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THE PAINTING MATERIALS AND CONSERVATION STATUS OF AN OLD ROMANIAN ORTHODOX ICON ATRIBUTTED TO SIMON THE PAINTER FROM BĂLGRAD

Olivia Florena NEMEȘ[1,*], Ion SANDU[2,3,4,5], Dan NEMEȘ[1], Marin COTEȚIU[1], Teofil TIA[1], Constantin MĂRUȚOIU[1]

[1] Babes-Bolyai' University, Faculty of Orthodox Theology, N. Ivan St., 400692, Cluj-Napoca, Romania
[2] Academy of Romanian Scientists AOSR, 54 Splaiul Independentei St., Sect 5, 050094 Bucharest, Romania
[3] Alexandru Ioan Cuza University of Iasi, Interdisciplinary Research Institute – Science Departament, 11 Carol I Bulevard, 700506 Iasi, Romania
[4] National Institute for Research and Development in Environmental Protection, 294 Splaiul Independentei, Sector 6, 060031 Bucharest, Romania
[5] Romanian Inventors Forum, Sf. Petru Movila St., L11, 3-3, 700089 Iasi, Romania

Abstract

The orthodox wooden icon "Saint Archangel Michael" attributed to the painter Simon from Balgrad is the only one known in the Cluj county and it is kept at the Metropolitan Museum from Cluj-Napoca, with an inventory number dating from 1976. The icon recently underwent a basic cleaning process and its conservation status was studied, together with the materials used for its manufacturing. The information gathered will offer information for continuing the restoration process and to document the materials and techniques used by the painter, useful for further researches regarding the author. The investigations employed nondestructive Fourier Transform Infrared Spectroscopy (FTIR), X-ray Fluorescence (XRF) measurements, photographic and microscopig imaging. Various degradation processes and damages were identified and preliminary conservation measures were taken. No previous restoration actions were identified. A frame repainting made at an unkown date was observed (and removed). The materials identified were appropriate for the time of execution: white lead, Prussian blue, cinnabar, natural earth brown and green pigments, copper green, silver and gold leaf and painting technique was identified as tempera.

***Keywords**: Fourier Transform Infrared Spectroscopy (FTIR); X-ray Fluorescence (XRF); Microscopy; Prussian blue; Degradation processes; Wooden icon; Tempera*

Introduction

The investigations carried out on the „Saint Archangel Michael" wooden icon aimed to characterize the physicochemical properties of the materials used by the author, to provide insight about the execution techniques and a detailed image of its current conservation status, past damages and interventions and ongoing degradation processes. The attributed author is a well-known painter from the Alba County, Simon from Balgrad [1]. His work impresses with the quality of the drawing, the color palette used and overcoming the conventionalism of post-Brâncovan art and expressing according to the new artistic taste that manifested in the

* Corresponding author: olivia.nemes@ubbcluj.ro

Romanian environment at the end of the 18th century [2]. The studied icon is the only one known within the Cluj County area and it is kept at the Metropolitan Museum from Cluj-Napoca. The attribution was made by the history and art experts from the Museum and were based on its stylistic and iconographic properties, as no signature was found on the artefact.

This old Romanian icon painted on wood has a beautiful representation of the Archangel Michael painted in the tempera technique (Fig. 1). Saint Archangel Michael is represented in half-length, dressed in military clothing with a silver cloak, holding a sword in his right hand from which flames come out and a chalice in his left hand. The Archangel wears a gray armor-like breastplate from under which short sleeves of a red shirt are visible and under it a blue shirt decorated with silver cuffs having strings of white pearls. Leather belts that appear from under the breastplate complete his military clothing. The background is painted in an intense blue color. The halo and the chalice are plated with a golden aspect metallic foil. The archangel's cloak, the cuffs of the shirt sleeves, the lower belts, the inner surface of the original frame are plated with a silver looking metallic foil.

Fig. 1. Saint Archangel Michael icon before and after the initial cleaning process with the investigated areas mapping

The icon's panel is made of a single board of coniferous tree wood obtained by tangential cutting from the tree trunk and has the dimensions of 31.5x24x2cm. The back of the panel has been finished in a rather neat way. The icon has an original frame attached to the front of the panel using animal glue and fixed with wooden nails on each stick. The icon currently had a second non-original but old frame (not pictured in Fig.1), fixed to the edges of the panel also by means of wooden nails (Fig. 1), that was originally provided with a glass plate to protect the icon (the glass no longer exists).

At the time of its restoration the icon of Archangel Michael was in an inadequate state of preservation, with several types of degradation at the level of the pictorial layer and the support. Some degradations were of an evolutionary nature, so it was urgently necessary to stabilize the degradation processes and then complex investigations and analyses were carried out.

Experimental part

Materials

The visual investigation of the icon shown that its state of conservation was inadequate. Numerous degradations were identified at the level of the color layer, the primer and at the level of the wooden panel on which the painting was made. The icon had never been properly restored before, but it was obvious that in the past improper cleaning had been carried out on the painting (and especially on the original frame). Because of excessive cleaning, the metal foil had been almost completely removed from the surface of the original polychrome frame and then it was painted over with golden paint.

The painting layer showed cleavages and the exfoliation process was evolutionary. Several fragments of the painting layer were lost resulting in deep gaps reaching the wooden panel and there was a risk of expanding and new ones appearing. Gradual abrasions were visible on the surface of the archangel's wings. Due to dimensional and flatness changes of the wooden panel under the influence of humidity variations, the painting layer showed several cracks in a predominantly longitudinal direction and there were micro cracks on the entire painted surface of the icon. The painting layer was dark mainly due to depositing of impurities that accumulated over time, but also because of the aging and alteration of the varnish.

