St. Nicholas (Russia) XIXth century

FT IR

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Holy Trinity (Transylvania)
XIXth century (second half)

Vermeil
Ochre
Ochre + lead white
Azurite + lead white + Au + Ag
Lead white
Ochre + chrome yellow + lead white

XRF
XRF

Holy Trinity (Transylvania) XIXth century (second half)

St. Stelian - child

Mantle

Aura

Mantle

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FT Raman

Holy Trinity (Transylvania) XIXth century (second half)

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FTIR

Holy Trinity (Transylvania)
XIXth century (second half)

[FTIR spectrum diagram]

Transmitance (a.u.)

Wavenumber (cm\(^{-1}\))

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ENAA

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

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<tr>
<th>L₁: Mater Dolorosa: ochre</th>
<th>Na (%)</th>
<th>Mg (%)</th>
<th>Cl (%)</th>
<th>K (%)</th>
<th>Ca (%)</th>
<th>Ti (%)</th>
<th>Fe (%)</th>
<th>Zn</th>
<th>As</th>
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<th>Sb</th>
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<td>P₂: Popular: red colour</td>
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<td>0.06</td>
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<tr>
<td>V: Holy Trinity: piece of wood</td>
<td>0.16</td>
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<td>0.08</td>
<td>--</td>
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19 fragments of colour, ground and pieces of wood of 8 icons

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<th>K</th>
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<th>Ti</th>
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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, Fourier-transform IR and Raman spectroscopy as well as Epithermal Neutron Activation Analysis evidenced a multitude of details such as mechanical defects, former interventions and 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