ON THE ARTISTIC MATERIALS OF TWO 19th CENTURY WOODEN ICONS FROM "ANNUNCIATION" CHURCH IN GALAȚI, ROMANIA

Victoria ATANASSOVA [1], Sultana-Ruxandra POLIZU [2,3]

This paper studies two 19th century wooden icons from the "Annunciation" church in Galați, Romania. The artistic materials of the paintings, investigated through optical microscopy, XRF, LIBS, and FTIR, comprised shellac varnish, metallic and earth pigments in oil binder in the pictorial layers, and calcite, lipid binder, gypsum, zinc and lead whites in the preparation layers. One of the icons had golden embellishment attached to the ground through lead-enriched adhesive of protein and resin.

These findings shed light on the painting techniques used in Eastern Orthodox art in the 19th century and also support the restoration process of both icons.

Keywords: 19th century wooden icons, FTIR, XRF, LIBS, aged oil paintings, golden decorations.

1. Introduction

The church dedicated to the "Annunciation", is a religious building in the central area of the city of Galați located in the eastern part of Romania. The church was built between 1856 and 1859, and the execution of the sculpture of the iconostasis and the painting of the icons were done in 1872, in a manner specific to the mid-nineteenth century [1]. The style of painting and the making of the iconostasis was strongly influenced by the western artistic currents which penetrated through the Greek space, but also through the Slavic one. The painting of the iconostasis presented a way of passing from tradition to novelty. The painting was done in tempera technique with egg yolk binder with the addition of oil (linseed). The polishing of the sculptural elements was done with gold leaf applied on a red polishing (bolus) [2].

Part of the iconography of the church is the 4 icons situated on the porch. Two

[1] Researcher, Center of Excellence for Restoration by Optoelectronic Techniques, National Institute of Research and Development for Optoelectronics – INOE 2000, Atomistilor str. no. 409, Magurele city, Ilfov County, Romania, e-mail: victoria.atanassova@inoe.ro

[2] Assist. Prof., Dept. of Systematic Theology, Practice and Sacred Art, Faculty of Orthodox Theology "Justinian the Patriarch", University of Bucharest, Str. Sfânta Ecaterina, Nr. 2-4, Post code 040155, Sector 4, Bucharest, Romania, e-mail: surupo@yahoo.com

[3] Paintings conservator (restorer), Iorux Restorations Laborator Conservare-Restaurare Pictură, Str. General Mihail Cerchez nr. 11, sector 4, Bucharest, Romania, e-mail: surupo@yahoo.com

of them depicting the *'Spring of Healing'* and *'Mother of God with the Child represented with crowns'* (Fig. 1) are the subject of the current investigation. The focus is to reveal part of the set of artistic materials used by the iconographer with the intent to gain important knowledge regarding the manufacturing of the icons and to assist the restoration process. The applied analytical methodology included optical microscopy (OM) investigating the morphology and, where possible, the cross-section of the pictorial layer, X-ray fluorescence spectroscopy (XRF) and laser-induced breakdown spectroscopy (LIBS) providing the elemental composition as the latter adds an in-depth investigation of the stratigraphy, and Fourier-transform infrared spectroscopy (FTIR) bringing details about the molecular composition of the painting materials.

2. Materials and methods

2.1. Wooden icons

The study was focused on two icons from the porch of the Annunciation church, which depict the *'Mother of God with the Child represented with crowns'*, hereafter named icon MD, and *'Spring of Healing'*, hereafter named icon IT. They were painted on panels of linden wood (the main material used by the iconographers applying the wooden icon technique [3]) with equal dimensions of 66 x 100 cm by an unknown painter in the second half of the 19th century. The icons were in a degraded state of conservation which hindered the aesthetical look and the long-term preservation of the paintings' integrity. Also, the initial varnishes of the icons were extremely aged, browned, thick, with a lot of dust, deposits, greasy smoke from candles and serious changes in their original chromaticity. Thus, the establishment of a proper restoration protocol was needed. It was supported by a detailed investigation which provided further insights into the pictorial materials used. For this purpose, small detached samples from four areas (Fig. 1) of each icon were collected by a restorer. The samples collected from MD had the pictorial layer strongly attached to the wooden support, while the samples from IT consisted of the pictorial layer with the ground fully detached from the wooden support which made the direct investigation of the preparation layer possible as well. All the analyses were performed only on the samples. Although the physical degradation of the icons was not monitored here, future studies could be done employing 3D models as demonstrated on similar artworks in [4], [5].

2.2. Microscopical observations

The samples were observed under a Leica M205FA fluorescence stereomicroscope. Photomicrographs were acquired with the 0.63 × PlanApo objective, at different magnifications, ranging from 12× to 100×. The acquired images with a relevant scale are shown in Table 1.

Fig. 1. The objects of investigation and the sampling areas are shown in the pictures. A) icon *'Spring of Healing'*. B) icon *'Mother of God with the Child represented with crowns'*. The description of the samples is given in Table 1.

2.3. Molecular analysis

FTIR was applied on the samples operated in attenuated total reflectance (ATR) mode using a Perkin Elmer Spectrum Two FTIR spectrometer equipped with a PIKE GladiATR accessory. Spectra were acquired in the 4000–380 cm^{-1} spectral region, at a resolution of 4 cm^{-1}, with an average of 32 scans. They are presented in transmission (%T), with automatic correction of the CO_2 lines and the baseline. Data processing was done with OriginPro 2021b. Peak identification was done based on the literature. Fig. 2 shows part of the acquired spectra. The spectra of the preparation layers of samples IT-1,2,4 are similar so only the spectrum of sample IT-1 is shown as representative. The spectrum of the preparation layer of IT-3 distinguishes it from the others, hence it is plotted separately. The spectrum of sample MD-1 is not presented here as it shows only degradation species of linden wood.