The wooden panel had degradations specific to old icons. It suffered a xylophage attack, as a result holes and galleries made in the wooden structure by xylophage insects appeared. The structure of the panel also showed some degradations represented by cracks caused by the introduction of the wooden nails. Over time, the panel also suffered changes in flatness, with a slight curvature towards the back being evident. The ends of the frame sticks were detached. The entire surface of the back panel was covered with adherent impurities.

Methods

Non-destructive analyses were performed using portable devices by approaching them to the paintings. These non-invasive methods were chosen because of restrictions over taking samples and were previously used for investigations [3-14].

Energy Dispersive X-ray Fluorescence

Non-destructive X-ray fluorescence elemental analysis (XRF) was performed with a handheld Bruker spectrometer, S1 TITAN series (EDXRF) configured with a Silicon diode PIN detector (SiPIN), Rh target X-ray tube with a maximum voltage of 50kV, 9µA current intensity and 30 seconds analysis time. The software used was Bruker S1 Data Tool.

FTIR reflectance spectroscopy

Fourier-transform infrared spectroscopy (FTIR) was performed using a tripod mounted Bruker Alpha II device with a contactless forward-looking reflection unit specialized for paintings, spectral domain 400-4000cm^{-1}, resolution 2cm^{-1}, using 100 scans. The software used was OPUS IR software. Basic atmospheric compensation was performed (CO_2 and H_2O compensation) and absorbance was selected as the output spectrum type (pseudo-absorbance, automatically converted by the software). Baseline correction was applied to the spectra.

Microscopy

The Q-scope 80200-P digital microscope with a magnification power of 10-50x, 8-megapixel CMOS sensor and polarization filter was used. Different magnification and polarization levels were used to study the painting layer and the metallic foils used by the author and to study later interventions made on the work of art.

Results and discussion

The investigations were carried out after a basic cleaning intervention was made on the painting layer and icon frame (more cleaning and restoration work being scheduled to be performed on this artefact). A small horizontal band-shaped section of the painting and frame area (shown on the top left image from Fig. 2) was left without cleaning interventions to constitute a recording of the prior condition of the painting layer and to display the additional paint and foil layers that were applied to the icon's frame at an unknown date. This section was investigated to acquire information about the materials used for repainting. The adjacent image on the top right of shows the original ground and paint layers from the frame that are degraded, which probably prompted the repainting. The painting layer inside the icon shows degradations but no signs of obvious later repainting.

The middle section shows the back panel of the wooden icon with signs of degradation due to xylophage insects attack and other degradations due to manipulation and nail insertions. It also shows a mark of inventory from the museum dating to 1976.

The bottom section shows examples of painting layer degradation. The left image shows the mechanical damage of the paint layer around the eye. The right image shows a degradation that can be a result of both mechanical degradation and specific paint properties.

Fig. 2. Top left: close-up of the unrestored frame area; top right: original frame paint layer; middle: section of the back of the wooden panel; bottom left: close-up of the eye; bottom right: close-up of the chalice

XRF and microscopy investigations

The investigations aimed to identify the metallic pigments used for the paint using the X-ray fluorescence technique. Microscopy imaging sought to obtain more information regarding the grain size of the pigments and their distribution, possible pigment mixing situations, the use of various types of metallic foils, investigation of possible repainting interventions and to show in greater detail the general conservation status of the painting layer. Various degrees of light polarization filtering were used to reduce the glare of the paint films/varnish layers or excessive reflections from the metallic foils (Fig. 3).

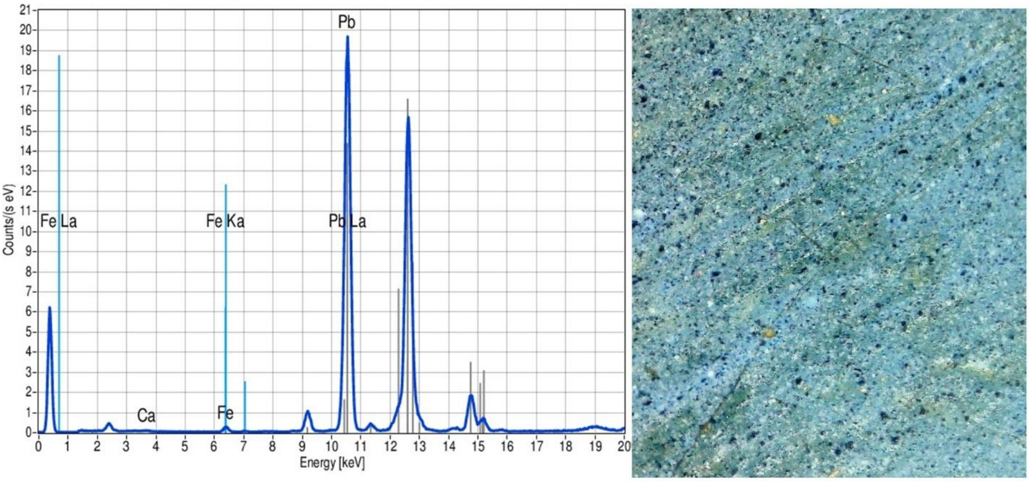

Fig. 3. Blue background around the Archangel; XRF spectrum and microscope image

The intense blue color (measured by XRF and imaged in the area A from Fig. 1) shows that a real blue pigment was used instead of a more common metod of obtaining a blueish-gray color by the high dilution of some black pigments [15]. This situation was due to the fact that historically the blue pigments were more expensive and difficult to obtain. The absence of copper (azurite being a relatively accessible pigment in the era, but relatively unstable chemically) and the presence of iron suggests the pigment used was Prussian blue [16], a synthetic pigment developed at the beginning of 18th century. The first signed work of the attributed author of the icon dates to 1771 [2], therefore the pigment is appropriate for the time the author was active. This also shows the author was open to use more modern materials (at the time of execution) that were developed in Western Europe.

