

**POLITEHNICA UNIVERSITY OF BUCHAREST**

**DOCTORAL SCHOOL OF  
MATERIALS SCIENCE AND ENGINEERING**



## **DOCTORAL THESIS**

**Studies and researches on the use of ferrous metals in the composition of easel paintings on metal supports and non-ferrous alloys in the structure of icon revetments with application in establishing authenticity and elaboration of restoration documentation**

*Studii și cercetări privind utilizarea metalelor feroase în componența picturilor de șevalet pe suporturi metalice și a aliajelor neferoase în structura ferecăturilor pentru icoane cu aplicare în stabilirea autenticității și elaborarea documentației de restaurare*

**Doctoral student: Lăcrămioara Raluca Bivol**

**Doctoral advisor: Prof. dr. habil. ing. Valeriu Gabriel Ghica**

**BUCHAREST 2023**



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## **SUMMARY OF DOCTORAL THESIS**

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**BUCHAREST 2023**

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## ABSTRACT

S-au efectuat analize în vederea identificării materialelor componente, tehnicilor de execuție originală, stabilirii autenticității (semnăturilor și datărilor - în cazul în care există) și evidențierea stării de conservare a unui număr de două picturi de șevalet pe suporturi metalice (neclasate, dintr-o colecție privată), respectiv a unui număr de șapte ferecături pentru icoane, dintre care trei ferecături pentru icoane din aliaj de argint de proveniență românească (executate în ateliere autohtone de prelucrare a metalelor prețioase), două ferecături pentru icoane din aliaj de argint de proveniență rusească (care au fost executate în ateliere rusești de prelucrare a metalelor prețioase, apoi au fost comercializate pe teritoriul românesc), precum și două ferecături pentru icoane din aliaje neferoase cu marcaje false (ce păreau a fi atât de proveniență românească, cât și rusească). În vederea identificării elementelor componente, a determinării tehnicilor de execuție originală, a stabilirii autenticității și evidențierii stării de conservare a artefactelor menționate mai sus s-au efectuat următoarele analize: examinare în lumină ultravioletă, radiografie digitală, tomografie computerizată, spectrometrie de fluorescență de raze X, microfluorescența de raze X, metalografie, microscopie electronică de baleiaj și spectroscopie de raze X cu dispersie de energie.

**Cuvinte-cheie:** pictură de șevalet pe suporturi metalice, ferecături pentru icoane din aliaje neferoase, documentație de restaurare, stare de conservare, stabilirea autenticității, examinare în lumină directă, metalografie, radiografie digitală, tomografie computerizată, spectrometrie de fluorescență de raze X, microfluorescența de raze X, metalografie, microscopie electronică de baleiaj și spectroscopie de raze X cu dispersie de energie.

Analyzes were carried out in order to identify component materials and original execution techniques, to establish the authenticity (signatures and dates - if there are any), and to highlight the conservation status of two easel paintings on metal support (unclassified, from a private collection), respectively of seven icon revetments, of which three silver alloy icon revetments of Romanian origin (executed in local workshops for processing precious metals), two silver alloy icon revetments of Russian origin (which were executed in Russian workshops for processing precious metals, then sold on Romanian territory), as well as two non-ferrous alloy icon revetments with counterfeit markings (which seemed to be both Romanian and Russian origin). In order to identify the components, to determine the original execution techniques, to establish the authenticity, and to highlight the conservation status of the artifacts mentioned above, the following analyzes were performed: examination in ultraviolet light, digital radiography, computed tomography, X-ray fluorescence spectrometry, X-ray microfluorescence, metallography, electron scanning microscopy and X-ray spectroscopy with energy dispersion.

**Keywords:** easel painting on a metal support, non-ferrous alloy icon revetments, restoration documentation, conservation status, authenticity, direct light examination, metallography, digital radiography, computed tomography, X-ray fluorescence spectrometry, X-ray microfluorescence, metallography, electron scanning microscopy and X-ray spectroscopy with energy dispersion.

## 1. Introduction

The doctoral thesis is divided into two parts: a theoretical study and personal contributions. The study focuses on the use of ferrous metals in easel painting on metal supports and non-ferrous alloys in the execution of icon revetments (figs. 1.1), as follows:

**Chapter 1. Introduction** - presents the context of the doctoral thesis, the scientific evaluation, the novelty and topicality of the doctoral thesis, the working hypothesis and the research objectives, the description of the structure, research limitations, and prospects for further research on easel paintings on metal supports and non-ferrous icon revetments.

**Part I. The theoretical study** includes four review chapters of the literature in the field of doctoral work.

**Chapter 2. The data analysis from the literature on the importance of preparing the restoration documentation** presents the current trends regarding the elaboration of artifact restoration documentation. Chapter 2 consists of subchapters such as movable cultural property, a brief history of legislation in the conservation and restoration of artifacts, establishing the first restoration laboratories, and the importance of conducting physico-chemical investigations to prepare the restoration documentation.