2.4. Elemental analysis

Due to the complex infrared spectra showing a lot of overlapping bands of the painting components in the fingerprint region, the XRF technique was used to provide complementary information about the pigments, possible fillers and the preparation

layer. XRF was performed with a portable, hand-held energy dispersive instrument from Brucker Elemental. The TRACER III-SD equipment has a Rh-anode X-ray tube and Si-PIN detector with a typical resolution of 190 eV at 10,000 cps and the spot size of the instrument is ~ 3 × 4 mm. The equipment has an integrated camera for precise positioning on the investigated area. For this study, the current intensity was set at 10.60 μA and the tube voltage was set at 40 kV. Measurements were recorded in air atmosphere, for 60 s, without filtering of the X-ray beam. The energy response was recorded between 0 and 40 keV, with the S1 PXRF software (Bruker AXS Handheld Inc.). The elemental identification was done by applying the standard Bayesian deconvolution with the ARTAX software (version 7.4.0.0, Bruker AXS MA) and data post-processing was performed with OriginPro 2021b. Part of the acquired spectra are shown in Fig. 3. Samples IT-1, 2 show spectral features similar to the rest of the samples and are not presented here. The spectra of the painting and the preparation layers of samples IT-3 and IT-4 are compared and shown on the graphs. Samples MD-2 and MD-3 have similar spectra, too. Thus, only MD-3 is shown as representative of both. Sample MD-1 containing wood was not analysed.

2.5. Stratigraphic elemental analysis

LIBS was applied as a complementary method for the in-depth elemental investigation of the MD samples aiming to obtain information about the materials used in the preparation layer of the icon. The potential of the technique for a nearly non-destructive depth-profiling with high accuracy was demonstrated in a lot of studies [6], [7]. The LIBS spectra were recorded by accumulating 10 pulses using a handheld spectrometer from SciAps that operates in Argon purge environment. The laser used for irradiation is a Q-switched Nd:YAG, generating at 1064 nm, an energy of 5 mJ, pulse width 8 ns, frequency 1-20 Hz, and a laser spot with a diameter of 50 μm. The system is equipped with three spectrometers that provide a spectral range from 190 nm out to 950 nm. The chemical lines within the spectra were identified using the NIST database [8]. Parts of the spectra acquired on sample MD-4 are shown in Fig. 4.

3. Results

The icons consist of polychrome paintings with different colours and shades laid on wooden panels. A large part of the results in this study is shown below. Table 1 presents them in a synthesised manner for better understanding.

3.1. Protective varnish

The visual inspection of IT showed the presence of a thick layer of yellowed aged varnish which was observed under the microscope on samples IT-1 and IT-2. According to traditional craftsmanship, transparent protective layers were applied to

the icons after drying for greater gloss and brilliance, enhancing the chromaticity of the painting. During the ages, natural resins were the most used varnishes. But their main drawback is the limited stability as ageing makes them hard and very brittle with a yellow to brownish hue owing to the natural photo-oxidation process [9]. Here, the protective varnish was identified as shellac resin by ascribing its main characteristic bands in the FTIR spectra (Fig. 2, A). The broad band centred at 3382 cm^{-1} is due to the O-H stretching vibrations. The peaks at 2920 cm^{-1} and 2855 cm^{-1} are attributed to the CH_2 asymmetric and symmetric stretching bands of the fatty acids, respectively. The sharp intense peak at 1708 cm^{-1} comes from the C=O stretching of the carboxylic acid. The peaks at 1453 and 1383 cm^{-1} arise from the bending or scissoring of the CH_2 groups, and the asymmetric and symmetric stretching vibrations of the CH_3 groups, respectively [10]. Other detected features are the band coming from the ester bending mode ranging from 1244 – 1253 cm^{-1} in all the spectra, the absorptions at 1162 cm^{-1}, 1109 cm^{-1}, 1034 cm^{-1}, and a broadened peak at 601 cm^{-1} [11], [12].

Although the presence of protective varnish on MD is expected, its characteristic IR bands couldn't be distinguished. A possible explanation could be the observed complex spectral features masking the prominent peaks.

3.2. Binder

Until the 19th century and even later, the icons were painted in the traditional tempera technique which consists in mixing the pigments with protein binder (chicken egg yolk) [3]. In the 19th century, the oil technique was introduced on large scale in the Romanian style and the iconographers started to paint in oil or mixed oil-tempera [3]. The FTIR analysis didn't distinguish any proteinaceous materials associated with the tempera technique. On the other hand, the characteristic bands of oil were detected (Fig. 2, A, C). The peaks at 2920 and 2855 cm^{-1} identified as moieties of the varnish, could be ascribed to oil as well. The main carbonyl (C=O) peak at 1732 cm^{-1} arising from the ester bonds between glycerol and fatty acids appeared broadened and lower in intensity owing to the addition of new poorly resolved features resulting from the ageing of the oil [13]. The peak at 1708 cm^{-1} was assigned to the carbonyl stretching absorption in carboxylic acid, and the shoulder at 1775 cm^{-1} was ascribed to long-term ageing oil [14], [9]. The formation of carboxylic acids is commonly associated with the oxidative processes in drying oils [13], [14]. The deformation of the ester triplet consisting of the peaks at 1246, 1162, and 1094 cm^{-1} is another characteristic of the aged oil [13]. This deformation could be influenced by the bands of the varnish, too, since in the infrared spectrum they overlap. Additional bands assigned to CH_2 bending mode (1453 cm^{-1}), moieties of carboxylic acid (1412 cm^{-1}) [13], and metal carboxylates (1620, 1383, and 1378 cm^{-1}) [14] were observed in the spectra of the MD samples (Fig. 2, C).

3.3. Pigments

The XRF spectra of samples IT-1, IT-2 (spectra not presented here) and MD-4 (Fig. 3) showed iron (Fe) via the characteristic K_α peak at 6.4 KeV as a minor element. The presence of Fe in sample MD-4 was corroborated by LIBS as well (Fig. 4). On the other hand, the corresponding FTIR spectra (Fig. 2, A, C) detected the characteristic peak of the stretching vibration of the nitrile group (C≡N) at 2093 cm^{-1} along with the Fe-N stretch at 605 cm^{-1} indicating the use of the pigment Prussian blue ($Fe_4[Fe(CN)_6]_3$) [15]. It is an iron-based pigment that explains the occurrence of Fe in the related XRF spectra. Possible traces of barium sulphate ($BaSO_4$) were identified as well via the weak peaks at 633 and 605 cm^{-1} (asymmetric bending of SO_4^{2-}), and the shoulder at 984 cm^{-1} (symmetric stretching of SO_4^{2-}) [16], [17]. This finding was verified by XRF (BaL_α line at 4.48 KeV and BaL_β line at 4.82 KeV) and LIBS (Ba II line at 493.4 nm) only for MD-4. Moreover, comparing the LIBS spectra of each of the 10 pulses penetrating in the depth of the layers, it can be seen that the signal of the barium line is stronger at the 3rd pulse (Fig. 4). It could be hypothesized that the barium sulphate might come from the pigment as it was used as an extender of Prussian blue [15]. In another similar study of a 19th century Lipovan icon [18], the occurrence of barium sulphate in the pictorial layer was suggested to originate from previous restoration interventions, as this substance is frequently used as mineral filler in modern conservation materials. To the authors' best knowledge, such previous interventions of the icons were not conducted.