Prussian blue is a lightfast pigment, has a very rich color and good coverage properties. The confirmation for the Prussian blue presence can be obtained by FTIR investigations, the ferrous ferrocyanide blue pigment having a distinctive spectrum peak. The pigment was applied over or mixed with a white lead paint. The microscope image shows grains of dark deep blue pigment and the lead white paint that was dyed and displays a blue hue. Small random yellow glittering flakes were also observed, which could represent contamination from nearby layers.

The high intensity lead peak suggests that the paint layer was rich in lead white. Calcium peaks from the ground layer are barely visible (due to shielding). The scale of the graph raised by the high intensity lead peak shows a relatively small iron peak. It also indicates a small concentration of iron based pigment was used, but the Prussian blue excelent coloring properties required only a moderate amount to be used to obtain this color.

Metallic foil (area B, Fig. 1) was applied over the calcium rich ground. Both gold and silver metals were detected. The general aspect from the microscope shows a rich gold color and suggested that a gold leaf was applied over the silver leaf (a silver rich alloy would present a paler nuance – Fig. 4).

The very small silver areas observable near the cracks where the material shows signs or erosion reinforce this assumption. A large silver area is also observable to the bottom right of the microscope image). The iron content can be explained by the traditional use of bole, an iron rich clay used to prepare the surface for gilding, offering better adherence and a smooth surface for the gold or silver leaf application by gilding techniques [17, 18].

The red pigment used for the sword (area C, Fig.1) is a red mercury sulfide (HgS) known as cinnabar (Fig. 5), a pigment used since Antiquity [19]. It could be found as a natural ore or was artificially synthesized and was a more expensive red pigment during the period this icon was manufactured (and still is), but could offer a richer, more vivid color than the alternative cheaper iron red pigments that were readily available.

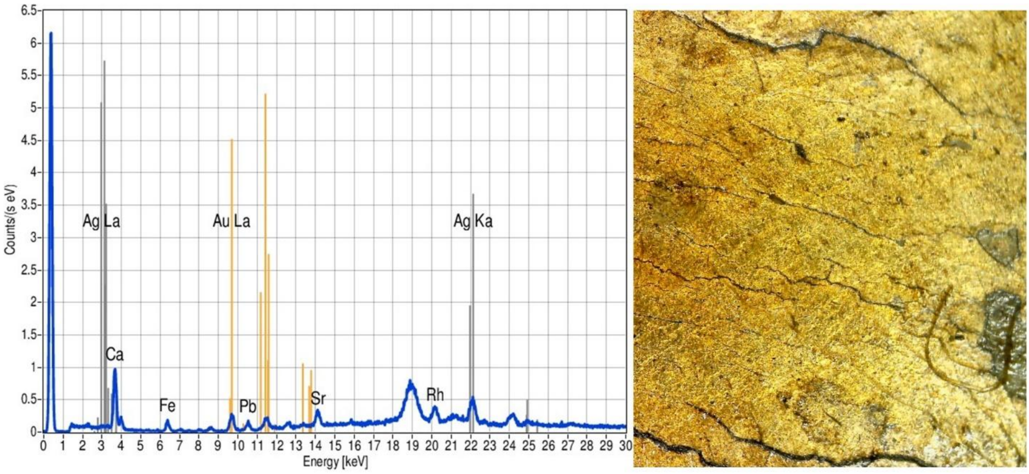

Fig. 4 . Gold aura around the Archangel’s head; XRF spectrum and microscope image

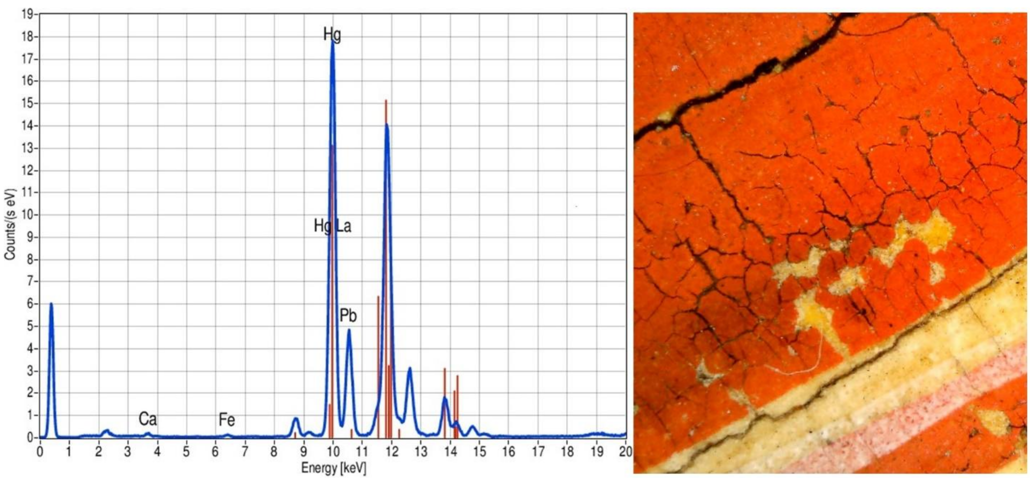

Fig. 5. Red Archangel’s sword; XRF spectrum and microscope image

A significant lead peak is present, due to the white lead paint present within the area or mixed into the paint. The second assumption is backed by similar (slightly higher) lead metal peaks intensity from a spectrum obtained investigating the mercury red shoulder garment area, which was measured away from the white lead paint used for the wings.

