BABEȘ-BOLYAI UNIVERSITY

Faculty of Chemistry and Chemical Engineering

Doctoral School of Chemistry

PhD Thesis Summary

Scientific Investigation of Materials of Works of Art that Belong to the Cultural Heritage of Transylvania

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Content resume

Keywords

List of abbreviations

Keywords

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chemical safety

cultural heritage

FTIR

XRF

GC-MS

DSC

List of abbreviations and symbols

IR	infrared
DSC	differential scanning calorimetry
GC-MS	gas chromatography-mass spectroscopy
r-FTIR	infrared spectroscopy in fourier transform in external reflectance
t-FTIR	infrared spectroscopy in fourier transform in transmission
SD	the second derivative of the t-FTIR spectrum
VIZ	visible
UV	ultraviolet
XRF	X-ray fluorescence spectroscopy
Kα si Kβ	the fluorescence emission lines of the K orbital of the atom
Lα și Lβ	the fluorescence emission lines of the L orbital of the atom
ν	stretching vibration (νas - asymmetric stretching vibration; νs - symmetric stretching vibration)
δ	bending vibration (în plane)
ρ	bending vibration (out-of-plane)

Chapter 1. Introduction

1.1. Justification of the research topic

The mural paintings of wooden churches and icons can be considered "a wonderful means of uplifting the soul, strengthening spiritual faith, and affirming national consciousness, towards the bright horizons of goodness and beauty" (Familia Română, 2009, pp. 20).

The materials of these invaluable artworks are the product of a past culture, created using technologies that, despite numerous studies by historians and scientists, still cannot be considered fully understood (Janssens et al., 2013). Moreover, they are subject to continuous and progressive deterioration. This decay is caused by several factors, such as the interaction between the constituent materials, the surrounding environment (Pozo-Antonio et al., 2018; Coccato, Moens, and Vandenabeele, 2017), and human factors. Regarding the latter, it is worth noting that wooden churches have always been built exclusively as religious sites, not as conservation spaces for artworks. This explains the presence of soot deposits on their surfaces and the loss of mural painting integrity after the electrification of the buildings in question or when various types of objects were added to their surfaces for various reasons.

The conservation-related issues have become more diverse in rural areas where, due to demographic dynamics, larger and more spacious churches made of modern materials, such as bricks, have been constructed. As a result, wooden churches have often remained closed for long periods of time without a prior conservation plan being adopted. This deficiency has led to the deterioration of roofs and their structures, resulting in the infiltration of rainwater into the mural paintings and other architectural elements. This, combined with the temperate continental climate in the Transylvania region, has created an inadequate indoor microclimate for the preservation of artwork materials.

The chemical and physical processes that have occurred at the molecular level in the paint layers are visible at the macromolecular level due to the alteration of the original colouration of the paintings, changes in texture or loss of integrity of the paint layers. These phenomena not only hinder the correct visualisation of the artwork's message, where each colour usually has its precise iconographic symbol, but they can also contribute - depending on the environmental conditions - to the structural instability of the painting, compromising its integrity.

Therefore, if these wooden places once invited the community not to words, but to silence and prayer, today, more than ever, they strongly invite each of us, due to their poor state of conservation, to save them from destruction. The salvation and valorisation of these priceless artistic treasures requires, above all, knowledge of them, as "only that which is known can be preserved!" (Appolonia and Volpin, 1999, pp. 12).

1.2. Importance and relevance of the research topic

Although the investigation of artworks began centuries ago, in recent decades, several global landmark projects in the field of conservation and restoration of cultural heritage can be noted. One of the priorities of these research projects is the investigation of the materials used in artworks. The development of diagnostic tools for the process of investigating artworks has had a significant impact.

One of the main objectives of consortium-type projects for the preservation of national cultural heritage in the past two decades has been the preservation of wooden churches in Transylvania. The interventions focused on the restoration of roofs (or even their reconstruction due to advanced deterioration) and the structural elements that were in direct contact with the ground (the foundation of the building), as well as the scientific investigation of the artworks in the respective churches.

Research projects coordinated by Prof. Dr. Măruțoiu Constantin, carried out in collaboration with various academic institutions and museums, are considered pioneering in applied science for the investigation of Transylvanian artworks in wooden churches.

Within these projects, mural paintings (Trifa et al., 2013), royal gates (Neamțu et al., 2021; Măruțoiu and collaborators, 2015) and icons (Bratu et al., 2020; Măruțoiu et al., 2019) of wooden churches.

1.3. Description of the project and objectives proposed in the research

Importance of the project and innovative aspects of scientific research

The doctoral research project was carried out within the framework of the project "Development of Complex Methodologies for Attribution and Authentication of Certain Medieval and Premodern Paintings in the National Heritage" (53-PCCDI/2018, code: PN-III-P1-1.2-PCCDI-2017-0812)

The scientific research of the doctoral project had the following objectives:

- identification and characterisation of the materials used in the creation of mural paintings in wooden churches located in the Transylvanian localities of Agârbiciu, Straja, and Someșul Rece.

- Identification and characterisation of the materials used in the creation of the painting *Entry of the Lord into Jerusalem* belonging to the Ethnographic Museum of Transylvania.
- Identification of artistic techniques used in the creation of the investigated artworks.
- Assessment of the conservation status of the materials of the investigated artworks.

The results of the scientific investigation will represent an important contribution in the following areas:

1°. archaeometry related to Transylvanian artworks from the 18th century, including:

- understanding the materials and chemical and biological processes that have influenced the current state of conservation of the investigated artworks.
- identification of artistic techniques used in their creation.
- understanding degradation factors contributing to the current state of conservation of the materials of the investigated artworks.
- authentication and dating of the investigated artworks.
- enrichment of the specialised literature in the field of archaeometry of Transylvanian cultural heritage with significant scientific results.
- obtaining indispensable information for the design of a proper methodology for future interventions in restoration operations (including digital restoration), conservation, promotion (including digital promotion), and valorization of cultural heritage.

2°. in the field of art history, by enriching the knowledge about two of the most famous religious painters of the 18th century: Grigore Ranite and Dumitru Ispas.

3°. obtaining essential information for planning a proper working methodology to ensure the occupational health protection of individuals who interact with artworks containing pigments (and degradation products) based on toxic metals (arsenic, lead, mercury).

4°. understanding aspects of social, economic, technological, and religious nature in the Transylvania region of the 18th century and even up to the present.

1.4. Contributions and originality of this scientific research

The research activity was based on an intra- and trans-disciplinary approach. The diagnostic techniques used in the scientific investigation of artworks were employed in a complementary manner. The design of the scientific investigation methodology took into account the availability of scientific equipment, the conservation status of the artworks, and the preservation of their integrity. The investigation of artworks was conducted using non-invasive diagnostic techniques (visible, ultraviolet, and infrared photography, XRF, and r-FTIR) as well as invasive diagnostic techniques for the artwork (t-FTIR, DSC, and GC-MS).

Knowledge of the scientific instrumentation used, the materials of the artworks, and the artistic techniques employed in painting aided in the understanding and interpretation of the data resulting from the scientific investigation of the artworks.

Chapter 2. Brief presentation of the typology of the investigated works of art and their materials

2.1. Wooden churches and mural painting

Wooden churches captivate the souls of all who set their eyes upon them or enter their threshold, through the nature of their materials, the grandeur of their architecture, their elegance, sacredness, and their inclination towards the infinite. The important elements of the building consist of the stone foundation (constructed by stacking several layers of stone), the base, and the eaves. The base consists of strong wooden beams that support the entire structure. On top of the base, walls are built using horizontal overlapping beams, secured with a traditional joining technique called “chetori” (dovetail joint system). A wooden church is typically comprised of three sections: the narthex, the nave, and the altar. Additional architectural features include the roof, bell tower, and entrance portal.

Inside a wooden church, particular significance is given to the iconostasis and mural paintings. The mural paintings adorning the walls of Transylvanian wooden churches are renowned worldwide for their simplicity, beauty, and unique artistic style.

2.2 Icon

Icons are an integral part of cultural heritage and represent an invaluable spiritual value for the Orthodox Christian religion. The materials used in creating an icon, as well as the process of its creation, reveal the close connection between material and spiritual aspects. For instance, gold, which is applied first in the creation of the image, serves as a reminder that every creation should be made in the Light, (“Let there be light!" (Genesis 1:3). The painting of the image begins with pure colours, then gradually incorporates increasing amounts of white pigment in successive layers. In certain iconographic areas, the final touch is the addition of gold pigment. Symbolically, all these stages depict the journey of human life and its spiritual evolution, the transition from darkness to light (Florensky, 1997).

2.3. The main pigments used in 18th and early 19th century iconography

Subchapter 2.3 of the thesis is dedicated to a brief presentation of the pigments used in the Transylvanian iconography of the 18th and early 19th centuries.

Tabel 1. A summary presentation of the main inorganic materials used in mural paintings and icons in the late 18th and early 19th centuries in Transylvania.

Pigments based on:	Pigments – brief information
Lead (Pb)	*White pigments* • **Lead white** - is composed of hydrocerussite ($Pb_3(CO_3)_2 \cdot (OH)_2$) and cerussite ($PbCO_3$) (Gliozzo and Ionescu, 2022). The pigment has been identified in different types of Transylvanian artworks (Nemeș et al., 2018; Măruțoiu et al., 2016). *Yellow pigments* **Letharga** (α-PbO) is a yellow-white pigment, **Massicot** (δ-PbO) is yellow-orange, **Lead and tin yellow (type I)** (Pb_2SnO_4), **Lead and tin yellow (type II)** ($PbSn_2SiO_7$), **Naples yellow ($Pb_3(SbO_4)_2$)** (Gliozzo and Ionescu, 2022). *Red pigment* • **Red lead** (Pb_3O_4) was obtained by calcining white lead. In painting it has been identified mixed with one or more pigments, such as lead white, calcite, cinnabar/vermilion and/or red ocher (Gliozzo and Ionescu, 2022). *Toxicity and degradation of lead - based pigments:* • lead is a toxic metal (Gliozzo and Ionescu, 2022), • due to lead's property of having multiple oxidation states, lead-based pigments are very unstable to degradation factors. The most frequent degradation products of lead-based pigments are lead sulfide (PbS), lead dioxide (PbO_2), lead-based soaps, lead carbonates and sulfates (Gliozzo and Ionescu, 2022; Mazzeo et al., 2018).
Mercury (Hg)	*Red pigments* • **Cinnabar** (HgS) – natural origins - and **vermilion (**α-HgS) produced by manufacturing process. • those has been identified in many works of art in Transylvania (Bratu et al., Măruțoiu et al., 2011).

Notes about toxicity and the degradation of mercury-based pigments:

- mercury-based pigments are toxic due to the presence of mercury (Gliozzo, 2022).
- mercury-based red pigments are very sensitive to degradation factors and their original colour may shift to other colours (Radepont et al., 2011).
- has an oxidizing action on binders (Coccato, Moens and Vandenabeele, 2017),

Arsenic (As) *Yellow pigment*

- **Orpiment** (As_2S_3) - the tonality of the colour of the pigment of natural origin varies from golden to orange, while in the case of artificially prepared pigment, brown shades predominate (Udrea, Măruțoiu and Nemeș, 2022).

Red pigment

- **Realgar** (α-As_4S_4) - the tonalities of the color of the pigment with natural origin are orange, while those of pigment made by manufacturing process are brown (Udrea, Măruțoiu and Nemeș, 2022).

Green pigments

1. **Scheele green** ($Cu_3(AsO_3)_2$) - the green pigment with yellow tones was discovered around 1778 (Udrea, Măruțoiu and Nemeș, 2022).
2. **Paris green** ($Cu(CH_3COO)_2$ x $3Cu(AsO_2)_2$) was invented in the period 1798-1812 (Udrea, Măruțoiu and Nemeș, 2022).

Blu pigments

- **Cobaltite** (CoAsS) *or* **Smaltite** *(*$CoAs_2$) was identified in the painting of the royal gates of the wooden church at Nicula (Bratu et al., 2017).

Notes about toxicity and the degradation of arsenic-based pigments:

- arsenic-based pigments are very toxic,
- their are very sensitive to factors or degradation, especially the light,
- the most common degradation products of arsenic-based pigments are: arsenic trioxide (As_2O_3), arsenite (As^{3+}) and arsenate (As^{5+}), arsine (AsH_3), metallic arsenic (As^0),
- arsenates (As^{5+}) are strongly absorbed on the surface of gypsum, carbonates, earth pigments, ochres and glues (contain Al and Fe),
- solid degradation products of arsenic-based pigments being soluble in water can migrate in the presence of humidity in the stratigraphy of the painting,
- some of the degradation products of the arsenic-based pigments are ten times more toxic than the pigments themselves, which is why it is necessary to adopt measures to protect the health of the people who work with the works of art (Udrea, Măruțoiu and Nemeș, 2022).

Iron (Fe)

Ochers

- can have of natural or synthetic origin,
- their colours and shades depend on the particle size and hydration state of the particles,
- the most widespread ochres are: hemetite (Fe_2O_3), goethite FeO(OH) and magnetite (Fe_4O_3),
- they are pigments quite resistant to degradation factors, but under certain conditions they can undergo chromatic shifts (Balakhnina et al., 2014).

Earth green pigments

- influences the degradation of the lipidic organic binder (Mecklenburg, Tumosa and Edward, 2012),
- in the presence of moisture and heat, the pigments tend to change the colour (Coccato, Moens and Vandenabeele, 2017).

Bolus (or bolus)

- has a brick red colour and a very fine granulometry, greasy consistency and good adhesion properties,
- it is used in the adhesion of gold foils and sometimes in the imprint layer (Grygar et al., 2003),
- the presence of iron influences the oxidation of lipid materials (Mecklenburg, Tumosa and Edward, 2012).

Blue pigments

Prussian blue - depending on the raw materials used in the preparation, the pigment can be classified as:

- **early Prussian blue** ($MFe^{3+}[Fe^{2+}(CN)_6]\cdot nH_2O$, where M can be, depending on the pigment preparation method, aluminium, sulphur, potassium, sodium, etc., and n = 14–16) and
- **modern Prussian blue** ($Fe_4^{3+}[Fe_{II}(CN)_6]_3$) (Grandjean, Samain and Long, 2016)
- The most common degradation factors of the pigment are: light, humidity, acidity, basicity, lack of oxygen (anoxia) and physical characteristics of the ground (Grandjean, Samain and Long, 2016).