The detection of a blue pigment on the sample taken from a green coloured area (IT-1) infers a mixture with yellow pigment. The XRF spectra didn't show any other specific lines except iron which could suggest the pigments used. The identification of kaolinite (1008 cm^{-1}, 912 cm^{-1}), quartz (799 cm^{-1}), and iron oxides (532 cm^{-1}, 467 cm^{-1}) in the infrared spectrum of IT-1 implies the use of an earth pigment [19]. Hence, it could be deduced that the pigment in the mixture is yellow ochre.

The elemental analysis of sample IT-4 unveiled the presence of the characteristic lines of mercury (Hg) at 9.9 KeV (L_α) and 11.8 KeV (L_β) as a major element (Fig. 3). This leads to the conclusion that the pigment is cinnabar (HgS). The corresponding FTIR spectrum couldn't corroborate this result since cinnabar doesn't have characteristic absorptions in the analytical IR region. On the other hand, lead white ($PbCO_3$) was identified only in this sample via the carbonate stretching vibrations at 1402 cm^{-1} (broad), 1041 cm^{-1} (sharp, overlapped), and 681 cm^{-1} (sharp) [20], [21]. The characteristic XRF lines of lead (Pb) at 10.6 KeV (L_α) and 12.6 KeV (L_β) were also detected in both the pictorial and the preparation layers but they were more intense in the pictorial layer rather than the preparation. The strong appearance of lead white in sample IT-4 could be explained by its addition in a mixture with cinnabar to prevent the red pigment's common darkening when exposed to light [22]. The characteristic XRF lines of Pb were detected in the pictorial layers of the other samples as well but

the related FTIR spectra didn't show any features of lead-based substance.

Characteristic FTIR peaks ascribed to natural earth pigments were registered in all the MD samples (Fig. 2, C). The aluminosilicate kaolinite was detected by its vibrations at 1033 cm^{-1} (Si–O–Si), 1007 cm^{-1} (Si-O-Al), and 912 cm^{-1} (Al-O-H). Low amounts of quartz were also noticed by the weak bands of the doublet at 799 cm^{-1} and 779 cm^{-1}. Diagnostic peaks of iron oxides present as hematite were identified at 523 cm^{-1} and 464 cm^{-1} as well [19]. For the black colour of sample MD-2, no characteristic bands were distinguished that could imply a possible animal origin of the black pigment such as bone black. The XRF analysis detected only traces of manganese (Mn) so the possibility of Mn-based black pigment was rejected. On the other hand, Fe was detected inferring that the pigment used is iron-based or carbon black [23].

The olive shade of the background of the scene from which the sample MD-3 was taken suggested that a mixture of colours was used composed of black and yellow pigments [24]. The XRF spectra of both MD-2 and MD-3 showed similar composition (Fig. 3), and the FTIR analysis indicated the presence of earth pigments inferring that the background was painted by mixing carbon black and yellow ochre pigments, although additional pigments could also have been used to obtain this specific shade such as green earth and burned or natural umber as indicated in a similar study [25].

The presence of zinc (Zn) was revealed via XRF, represented by the K_α line at 8.64 KeV and the K_β line at 9.56 KeV, as a major element in both the painting and the ground layers, with the characteristic lines being more intense in the first. Such high zinc signal is not uncommon in religious painting [26], as zinc white (ZnO) could have been used both as a pigment and in the preparation layer. On the contrary, the LIBS analysis revealed that Zn lines (Zn I at 481.1 nm) were more intense at higher pulses (Fig. 4) suggesting that it might be an additive in the preparation layer of MD. The appearance of Zn in the pictorial layer was confirmed via FTIR as well by the detection of zinc carboxylates (degradation products of the interaction of Zn-based pigment with the drying oil) via a sharp band ranging between 1537 and 1554 cm^{-1} for the different samples [27]. Zinc white has been used as a pigment since 1834 [28] which follows the initial estimation that the icons were manufactured in the second half of the 19th century.

A significant presence of gypsum ($CaSO_4 \cdot 2H_2O$) in all the samples of MD was found through FTIR with the main contributions at 3529, 3396 cm^{-1} (stretching O-H), 1683, 1618 cm^{-1} (bending O-H), 1111 cm^{-1} (stretching SO_4^{2-}), and 663, 601 cm^{-1} (bending SO_4^{2-}) [26], [29]. This component might come either from the pigments used as an extender [30] or from the preparation layer.

Weak absorptions ascribed to calcite ($CaCO_3$) (broad overlapped band around 1400 cm^{-1} assigned to the CO in-plane asymmetric stretch, and weak sharp peaks at 875 and 713 cm^{-1} assigned to CO_3^{2-} out-of-plane bending mode and Ca-O in-plane bending mode, respectively [31]) along with calcium oxalate (1318 cm^{-1} assigned to the asymmetric stretch of the CO group [32]) which is a degradation product of the

organic binder [33] were detected in the pictorial layer of all of the samples. This finding was confirmed by the detection of the diagnostic K_α and K_β lines of calcium (Ca) at 3.69 KeV and 4.02 KeV, respectively [20] through the XRF technique. It could be assumed that $CaCO_3$ was used as a pigment extender or the detected bands could come from the preparation layer.