Both the face (area D, Fig. 1) and the wing (area E, Fig. 1) white were obtained using lead white paint. The paint layer of the Archangel's face is much richer/thicker, as shown by the relative lead peak heights difference. The reddish hue of the Archangel's face was obtained by applying a small quantity of cinnabar to give it a more natural skin tone (with varying concentration levels depending on the face area). The mercury sulfide is absent in the wing area, being a simple white (Fig. 6).

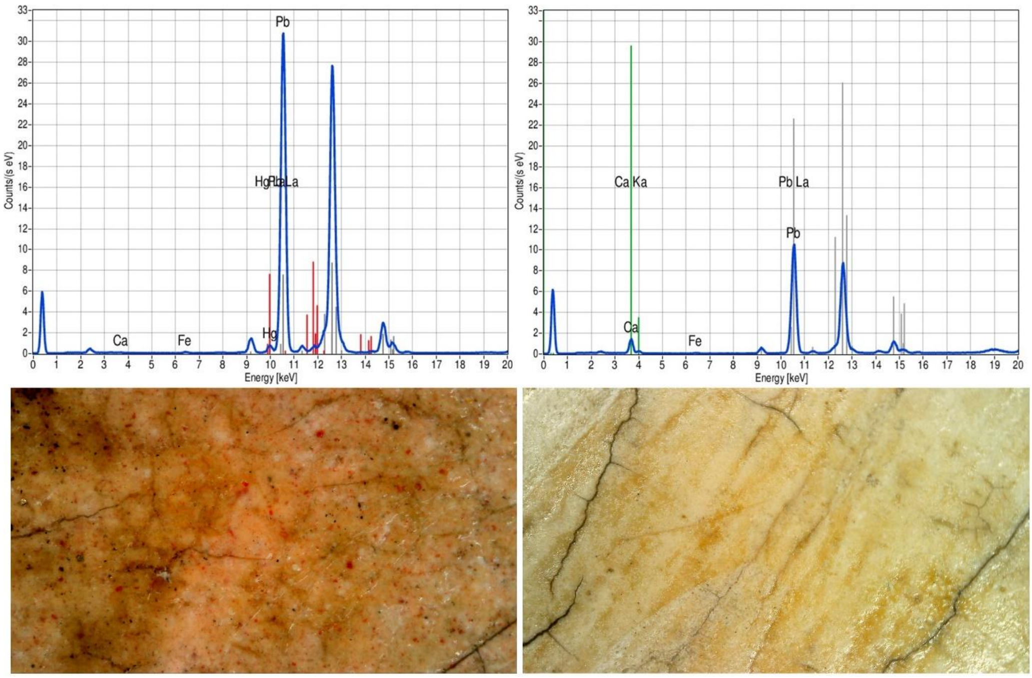

Fig. 6. White paint spectra comparison: Archangel's white face (left) and Archangel's white wing (right); microscopic images of the studied areas

The calcium peak from the ground layer is clearly visible in the Archangel's wing area which has a smaller quantity of lead white applied over it and it is and not visible in the Archangel's face area where the thickness of the lead paint layer shields against X-ray penetration and against the low energy specific calcium lines emerging from underneath the rich lead paint. The cracking of paint layer is a common sight for historical lead white paints, being observed on this icon both where the white lead paint was alone or mixed with other pigments.

Different metallic foil types were used for this icon. The silver-gray area of the Archangel's shoulder ornament (area F, Fig. 1) was obtained using silver leaf (Fig. 7). The XRF spectrum shown a moderate silver peak, suggesting a very thin foil application. The thin foil application allows for a strong calcium signal from the ground layer with the accompanying strontium from the natural deposits [17, 18]. The iron peak can be explained by the traditional use of bole. Traces of lead can be observed, similar to other foil areas. The omnipresence of lead could suggest a small quantity was applied on the calcium ground layer [20].