**Chapter 3. The use of metals in plastic art** includes a short history of easel paintings on metal supports and easel painting on Romanian territory, a description of the stratigraphy of easel paintings on metal supports, and the use of metals in easel painting and non-ferrous alloys for performing artifacts.

**Chapter 4. The analysis of data from the literature of icon revetments made of non-ferrous alloys** presents the establishment and organization of silver work guilds in Romanian Countries, the importance of Transylvanian silversmithing workshops in the development of worship, the legislation of the Romanian Countries regarding the field of processing of precious metals, marking of silver workpieces in the Romanian Countries, techniques for processing metals and non-ferrous alloys, the origin and development of icons and the art of icon revetments, as well as the circulation of religious silver works of Russian origin on the Romanian territory.

**Chapter 5. The analysis of data from the literature on establishing the authenticity of movable cultural property** includes a brief history of forgeries, reproductions, and replicas in fine arts, respectively counterfeiting and forgery in easel paintings on metal supports, as well as the application of counterfeit and forged marks on iconic revetments.

**Part II. Experimental research** is represented by own studies on using metals in easel paintings on metal supports and non-ferrous alloys in the execution of iconic revetments.

**Chapter 6. The Research methodology of easel paintings on metal supports and non-ferrous alloy icon revetments** includes the presentation of the equipment and the way of working.

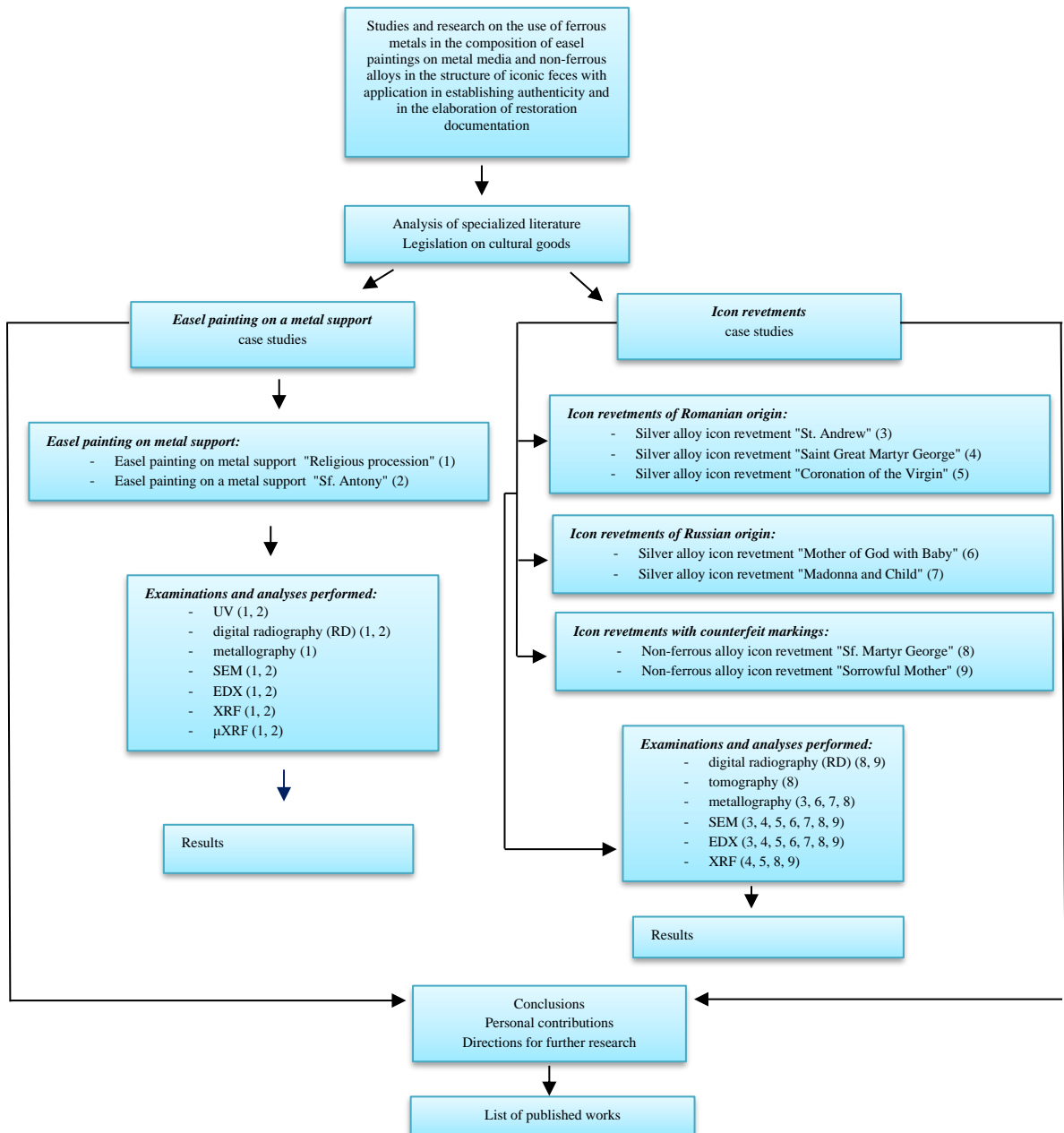
**Chapter 7. Studies and research on easel paintings on metal supports** show research, results of examinations, and physico-chemical investigations, including metallographic analysis, discussions, and conclusions on easel paintings on metal supports "Religious procession" and "St. Antonie."