The FTIR spectrum of sample MD-4 revealed the strong presence of beeswax detected via the C-H stretching vibrations at 2956 cm^{-1} (CH_3), 2920 cm^{-1} (CH_2), and 2850 cm^{-1} (CH_2), the carbonyl stretching band at 1737 cm^{-1} overlapping with the oil, the sharp C-H bending vibrations at 1472 cm^{-1} (CH_2) and 1462 cm^{-1} (CH_3), and the sharp doublet at 731 and 719 cm^{-1} [34]. This discovery agreed with the microscopical observations as well. Usually, beeswax was used as either a protective coating or for the consolidation of paint layers and masking of defects [16]. However, the absence of characteristic features of beeswax in the other samples and the lack of documents regarding some previous restoration of the icon suggested that it is a contamination product from the candles in the worshipping ceremonies in the church.

3.4. Metallic embellishment

Sample IT-3 was taken from the golden background of the scene depicted on the icon. Its cross-section is observed under the microscope (Table 1). Three layers can be seen: a thin golden leaf (approx. 10 μm), attaching layer (approx. 10 μm), and the preparation layer. A common practice during the post-Byzantine period was the embellishing of fields, haloes, and various other details on the icons by applying a golden leaf with minor admixtures of silver and copper [35]. The XRF spectra identified the L_α line at 9.7 KeV and the L_β line at 11.4 KeV of gold (Au). Copper (Cu) was also identified with the K_α line at 8.04 KeV and the K_β line at 8.9 KeV. Given that Cu is detected in all of the samples as a minor element, it is not clear if it originates from the metallic leaf or some impurity. Other elements indicating the use of metal alloy were not detected. Another similar study on 19th century wooden icons from the same region indicated that the gold leaf was replaced with a silver leaf covered with varnish or with yellow metallic pigments (realgar or orpiment) [25]. However, the current study is not following these findings which infers diverse trends in the 19th century craftsmanship from this area.

Usually, the metal leaf was attached to the surface through proteinaceous or oily gluing earth bolus [35]. The initial observations of the iconostasis in the church [2] showed the use of a red bolus under the golden leaf, which is a common practice of the iconographers. However, the microscopic examination of the cross-section of the sample IT-3 didn't indicate the use of such material. Moreover, the FTIR spectrum (Fig. 2, A) detected some broad bands around 1621 cm^{-1} (C═O stretching of amide I), and 1539 cm^{-1} (combination of N─H bending and C─N stretching of amide II) ascribed to proteinaceous material (animal glue) [16]. The sharp bands at

2922 and 2853 cm^{-1} together with the poorly resolved triplet at 1773, 1732, and 1708 cm^{-1} infer the presence of lipids which might be due to the varnish or oil moieties in the attachment layer. The infrared spectrum of the preparation layer (Fig. 2, B) showed the presence of calcite, proteins (1657 cm^{-1}, and 1530 cm^{-1}), and some distinctive features of shellac resin (the C-H stretching modes at 2922 and 2850 cm^{-1}, the ester band at 1708 cm^{-1}, the absorptions at 1162 cm^{-1}, 1109 cm^{-1}, 1034 cm^{-1}, and the broadened peak at 601 cm^{-1}) which were not observed in the preparation layers of the rest of the samples. The XRF spectrum of the pictorial layer of sample IT-3 revealed the presence of Pb lines at relatively higher net count rates compared with the other elements detected. The appearance of this element in the adhesive mixture is not unusual as it is known that lead could be used as a drier in adhesives [35]. Thus, it could be deduced that the gold leaf was applied over a resin layer in a lead-enriched mixture with animal glue which served as attaching medium to the ground. A similar case is documented in another study on an 18^{th}-century Taskin harpsichord [36].

3.5. Preparation layers

The photomicrographs of the cross-sections of the MD samples revealed a thin whitish preparation layer under the examined pictorial layer. As there was no possibility for a direct investigation of this layer, we applied an in-depth stratigraphic analysis performed by LIBS. Fig. 4 shows Ca as a major element rather coming from the preparation layer as the intensity of the presented line (Ca II at 396.84 nm) becomes higher at the higher pulses. Lead was also found to be with higher intensity of the lines (Pb I line at 406.7 nm in Fig. 4) at the higher pulses. We could assume that the ground layer consists of a mixture of calcite, gypsum, and/or lead.

On the other hand, the XRF analysis of the preparation layer of the IT samples showed Ca as a major element. It was observed that the lines in the ground layer were more intense compared to the lines detected in the painting (Fig. 3), which was in accordance with the molecular analysis. The characteristic FTIR bands of calcite (weak peaks at 2514 cm^{-1}, 1794 cm^{-1}, intense broad band at 1390 cm^{-1}, and strong sharp peaks at 873 cm^{-1} and 713 cm^{-1}) were found more prominent in the ground compared with the painting (Fig. 2, B) as well. Additionally, some features of lipid-containing binder applied as a sizing agent in the preparation layer were observed via the sharp C-H absorptions at 2924 and 2852 cm^{-1}, and the broadened band including the poorly resolved carbonyl stretching absorptions of the ester bond at 1737 cm^{-1} and the carboxylic acid at 1713 cm^{-1}. Similar preparation layers were reported in the studies of other artworks [32] and icons [16] from different ages as well.

In early times, a mixture of calcite and animal glue was used to make the ground layer of panel paintings aiming to produce a proper white background for painting [20]. In the current case, proteinaceous materials were not found, but only small amounts of

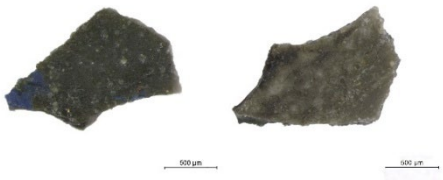
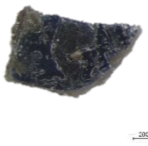
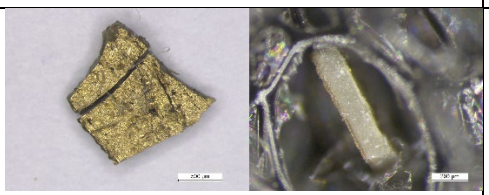
lipids inferring the use of oil. The detection of Zn and Pb might come from the pictorial layer given that the characteristic XRF lines are stronger compared with the ground. Nevertheless, it is documented that sometimes lead white and zinc white could be mixed with calcite to make the preparation layer denser and whiter [20].