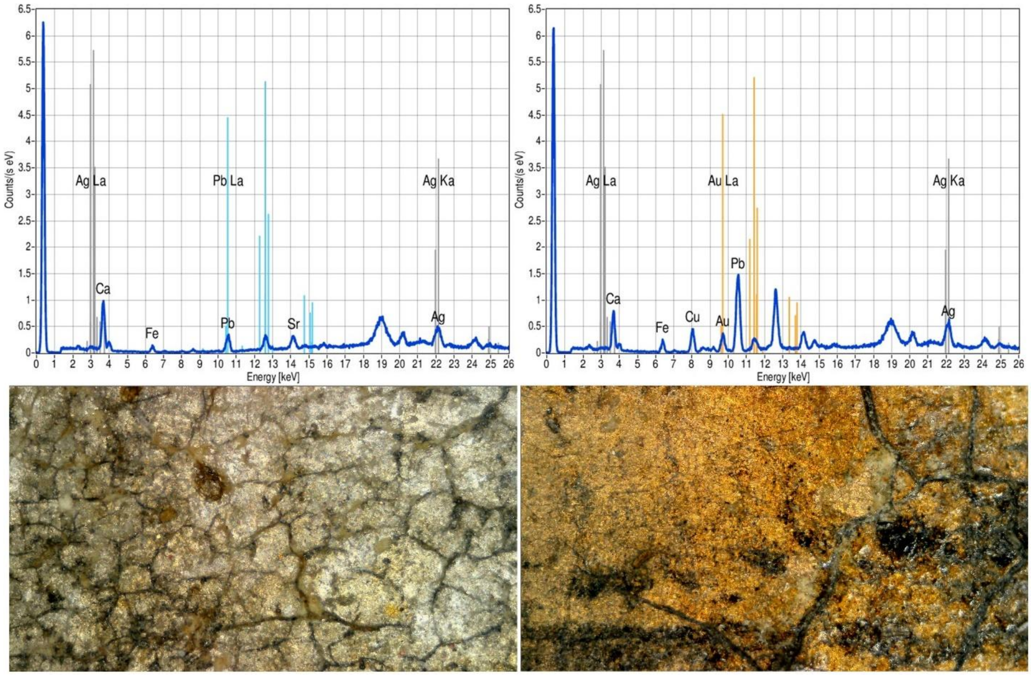

Fig. 7. Silver shoulder ornament (left) and golden chalice (right) spectra and microscopic images

The silver leaf application is not limited to the ornament sitting above the shoulder, but also to the whole brown upper garment stretching over the chest from shoulder to shoulder and it is also found at the lower vestment ornaments. The brown color partially covering these other silver leaf areas could be explained by the microscopy images showing a thin brown film and occasional accumulations under the form of droplets of dark brown matter resembling tainted varnish. The scheduled second phase of cleaning could reveal more details. Very low observed traces of copper and zinc (not visible at the above graph scale) could suggest contamination from other areas rather than an intentional use of a brass powder to obtain a yellow shine.

The area of the golden chalice (area G, Fig. 1) presents both silver and gold peaks. This situation is similar to the metallic foils that were observed studying the Archangel's aura. Unlike the aura, a significant copper peak was surprising and suggested that the small green areas visible on chalice were obtained using a copper green pigment (malachite or verdigris). To further investigate the copper origin and distinguish between a possible gold-copper alloying situation, a tarnishing of a bronze or brass powder paint/foil or the existence of a simple green copper pigment, a series of four measurements were made targeting different areas of the golden chalice. As the icon is relatively small and the chalice size allowed a difference in positioning is measured in millimeters, it is possible that the measuring spots of the XRF device tangentially overlap.

The four spectra of the golden chalice were loaded simultaneously and compared to establish a basic map of copper distribution. The top (blue mark) and left (red mark) measurement spots from the chalice shown very low copper contents, significantly lower than the original central measuring spot (thus excluding a gold alloy rich in copper applied all over the chalice). The gold, silver, calcium, iron and lead contents were similar for all four spectra, showing remarkable peak similarities (Fig. 8). Contrasting to the first two spectra, the right (dark green mark) and bottom (yellow green mark) shown much higher copper concentrations and match the green paint aspect observed in those areas. No significant zinc or tin contents were observed to suggest the existence of a copper alloy powder/foil used locally that tarnished.

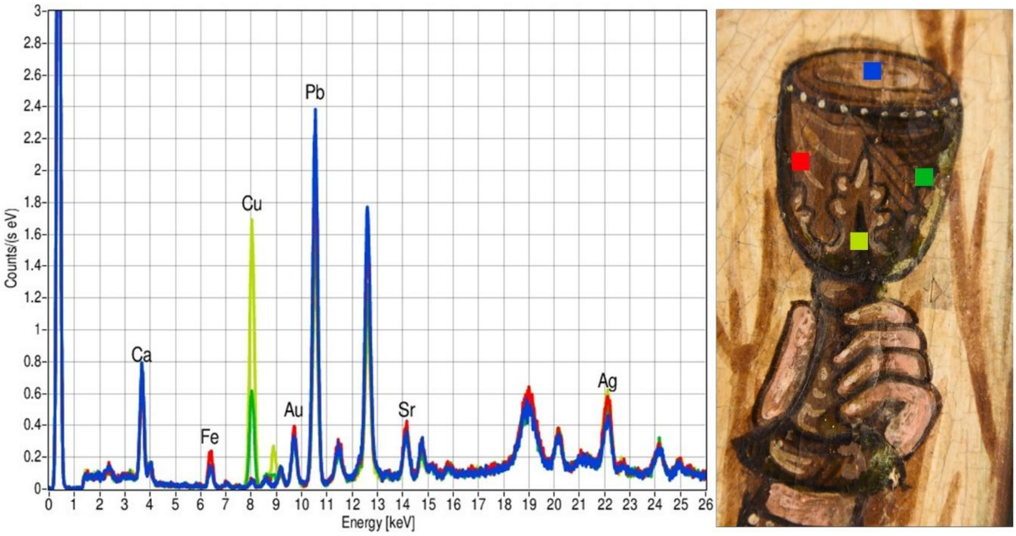

Fig. 8. Spectra comparison for golden chalice investigated areas

A detail of note is that the green paint areas (representing the shadows cast on the chalice) experienced much more severe degradation and exfoliation, visible even on the base of the chalice (below the hand) where the green area also experienced significant degradation. The dark outline of the chalice goes beyond the exfoliated area. This shows the green paint experienced significantly more degradation than the surrounding layers. The green color from this area has a different aspect and it is chemically different from the one used for the larger dark green areas of the Archangel's clothing, which was studied next.