**Chapter 8. Studies and research on icon revetments** include research, results of physico-chemical examinations and investigations, including metallographic, as well as discussions and conclusions on the following types of icon revetments:

- icon revetments - of Romanian origin ( silver alloy castings "Sf. Apostol Andrei ", "Sf. Great Martyr George," and "Coronation of the Virgin");

- icon revetments - of Russian origin ( silver alloy icon revetments "Mother of God with Baby" and "Virgin with Baby" );
- icon revetments with false markings (icon revetments made of non-ferrous alloys „ Sf. Martyr George" and „ Mother of God Sorrowed").

**Chapter 9. Conclusions, personal contributions, and directions for further research** present the conclusions related to theoretical and experimental studies and summarize personal contributions and research perspectives after the doctoral work.



**Figure 1.1.** The structure of the doctoral work

*Highlighting the interdisciplinary nature of the research carried out*

Research on the doctoral thesis entitled "Studies and research on the use of ferrous metals in the composition of easel paintings on metal supports and non-ferrous alloys in the structure of icon revetments with application in establishing authenticity and developing restoration documentation" are interdisciplinary, involving several areas of activity such as materials science (metallography - to identify and analyze metals and non-ferrous alloys ), materials technology, art history and restoration of cultural goods. This interdisciplinary character allows an in-depth approach and research of non-ferrous metals and alloys in the composition of easel paintings on metal supports and icon revetments, providing a complex picture of the possibilities for developing the (restoration documentation required for future restoration interventions) and establishing the authenticity of artifacts based on the results of physico-chemical investigations performed, of the historical and artistic context, of the original execution techniques and the conservation status.

*Indication of the limits of the research carried out during the elaboration of the doctoral thesis and the perspectives of further research*

The doctoral thesis "Studies and Research on the Use of Ferrous Metals in Easel Paintings on Metal Supports and Non-ferrous Alloys in Icon Revetments for Authenticity and Restoration Documentation" has certain limitations. Only two easel paintings on metal supports and seven icon revetments were analyzed, so the results cannot be applied to all such artifacts. Improving the methodology would involve using more analysis techniques to characterize better both the ferrous metals used in easel paintings and the non-ferrous alloys used in icon revetments. Future research should focus on conducting more physico-chemical and metallographic investigations on a larger number of artifacts in order to gain a deeper understanding.

## **PART I: TECHORETICAL STUDY**

### **2. Analysis of data from the literature on the importance of preparing restoration documentation**

#### **2.2. Legislation on the conservation and restoration of artifacts - a brief history**

Restoration of mobile cultural goods with artistic significance requires understanding art pieces' materiality, vulnerabilities, and uniqueness [3]. Restoration, as a discipline and profession, was formed under indispensable conditions of interdisciplinarity [4], restoration specialists being forced to acquire skills of researchers trained in the knowledge of techniques and materials of cultural goods [5].

By the Decree of the State Council, no. 724 of 1969 was enacted law no. 64 on the protection and conservation of goods of special artistic significance, including parts made of precious metals [21]. Law No. 63 of 1974 on protecting the national cultural heritage, adopted by the Great National Assembly, highlighted the importance of restoration and conserving artifacts within museum institutions. [21]. After 1990 the status of specialists in the field of cultural heritage, priorities in decision-making on research or restoration of goods with artistic significance, and the organization and establishment of the objectives of the specialized institutions and bodies were regulated [1] by a series of laws, decrees, and instructions [22]. On February 12, 2001, the 2008 Order approved the certification standards for conservatives and restorers. [23]. In support of the protection of national and international cultural heritage, international organizations such as the UN, UNESCO, and the EU have developed several legal criteria to ensure respect for human rights regarding cultural identity. [2].

#### **2.3. Establishment of the first restoration laboratories and the importance of conducting physico-chemical investigations in order to prepare the restoration documentation**

##### *Establishment of the first laboratories for the restoration and research of artifacts*

Ensuring the continuity and permanence of works of art has led to the imperative need to practice restoration and conservation based on scientific norms and principles. For this purpose, various international cooperation bodies, institutions, and laboratories have been established. [21]. In Germany, the first Restoration Laboratory was established in Berlin in 1882 [4], in 1888 Friedrich Rathgen ( 1862-1942 ) founded the Research Laboratory at the Royal Museums in Berlin [24], [25], and in 1920 Alexander Scott founded the Research Laboratory of the British Museum [26], [25]. Edward Forbes founded the Department of Technical Studies at the Fogg Museum at Harvard University in 1928, in which chemist Rutherford John Gettens and restorer George Stout [27], [25] were used to research the materials and techniques used to make works of art [25]. The Louvre Museum founded the Restoration Laboratory in France in 1936[4]; while the Central Restoration Institute of Rome was established in 1940[4].