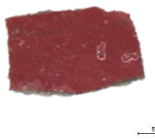
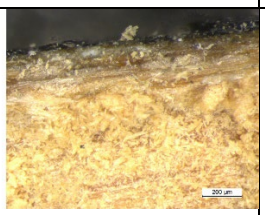
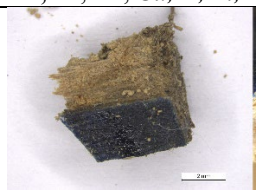
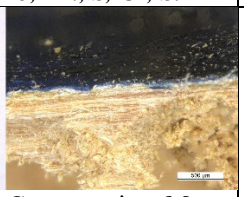
3.6. Wooden support

Sample MD-1 taken from the wooden support of the icon was analysed only by FTIR for complementarity and to exclude possible bands of wood interfering with the rest of the spectra. Its spectrum (not presented here) showed decaying linden wood indicating features of lignin (1593, 1504, and 1456 cm^{-1}), cellulose (1422, 1319, 1160, 1107, 1033, and 898 cm^{-1}), and hemicellulose (1370, 1160, 1107, and 1033 cm^{-1}) [29], [37], [38].

Table 1

Synthesised results of the physicochemical analysis of the icons' samples

ID	Description	Micro details	FTIR identified compounds
IT-1	background green colour taken from the right side of the composition, towards the bottom	 Painting, M* x50 Ground, M x50 XRF detected elements** Painting: **Zn, Ca**, Fe, Pb, Cu, Ti, Mn, *S, Cr, Si*	Protective varnish: shellac; Pigment: Prussian blue, yellow ochre (kaolinite, quartz, iron oxides), barium sulphate; Binder: linseed oil Preparation layer: calcite, lipids; Degradation products: carboxylic acid, metal carboxylates (zinc stearate), calcium oxalate
IT-2	blue colour taken from the sleeve of the figure's coat placed on the right side of the scene, towards the bottom	 Painting, M x80 XRF detected elements** Painting: **Ca, Zn**, Fe, Cu, Ti, Mn, Pb, *S, Si* Ground: **Ca**, Zn, Fe, Cu, Mn, *Ti, Pb, S, Si*	Protective varnish: shellac; Pigment: Prussian blue, barium sulphate; Binder: linseed oil; Preparation layer: calcite, lipids; Degradation products: carboxylic acid, metal carboxylates (zinc stearate), calcium oxalate
IT-3	gold background taken from the top side	 Painting, M x50 Cross-section, M x50	Protective varnish: shellac; Metal leaf attachment: protein (animal glue), resin; Preparation layer: calcite, gypsum, resin; Degradation products: carboxylic acid, metal

		XRF detected elements** Painting: **Zn, Pb,** Ca, Fe, Cu, Au, Ba, *S, Si* Ground: **Ca, Zn, Pb,** Fe, Cu, *Ti, Sr, Si, S*	carboxylates (zinc stearate), calcium oxalate
IT-4	red colour taken from the left sleeve of the archangel's robe holding the crown of the Mother of God, the top side	 Painting, M x50 XRF detected elements** Painting: **Zn, Hg,** Fe, Ca, Pb, Cu, *Ti, S, Si* Ground: **Zn, Ca,** Fe, Pb, Cu, Hg, Mn, Ti, *Cr, S, Si, P*	Protective varnish: shellac? Pigment: lead white, cinnabar doesn't show absorption in the mid-IR; Binder: linseed oil; Preparation layer: calcite, lipids; Degradation products: carboxylic acid, metal carboxylates, calcium oxalate
MD-2	black colour taken from the border, left bottom side	  Painting, M x15 Cross-section, M x80 XRF detected elements** **Zn,** Fe, Ca, *Pb, Cu, S, Ti, Cr, Mn, Sr, Si, K*	pigment: earth pigment – kaolinite, quartz, iron oxides, gypsum; preparation layer: gypsum, calcite; binder: linseed oil; degradation products: carboxylic acid, metal carboxylates (zinc oleate), calcium oxalate
MD-3	background ochre colour taken from the right bottom side	  Painting, M x15 Cross-section, M x100 XRF detected elements** **Zn,** Fe, Ca, *Cu, K, Ti, Pb, Mn, S, Cr, Si*	pigment: kaolinite, quartz, iron oxides, gypsum; preparation layer: gypsum, calcite; binder: linseed oil; degradation products: carboxylic acid, metal carboxylates (zinc stearate), calcium oxalate
MD-4	blue colour taken from the garment of the Mother of God, bottom side	  Painting, M x12 x50 Cross-section, M XRF detected elements** **Zn,** Fe, Ca, Pb, *Ba, S, Cu, Mn, K, Sr, Si, P*	Pigment: Prussian blue, gypsum, barium sulphate; preparation layer: calcite, gypsum; binder: linseed oil; degradation products: carboxylic acid, metal carboxylates (zinc stearate), calcium oxalate; contamination product: beeswax

*M – magnification;
**bold letters denote major elements, regular letters denote minor elements, and italic letters denote trace elements