The green pigment (area H, Fig. 1) used on large areas of the Archangel's clothing contained no copper, contrasting to the green observed on the right and lower side of the golden chalice (Fig. 9).

The lead based paint shown a significant quantity of iron (significant but small compared to the high intensity lead peaks, which raise the scale) and potassium which had a weaker signal (being a specific low energy peak and also being the lower limit of the XRF device SiPIN detector measurement range). This suggests that the green pigment used was a common green earth pigment, Terra Verde, used since Antiquity [21]. This green pigment also contains magnesium, aluminum, silicon – elements that are lighter than potassium and not detectable by the portable device used.

The frame area was repainted at an unknown date, which was a common practice to restore the aspect of an area subjected to manipulation and degradation (there was significant damage and exfoliations of the red paint) or as a method to further adorn the icon.

Investigation were conducted on the outer frame to identify the repainting materials on the bottom left witness area (area I, Fig. 1). The spectrum (top left of Fig. 10) clearly demonstrates a copper – zinc alloy (brass) was used to obtain the golden color. The iron signal from the original red paint layer is visible. The microscope image shows agglomerations of glittering flakes with spaces inbetween.

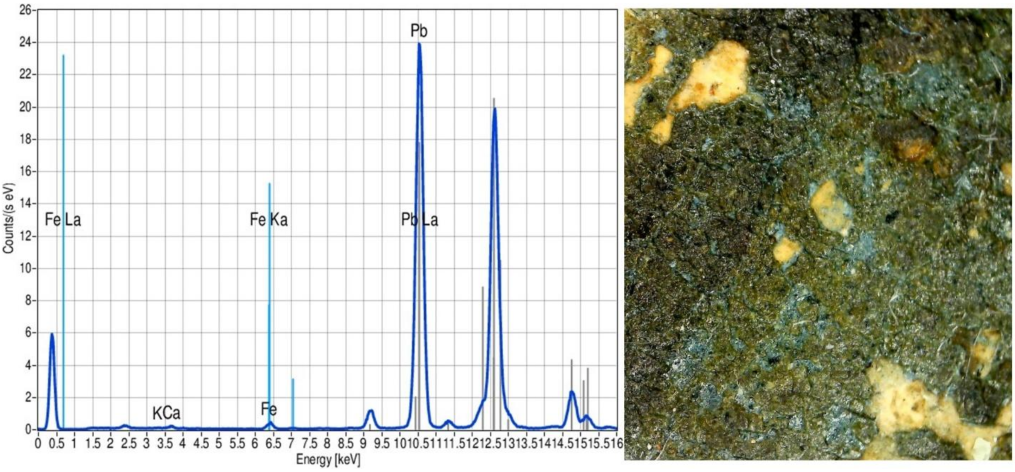

Fig. 9. XRF spectrum and microscopic image of the green paint from the Archangel's vestment

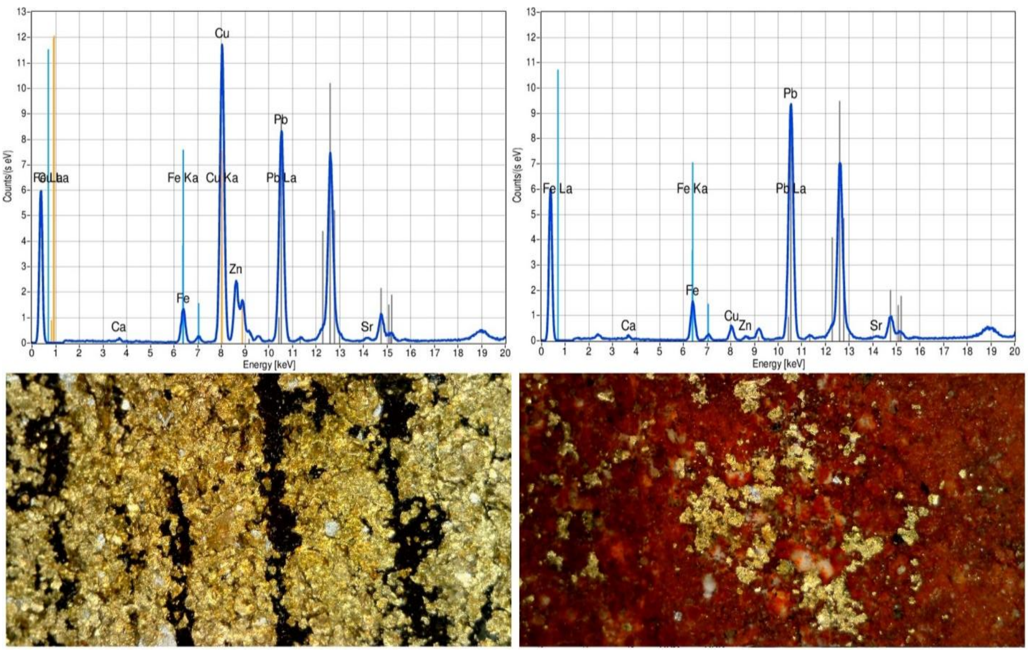

Fig. 10. Spectra comparison and microscopic images for unrestored (left) and cleaned area (right) of the outer frame

The paint application is not uniform and the flakes look spread out and not binded very well together, explaining the contamination that spread all over the icon.