”



### **3. The use of metals in plastic art**

#### **3.2. Easel painting on Romanian territory**

Throughout Romania's Middle Ages and transition to modern times, painting was mainly focused on frescoes, wood icons, and miniatures [40]. Towards the end of the 18th century, easel painting began to appear in Moldova as an artistic genre. This was influenced by the Fanar kings of the political elite and foreign artists who brought new and innovative techniques to Romanian art, including painting on metal, ivory, and miniature enamel [41]. In the 19th century, the easel painting ( which made the transition from ecclesiastical to secular painting ) was a particular development on Romanian territory [40].

#### **3.3. Stratigraphy of easel paintings on metal supports**

In general, the stratigraphy of the painting of easel [5], [4] include:

- metal support;
- color layer;
- vernis or ( solution consisting of a resin - natural or synthetic -, solubilized in a solvent which, after application over a painting and evaporation of the solvent form a layer or film with a degree of solubility different from that of the color layer - and therefore reversible-, which acts as both a protective layer and a solution for saturation of the base color [39].

The material structure of a painting, whose objective is to maintain the painting layer applied on its surface, is called the support. [6]. Support is of fundamental importance in compiling a painting both in terms of durability [42], [43], and aesthetics [43].

Depending on the degree of elasticity characteristic of each type of material, the supports can be classified into:

- *flexible supports* - canvas, paper [6], [42], parchment [44];
- *semi-rigid supports* - cardboard, paper backed with canvas, canvas backed with cardboard [6], [42] papyrus [44];
- *rigid supports* - metal, plaster, stone, wood, glass [6], [42], mother-of-pearl, ivory, and bone [44].

### **4. The use of non-ferrous alloys in the Romanian religious silver work**

#### **4.1. Establishment and organization of the guilds of silversmiths in the Romanian Lands**

The Saxons, displaced from western Germany to Transylvania ( in the middle of the 12th century ) by King Géza II of Hungary, developed the art of precious metal processing on Romanian territory. [57]. During the 14th century, Saxon craftsmen created silver works that showed a clear connection between Western art and Byzantine traditions [58]. This is because, until the 12th century, the art of precious metalworking was heavily influenced by the artistic style of Byzantium [57].

During the 14th century, the first silversmith guild was established in Transylvania [22]. This marked the beginning of guilds in Romanian Lands, with Wallachia and Moldova soon forming their own guilds as well [61].

The first goldsmiths' guild statute on the Wallachian territory was established in Cluj in 1473[57]. In 1494, the regulations of the silversmith guilds in Sibiu and Mediaş were modernized [60], and in 1511, around 40 silversmiths from Braşov were organized in the guild [60], [61].

During the XV-XVI centuries in Transylvania, the goldsmiths' guilds enacted policies that limited foreign competition, maintained professional secrecy, and increased the production of silver pieces [41]. The reputation of the association of Transylvanian silversmiths was secured and developed through adherence to the guild's rules, conscience, and professionalism [41]. Until the mid-15th century, artisans from Transylvania's Saxon community exclusively produced parts made of precious metals [57].

Since the 16th century, the silversmiths from Moldova and Wallachia have contributed to developing the silver-work in the Romanian Middle Ages. [22]. The guild of silversmiths in Wallachia was founded in 1634, only two years after Matei Basarab took the throne. In 1669, the Guild of Moldovan Silversmiths was established in Iaşi. Silver workshops were established in the monasteries of the Romanian Lands. [60], [61], [41]. Starting with the second half of the 18th century and during the 19th century, due to the presence of Russian and Austrian pieces of silversmith on the territory of Romanian Lands, the number of local silverware workshops in Wallachia, Moldova and Transylvania has decreased significantly [66].

#### **4.2. The importance of Transylvanian silversmithing workshops in the development of the cult silver work**

To realize the pieces in the silver-work workshops in Transylvania, the sponsors from Moldova and Wallachia sent to the Transylvanian artisan's precious metals either in the form of coins or in their native state [65]. The sale of silver and gold between Moldova and Wallachia - on the one hand - and Transylvania - on the other - was limited and strictly regulated [65].

At the growing demand of the voivodes, especially the rulers Şerban Cantacuzino (1640-1688) [67] and Constantin Brâncoveanu (1654-1714) [68], Saxon silversmiths modified their iconography, ornamentation and models to meet the requirements of liturgical silver-work [60], [41].

## **PART II: EXPERIMENTAL RESEARCH**

### **7. Studies and researchs on easel paintings on metal supports**

Identifying the chemical components of easel paintings on metallic supports is essential to diagnose and determine the appropriate restoration treatment accurately.