Vivianite ($Fe_3PO_4)_3$ – the pigment has a sedimentary origin (van Loon, 2008, pp. 56)

Crocidolite or **"blue asbestos"** - is part of the glaucophane-riebeckite class (Eastaugh et al., 2004, pp. 183).

Copper (Cu) **Malachit** $Cu_2(OH)_2CO_3$

- the pigment has green colour and can have mineral origins o can be prepared (Feller, 1986. pp. 183-202).
- under certain conservation conditions, it can transform into azurite, a blue pigment (Feller, 1986. pp. 183-202)

Verdigris ~ $2Cu(CH_3CO_2)_2.Cu(OH)_2$)

- the optical properties of the green pigment (weak colour intensity and covering power) determine its use in painting mixed with other pigments,
- it is sensitive to degradation factors (Feller, 1986, pp. 141-147)

Copper resinate ($Cu_2(C_{19}H_{29}COO)_4{\cdot}2H_2O$)

- is obtained by dissolving verdigris in resin (venetian turpentine or rosin). The pigment, due to the presence of resin, is sensitive to degradation factors (Feller, 1986, pp. 148-158).

Calcium (Ca)

- **Calcite**($CaCO_3$)
- the mineral was often used both in the preparation of the painting ground as well as a pigment (Roy, 1993, pp. 203-244).

2.4. The main minerals used in making primer in the 18th and early 19th centuries

In Transylvania, in making the ground layer, the most used white mineral was based on calcium sulphate ($CaSO_4$) (Bratu et al., 2020; Bratu et al., 2017; Măruțoiu et al., 2011). This mineral is found in various states of hydration (anydrite, bassanite and *gesso*) and granulometry (*gesso grosso* and *gesso sottile*) (Udrea, Măruțoiu and Nemeș, 2022; Wallert, Hermens, Peek, 1995, pp. 58-64).

2.5. The main organic materials used in 18th and early 19th century art

Organic materials in mural painting and icons are mainly used as a binder (in the primer layers and painting) and varnish. The most commonly used primer binder is animal glue, while the painting binder is *tempera* (egg yolk emulsion) or *tempera grassa* (egg yolk and oil). As for the varnish, the main organic material was linseed oil. It was processed hot (in order to improve its exicative property) and successively, it could also be mixed with other organic materials (such as various resins).

Over time, depending on the conservation conditions, the materials of the works of art have undergone various types of chemical, biological and mechanical degradation processes. These had as consequences, the modification of the chroma and the loss of the integrity of the painting's stratigraphy.

The most common degradation products, resulting from chemical reactions, encountered in works of art are metallic soaps, oxalates, carbonyl compounds.

Chapter 3 - Analytical instrumentation used in scientific investigation

Chapter 3 provides a review for each technique used in the scientific investigation of artworks presented in this thesis.

The scientific investigation of artworks was conducted using complementary non-invasive methods (photographic examinations, XRF, and r-FTIR) and invasive methods (t-FTIR, DSC, and GC-MS) for a specific artwork (Ceroni and Elia, 2008, pp. 25-30).

It is important to specify that an investigative technique is considered non-invasive if it does not involve taking samples from the work of art (it is carried out *in situ*), while an invasive investigative technique includes the taking of samples for the purpose of analysing them in the laboratory (Ceroni and Elia, 2008, pp. 25-30).

4.1. Scientific investigation of the mural painting in the wooden church of Agârbiciu, Cluj County

4.1.1 Introduction

This section presents the scientific investigations carried out on the mural painting inside the wooden church situated in the Agârbiciu Valley (Căpușu Mare, Cluj country). The church, built in 1792, has relatively small dimensions, measuring 14.0 m in length, 6.5 m in width, and 19.45 m in height. The foundation is made of locally sourced stone, while the walls are constructed using horizontal oak beams joined in a distinct "swallowtail" pattern. The church features a porch on the south and west sides and the narthex has a wooden ceiling with a bell tower rising above it. The bell tower, boasts a square-shaped balcony, and is adorned with four small towers at each corner (Figure 4.1.(Summary 1) (Măruțoiu et al., 2020).

Figures 4.1. (Summary1)
The wooden church of Agârbiciu alongside several examples of mural painting from the altar, nave and narthex areas (Udrea, Măruțoiu and Nemeș, 2022; Măruțoiu et al., 2020).

The mural painting within the church was created by the painter Dimitrie Ispas from the village of Gilău (Cluj) in two stages: the altar and nave were decorated in 1801, while the narthex was completed in 1818 (Măruțoiu et al., 2020).

4.2.2 Experimental methods

For the scientific investigation of the mural painting, various diagnostic methods were employed. Non-invasive techniques like XRF, r-FTIR were used, along with invasive methods such as t-FTIR and GC-MS (Măruțoiu et al., 2020).

4.1.3. Results and Discussions

4.1.3.1. XRF Investigation results

The elemental chemical composition and colour of the investigated painting area provided information about the type of pigment or pigment mixtures present in that specific area.

Figures 4.1.(Summary 2) and 4.1.(Summary 3) in this rèsume provide a brief representation of Figures 4.1.8-4.1.18 presented in the thesis.

From the XRF investigations in the nave area (Figure 4.1.(Summary 2) it was suggested that the blue colour was achieved using calcite ($CaCO_3$) and an early form of Prussian blue pigment. The latter pigment only needed to be used in small quantities in the painting due to its high colouring power. The dark red area of the painting shows a strong intensity of colour. According to the XRF spectrum, it contains calcite and hematite (Fe_2O_3). The signal of lead, on the other hand, is quite weak, which suggests that it might be present in the painting as a pigment, possibly red lead (Pb_3O_4), or it could be used as a drying additive for the oil, or even as a product of degradation (metallic soaps, lead carbonates, etc.).

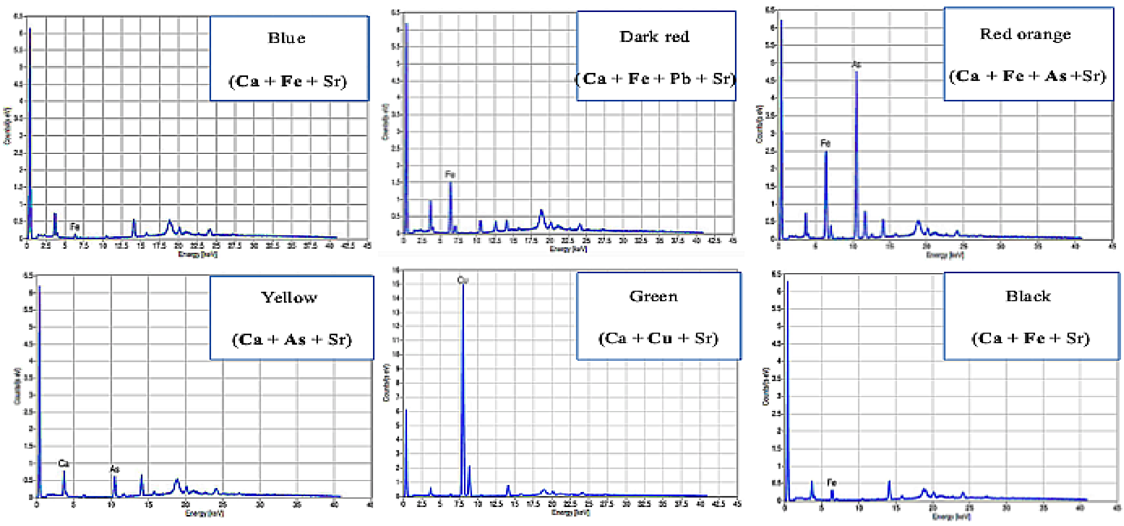


Figure 4.1.(Summary 2)
XRF spectra of the painting areas of various colors in the nave

The red-orange painting was created by mixing hematite with an arsenic-based pigment, most likely realgar (α-As_4S_4) (Măruțoiu et al., 2020). When analysing the yellow mural painting (halos) using XRF, the presence of orpiment (As_2S_3) and calcite was suggested (Măruțoiu et al., 2019; West-Fitzhugh, E., 1997, pp. 63). The weak intensity of the arsenic signals in the corresponding spectrum is also explained by the specific conservation condition of that area. As for the green-coloured painting, the primary pigment used was copper-based, possibly malachite. The XRF spectrum of the black-coloured area suggests that both iron oxide (magnetite, Fe_3O_4) and bone black were used in the painting (Măruțoiu et al., 2019). Bone black can be identified in the XRF spectrum by the signals of calcium, iron, and potassium (with a very weak signal around 2 KeV) (Bezur et al., 2020, pp. 113-115). The calcium in the bone black pigment derived from hydroxyapatite ($Ca_5(PO_4)_3(OH)$) (Udrea et al., 2023).

The XRF investigations in the narthex area are presented in Figure 4.1.(Summary 3). Conducted seventeen years later than the nave area, the narthex area was painted by Dumitru Ispas using the same pigments for the blue, yellow, and black-coloured painting, as seen in the comparison of spectra in Figure 4.1.(Summary 2) and 4.1.(Summary 3).

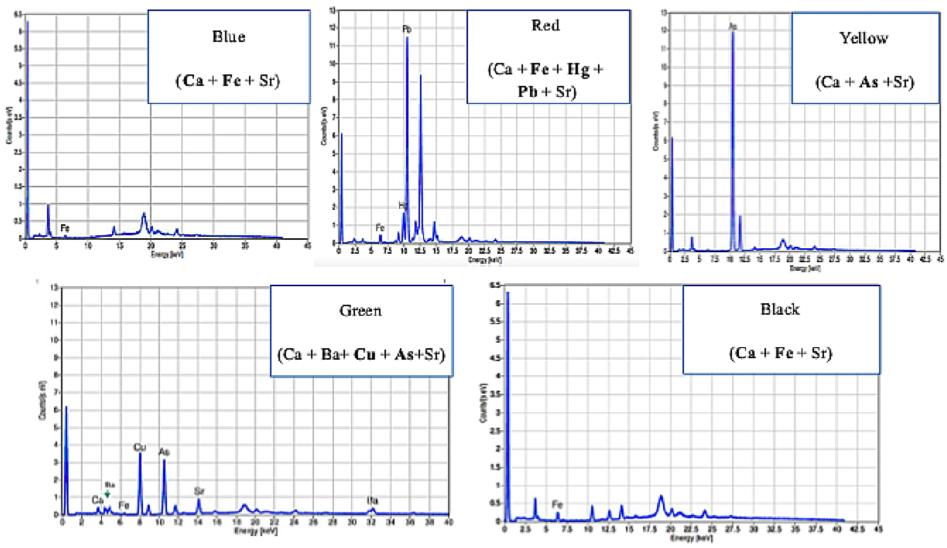


Figure 4.1.(Summary 3).
XRF spectums of the investigation from narthex

The red-coloured pigments used in the painting were hematite, cinnabar/vermilion, and red lead. The presence of these three pigments in the mixture can be justified by several reasons:

- red lead provides enhanced resistance to fading for the mercury sulphide-based pigment against fading (Coccato, Moens, & Vandenabeele, 2017; van Loon, 2008, pp. 84).
- the pigment HgS does not have good drying properties, so it was combined with hematite and red lead, pigments that had good drying properties (van Loon, 2008, pp. 65).

For the green-coloured painting, based on the presence of copper (Cu), arsenic (As), and barium (Ba), it can be inferred that the artist Dumitru Ispas used a late variant of Scheele green or early emerald green as pigment (Wes, 2014; West-Fitzhugh, 1997, pp. 221-222; Fabbi Reno, 1965).

From the comparative analysis of the XRF data, it is evident that there are signals of fluorescence emission corresponding to calcium (Ca) and strontium (Sr). Calcium was intentionally introduced into the painting as a mineral in the primer (calcium sulphate) and as a white pigment (calcium carbonate). Alternatively, it could have formed in the painting as oxalates, carbonates, or metal soaps due to degradation processes.

Strontium can originate from various sources, such as:

- calcium sulphates and carbonates (Franceschi et al., 2014)
- pigments with a limestone origin (or containing limestone impurities) (Murcia-Mascar et al., 2010),
- pigments obtained from the carbonisation of animal bones (Dalle et al., 2022), or derived from plants (vine black) (Larsen, Coluzzi, & Cosentino, 2016)
- animal glue used as a binder for the primer (Dalle et al., 2022).

4.1.3.2. Results of the r-FTIR investigation

The r-FTIR investigation revealed that the primer used was based on calcium sulphate in all three hydrated states (Figure 4.1.19).