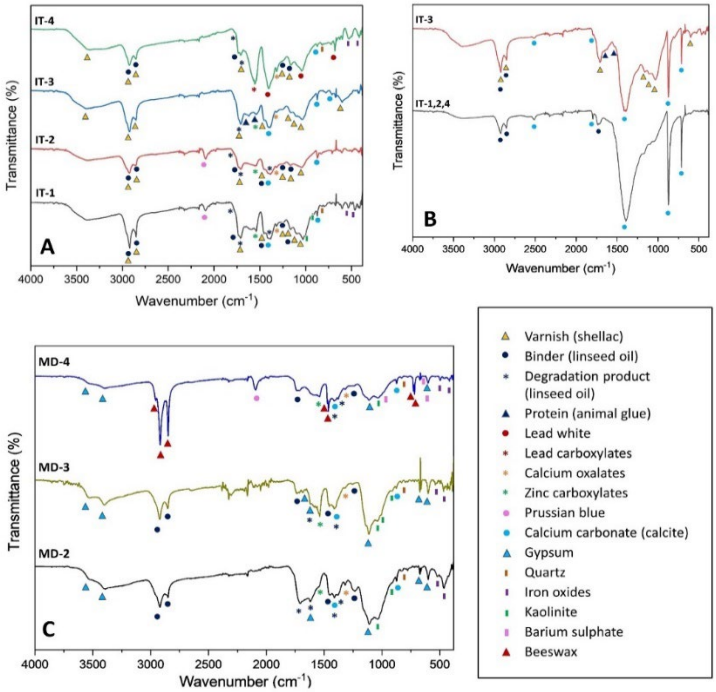


Fig. 2. FTIR spectra of the analysed samples of the icons

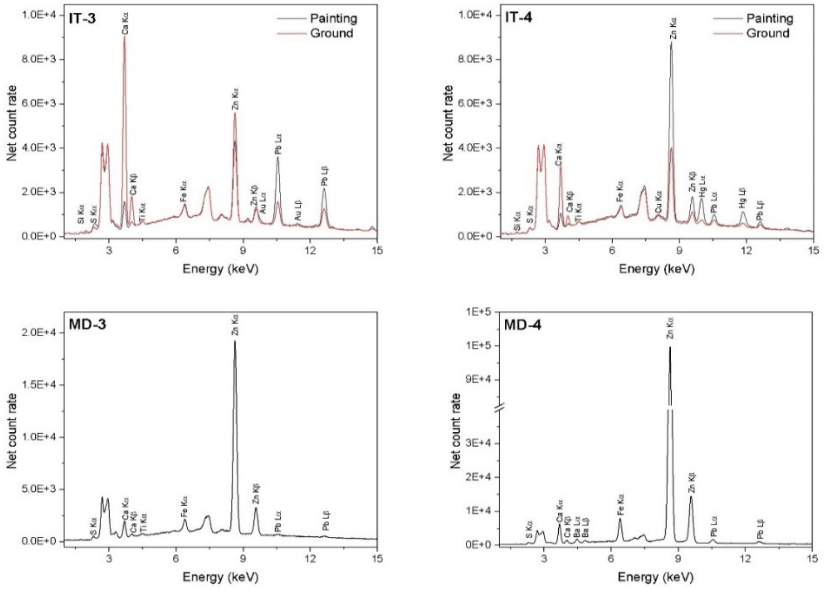


Fig. 3. XRF spectra of the analysed samples of the icons

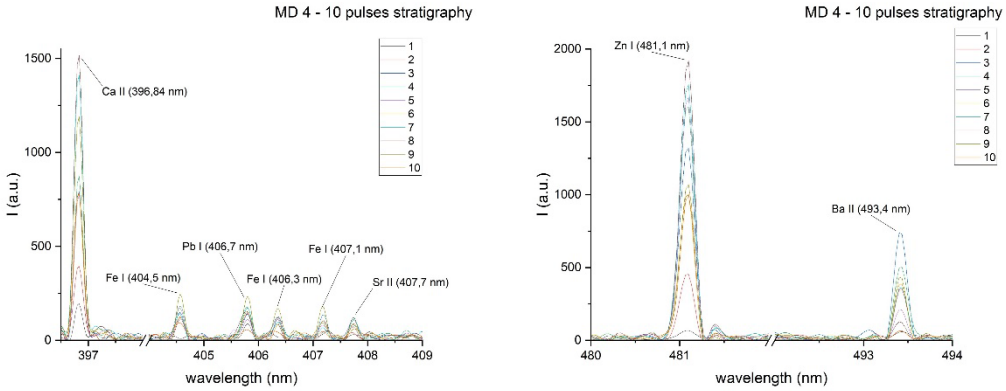


Fig. 4. Parts of the LIBS spectra of sample MD-4.

4. Conclusion

The artistic materials of two 19th century wooden icons from "Annunciation" church in Galați, Romania, depicting *'Spring of Healing'* (IT) and *'Mother of God with the Child represented with crowns'* (MD) were studied. Micro details of the painting layers were investigated via optical microscopy. X-ray fluorescence, laser-induced breakdown spectroscopy, and Fourier transform infrared spectroscopy were employed to identify both the organic and inorganic materials used in the pictorial and the preparation layers. It was found that the icons were painted in oil technique. A thick layer of degraded varnish, most probably shellac, was observed as a coating on IT. Part of the color palette was revealed including earth, iron- and mercury-based pigments. A mixture of cinnabar and lead white, Prussian blue, and its mixture with yellow ochre were used for the red, blue and green shades of IT, respectively. On the other hand, carbon black, a mixture of carbon black with yellow ochre, and Prussian blue were identified for the black, olive-green, and blue hues of MD, correspondingly. Small amounts of barium sulfate were detected most probably used as an extender of Prussian blue. The preparation layers were composed mainly of calcite in a mixture with a lipid-containing binder. They were applied on panels that showed features of decaying linden wood.

Very often, zinc and lead whites have been applied to the paintings to give lighter shades of the colors, to highlight parts, or to model the bodies under the paint, which explains their presence in the pictorial layer. They have been often added to the ground mixture as well to achieve the effect of a denser and whiter preparation layer which might justify their occurrence there. Moreover, zinc white has been used as a pigment since 1834 which confirms the initial estimation that the icons were manufactured in the second half of the 19th century.

FTIR analysis of the samples from MD detected a strong presence of

gypsum as well. It could originate from the pictorial layer being used as a pigment filler or from the ground layer.

The observations of both icons suggest a similar mechanism of aging based on the detected calcium oxalate, moieties of carboxylic acids, and zinc carboxylate which is the product of the long-term interaction of the Zn cations in zinc white and the free fatty acids in the oil binder.

The metallic leaf used as the embellishment of the background of IT was made by golden leaf attached to the preparation layer by a lead-enriched mixture of proteins (animal glue) and a resin (shellac). During the ages, such metal-leaf decorations became a common feature of the icons and besides the given aesthetic value, in the context of Eastern Orthodox art, they represented the divine glory.

Residues of beeswax were found on the surface of MD suggesting that it is a contamination product from the candles in the worshipping ceremonies in the church.

These findings shed light on the painting techniques and the materials used in Eastern Orthodox art in the second half of 19th century. They also present important information supporting the restoration process undertaken on both icons.