Easel paintings technique on metal supports ( iron, copper sheet, etc. ) has its origins in medieval Europe [129]. Copper plates began to be widely used by Dutch and German painters from the second half of the sixteenth century to the middle of the seventeenth century, especially for oil painting [130]. At the end of the 18th century, iron support was often used for mass religious painting in Spanish colonies [29]. Metal surfaces have often been covered with a thin layer of tin for corrosion protection [129].

The paint layers consist of a wide range of inorganic pigments with well-established chemical formulas. Painters have used these pigments on a large scale over time due to their stability (to microclimate conditions) and high coverage power [131].

*The specific objectives of the research* were to identify the component materials, to establish the authenticity ( signatures and dates - if there is ) and highlighting the state of

conservation of the following easel paintings on unclassified metal supports from a private collection:

- "Religious procession", anonymous author; execution technique: oil colors on metal support; size: 19 x 14 cm;
- "Sf. Antony", signed and dated ( on the front in the lower right corner - "Lecca 1866" and on the verso, in the central upper part: "Leca / O ΑΓΙΟΣ ΑΝΤΩΝΙΟΣ 1866"); execution technique: oil colors on metal support; size: 33 x 26 cm.

To identify the component materials of the paintings made on metal supports, the following analyzes were performed to establish authenticity and highlight the state of conservation: digital radiography (RD), X-ray fluorescence spectrometry (XRF), X-ray microfluorescence ( $\mu$ -XRF), metallography and electron scanning microscopy coupled with X-ray spectroscopy with energy dispersion (SEM-EDX).

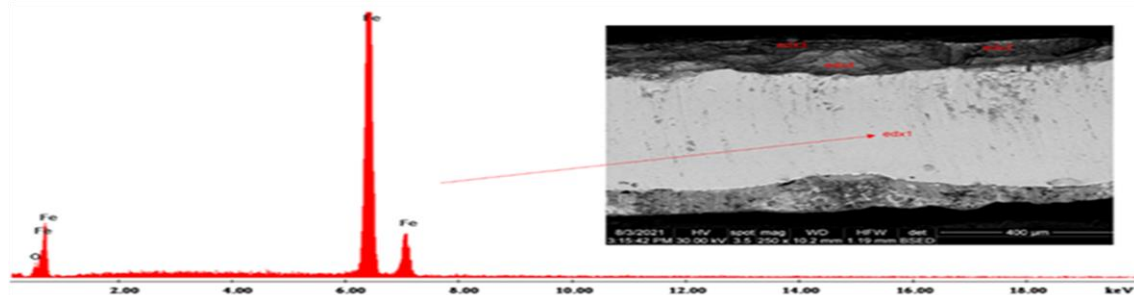
### 7.1. Studies and researchs on easel painting on metal support "Religious procession"

The painting "Religious Procession" is attributed to an anonymous Italian painter from the end of the 18th century ( fig. 7.1 ).

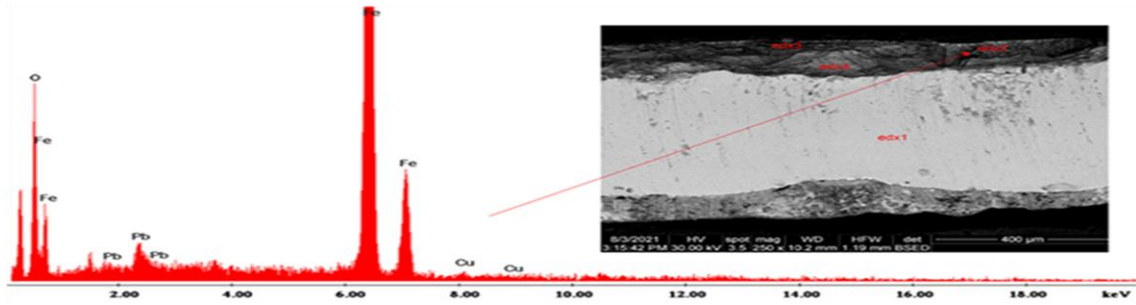


**Figure 7.1.** Easel painting on metal support "Religious procession, "overall images: a ) face and b )verso.






Easel painting on metal support "Religious procession" is made in oil colors on iron and not copper, as erroneously indicated on the authentication label on the verso of the painting. Based on the electron microscopy analysis ( SEM-EDX ) performed on the sample taken from the metal support, we identified the key chemicals such as Fe, Pb and Cu. The color palette consists of lead white, barium white, vermilion red and iron oxide-based pigments.

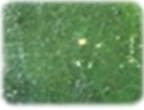


**Figure 7.6.** EDX 1 spectrum ( left ) in which the main iron spectral line and the SEM micrograph ( right ), 400 microns, magnification power 250: 1 are visible.