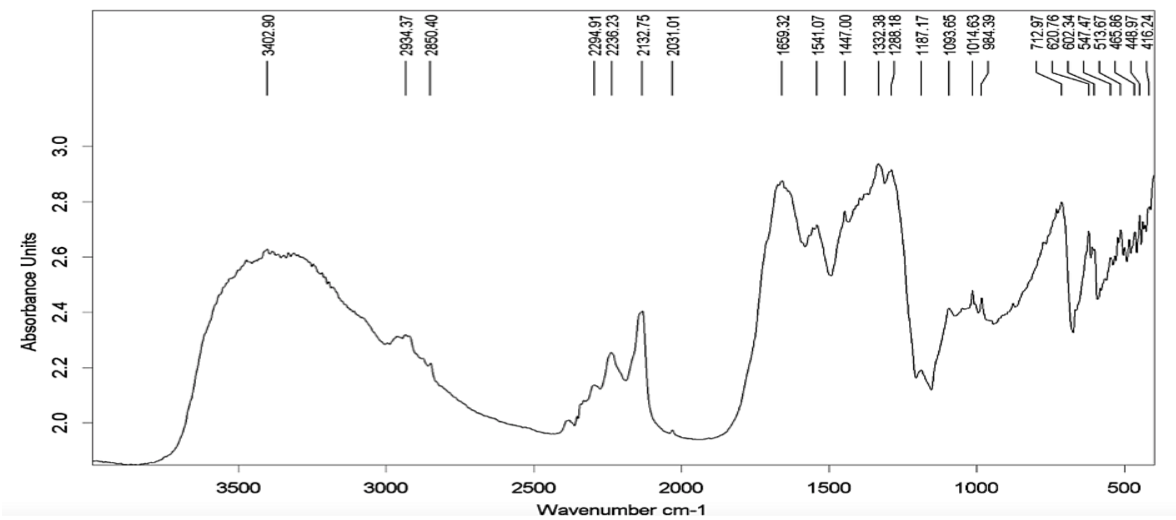


Figure 4.1.19.

r-FTIR spectrum of the blue zone of the mural painting (Măruțoiu și colaboratorii, 2020)

This was identified through vibrations at 3403, 2241, 2235, 2132, 2030, and 620 cm^{-1} (Măruțoiu et al., 2019; Miliani et al., 2012). The presence of early Prussian blue was identified through the vibrations of the Fe-CN bond (527-440 cm^{-1} and 450-430 cm^{-1}), Fe-C bond (600-550 cm^{-1}) (Kendix, 2009, pp. 119), as well as the presence of iron oxides (1037 and 1080 cm^{-1}) and kaolin (1020 and 3650 cm^{-1}) (Udrea et al., 2023; Rosi, Miliani, Clemente, et al. 2010). Calcium carbonate, the mineral suggested to be mixed with early Prussian blue by XRF, was also detected through its characteristic vibrations collocated around 2900, 2512, 1800 și 1447 cm^{-1} (Măruțoiu și colaboratorii, 2019; Rosi, Miliani, Clemente și colaboratorii, 2010). The weak intensity of the band at 2512 cm^{-1} can be due to either the large particle size of the pigment or the organic binders used in the mural painting.

Organic materials of a proteinaceous nature were identified by specific bands around 1650 cm^{-1} (ν C=O from amide I), 1550 cm^{-1} (ν C-N and N-H from amide II), and 1450 cm^{-1} (δ CH from amide III) (Rosi, Miliani, Clemente, et al. 2010). These protein compounds could have come from animal glue, as suggested by specific bands related to collagen at 1288 cm^{-1} and 712 cm^{-1} used as a binder for the primer (Măruțoiu et al., 2019). Alternatively, they could have originated from egg yolk, used as an ingredient in the oil-based tempera layers of the painting. Lipid materials were also detected showing vibrations at around 2928 and 2850 cm^{-1} (ν C-H), a broad and intense band between 1800-1580 cm^{-1}, and a shoulder peak at 1740 cm^{-1} (ν C=O from ester) (Miliani et al., 2012).

The main degradation products identified with r-FTIR were calcium soaps (1541 and 1578 cm^{-1}), lead soaps (1045, 1405, and 1519 cm^{-1}) (Henderson et al., 2019), and lead carbonates (3540, 2430, 2410, 1730-1740, 1392-1504, and 1000 cm^{-1}) (Monico et al., 2013; Miliani et al., 2012).

4.1.3.3. Results of the t-FTIR investigation

The t-FTIR spectra for the red-coloured mural painting on the north, west, and south walls are shown in Figures 4.1.20 – 4.1.21.

Red lead (Pb_3O_4) was identified through bands in the range of 419-443 cm^{-1} and 512-528 cm^{-1} (Mărutoiu et al., 2019). Hematite (Fe_2O_3) was detected through vibrations at 558 and 472 cm^{-1} (Gimenez et al., 2022; Vahur, 2010). Realgar (α-As_4S_4), due to its lack of vibrations in the range of 4000-400 cm^{-1}, was indirectly suggested by the band at 1040 cm^{-1} (Čiuladienė, Kareiva, Raudonis, 2020) and the presence of its degradation products, such as arsenolites (415, 470, and 780 cm^{-1}), arsenites (680-780 cm^{-1}), and arsenates (791-930 cm^{-1}) (Udrea, Măruțoiu, Nemeș, 2022). The identification of aragonite ($CaCO_3$) and dawsonite ($NaAl(CO_3)_2(OH)_2$) suggests that the realgar pigment and certain minerals from the carbonate class might have originated from the eastern part of the Transylvania basin (Kristály et al., 2006; Attila, 2002).

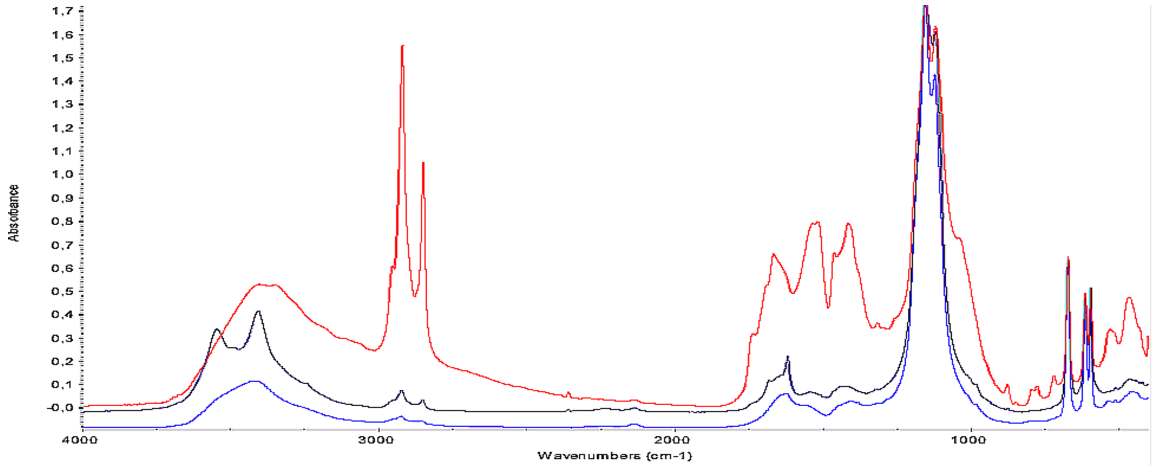


Figure 4.1.20. t-FTIR spectra of red paint samples
(the blue colour spectrum corresponds to the CrNord sample; the grey colour spectrum corresponds to the CrVest; the red colour spectrum corresponds to the CrSud sample).

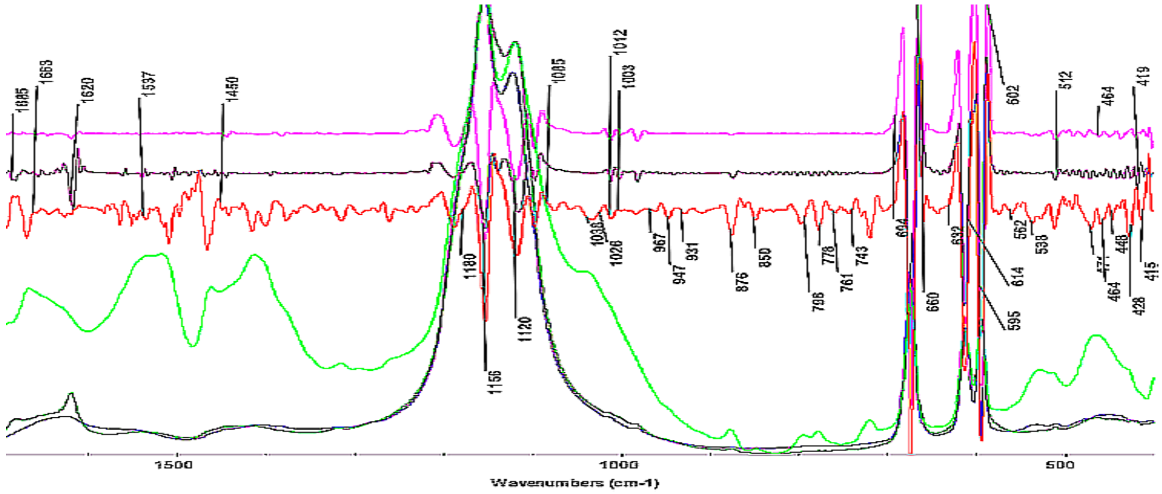


Figure 4.1.21. t-FTIR spectra of red paint samples and the relatives SD spectra.
The SD spectra representated by: the light purple line corresponds to the CrNord sample;
the dark purple line corresponds to the CrWest; the red line corresponds to the CrSud sample.

Cinnabar (HgS) has been suggested based on the very weak intensity bands observed at 1660, 1537, and 1450 cm^{-1} (Vahur 2010), as well as the presence of vibrations around 1175-1080, 778, 695, and 464 cm^{-1} characteristic of quartz (SiO_2) (Spring and Grout, 2002). The vibration at around 695 cm^{-1} indicates the crystalline nature of quartz (absent in amorphous quartz) (Saikia, 2014).

White lead was found by looking at certain bands at 1400, 1045, and 682 cm^{-1}, while the three types of calcium sulphate (anhydrite, bassanite, and gypsum) were identified based on specific vibrations around 595-665, 1110-1156, and 1620 cm^{-1}. Bands at 3490, 2341, and 2360 cm^{-1} indicate that anhydrite became hydrated due to absorbing water molecules from the atmosphere or from rainwater seeping în (Wallert, Hermens și Peek, 1995, pp. 58-64).

Regarding the organic materials, all three samples of red paint showed the presence of both the primer binder (animal glue) and the pigment binder (*tempera grassa*) (Table 4.1.2).

Table 4.1.2. Materials of organic nature identified in the red sample on the south wall

Organic materials	The characteristic wavelengths (cm^{-1})	References
Protein	~1657 (ν C=O), ~1634, ~1545 (ν C-N și δ N-H), ~1400-1300 (δ C-H), 1250-1000 (ν C-O)	Centeno et al, 2004
Lipids	3466 (νO-H), 2924(νas CH_2), 2852 (νs CH_2), 1740 (ν C=O esters), 1710-1705 (ν C=O acid), 1643 (ν C=O si C=C), 1463 (δas CH_3), 1423 (ν CO + OH), 1384 (δas CH_3), 1241 (ν C-O), 1169 (ν C-O-C), 1110 (ν C-O) , 979.	Poli et al., 2021
Shellac	2930 (νas CH_2), 2860 (νs CH_2), 1738-1730 (ν C=O esters or aldehyda), 1715 -1720 (ν C=O acid or ketones), 1636 (ν C=C), 1466 (δ CH_2), 1414 (δ CH2),1376 (δas CH_3), 1241 (ν C- O) , 1178 (ν C-O-C) , 1112 (ν C-O), 945 (δ CH_2), 930 (δ CH_2), 730 and 720 (δ rocking CH_2)	Derrick, 1989
Sandarac	2955 (νas CH_3), 2870, 2871, 1715-1695 (νC=O acid), 1448 (δ CH_2), 1382 (δas CH_3), 1321 (ν C-O-C), 1180 si 1078 (ν C-O), 793 and 673 (δ CH)	Derrick, 1989
Beeswax	2918, 2850 (νs CH_2), 2955 (νas CH_3), doublets at: 1742- 1736 (ν C=O esters), 1471 si 1460 (δ CH_2), 730 si 720 (δ rocking CH_2)	Derrick, 1989
Conifer resin (Pine tree)	3420 (νO-H), 2922 (νas CH_2), 2865, 1710 (ν C=O acid), 1689 (ν C=O al α, β – ketones), 1610 (ν C=C), 1544 (νas COO-), 1465 (δ CH_2), 1440 (ν CO + OH), 1393 (δas CH_3), 1280 (δ OH from COOH), 1199 (ν OH from COOH), 1161 (ν C-O-C), 962 (δ CH)	Zumbühl, Soulier și Zindel, 2021; Derrick, 1989
Colophony	2920 (νas CH_2), 2860 (νs CH_2), 1710 (ν C=O acid), 1457 (δ CH_2), 1381 (δas CH_3), 1241 (ν C- O), 1161 (ν C-O-C), 1038 (ν C-O), 983 (δ CH), 899 (δ CH)	Poli et al. 2021

The sample taken from the south wall also indicated the presence of an oleo-resinous varnish made up of various ingredients, including shellac, sandarac, beeswax, conifer resin, and rosin. Another material identified in this sample, through the vibrations of hydroxyapatite ($Ca_5(PO_4)_3(OH)$), was bone black (Udrea şi colaboratorii, 2023). Bone black could be used in painting for drawing and as an additive to help the oil in varnish or *tempera grassa* to dry and stay stable (Zumbühl, Soulier şi Zindel, 2021).

In addition to the original materials used in the mural painting, degradation products such as carbonyl compounds, metallic soaps, oxalates, nitrates, and plumbonacrit have also been identified.

Metallic soaps were highlighted in all red painting samples by the decrease in intensity of bands around 3500-3300 cm^{-1} and 1708 cm^{-1} corresponding to acids (fatty acids, abietic acids or acids derived from protein degradation) and the appearance bands in the range 1600-1400 cm^{-1}. The intensity of the band at 1514 cm^{-1} suggests that the largest amount of metal soaps is found in the CrSud sample. This aspect is in full agreement with the presence of organic materials in that sample.

Calcium oxalate monohydrate was identified by the bands around 1620-1640, 1320 and 779 cm^{-1}, while the oxalate dehydrated at 1643, 1330 and 783 cm^{-1} (van Loon, 2008, pp. 133).

Plumbonacrite ($Pb_{10}O(OH)_6(CO_3)_6$) was identified by bands located at 419, 466, 685, 1400, 3542, and 3560 cm^{-1} (Brooker et al., 1983). Sodium nitrate was suggested by the bands at 1395, 1068, 838 and 727 cm^{-1}, while potassium nitrate is represented by the characteristic bands at 1050, 827, 1420 and 714 cm^{-1} (Weir and Lippincott, 1961).

4.1.3.3. Results of the GC-MS investigation

In the analysis of the mural painting at the wooden church from Agârbiciu, GC-MS analysis played a significant role in confirming the presence of egg yolk and identifying the type of oil added to tempera grassa. The identification of the oil was based on the ratio of palmitic acid (C16:0) to stearic acid (C18:0) (Figures 4.1.23 - 4.1.24 and Table 4.1.3.) (Măruțoiu et al., 2019).

For the selection of painting samples, was taken care to avoid those containing pigments such as lead, mercury, or iron, which could greatly influence the ratio of saturated fatty acids in the oil due to degradation processes (Mazzeo et al., 2018). In this context, the colour area most suitable for GC-MS analysis was the one containing copper-based pigments (Tumosa and Mecklenburg, 2005).