Acknowledgements

This work was supported by the Romanian Ministry of Research, Innovation and Digitalization, through P 1- Development of the national research-development system, 1.2 - Institutional performance - Projects to finance the excellence in RDI - 18PFE/30.12.2021 and Core Program 18N/08.02.2019, project PN 19-18.01.02.

REFERENCES

[1]. *P. Păltănea*, Istoria orașului Galați (History of the city of Galati), Editura Porto-franco, **vol. 1,2**, 1994.

[2]. *D. Handrea*, expert restaurare pictură, Proiect de conservare-restaurare a iconostasului, amvonului, tronului arhieresc, a icoanelor cu ancadrament și a icoanelor individuale aparținând bisericii Bunavestire, Municipiul Galați (Conservation-restoration project of the iconostasis, the pulpit, the hierarchical throne, the framed icons and the individual icons belonging to the church of the Annunciation, Galati Municipality), București, 2018.

[3]. *A. Baciu et al.*, "Comparative Study of the Painting Materials of a Series of Orthodox Icons on Wooden and Glass Support from Transylvania," in Current Analytical Chemistry, **vol. 6**, no. 1, Dec. 2009, pp. 53–59, doi: 10.2174/157341110790069655.

[4]. *L. M. Angheluță and R. Rădvan*, "Macro Photogrammetry for fhe Damage Assessment of Artwork Painted Surfaces," The International Archives of the Photogrammetry, Remote Sensing and Spatial Information Sciences, **vol. XLII-2/W15**, 2019, pp. 101–107, doi: 10.5194/isprs-archives-XLII-2-W15-101-2019.

[5]. *L. M. Angheluţă and A. Chiroşca*, "Physical degradation detection on artwork surface polychromies using Deep Learning models," Romanian Reports in Physics, **vol. 72**, 2020, p. 805.

[6]. *U. Pacher, M. Dinu, T. O. Nagy, R. Radvan, and W. Kautek*, "Multiple wavelength stratigraphy by laser-induced breakdown spectroscopy of Ni-Co alloy coatings on steel," Spectrochimica Acta Part B: Atomic Spectroscopy, **vol. 146**, pp. 36–40, Aug. 2018, doi: 10.1016/J.SAB.2018.04.006.

[7]. H. Sadek, A. Khedr, M. Simileanu, and R. Radvan, "Characterisation of lustre compositions from Egypt

by LIBS and IBA.," Dig J Nanomater Biostruct, **vol. 8**, no. 4, 2013, pp. 1357–1363.
[8]. A. Kramida, Yu. Ralchenko, J. Reader, and NIST ASD Team, "NIST: Atomic Spectra Database (version 5.9), [Online]," NIST Atomic Spectra Database (version 5.9), [Online]. Available: https://physics.nist.gov/asd [Mon Jul 11 2022]. National Institute of Standards and Technology, Gaithersburg, MD., 2021. https://physics.nist.gov/PhysRefData/ASD/Html/verhist.shtml (accessed Jul. 11, 2022).
[9]. *V. Ganitis, E. Pavlidou, F. Zorba, K. M. Paraskevopoulos, and D. Bikiaris*, "A post-Byzantine icon of St Nicholas painted on a leather support. Microanalysis and characterisation of technique," in Journal of Cultural Heritage, **vol. 5**, no. 4, Oct. 2004, pp. 349–360, doi: 10.1016/J.CULHER.2004.03.004.
[10]. *M. Abdel-Ghani*, "Dating A Coptic Icon of Anonymous Painter by Spectroscopic Study of Pigment Palette," in Mediterranean Archaeology and Archaeometry, **vol. 15**, no. 1, 2015, pp. 23–37.
[11]. *C. Mcglinchey, K. Buchberg*, M. Schreiner, and C. Org, "The examination of drawings by Georges Seurat using Fourier transform infrared micro-spectroscopy (micro-FTIR)," in e-Preservation Science, **vol. 6**, 2009, pp. 118–121.
[12]. *S. Vahur, A. Teearu, P. Peets, L. Joosu, and I. Leito*, "ATR-FT-IR spectral collection of conservation materials in the extended region of 4000-80 cm–1," in Analytical and Bioanalytical Chemistry, **vol. 408**, no. 13, May 2016, pp. 3373–3379, doi: 10.1007/S00216-016-9411-5/TABLES/1.
[13]. *J. van der Weerd, A. van Loon, and J. J. Boon*, "FTIR Studies of the Effects of Pigments on the Aging of Oil," in Studies in Conservation, **vol. 50**, no. 1, 2013, pp. 3–22, doi: 10.1179/SIC.2005.50.1.3.
[14]. *J. Pilc and R. White,* "The Application of FTIR-Microscopy to the Analysis of Paint Binders in Easel Paintings," in National Gallery Technical Bulletin, **vol. 16**, 1995, pp. 73–84.
[15]. *E. W. FitzHugh*, Artists' Pigments: a Handbook of Their History and Characteristics, **vol. 3**, National Gallery of Art, Washington, DC, 1997.
[16]. *I. M. Cortea, L. Ratoiu, A. Chelmuș, and T. Mureșan*, "Unveiling the original layers and color palette of 18th century overpainted Transylvanian icons by combined X-ray radiography, hyperspectral imaging, and spectroscopic spot analysis," in X-Ray Spectrometry, **vol. 51**, no. 1, Jan. 2022, pp. 26–42.
[17]. *S. Akyuz, T. Akyuz, G. Emre, A. Gulec, and S. Basaran*, "Pigment analyses of a portrait and paint box of Turkish artist Feyhaman Duran (1886–1970): The EDXRF, FT-IR and micro Raman spectroscopic studies," in Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, **vol. 89**, Apr. 2012, pp. 74–81, doi: 10.1016/J.SAA.2011.12.046.
[18]. *L. Ghervase, I. M. Cortea, R. Rădvan, L. Ratoiu, and A. Chelmuș*, "Complementary investigations of two Lipovan-style icons," in Microchemical Journal, **vol. 138**, May 2018, pp. 509–518.
[19] *C. Genestar and C. Pons*, "Earth pigments in painting: Characterisation and differentiation by means of FTIR spectroscopy and SEM-EDS microanalysis," in Analytical and Bioanalytical Chemistry, **vol. 382**, no. 2, May 2005, pp. 269–274, doi: 10.1007/S00216-005-3085-8/TABLES/6.
[20]. *R. Ashok*, Artists' Pigments: a Handbook of Their History and Characteristics, **vol. 2**, National Gallery of Art, Washington, DC, 1993.
[21]. *R. J. Meilunas, J. G. Bentsen, and A. Steinberg*, "Analysis of aged paint binders by FTIR spectroscopy," in Studies in conservation, **vol. 35**, no. 1, 1990, pp. 33–51.
[22]. *A. Coccato, L. Moens, and P. Vandenabeele*, "On the stability of mediaeval inorganic pigments: a literature review of the effect of climate, material selection, biological activity, analysis and conservation treatments," in Heritage Science, **vol. 5**, no. 1, Mar. 2017, pp. 1–25, doi: 10.1186/S40494-017-0125-6.
[23]. *E. Tomasini, G. Siracusano, and M. S. Maier*, "Spectroscopic, morphological and chemical characterization of historic pigments based on carbon. Paths for the identification of an artistic pigment," in Microchemical Journal, **vol. 102**, May 2012, pp. 28–37.
[24]. *S. Daniilia, E. Minopoulou, K. S. Andrikopoulos, A. Tsakalof, and K. Bairachtari*, "From Byzantine to post-Byzantine art: the painting technique of St Stephen's wall paintings at Meteora, Greece," in