**Figure 7.7.** EDX 2 spectrum (left) in which the main spectral line of iron and the lead and copper spectral lines, respectively SEM micrography (right), 400 microns, magnification power 250:1

XRF / photographic details from the areas of the XRF analysis points	Name and concentration of detected chemical elements (% wt) (displayed in descending order)	Result / Interpretation ( name of the pigments )
 1. Priest, garment, white gray	<p><b><u>Pb 37,41</u></b>  <b><u>Ba 2,42</u></b>                      Fe 0,38                      Cr 0,16                      Cu 0,03</p>	Lead white (2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub> , PbCO <sub>3</sub> ), predominantly at all XRF analysis points performed, possible traces of ochre and other colors based on iron oxides.
 2. Faithful, right, down, garment, reddish-brown blouse	<p><b><u>Pb 9,12</u></b>  <b><u>Hg 6,86</u></b>  <b><u>Ba 2,66</u></b>                      Fe 2,41</p>	Lead white (2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub> , PbCO <sub>3</sub> ) predominantly at all XRF analysis points performed, vermilion ( HgS synthetic mercury sulfide ), ochres, and other colors based on iron oxides.
 3. Faithful, right, down, garment,, brown reddish blouse	<p><b><u>Pb 17,02</u></b>  <b><u>Ba 10,01</u></b>                      Fe 2,77                      Hg 0,62</p>	Lead white (basic lead carbonate 2 PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub> and lead carbonate PbCO <sub>3</sub> ), predominantly at all XRF analysis points performed, vermilion ( synthetic mercury sulfide), lead white, possible BaSO <sub>4</sub> barium sulfate, ochres and other colors based on iron oxides.
 4. Faithful, bottom right, garment, sleeve, gray white	<p><b><u>Pb 10,69</u></b>  <b><u>Ba 2,18</u></b>                      Fe 1,55</p>	Lead white (basic lead carbonate 2 PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub> and lead carbonate PbCO <sub>3</sub> ), predominantly at all XRF analysis points performed, possibly barium sulfate BaSO <sub>4</sub> , ochre, probably carbon black.
 5. Faithful, bottom right, garment, blue skirt	<p><b><u>Pb 6,71</u></b>  <b><u>Ba 2,47</u></b>                      Fe 0,73</p>	Lead white (basic lead carbonate 2 PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub> and lead carbonate PbCO <sub>3</sub> ), predominantly at all XRF analysis points performed, Prussian blue ( complex inorganic salt, consisting of differently loaded iron ions and negatively charged ions of hexacyanoferrate Fe <sub>4</sub> [Fe(CN) <sub>6</sub> ] <sub>3</sub> x H <sub>2</sub> O) or ultramarine blue ( sodium complex silicate Na <sub>7</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> S <sub>3</sub> ), possible barium BaSO <sub>4</sub> .

XRF / photographic details from the areas of the XRF analysis points	Name and concentration of detected chemical elements (% wt) (displayed in descending order)	Result / Interpretation ( name of the pigments )
 <p>6. Faithful, median right, garment, green skirt</p>	<p><i>Pb</i> 7,95  <i>Ba</i> 2,17  <i>Fe</i> 0,68  <i>As</i> 0,85  <i>V</i> 0,30</p>	<p>Lead white (basic lead carbonate <math>2 \text{PbCO}_3 \cdot \text{Pb(OH)}_2</math> and lead carbonate <math>\text{PbCO}_3</math>), predominantly at all XRF analysis points performed, possibly barium sulfate <math>\text{BaSO}_4</math>, green earth, possibly ochre. No copper or chromium is present.</p>

## 7.2. Studies and researches on easel painting on metal support "Saint Anthony"

This "Sf. Antonie" artwork is an oil painting created on a metal support. It is signed and dated on both the front (in the lower right corner as "Lecca 1866" - see fig. 7.20.a) and the verso (in the central upper part as "Leca / O ΑΓΙΟΣ ΑΝΤΩΝΙΟΣ 1866" - phonetically translated as "AGIOS ANTONIOS" in Greek, meaning St. Antonie - see fig. 7.20.b). The work was purchased on a "principle seen, pleasantly, bought" and is part of a private collection.



Figure 7.20. Easel painting on metal support" Sf. Antonia ", direct light overview: a ) front and b ) back.

In the lower right corner of the easel painting on a metal support, you can see the hard-readable traces of the signature (from the second plane) "Lecca," which was applied to the upper left side of the signature and dating "Lecca 1866" from the foreground (fig. 7.23.a - 7.25.a). In the upper central area of the verso of the painting (fig. 7.23.b, 7.24.b, 7.25.c, d, e), the signature "Leca" is applied. The lower part of it is visible in the dating "1866" and the entry "O ΑΓΙΟΣ ΑΝΤΩΝΙΟΣ" (in phonetic transcription AGIOS ANTONIOS, translation from the Greek language St. Antonie).