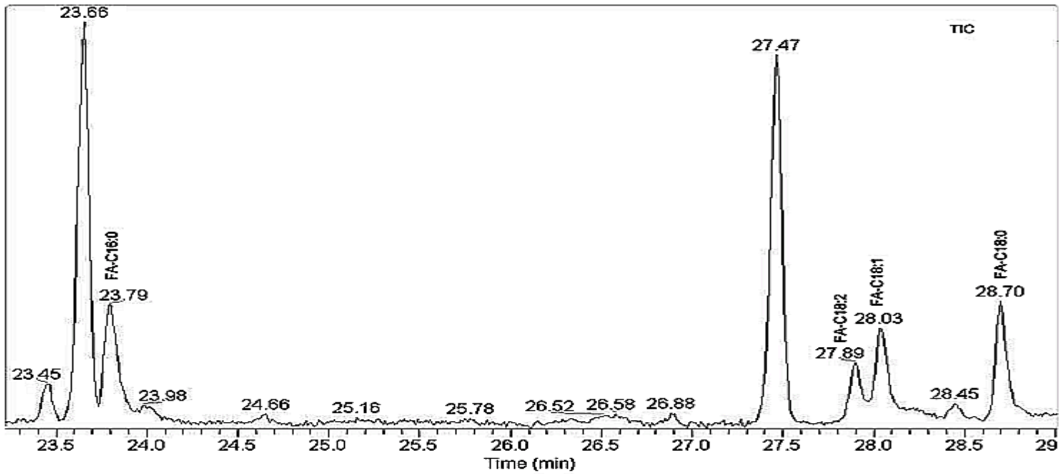


Figure 4.1.23. Total ion chromatogram of ethyl ester of palmitic acid (16:0), linoleic acid (18:2), oleic acid (18:1) and stearic acid (18:0) identified in the green painting sample (Māruțoiu et al., 2020).

Table 4.1.3. Chromatographic characteristics of ethyl ester fatty acids identified in the green paint sample (Măruțoiu et al., 2020).

Nr.	Ethyl ester of:	m/z characteristics	Proba 1 (%)	Proba (2 %)
1	palmitic acid (16:0)	73, 87, 101…. 255, 284	29.78	41.35
2	linoleic acid (18:2)	67, 81, 95, 109, 262, 308	15.68	2.68
3	oleic acid (18:1)	67, 81, 95, 109, 264, 310	25.35	17.09
4	stearic acid (18:0)	73, 87, 101 … 283, 312	29.19	38.86

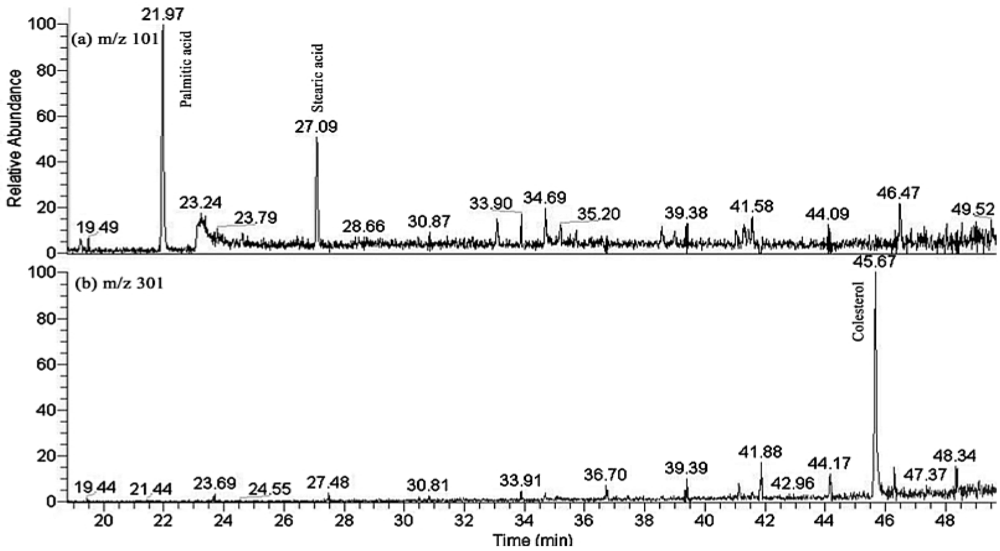


Figure 4.1.24. Selected mass chromatogram of molecular fragments

m/z = 101 of palmitic acid and stearic acid and m/z = 301 of cholesterol (Măruțoiu et al., 2020).

The P/S ratio values for the two samples were 1.02 (sample 1) and 1.06 (sample 2), indicating the use of linseed oil as a component of *tempera* (Măruțoiu et al., 2020). The presence of linseed oil and egg yolk (indicated by m/z = 301 corresponding to cholesterol) confirms the artistic technique used by the painter Dumitru Ispas in creating the tempera grassa mural at Agârbiciu.

4.1.4. Applications of scientific investigation results in digital restoration

Based on the identification of materials in the Agârbiciu mural painting, laboratory replicas of the colours were produced. After digitalisation, they formed the fundamental basis for both the digital restoration of the mural painting and its virtual promotion as an art and religious monument (Măruțoiu et al., 2020).

4.1.5. Conclusions

Using XRF, r-FTIR, t-FTIR, and GC-MS investigations, the main materials and artistic techniques used by Dumitru Ispas in creating the mural painting at the wooden church in Agârbiciu were identified and characterised. In 1801, during the painting the nave and altar, the painter used the following pigments: calcite, Prussian blue, hematite, lead red, realgar, orpiment, malachite (or verdigris), carbon black, and magnetite. Seventeen years later, when painting the narthex, the pigments used were: calcite, Prussian blue, hematite, lead red, lead white, cinnabar, orpiment, late Scheele green or early emerald green, carbon black, and magnetite. The ground layer was composed of *gesso grosso*, *gesso fino*, and animal glue. The pigments mixed with egg yolk and linseed oil (*tempera grassa*) were applied to the completely dried ground layer using the *a secco* technique. Identifying certain minerals in smaller quantities was also significant. For instance, the presence of calcite, aragonite, and dawsonite suggested that some pigments, like realgar, might have come from the eastern part of Transylvania. The detection of barium was crucial in determining the use of green pigment in the narthex, either a late variant of Scheele green or an early variant of emerald green.

The presence of strontium in all XRF spectra, along with calcium and/or sulphate carbonates, pigments with carbonate impurities, black carbon-based pigments, and animal glue, suggested the originality of the materials (the mural painting had not undergone restoration interventions) (Franceschi et al., 2014).

Moreover, the identification of heavy metal-based pigments (As, Hg, and Pb) and degradation products of arsenic-based pigments was vital from a health and occupational protection standpoint in the field of artwork (Udrea, Măruțoiu, and Nemeș, 2022).

Acknowledgments

Figures 4.1.5. and 4.1.7 were reprinted from the article *Udrea, I., Marutoiu, C., Nemes, F., Pigments based on arsenic-Sola dosis facit venenum. Book: Restoration notebooks, 2022, number 10, pages 250-265,* with the permission of Art Conservation Suport Publishing House, Bucharest.

4.2. Characterisation of Dumitru Ispas's mural painting in the wooden church of Straja, Cluj County, Romania

4.2.1. Introduction

The wooden church of the Holy Archangels Michael and Gabriel in Straja, Cluj, follows the usual design of wooden churches with its semicircular-shaped altar, nave, narthex, bell tower, and a porch on the southern side. The beautiful mural paintings inside the church were created in 1806 by the painter Dumitru Ispas and his son, Ștefan (Nemeș et al., 2020).

Figure 4.2.1
The wooden church in Straja, Capușu Mare, Cluj country (Nemeș et al., 2020)

Figure 4.2.3 Sequence of the mural painting in the altar area where some of the non-invasive investigations (XRF and r-FTIR) were conducted (Nemeș et al., 2020)

Figure 4.2.4
Sequence of the mural painting in the iconostasis area (Nemeș et al., 2020)

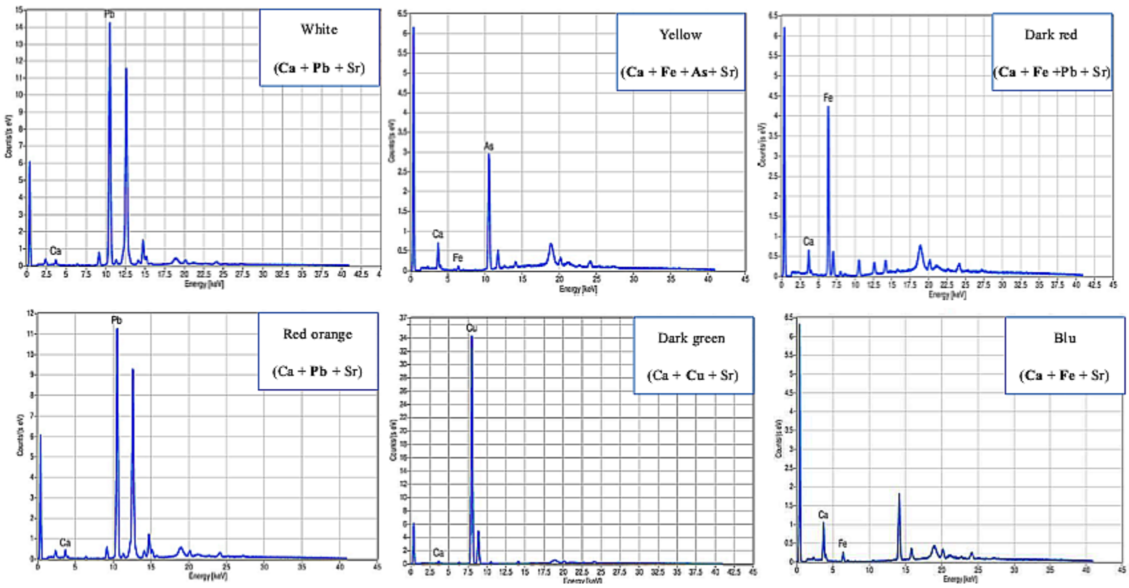
4.1.2. Experimental Methods

The scientific investigation of the mural painting was conducted using non-invasive diagnostic methods (XRF and r-FTIR) and invasive techniques for artworks (t-FTIR and DSC).

4.2.3. Data Interpretation and Results

4.2.3.1 XRF Investigation Results

The XRF investigation reveals that the white parts of the mural painting were made using white lead. For the yellow colour, a pigment called orpiment was used, which is based on arsenic sulphide (As_2S_3), along with calcite and goethite. For the yellow pigment, arsenic sulphide-based orpiment (and/or para-realgar (β-As_4S_4)) was used in combination with calcite and goethite (FeO(OH)). To achieve the dark red shade they mixed hematite with calcite and small amounts of red lead.



Figures 4.2. (Summary 1) contaings Figures 4.2. 5 - 4.2.10 (from the thesis) corresponding to the areas of painting investigated with XRF

The faint signals of lead may originate from the oil additive used in *tempera grassa*, or from a degradation product (metallic salts). In the reddish-orange painting, red lead was the main pigment used, and in the olive green one, copper-based pigments like malachite and green earth pigments were employed. The blue colour was made by mixing early Prussian blue pigment with calcite. The presence of calcium and strontium in all spectra was explained in the previous chapter.

4.2.3.2. The results of the r-FTIR investigation

In the r-FTIR investigation, which corresponds to the dark red and reddish-orange paintings, the results are represented in Figures 4.2.11 and 4.2.12. The first spectrum revealed the presence of iron oxide pigment (hematite) with a band at 485 cm^{-1}, while the spectrum in Figure 4.2.12 indicated the use of red lead (Pb_3O_4) through a doublet around 530 and 486 cm^{-1} (Nemeș et al., 2020; Čiuladienė et al., 2018).

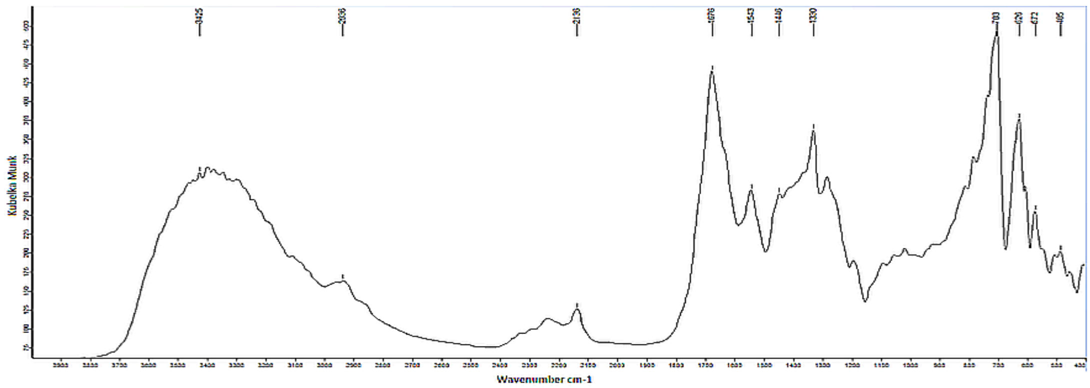


Figure 4.2.11.

r-FTIR spectrum of the dark red coloured painting (Nemeș et al., 2020)

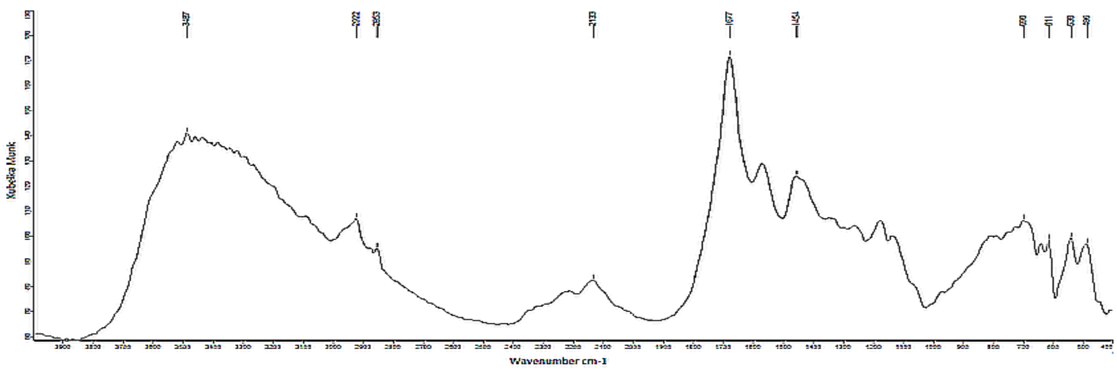


Figure 4.2.12

r-FTIR spectrum of the red-orange coloured painting (Nemeș et al., 2020)

Calcium sulphate, a mineral used in the ground layer, was suggested by the bands at 3487, 2132, 2114, 1150 (inverted band), 670, and 617 cm^{-1} (Nemeș et al., 2020; Melchiorre Di Crescenzo et al., 2013). Organic materials of protein nature (animal glue and egg yolk) were indicated by vibrations around 3350-3180, 3090, 1677, 1543, and 1450 cm^{-1} (Nemeș et al., 2020; Rosi, Miliani, Clemente et al., 2010), while lipid materials (egg yolk and oil) were highlighted by bands at 3000-2800, 1800, 1460, 1384, 1240, and 1163 cm^{-1} (Nemeș et al., 2020; Piqué and Verri, 2015). The band around 2950 cm^{-1} is a marker of *tempera grassa* (Bell, Nel, and Stuart, 2019, pp. 104). Calcium carbonate was suggested by the bands at 1454 and 698 cm^{-1} (Nemeș et al., 2020), lead carbonate by the bands at 1400 and 838 cm^{-1}, and early Prussian blue by the specific Fe-CN, Fe-C, and Fe-O bands at wavelengths below 600 cm^{-1} (Udrea et al., 2022; Čiuladienė et al., 2018).