The original paint layer (area J, Fig. 1) XRF spectrum and microscope image are shown on the right side of figure 10. After the initial cleaning process there were still traces of glittering yellow material over the original red paint layer. The traces were investigated to establish if they represented remnants of a degraded original metallic foil or residue left after the cleaning process. The spectrum shows that it is the same brass powder used to repaint the outer frame, as does the microscopic image showing the same type of glittering golden flakes.

The cleaning process didn't remove the powder from all areas (more visible traces were found on the top right corner). No traces of gold were found and it was concluded that the original paint was a red iron oxide paint mixed with white lead. As the repainting was done both on the inner and outer frame, further investigations were carried out on the inner frame to identify possible original materials.

The spectrum of the brass powder paint (left) (area K, Fig. 1) revealed the usual copper and zinc alloy that was used to obtain the golden color. Both the original layer (right) (area L, Fig. 1) and the repainted spectra showed the presence of gold and silver, which represented the original materials (Fig. 11).

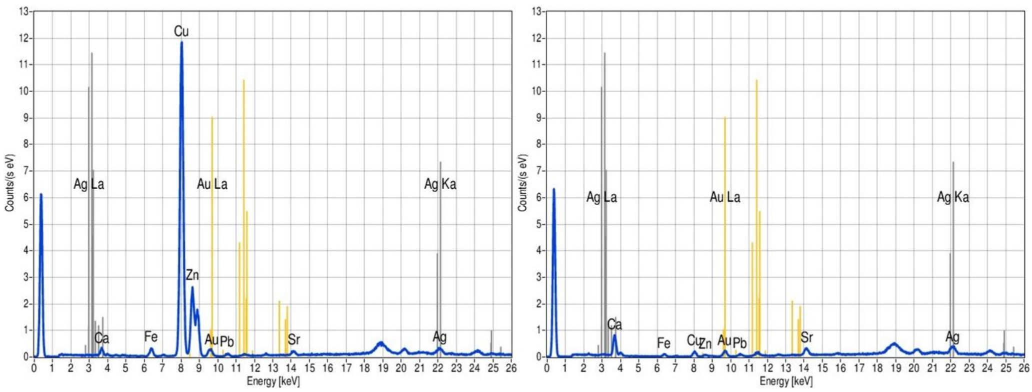

Fig. 11. Spectra comparison of the repainted inner frame (left) and the original area (right)

This is similar to the Archangel's aura and the golden chalice metallic foils. The peaks were weak, reflecting the general state of degradation and exfoliation. An important observation regards the lead content, which is extremely low. This suggests the inner frame wasn't painted over with a white lead based paint before the metallic foil application.

The brown hair color (area M, Fig.1) was obtained using an iron oxide pigment, the reddish aspect suggesting a burnt sienna or umber pigment. Heating the natural earths sienna or umber partially dehydrates the iron oxides being transformed into the red hematite, or iron oxide Fe_2O_3 - matching the general aspect observed under microscope). The observed traces of manganese are expected for either of the two natural earth pigments (Fig. 12).

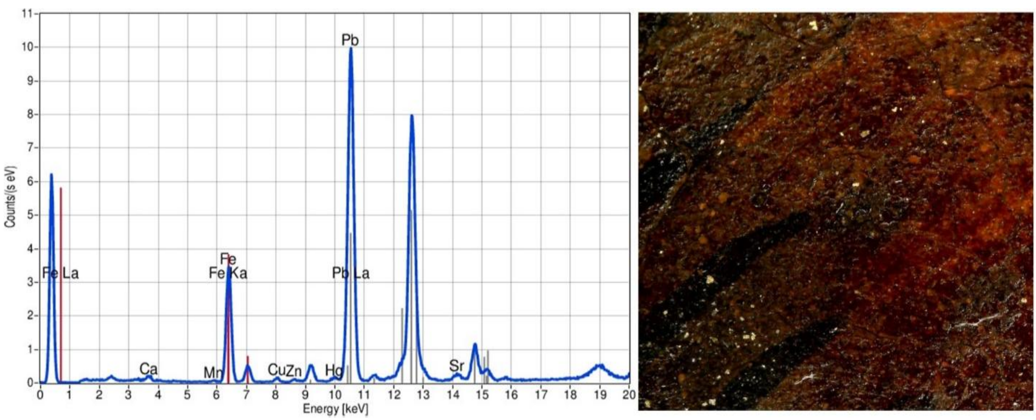

Fig. 12. XRF spectrum and microscopic image of the brown hair

The traces of copper and zinc can be explained by contamination from the frame repainting, the microscopic image showing a small number or glittering flakes being present. A small quantity of mercury was also observed, probably used to enrich the color hue. Similar traces of manganese and cinnabar were also observed on the brown paint from the eyes.

FTIR investigations

FTIR investigations were conducted to obtain information about the pigments and binders used for the paint. Two spectra were simultaneously loaded in the software, one for the blue background color (area A, Fig. 1), to obtain confirmation about the Prussian blue pigment suggested by the XRF results. The other spectrum was for the brown hair color (area M, Fig. 1) to confirm the iron oxide based pigments suggested by the XRF results and to compare/verify against the blue spectrum specific pigment peak (the absence of it). The two spectra were also studied to show common peaks attributed to the binder media (Fig. 13).