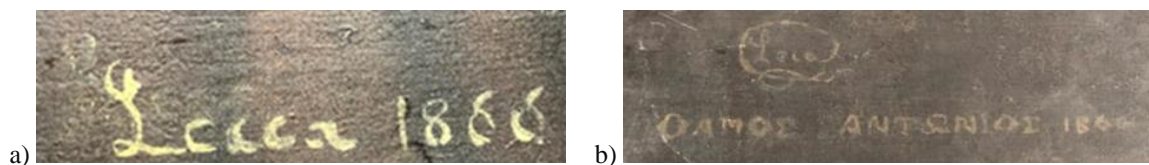
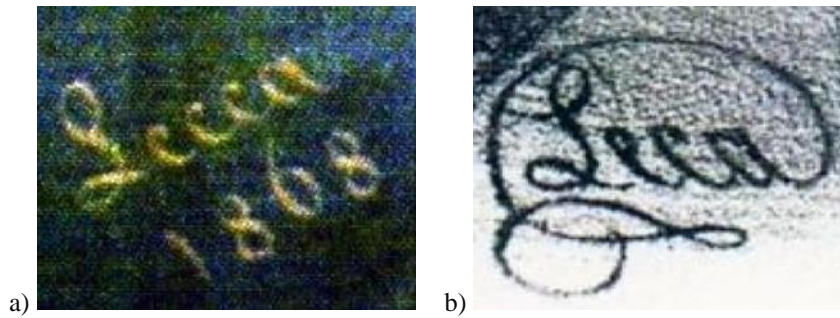


Figure 7.24. Signatures and dates: a ) front, bottom left, and b ) back, upper center.

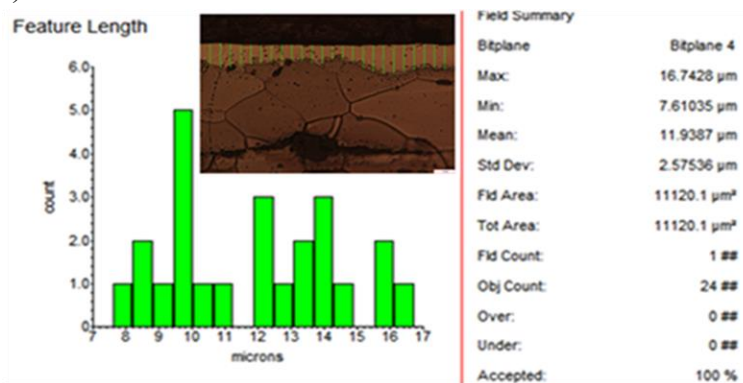




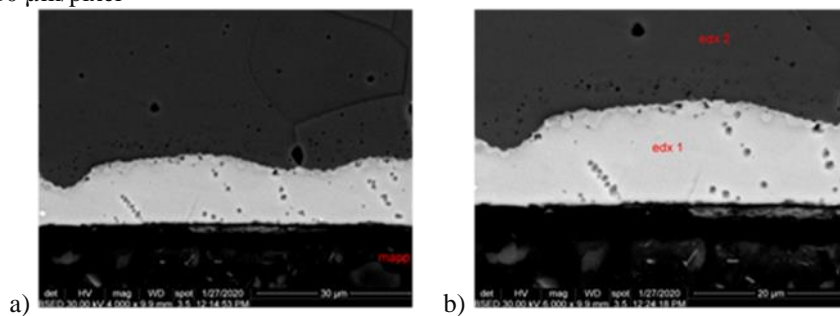
**Figure 7.28.** Details of the authentic signatures of the painter Constantin Lecca ( a, b ) [ 154 ].

The color palette used by the painter consists of pigments based on iron oxides ( ores, brunettes ), charcoal black, possibly asphalt, and lead white.

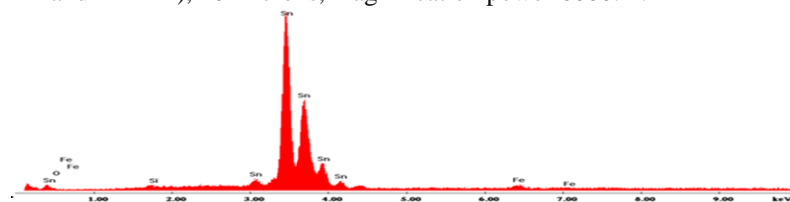
The measurements' results established that the support is made of wrought iron and is covered with tin. The thickness of the deposited layer ( fig. 7.33 ) on the metal support was examined using an optical microscope. According to the results of the measurements, the tin layer deposited on the wrought iron support has thicknesses between 7.61 and 16.74 micrometers. The micro-probe has a non-uniform deposited tin layer thickness of almost 12 micrometers (  $\mu\text{m}$  ).



**Figura 7.33.** Măsurători ale grosimii stratului subțire de staniu care a fost depus peste suportul din fier forjat, calibrare: 0.07610  $\mu\text{m}/\text{pixel}$



**Figure 7.35. a )** Overall SEM micrography, 30 microns, magnification power 4000: 1, and b ) SEM micrography ( indicating the EDX 1 and EDX 2 ), 20 microns, magnification power 6000: 1.