4.2.3.3. Results of the t-FTIR investigation

The t-FTIR investigation was conducted on three samples of red-coloured paint (D_3, D_6, and D_9), one sample of green paint, and two canvas samples.

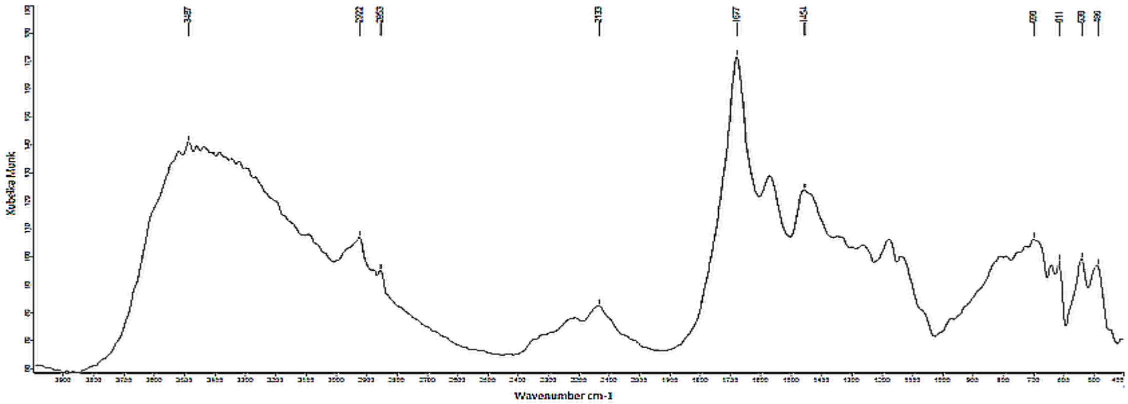


Figure 4.2.13. t-FTIR spectra corresponding to the red-coloured paint samples (D_3, D_6, and D_9) representing different shades of red, dark red, and orange-red.

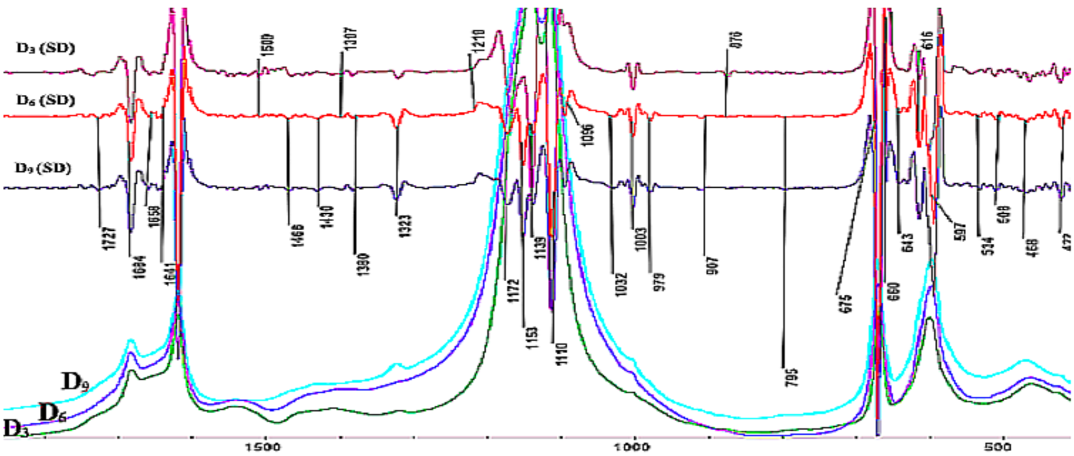


Figure 4.2.14. Second derivative (SD) spectra from the spectra series presented in Figure 4.2.13 in the spectral range of 1750 - 420 cm^{-1}. The spectra D_3, D_6, and D_9 correspond to the paint samples of red, dark red, and orange-red colours.

Through the comparative analysis of the spectra, it was confirmed that the mineral used in the ground layer was hydrated calcium sulphate, as indicated by the bands at 3620, 3550, 3400 cm-1 (with a shoulder at 3492 cm^{-1}), 1684, 1620, 1141, 1111, 672, and 595 cm^{-1} (Nemeș et al., 2020; Wallert, Hermens, and Peek, 1995, pp. 46-64).

Organic materials of protein and lipid nature were suggested by the bands at 3230, 1660-1640, 1566, and 1450 cm^{-1} for protein, and 2919-2850, 1736-1700, 1462, 1386, and 1165 cm^{-1} for lipids (Nemeș et al., 2020; Mazzeo et al., 2018).

The bands around 512, 450, and 441 cm^{-1} revealed the presence of red lead (Vahur, 2010), while those at 485-430 and 580-510 cm^{-1} indicated hematite (Čiuladienė et al., 2018). The bands at 1001, 913, 526, and 465 cm^{-1} confirmed the presence of red ochre. The presence of hematite and red ochre was further supported by the bands of silicates (1030 cm^{-1}), aluminosilicates (692 and 773 cm^{-1}) (Vargas et al., 2019), quartz (797 and 777 cm^{-1}), and kaolin (3690-3620 and 1010-700 cm^{-1}) (Čiuladienė et al., 2018). The low-intensity bands in the spectral region of 1040-478 cm^{-1} in spectra D_6 and D_9 may derive from degradation products of arsenic-based pigments (Udrea et al., 2022; Čiuladienė et al., 2020) or indicate contamination of iron-based pigments (hematite and/or red ochre) with arsenic (Manasse și Mellini, 2006). Besides the red pigments, calcite (1396, 1089, 872, and 713 cm^{-1}) and lead white (1393, 1045, 837, and 677 cm^{-1}) were also identified (Hans and Paul, 1963). In the green paint sample, malachite, whose spectrum is presented in (Nemeș et al., 2020), was identified by the bands around 3400, 3322, 1520-1390, 1098-875, 820, 748, 580-565 cm^{-1}, and 520-420 cm^{-1} (δ CO_3^{2-}). The spectrum and description of t-FTIR bands corresponding to the blue paint sample (with grey tones due to degradation) resulting from the mixture of Prussian blue pigment and calcite were presented in chapters 4.1 and 4.3.

The most abundant degradation products identified were lactones or anhydrides (1790-1770 cm^{-1}), lead soaps (2933 and 2849, 1540 and 1513 cm^{-1}) (van Loon, 2008, pp. 140), calcium carboxylates (1566 and 1538 cm^{-1}), calcium oxalates (1322 cm^{-1}), and copper oxalates (1365 and 1320 cm^{-1}) (Keune et al., 2016).

The canvas investigation, by means of spectroscopic analysis, aimed at finding out what type of cellulose fibre was used to make the canvas and assess its state of preservation. The condition of the cellulose fibres in the investigated canvas samples was evaluated by comparing the specific vibrations of the specific bands of functional group vibrations of the chemical components of hemp fibres in the samples, using a hemp reference spectrum (Figures 4.2.15 - 4.2.17).

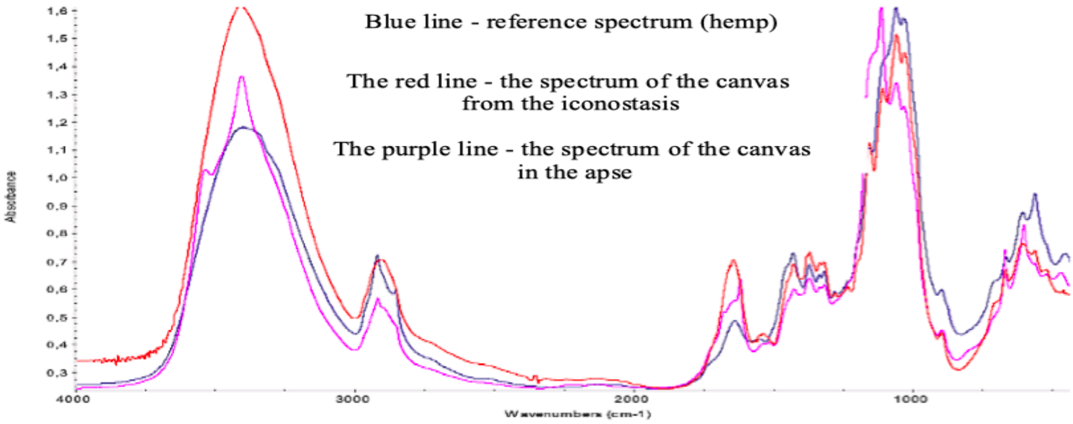


Figure 4.2.15. Comparative analysis of the two canvas samples taken from the mural painting with the reference spectrum (hemp)

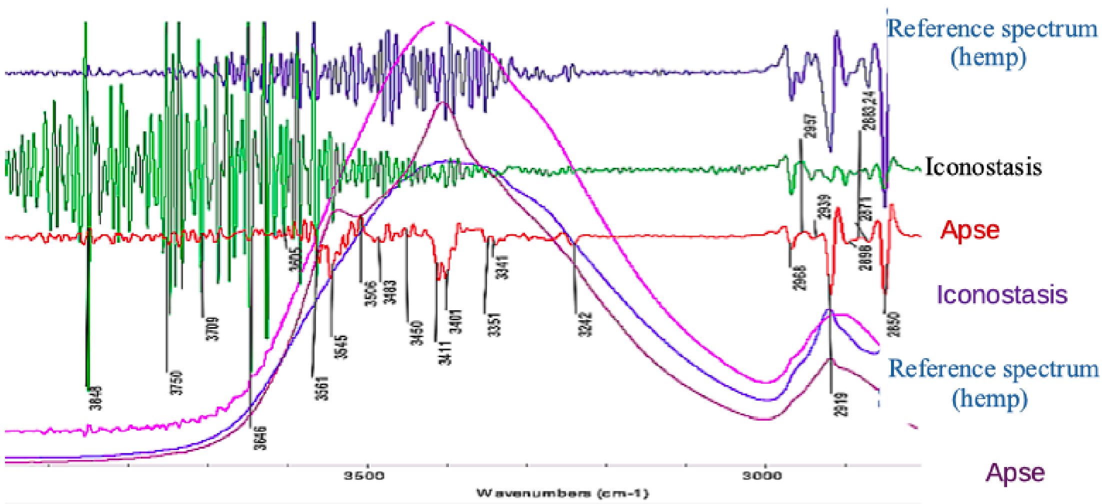


Figure 4.2.16. Detail of the spectral region 3700 - 2800 cm^{-1} spectra in second derivative spectra of the t-FTIR spectra of the canvas samples

The spectrum of the canvas sample from the apse also contains bands related to the painting materials. The degradation of cellulose fibres was indicated (according to Figures 4.2.15-4.2.17) by changes in the intensities of hydrogen bond-specific bands (3500-3000 cm^{-1}), increased intensity of carbonyl compounds (1750-1650 cm^{-1}), and decreased intensity of C-O-C, C-O, and C-C-C vibrations in the range of 1200-800 cm^{-1} (Calvini and Gorrossini, 2002).

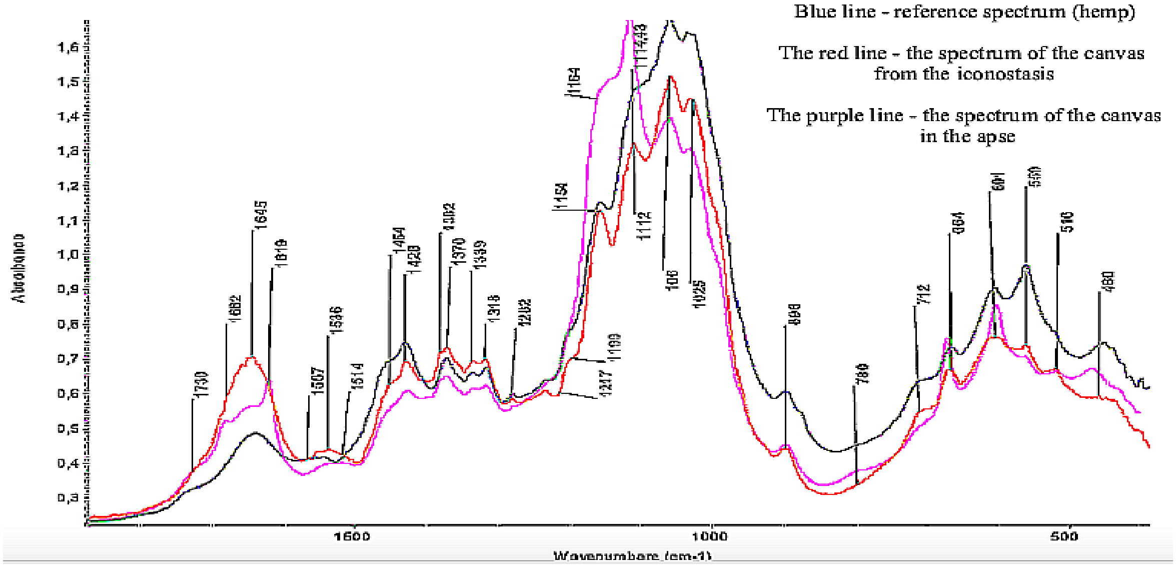


Figure 4.2.17. *Fingerprint* region (1800 - 400 cm^{-1})
of the t-FTIR spectra of the canvas samples

4.2.3.4. Results of the DSC investigation

The type of fibre used in the canvas and its state of conservation were confirmed, by the results of the differential scanning calorimetry (DSC) analysis (Figure 4.2.18) (Nemeș et al., 2020).