Journal of Archaeological Science, **vol. 35**, no. 9, Sep. 2008, pp. 2474–2485, doi: 10.1016/J.JAS.2008.03.017.

[25]. *M. Marius, I. Sandu, I. Huţanu, and L. Nica*, "The Study of Stages and Operations Involved in the Preservation and Restoration of two XIX-th Century Icons, on Wooden Support," in Present Environment and Sustainable Development, **vol. 8**, no. 2, Jan. 2015, pp. 131–150, doi: 10.2478/PESD-2014-0030.

[26]. *I. Huică, I. M. Cortea, L. Ratoiu, L. Ghervase, R. Rădvan, and D. Mohanu*, "Multidisciplinary approach for time-framing of an overpainted wooden iconostasis from Southern Romania," in Microchemical Journal, **vol. 155**, Jun. 2020, p. 104685, doi: 10.1016/J.MICROC.2020.104685.

[27] *V. Otero et al.*, "Characterisation of metal carboxylates by Raman and infrared spectroscopy in works of art," in Journal of Raman Spectroscopy, **vol. 45**, no. 11–12, Nov. 2014, pp. 1197–1206, doi: 10.1002/JRS.4520.

[28]. *R. L. Feller*, Artists' Pigments: a Handbook of their History and Characteristics, **vol. 1**, National Gallery of Art, Washington, DC, 1986.

[29]. *G. Abdel-Maksoud, M. Ibrahim, Y. M. Issa, and M. Magdy*, "Investigation of painting technique of Coptic icon by integrated analytical methods: imaging, spectroscopic and chemometric methods," in Journal of Archaeological Science: Reports, **vol. 29**, Feb. 2020, p. 102085, doi: 10.1016/J.JASREP.2019.102085.

[30]. *D. Hradil, T. Grygar, J. Hradilová, and P. Bezdička*, "Clay and iron oxide pigments in the history of painting," in Applied Clay Science, **vol. 22**, no. 5, Apr. 2003, pp. 223–236, doi: 10.1016/S0169-1317(03)00076-0.

[31]. *S. Gunasekaran, G. Anbalagan, and S. Pandi*, "Raman and infrared spectra of carbonates of calcite structure," in Journal of Raman Spectroscopy, **vol. 37**, no. 9, Sep. 2006, pp. 892–899, doi: 10.1002/JRS.1518.

[32]. *Z. Kaszowska, K. Malek, M. Pańczyk, and A. Mikołajska*, "A joint application of ATR-FTIR and SEM imaging with high spatial resolution: Identification and distribution of painting materials and their degradation products in paint cross sections," in Vib Spectrosc, **vol. 65**, Mar. 2013, pp. 1–11, doi: 10.1016/J.VIBSPEC.2012.11.018.

[33]. *V. Otero, M. Vilarigues, L. Carlyle, M. Cotte, W. de Nolf, and M. J. Melo*, "A little key to oxalate formation in oil paints: protective patina or chemical reactor?," in Photochemical & Photobiological Sciences, **vol. 17**, no. 3, Mar. 2018, pp. 266–270, doi: 10.1039/C7PP00307B.

[34]. *D. Kovala-Demertzi, L. Papathanasis, R. Mazzeo, M. A. Demertzis, E. A. Varella, and S. Prati*, "Pigment identification in a Greek icon by optical microscopy and infrared microspectroscopy," in Journal of Cultural Heritage, **vol. 13**, no. 1, Jan. 2012, pp. 107–113, doi: 10.1016/J.CULHER.2011.06.003.

[35]. *G. P. Mastrotheodoros, K. G. Beltsios, Y. Bassiakos, and V. Papadopoulou*, "On the Metal-Leaf Decorations of Post-Byzantine Greek Icons," in Archaeometry, **vol. 60**, no. 2, Apr. 2018, pp. 269–289, doi: 10.1111/ARCM.12287.

[36]. *I. M. Cortea, L. Ghervase, L. Ratoiu, M. Dinu, and R. Rădvan*, "Uncovering hidden jewels: an investigation of the pictorial layers of an 18th-century Taskin harpsichord," in Heritage Science, **vol. 8**, no. 1, Dec. 2020, pp. 1–19, doi: 10.1186/S40494-020-00401-3/FIG.S/9.

[37]. *C. M. Popescu, M. C. Popescu, and C. Vasile*, "Structural analysis of photodegraded lime wood by means of FT-IR and 2D IR correlation spectroscopy," in International Journal of Biological Macromolecules, **vol. 48**, no. 4, May 2011, pp. 667–675, doi: 10.1016/J.IJBIOMAC.2011.02.009.

[38]. *I. Bratu, Z. Moldovan, I. Kacso, C. Marutoiu, L. Trosan, and V. C. Marutoiu*, "A Transylvanian Diptych Wooden Icon: Wooden Support and Painting Materials Investigations," in Revista de Chimie - Bicharest , **vol. 64**, no. 5, May 2013, pp. 524–528.