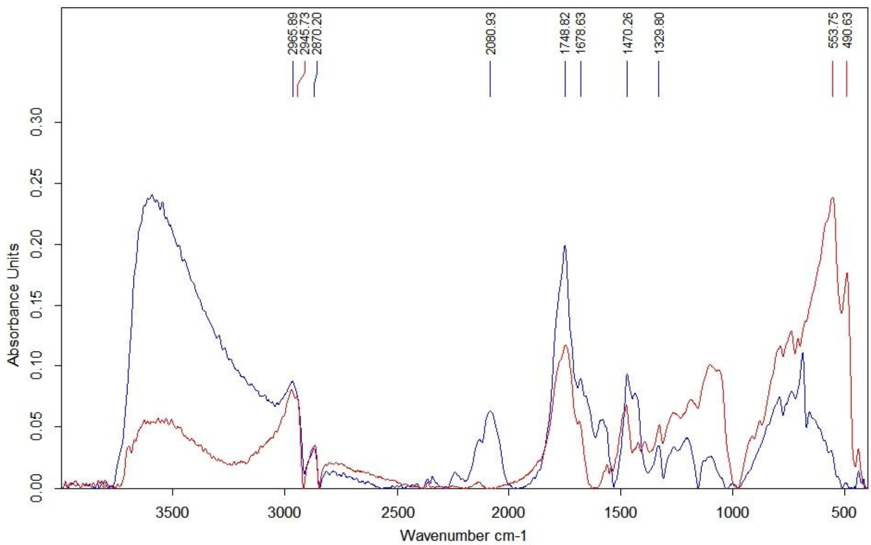

Fig. 13. FTIR compared spectra of blue background (blue line) and brown hair (red line)

FTIR peaks studied regarding the use of pigments [22, 23]:

- 2081cm^{-1} – specific Prussian blue pigment, confirming the initial assumption and XRF results; this specific peak was absent on the red iron spectrum.
- 554 and 491cm^{-1} – iron oxide/hematite specific pair of peaks

FTIR peaks studied regarding the use of binders [24-26]:

- 2966, 2946 and 2870cm^{-1} – stretching bands from CH_2 and CH_3 groups;
- 1749cm^{-1} – C=O ester stretching band – the high peak intensity suggesting the use of linseed oil used in the paint or varnish [27]; the peaks are also common for the egg yolk binding medium;
- 1679cm^{-1}- C= and C-N stretching from Amide I;
- 1470cm^{-1} C–H bending of Amide II;
- 1330cm^{-1} – C-N stretching, N-H bending of Amide III – suggesting the existence of proteins from the egg yolk, commonly used as a binding medium for the tempera technique.

Conclusions

The icon of Archangel Michael (Fig. 1) was investigated during a cleaning and restoration process. The icon shown signs of degradation, some of them ongoing. Interventions were made to clean and stabilize the icon. The materials used for manufacturing the work of art were investigated. Details about the technique, degradation processes, current and original aspect were discussed.

The icon was painted on a single wooden plank, on which a calcium based primer was applied and a thin layer of white lead (lead was omnipresent in all the spectra including metallic foils, except for the inner icon frame which was not part of the painting area). The palette used was relatively varied, using a combination of natural and synthetic pigments, old and modern at the time of execution: white lead, cinnabar, Prussian blue, green earth pigment (Terra Verde), a copper based green pigment (malachite or verdigris), red-brown natural earth pigments that were processed (burnt sienna or umber). Both cheap and expensive materials were used for the manufacturing. The use of the more expensive pigments (cinnabar) and metallic foils (gold and silver leaf used in many places and over extensive areas) offered an insight about the financial status of the person or community who ordered the manufacturing of the icon. The gilding technique was traditional, using bole as a substrate.

The icon shown signs of degradation in various places, but some areas experienced more, especially visible around the green copper pigment application area and on the icon’s frame. The degradations can be attributed to mechanical wear (by handling and cleaning of the frame), humidity variances (geometry distortions), biological attacks (xylophage insect attacks) or to the specific properties of the used pigment (for the copper green pigment). Similar degradation of the copper green pigment was encountered before by the investigating team [7, 28] and could be further studied to establish its mechanism and the possible effects of the cleaning process.

The icon’s frame experienced extensive surface degradation that probably prompted the repainting at an unknown date. The frame was repainted using a copper based alloy powder (brass), that was removed during the cleaning process. Still, contamination with small glittering flakes was noticed under microscope over all studied surfaces and was still visible with the naked eye on the concave areas of the frame, even after the first cleaning process was finalized. The varnish used for the painting layer was degraded and still covered large surfaces modifying their appearance. A second phase of cleaning and stabilization is scheduled to take place.

The painting technique used was tempera, as confirmed by the FTIR results. This technique consisted in the mixing of egg yolk (as a binding medium) with the desired pigments and water. The resulted emulsion was used as paint. The materials used were typical for the period. No previous restoration interventions were identified.

The pigments that suffered a particular degradation rate, along with very thin metal sheets with different forms of physical damage, presented a special interest, especially since the icon has both small lacunar areas and disproportionate exfoliation compared to all other pigments, explained by mechanical erosion to the touch, on a series of multiple microzones of the icon [29, 30]. The limiting factor for further investigations requires the use of semi-destructive methods, by sampling micro samples, which require the owner's approval, being highly discouraged by restorers.

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