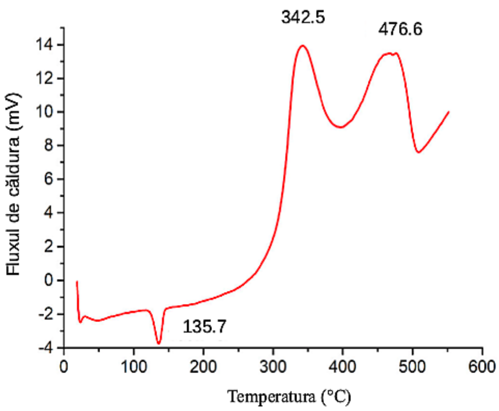


Figure 4.2.18

DSC profile of the canvas from the altar, where the endotheRmic peak at 135.7°C corresponds to the loss of water molecules from the fibre, while the exothermic peaks at 342.5°C and 476.6°C indicate the depolymerisation of hemicellulose and cellulose, and the decomposition of lignin and other fibre compounds (Nemeș et al., 2020)

4.2.4. Conclusions

Dumitru Ispas used a variety of pigments to create the mural painting at the wooden church in Straja. These included white lead, calcite, orpiment, goethite, malachite, early Prussian blue, hematite, lead red, and possibly realgar. He applied these pigments on a dry ground layer (*a secco*) using the *tempera grassa* artistic technique.

The paint layers showed signs of degradation, with the most abundant degradation products being metal soaps, oxalates, and carbonyl compounds. These products can affect the appearance and preservation of the painting over time.

The materials used for the ground layer were calcium sulphate and animal glue. The canvas used in the church, in some areas, it served as a lining between beams, while in others, it acted as a support for the painting. This canvas was made from hemp fibre. Through the t-FTIR and DSC analyses, the nature of the fibre and its state of preservation were confirmed. The diagnostic methods indicated that the canvas in the iconostasis area had experienced more degradation compared to the canvas in the apse. This information gathered from these diagnostic methods helps us understand the condition and materials used in creating this beautiful mural painting at the wooden church.

Acknowledgment

Figures 4.2.1, 4.2.3, 4.2.4, 4.2.11, 4.2.12, 4.3.13 were reprinted from the article *Characterization of the paint used by Dumitru Ispas in the wooden Straja church, Cluj County, Romania*, *Nemeș, D., Maruțoiu, C., Bratu, I., Neamțu, C., Kacso, I., Nemeș, O. F., Udrea, I. Analytical Letters, 2021, 54:1-2, 255-264.* Copyright © [2021], with the permission of Informa UK Limited - Taylor & Taylor & Francis Group, http://www.tandfonline.com

4.3. Scientific Investigation of the Icon

"Entry of Our Lord into Jerusalem" by Dumitru Ranite

Figure 4.3.1. The Icon *The Entry of the into Jerusalem*
by Grigore Ranite

4.3.1. Introduction

The artwork under scientific investigation is the wooden icon "Entry of Our Lord into Jerusalem," created around 1745 by the painter Grigore Ranite. Originally, this icon was part of the iconostasis in the church of Garda de jos (Alba Iulia), but it is currently housed at the Ethnographic Museum of Transylvania (inventory number B 4 513) (Udrea et al., 2023).

4.3.2. Experimental Methods

The investigation of the icon involved the use of ED-XRF and t-FTIR. The XRF investigation was performed on various colour areas of the icon, while for the t-FTIR analysis, three paint samples (blue-grey, green, and red) and two wood samples (one from the back of the icon and the other from the frame) were collected.

4.3.3. Results and Discussions

4.3.3.1. XRF Investigation Results

The elemental composition obtained from the XRF investigation of the different colour areas of the icon and the possible attribution of pigments were extensively presented in the thesis and the article by Udrea et al. (2023); here, a summary is provided in Table 4.3.3.1.

Table 4.3.3.1. Summary of XRF scientific investigation

Zone of painting colour investigated:	Elemental Composition	Possible pigment attribution
Gilded (central part and icon frame)	Ca, Fe, Au, Sr	High-purity gold leaf (Au) on red *bolo* layer
Gilded (Jesus Christ's garment)	Ca, Fe, Au, Sr	Gold (pigment)
Red (Jesus Christ and other character's garments – on right side of icon)	Ca, Fe, Pb, Au, Hg, Sr	Cinnabar, red lead, hematite, gold pigment
Red (city building and rocks)	Ca, Fe, Hg, Pb, Sr	Cinnabar, red lead, hematite
Red (icon frame)	Ca, Fe, Hg, Pb, Sr	Red lead and hematite
Light blue and dark blue (tower)	Ca, Fe, Pb, Sr	Lead white and early prussian blue
Green (tree and left character)	Ca, Fe, Cu, Pb, Sr	Lead white, copper-based pigments, earth pigments
Green-brown (rocks)	Ca, Fe, Cu, Pb, Sr	Lead white, copper-based pigments, earth pigments
Brown (rocks)	Ca, Fe, Pb, Sr	Lead white, goethite, and possibly carbon black
Light brown (central area of rocks)	Ca, Fe, Pb, Sr	Lead white mixed with ochre

The signals of calcium (Ca) and strontium (Sr) were present in all XRF spectra, and their relationship was described in Chapter 4.1. The signals of iron (Fe) and lead (Pb) were present in all XRF spectra of the analysed points, except for the spectrum of the area covered with gold leaf, indicating the possible presence of an *imprimitura,* lead-based imprinting layer (lead white and/or red lead) and iron-based pigments (hematite) above the ground layer (Serendan et al., 2013). The potential presence of an *imprimitura* layer in the icon "Transfiguration of Jesus Christ," also painted by the same iconographer Grigore Ranite, was supported by Bratu et al. (2020).

The gilded area was made with high-purity gold, both in the form of leaf and pigment. The presence of calcium and iron in the area covered with gold leaf indicates the use of *bolo* for its application. Gold pigment was used in the red-coloured painting, where cinnabar (HgS), a precious pigment, was also identified. The use of these two pigments corresponds to the iconographic significance of the depicted scenes. Figures 4.3.3 and 4.3.4 illustrate, as examples of the XRF investigation, the spectra corresponding to the gilded areas of the icon's frame and the garment of Jesus Christ.

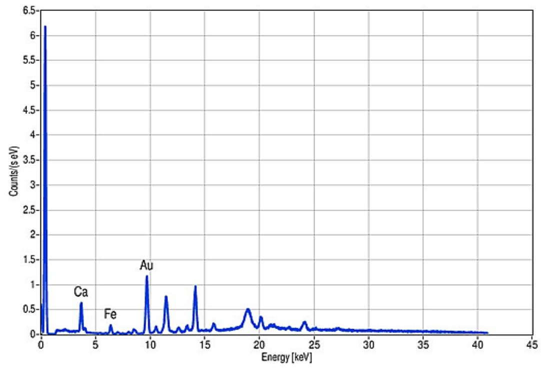


Figure 4.3.3

XRF Spectrum of the gilded area on the icon frame

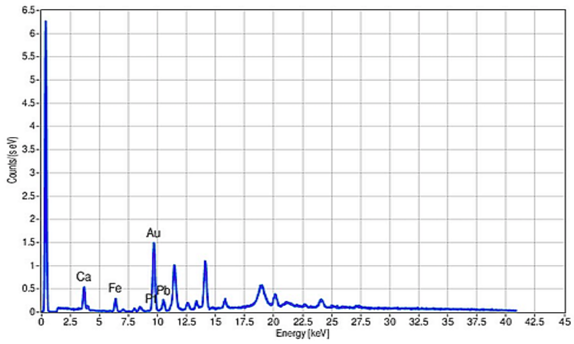


Figure 4.3.4.

XRF Spectrum of the gilded area corresponding to Jesus Christ's garment

Other red pigments identified were hematite and red lead, and possibly pigments of Greek origin known as *sandyx* and *syricum*. *Sandyx* was obtained by calcining a mixture of hematite and lead white (in a 1:1 ratio), while *syricum* was obtained by mixing sandyx with hematite (also in a 1:1 ratio); the latter was commercially known as minium (Pb_3O_4) (Udrea et al., 2021).

In the green colour area (with various shades), the XRF investigation suggested the use of lead white, copper-based pigments, and iron-based pigments. In art, lead white was mixed with pigments not only to enhance brightness but also, as in the case of verdigris, to increase its resistance to degradation (Wallert, Hermens, and Peek, 1995, pp. 124-125).

The brown-coloured painting was likely obtained with brown ochre, as well as goethite and lead white.

4.3.3.2. t-FTIR investigation results

The t-FTIR investigation of wood samples from the icon's support was conducted to determine the wood type and identify and characterise its main chemical components.

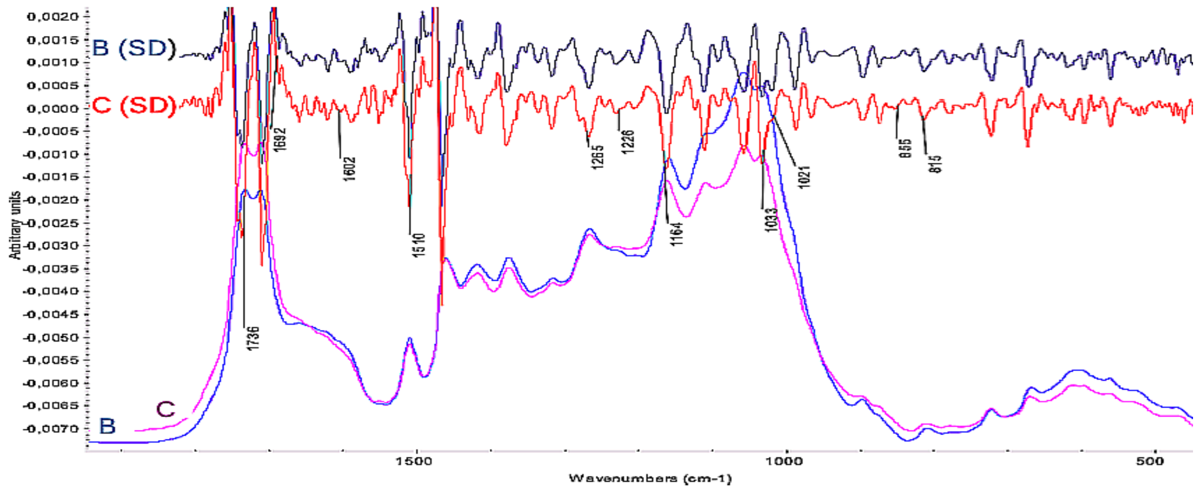


Figure 4.3.16. t-FTIR spectra (average and second derivative) in the spectral region 1800-400 cm^{-1} of the wood samples from the icon support (B-sample taken from the back of the icon, C-sample of wood taken from the back of the icon frame) (Udrea et al., 2023).

The investigated wood samples (Figure 4.3.16) were identified as coniferous wood due to several features:

- higher intensity of the band located at 1264 cm^{-1} than the one at 1221 cm^{-1} (Ishii and Shimizu, 2001; Łojewska et al., 2005)
- absorption band of the carbonyl group at a lower frequency than 1738 cm^{-1} (indicating a high lignin content) (Łucejko et al., 2015)
- higher intensity of the guaiacyl-specific absorption vibration at 1510 cm^{-1} compared to 1600 cm^{-1} (Łojewska et al., 2005; Ishii and Shimizu, 2001)
- paired bands around 1140/1031 cm^{-1} and 860/816 cm^{-1} (with similar intensity in coniferous wood) (Ishii and Shimizu, 2001)
- absorption bands at 1695 cm^{-1} and 1022 cm^{-1} specific to the carbonyl groups of dehydroabietic acid and pimaric acid, respectively (Udrea et al., 2023).

The results were validated (Figure 4.3.17) by comparing the two spectra of panel samples with a reference spectrum (coniferous wood) (Udrea et al., 2023).

The assessment of the state of preservation of the wooden support was conducted by identifying and characterising its chemical components (cellulose, hemicellulose, lignin, extractives). The specific bands for each component were described by Udrea et al. (2023).

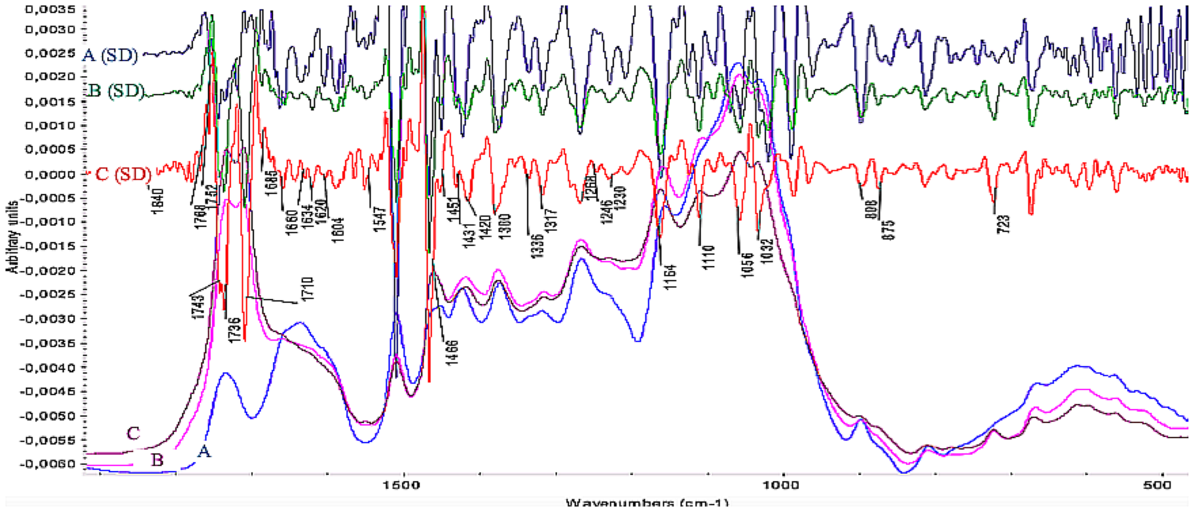


Figure 4.3.17 shows the t-FTIR spectra (average and second derivative) in the spectral region of 1800 - 400 cm^{-1} for the reference sample (A), the wood sample taken from the back of the icon (B), and the wood sample taken from the back of the icon frame (C) (Udrea et al., 2023).

The degradation of cellulose and hemicellulose was suggested, among other factors, by the decrease in intensity of absorption related to amorphous regions (1317 cm^{-1}), crystalline regions (~1448 cm^{-1}), and β-(1→4) glycosidic linkages in the cellulose fibre (Udrea et al., 2022; Udrea, 2013, pp. 63-73). Photo-oxidation of lignin was indicated by the increased intensity of absorption bands related to aromatic groups at around 1604, 1519, 1455, 1422, 1264, and 875 cm^{-1} and the formation of compounds in the carbonyl region (1700-1780 cm^{-1}) and quinones (~1685 cm^{-1}) (Chang et al., 2010; Łojewska et al., 2005; Mosini et al.,1990). Degradation of extractives was recognised through the band at 1245 cm^{-1}, representative of the most oxidised form of resin, the 15-hydroxy-7-oxodehydroabietic acid (Udrea et al., 2023).

The degradation of the wooden support resulted in the formation of acid-character degradation products in the spectra of wood samples (spectra B and C). These products influenced the increased hydrophilic properties of wood, along with the environmental factors (temperature and humidity) where the artwork was stored, leading to biodegradation processes. The conifer wood extractives played a significant role in this process, as they provided nutrients for biotic agents that caused wood-decay (Udrea et al., 2023).

Biotic agents were identified by specific vibrations of their biochemical compounds, such as amide I and amide II (1635 and 1540 cm^{-1}), glycogen (1030 cm^{-1} and 576-583 cm^{-1}), phosphate compounds (1080, 1247, and 875 cm^{-1}) and oxalates (1318 cm^{-1}). Bands at 3006 and 723 cm^{-1}, attributed to the cis-trans isomerization of double bonds in the fatty acids of triglycerides, were not present in aged oil (a component of the binder and varnish), confirming the presence of active wood-decay by biotic agents (Udrea et al., 2023). Moreover, the band at 1560 cm^{-1}, together with the increased intensity of the amide II band (1540 cm-1) compared to amide I (1635 cm^{-1}), indicated the presence of protein compounds such as chitin or chitosan. These were associated with xilophagous attack (Zotti, Ferroni, and Calvini, 2011). The wood from the icon frame, due to its marginal position in the icon's architecture, showed a much more pronounced chemical and biogical degradation process.

The t-FTIR investigation of the three paint samples indicated, through sulphate group (SO_4^{2-}) signals, that the mineral used for the ground layer was calcium sulphate (*gesso)* (Figures 4.3.18 - 4.3.19). This mineral was identified in all three hydration states: anhydrous (1098, 672,

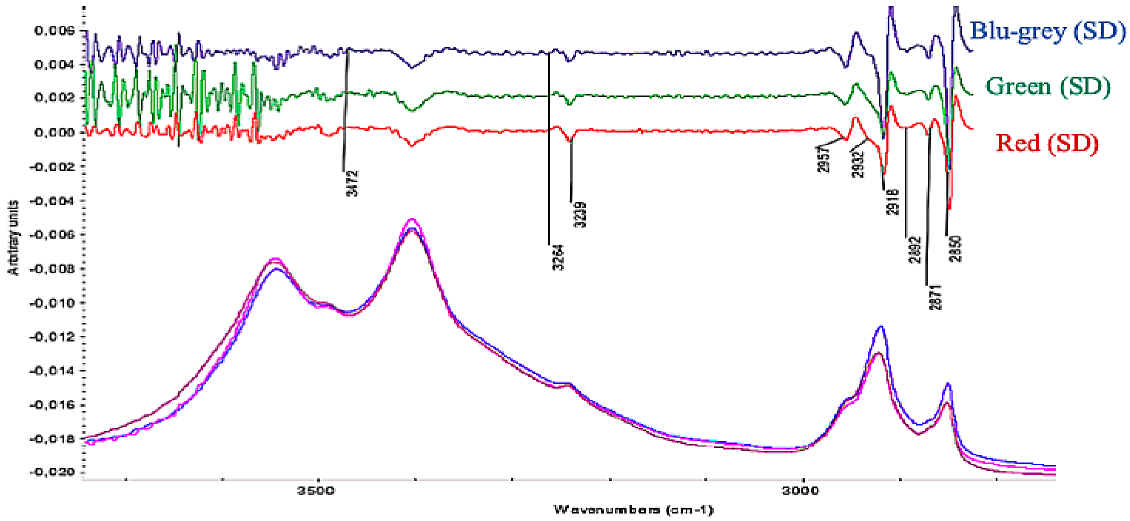


Figure 4.3.18 shows the t-FTIR spectra of the paint samples
in the blue-grey, green, and red colours in the spectral region of 3700 – 2800 cm^{-1} (Udrea et al., 2023).

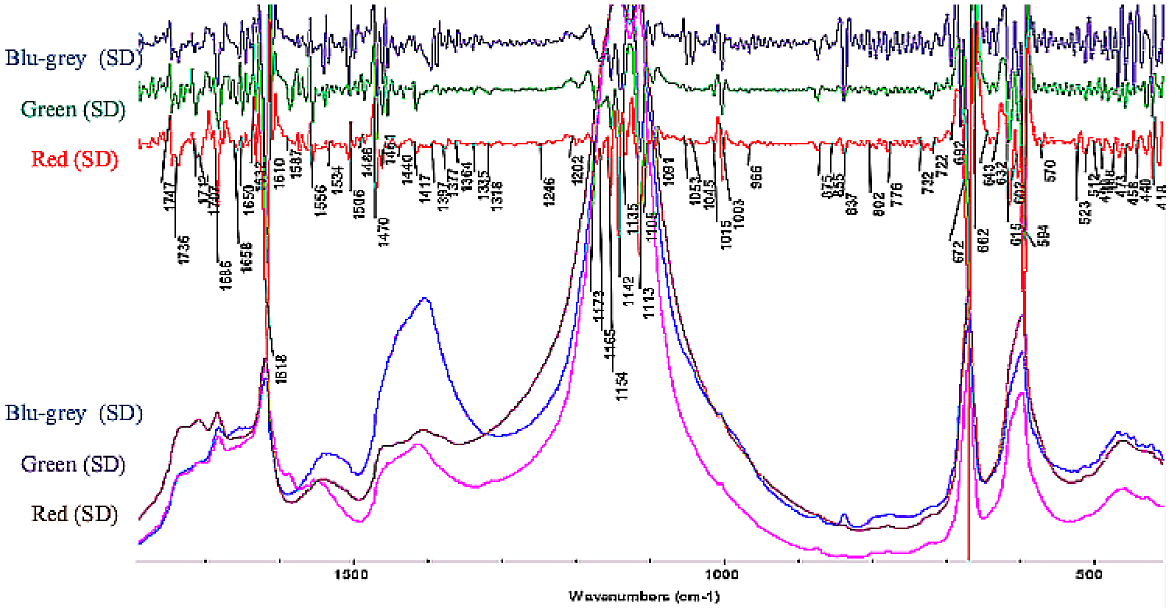


Figure 4.3.19. Detail of the spectral region of 1800-400 cm^{-1} from the t-FTIR spectra corresponding to the paint samples in the blue-grey, green, and red colours (Udrea et al., 2023).

614, and 595 cm^{-1}), bassanite (3553, 3605, 1617, 1114, 659, and 595 cm^{-1}), and gypsum (3395, 3489, 1686, 1620, 1103, 670, and 596 cm^{-1}) (Udrea et al., 2022). The prominent and sharp bands in the spectral regions of 1050-1250 cm-1 and 500-700 cm^{-1} (Lane, 2007) indicate that both *gesso grosso* and *gesso sottile* were used in creating the ground layer (Udrea et al., 2023).

The presence of proteinaceous materials was identified through vibrations located at 1645, 1552, and 1453 cm^{-1} (Udrea et al., 2023), while lipidic materials were suggested by the absence of the band at 3009 cm^{-1} (corresponding to cis–trans isomerization), the decrease in intensity, and the broadening of bands at 724 cm^{-1} (cis-C=C–H), 990 cm^{-1}, and 3435 cm^{-1} (Balakhnina et al., 2011), and the presence of free fatty acids like palmitic acid (2956, 2916, 2849, 1695, 1564, 1315, 1299, and 1290–1180 cm^{-1}) (Poli et al., 2021). The presence of proteinaceous and lipidic signals confirms that the artistic technique used was *tempera* or *tempera grassa* (Udrea et al., 2023). It is important to mention that lipids refer to both the egg yolk and the oil. The oil was used in *tempera grassa* as well as the main ingredient of varnish (Udrea et al., 2023).

For the red paint, the bands at 530, 512, and 454 cm^{-1} suggested the use of red lead, and bands at 580-520 cm^{-1} and 480-420 cm^{-1} indicated hematite. In the blue-grey paint sample, bands at 3565, 3533, 1397, 1360, 1044, 855, 838, 776, 680, and 410 cm^{-1} confirmed the use of lead white (Udrea et al., 2023). Considering the historical period and the presence of lead white, it was assumed that early Prussian blue was used as the blue pigment. This pigment's specific vibration at around 2080-2090 cm^{-1}, usually corresponding to the cyanide group, was not detected due to its sensitivity to degradation factors. Instead, its degradation products and additives were identified. The degradation products found were ferrocyanide [FeII(CN)6]4, ferricyanide $[Fe_{III}(CN)_6]_3$, and polymorphic FeOOH compounds. The former two compounds were recognised based on IR absorptions at around 2120 and 2230 cm^{-1}, while the latter around 799 and 875 cm^{-1} (Udrea et al., 2023). The additives added to the pigment were identified as aluminium-based compounds AlO(OH) (1072, 884, 740, 621, and 479 cm^{-1}), Al_2O_3 (759, 652, 630, 617, 554, and 465 cm^{-1}), quartz (1168, 1087, 1032, 798, and 775 cm^{-1}), and calcite based on its characteristic bands at 1428, 873, and 712 cm^{-1} (Udrea et al., 2023). Due to the complexity and difficulties associated with identifying this pigment and the detection limit of the FTIR instrument, further scientific investigation with complementary analysis methods is recommended for absolute confirmation (Udrea et al., 2023; Polkownic and Buisman, 2020).

Results from the t-FTIR investigation of the green-coloured painting revealed the use of malachite (1488, 1384, 1096, 875 si 820 cm^{-1}), verdigris (3482, 3374, 3272, 2985, 2935, 1560-1610, 1417 și 1606, 1445 și 692 cm^{-1}), and copper resinate (1710, 1695, 1247 și 1198 cm^{-1}). The black bone pigment, employed for outlining the iconographic details and mixed with other pigments to achieve various colour tones, was identified based on specific vibrations at 1087, 1038, 875, 966, 632, 803, 564 și 467 cm^{-1} specific to phosphate from hydroxyapatite ($Ca_5(OH)(PO)_4$) (Udrea et al., 2023).

As for the varnish, besides linseed oil, it contained other ingredients such as dipentene resin (1469, 1244, 1200, 1020 cm^{-1}), beeswax (2950 , 2919, 1470, 1460, 730 și 720 cm^{-1}), and shellac (2857, 2937, 2895, 1737, 1710, 1639 și 1247 cm^{-1}) (Udrea et al., 2023). The strong intensity of the bands at 1745 and 1172 cm^{-1} indicates the possibility, according to Svečnjak et al. (2015), that the beeswax was contaminated with beef tallow.

Degradation products identified in the three colour samples included calcium oxalates and metal soaps. The presence of various metal soaps like copper-based (1585 and 1417 cm^{-1}) and lead-based (1510, 1420, and 1461 cm^{-1}) was detected. Iron-based (1530, 1467, and 1444 cm-1) and calcium-based (1579-1540 cm^{-1}, 1469-1434 cm^{-1}, and 1418 cm^{-1}) metal soaps were also present.

4.3.4. Conclusions

The investigation confirmed that the wooden support of the icon belongs to the conifer species. The icon's primer was made using calcium sulphate in various hydrate forms and animal glue. Strontium was found in all painting samples. The gold used in the artwork, both as metallic leaf and pigment, was of superior quality. The metallic leaf was applied on a red bole layer, likely enhanced with red lead.

The identified pigments, including lead white, cinnabar/vermilion, hematite, Prussian blue (early type), malachite, verdigris, resinates, earth pigments, carbon black, and possibly ochre pigments, were applied with tempera grassa technique. The varnish used on the icon consisted of linseed oil, conifer resin, shellac, and beeswax.

Various materials in the painting exhibited signs of degradation. Both chemical and biological degradation affected the wooden frame support more intensely than the painting surface. The green and blue-coloured areas experienced chromatic changes, shifting towards darker tones. The most commonly identified degradation products were metal soaps and oxalates.

Acknowledgment

Figures 4.3.4, 4.3.5, 4.3.8, 4.3.12, 4,3.14 were reprinted from the article *Udrea, I., Maruțoiu, C., Nemeș, O. F., Bratu, I., Nemeș, D., Toader , D., Spectroscopic analysis of the Romanian icon "The entry of the Lord into Jerusalem" by Grigore Ranite, Analytical Letters, 2023, 56:2, 312-330*, Copyright © [2023], with permission from Informa UK Limited-Taylor & Taylor & Francis Group, http://www.tandfonline.com

4.4. Investigation of XRF on the component materials

of the mural painting in the wooden church of Someșul Rece village, Cluj county

Figure 4.4.1.
Front view of the wooden church in Someșul Rece

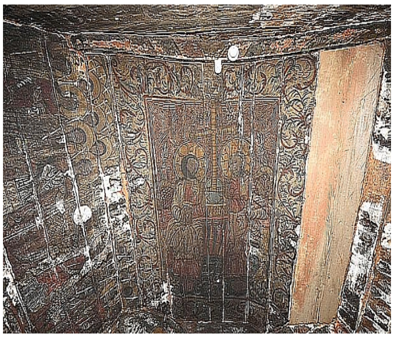


Figure 4.4.3
The mural painting of the apse vault

Figure 4.4.4. Detail of the mural painting in the altar (medallion), where part of the XRF investigation was carried out

The church is dedicated to the "Descent of the Holy Spirit" and, according to the inscription at the entrance, it was built in the year 1763. The mural painting inside the church, whose state of preservation is precarious, was created in 1768, as confirmed by the inscription written in the old Romanian language (Cyrillic alphabet) on the wall of the altar. Over time, the church has undergone various restoration interventions.

4.4.2. Experimental methods

X-ray fluorescence (XRF) was used as a non-invasive diagnostic method to investigate the pigments in the mural painting. The portable Bruker spectrometer (S1 Titan) used in this study is the same as in previous cases.

4.4.3. Results and Discussions

The XRF scientific investigation demonstrated that many of the materials identified in the mural painting correspond to the period of its creation. From the comparative analysis of all XRF spectra data (presented in Table 4.4.) it was noted that strontium (Sr) and calcium (Ca) were found in all the spectra of the analysed painting areas. Iron (Fe) was also present in all the XRF spectra, except in the white-coloured area.

Table 4.4. Summarises the elemental chemical composition in different chromatic areas of the mural painting in the altar, iconostasis, naos, and narthex.

Picture colour	**Altar**	**Iconostasis**	**Nave**	**Narthex**
White	1452 – Ca, Si.			
White pink	1457- Pb, Ca, Fe, Sr.			1324 - Ca, Fe, Hg, Sr.
(skin)				1303 - Ca, Fe, Sr.
				1310 - Ca, Fe, Pb, Sr.
	1361- Hg, Ca, Fe, Sr.	1338 – Pb, Ca, Fe, Sr.	1332 – Ca, Fe, Hg, Pb, Sr.	1318 - Ca, Fe, Sr.
	1455 - Hg, Ca, Fe, Sr.	1341 – Pb, Fe, Ca, Sr.		1314 – Ca, Fe, Sr
Red	1450 – Ca, Pb, Fe, Sr.	1340 – Pb, Fe, Ca, Sr.		1315 – Ca, Fe, Hg, Pb, Sr.
	1451 – Pb, Ca, Fe, Sr.			1320 – Ca, Fe, Hg, Pb, Sr.
				1319 – Ca, Fe, Hg, Sr.
				1306 – Ca, Fe, As, Sr.
				1300 – Ca, Fe, Hg, Pb, Sr.
Blu	1454 – Pb, Ca, Fe, Sr.	1343 - Ca, Fe, Sr.	1333 – Ca, Fe, Pb, Sr.	1307 – Ca, Fe, As, Sr.
		1344 - As, Ca, Fe, Sr.		
	1453 - As, Ca, Fe, Sr.	1348 - Ca, Fe, Pb, Sr.	1337 - Ca, Fe, Pb, Sr	1313 – Ca, Fe, As, Sr.
Green	1433 – As, Ca. Fe, Sr.	1349 - Ca, Fe, Cu, Pb, Sr.	1334 – Ca, Fe, Cu, Pb, Sr.	1321 – Ca, Fe, As, Sr.
	1365 – As, Ca, Fe, Sr.			
	1458 - As, Ca, Fe, Sr.			1312 – Ca, Fe, As, Sr.
Yellow	1456 - As, Ca, Fe, Sr.			
	1364 – As, Ca, Fe, Sr.	1342 - Cu, Pb, Ca, Fe, Sr.		1309 – Ca, Fe, As. Sr.
				1311 – Ca, Fe, Pb, Sr.
				1305 – Ca, Fe, As, Sr.
Brown				1304 – Ca, Fe, Sr.
Black		1347 – Ca, Fe, Pb, Sr.		1302 – Ca, Fe, Sr.

The investigation revealed that the white pigments used in the painting were lead carbonate (lead white) and calcium carbonate (calcite). Red pigments used in the red-coloured areas included hematite, red lead, cinnabar/vermilion, realgar, and possibly lepidocrocite

(γ-Fe(OH)O). Cinnabar/ vermilion was not used alone but in a mixture with hematite and red lead. Hematite was used alone only for red ornaments, while in certain symbolically significant iconographic details, it was found alongside cinnabar/vermilion and red lead. The arsenic and mercury-based pigments could be of Transylvanian origin.

The blue-coloured area was identified as Prussian blue pigment. It was mixed with lead white in the altar and naveareas (XRF spectra 1454 and 1333) and with calcite in the iconostasis and narthex areas (XRF spectra 1344, 1307, and 1343). The presence of arsenic in the XRF spectrum 1343 could be attributed to degradation products of arsenic-based pigments used in adjacent blue-coloured areas (Udrea, Măruțoiu, and Nemeș 2022), or it could be due to iron pigment impurities (Cruells and Roca, 2012). However, there is a possibility of other blue pigments being used (as described in chapter 2 of the thesis), which is why further investigations are recommended.

The green colour in the altar and narthex areas suggested the use of a green earth pigment contaminated with arsenic or a mixture of yellow pigment (orpiment) with Prussian blue or goethite (*vergaut* technique). In the iconostasis and nave areas, two distinct chemical compositions were identified, consisting of Ca, Fe, Pb, Sr (XRF spectra 1348 and 1337), and Ca, Fe, Cu, Pb, Sr (XRF spectra 1349 and 1334), respectively. The presence of copper suggested the use of copper-based pigments. Iron might be associated with earth pigments, while lead, as described earlier, could have multiple sources.

The investigation of the yellow-coloured painting revealed diverse elemental chemical compositions in the four investigated areas (altar, narthex iconostasis, and naos). The yellow painting in the altar and narthex areas was achieved by using a mixture of orpiment and yellow ochre or by using yellow ochre contaminated with arsenic (Cruells and Roca, 2012). In the narthex area, the presence of lead and iron indicated a mixture of one of the lead-based pigments (lead white, massicot, litharge) with yellow ochre. In the iconostasis, the elemental chemical composition of the yellow painting areas consisted of copper (Cu), lead (Pb), and iron (Fe). The materials possibly used for this could be chalcopyrite pigment (CuFeS2) or, according to Salem's publication (2017), a synthetic dye (azo-azomethine dyes) (Salem, 2017). The latter product might indicate a restoration intervention. Deposits of chalcopyrite have been found in Romania, but its use as a pigment in Romanian painting has still not been described in national literature. At the European level, only recently, has do Nascimento Campos and his collaborators (2023) identified this pigment in a painting made by Lèon Palliére (1787 – 1820).

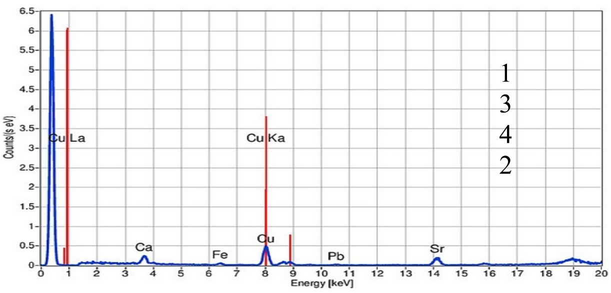


Figure 4.4.10.

XRF spectrum 1342 of the yellow-coloured (aura) painting area in the iconostasis.

The XRF investigation of the brown-coloured painting suggested the use of ocher pigments, such as goethite and/or jarosite. The black-coloured areas possibly used iron-based pigments like magnetite or maghemite, as well as carbon black.

4.4.3.4. Conclusions

The scientific investigations showed that many of the identified pigments in the mural painting align with both the period of its creation and the artistic technique used (*a secco*). Based on the findings described above, it can be concluded that XRF is highly valuable in obtaining essential information about a significant portion of the pigments used in 18th-century paintings. However, it also revealed some uncertainties and complexities, prompting the need for further analysis. To fully grasp the pigments used (especially as yellow, blue, and green pigments), the painting's artistic techniques and restoration history, additional research and in-depth examinations are essential. The investigation sets the foundation for a more comprehensive understanding of this precious artwork's story and conservation needs.

Besides pigment identification, the XRF also highlighted the possible presence of the migration process of degradation products of arsenic-based pigments. Their presence in different areas from the initial pigment placement calls for measures to ensure the safety of conservation work and the development of appropriate cleaning methodologies for the painting (Udrea, Măruțoiu, and Nemeș 2022).

Chapter 5. Final Conclusions

The results of the investigation have provided valuable insight into the identity and character of the materials used in some artworks, created by two of the most important Romanian iconographers of the 18th century: Dumitru Ispas and Grigore Ranite. Dumitru Ispas was an active painter in the Cluj and Sălaj regions of Romania, while the artworks of Grigore Ranite can be found throughout Transylvania, Oltenia, and Banat in Romania.

The detailed conclusions and recommendations corresponding to the scientific investigation of each artwork have been presented in Chapters 4.1-4.4. Here, the general conclusions will be summarised.

The mural paintings in the investigated artworks had a wooden support. The ground layers were made using gesso grosso, gesso sottile, and animal glue. The painting layers were applied on dry ground (*a secco technique*) using *tempera grassa* as a binder.

Dumitru Ispas, the iconographic painter who created the mural paintings in the wooden churches of Agârbiciu and Straja, used various pigments, including hematite, red lead, cinnabar, realgar, orpiment, calcite, lead white, goethite, early Prussian blue, bone black, magnetite, malachite, and late Scheele green or early emerald green. He often mixed orpiment with calcite and early Prussian blue with calcite to achieve certain colours.

The mural painting in the wooden church of Someșul Rece proved to be more complex, with different pigments used for paintings of the same colour in the investigated areas of the altar, iconostasis, nave and narthex. For instance, green earth pigment and copper-based pigments were used for the green colour in the altar and narthex, while in the nave, the green colour was obtained either by mixing orpiment with early Prussian blue or by using a green earth pigment contaminated with arsenic. The presence of arsenic contamination can be correlated with its natural origin and the degradation of arsenic-based pigments in the painting, influenced by the migration of water molecules in the stratigraphy. The yellow areas were created with orpiment and yellow ochre, and possibly with chalcopyrite or synthetic colourant (azo-azomethine dyes) (Salem, 2017). The latter two materials have not been found in the Transylvanian artworks, according to the literature. Other identified pigments include hematite (and probably lepidocrocite), red lead, cinnabar/vermilion, realgar, and early Prussian blue. The latter pigment was mixed with lead white in the altar area and with calcite in the iconostasis and narthex areas.

In Grigore Ranite's icon, the scientific investigation of the wood support identified the essence and state of preservation of the main components of the cellulose fibre. The pigments used in the icon included red lead, cinnabar / vermilion, white lead, early Prussian blue, malachite, verdigris, copper resinate, earth pigments, bone black, and various ochres (hematite, goethite, magnetite). Gold leaf was also used in the artwork. The variety of varnish ingredients (linseed oil, beeswax, shellac, colophony, sandarac, resin from conifers), as well as the degradation products of the painting materials, confirmed the authenticity of the icon.

The complementary diagnostic techniques were helpful in identifying and characterising the materials used in the artworks. XRF was particularly valuable due to its rapid execution and non- invasive nature, allowing for the identification of the elemental chemical composition of the paintings in several representative areas. Strontium in the XRF-investigated painting areas could confirm the authenticity of the materials, while the presence of barium was essential in identifying the late Scheele green or early emerald green pigment in the narthex painting of the Agârbiciu church.

The r-FTIR technique was extremely useful in quickly identifying the minerals in the ground layer, certain pigments, and the type of tempera and artistic techniques used in the investigated artworks. On the other hand, the t-FTIR technique played a vital role not just in identifying and characterising the organic and inorganic materials in the paintings, but also in identifying additives and degradation products. Their identification played a crucial role in our analysis. Notably, it enabled the early identification of Prussian blue. For instance, when pinpointing this pigment, the elemental chemical composition acquired via XRF investigation proved to be a pivotal factor. In the context of the mural painting within the wooden church of Agârbiciu, the presence of cinnabar in the form of mercury sulphide was revealed by the quart, shedding light on the materials used. This same mural unveiled the existence of carbonate compounds such as aragonite, calcite, and dawsonite, alongside realgar. This combination strongly suggested these materials likely originated from the eastern part of the Transylvania basin.

Another group of pigments, whose presence was confirmed through the analysis of degradation products using t-FTIR, pertained to those based on arsenic sulfide. The identification of these degradation products holds paramount significance due to their heightened toxicity compared to the pigments themselves. A concise overview of the various arsenic compounds and their behaviour in the context of painting was briefly outlined in the article (Udrea, Măruțoiu, and Nemeș, 2022).

FTIR was also used with GC-MS to identify the type of lipid-based binder used in the mural painting of the Agârbiciu church. This chromatographic technique showed that linseed oil was used in *tempera grassa* and confirmed the presence of egg yolk. Additionally, the DSC technique was used to identify and to assess the state of preservation of the canvas used between the wooden beams of the support and the ground layer of the mural painting in the Agârbiciu church.

The knowledge of the aspects described in this thesis is of particular importance both for the dating and authentication of the investigated works of art, as well as in the planning of future methodologies for the diagnosis, restoration and conservation of the works of art, as well as regarding the protection measures at work and health of personnel involved in the field of research and/or conservation of cultural heritage.

Comprehending the facets described in this thesis holds paramount significance, serving dual purposes: firstly, aiding in the precise dating and authentication of the examined artworks; and secondly, informing the blueprinting of prospective methodologies for the diagnosis, restoration, and conservation of these artworks. Furthermore, it bears relevance to the implementation of protective measures for both the artworks themselves and for the well-being of those personnel engaged in research and cultural heritage conservation efforts.

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