**Figure 7.36.** EDX 1 spectrum in which the main tin spectral lines are visible.

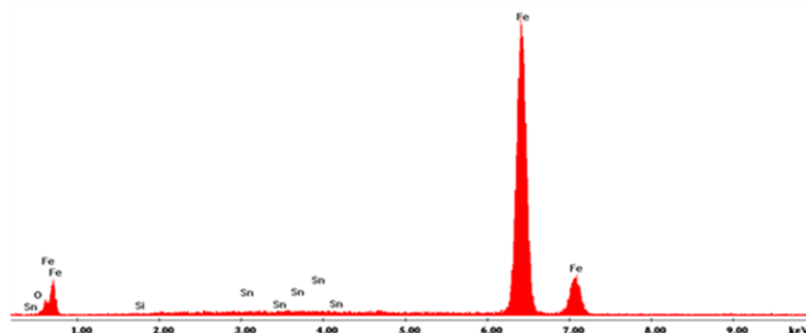


Figure 7.37. EDX 2 spectrum in which the main iron spectral lines are visible.

## 8. Studies and research on icon revetments

The specific objectives of the research were to identify the component chemicals, determine the original execution technique, establish the authenticity of the markings, and highlighting the conservation status of a number of seven wipes for ( unclassified icons, from a private collection ) divided into three categories, as follows:

1. *Icon revetments of Romanian origin (executed in local workshops for processing precious metals):*

- Silver alloy icon revetment "St. Andrew" - 15 x 12 cm, 56 grams (51 grams without halo, 5 grams removable halo);
- Silver alloy icon revetment "Saint Great Martyr George"- 18.5 x 14 cm, 197 grams (193 grams without halo, 4 grams removable halo);
- Silver alloy icon revetment "Coronation of the Virgin" - 25.7 x 19.5 cm, 304 grams.

2. *Icon revetments of Russian origin (which were executed in Russian workshops for processing precious metals, after which they were sold on Romanian territory):*

- Silver alloy icon revetment "Mother of God with Baby" - 26.04 x 21.5 cm, 184 grams (123 grams without halo, 61 grams removable halo);
- Silver alloy icon revetment "Madonna and Child" - 19.5 x 14 cm, 94 grams.

3. *Icon revetments with counterfeit markings:*

- Non-ferrous alloy icon revetment "Sf. Martyr George" - 17.08 x 14.02 cm, 110 grams (105 grams without halo, 5 grams removable halo);
- Non-ferrous alloy icon revetment "Sorrowful Mother"- 27.5 x 23 cm, 187 grams (167 grams without halo, 20 grams removable halo).

To identify the materials and techniques of execution, as well as to highlight the state of conservation and to establish the authenticity of icon revetments, a wide range of analyzes (metallographic was performed, of X-ray fluorescence spectrometry, electronic scanning microscopy, X-ray spectroscopy with energy dispersion, digital radiography, and computed tomography).

### 8.1. Icon revetments of Romanian origin

#### 8.1.1. Silver alloy icon revetment "St. Andrew"

On the "Sf. Ap. Andrei" ( fig. 8.1 ), two punches are stamped in the right central area ("EF" and "12").



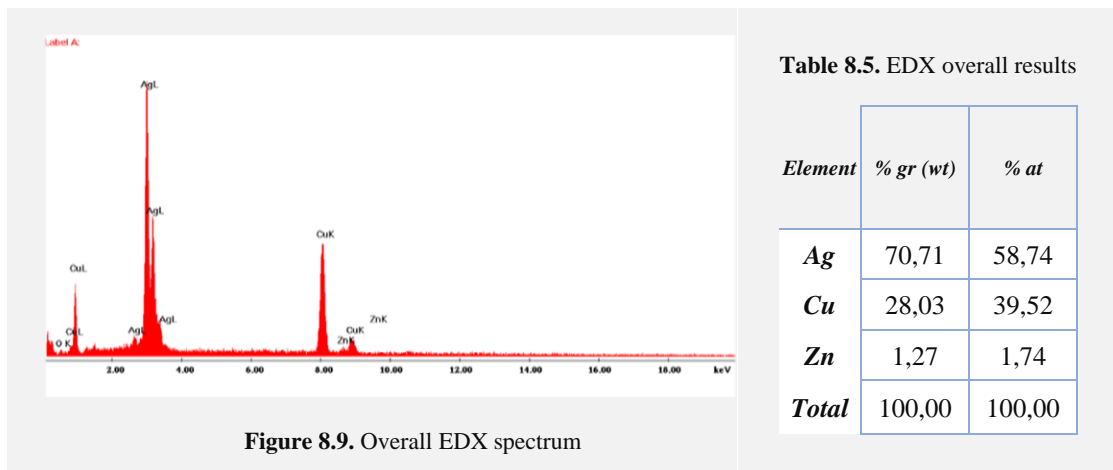
**Figure 8.1.** Overview of the icon "Sf. Apostle Andrei": a ) front and b ) verso.

Icon revetment "St. Andrew" has two marks: "EF" ( Latin letters ) - silversmith monogram ( fig 8.2.c ) and silver title mark "12" ( fig. 8.2.b).



**Figure 8.2.** a ) Details of the markings stamped on the lower right edge of the icon revetment "St. Andrew", b ) monogram of the silversmith "EF," and c ) standard silver mark "12 ".

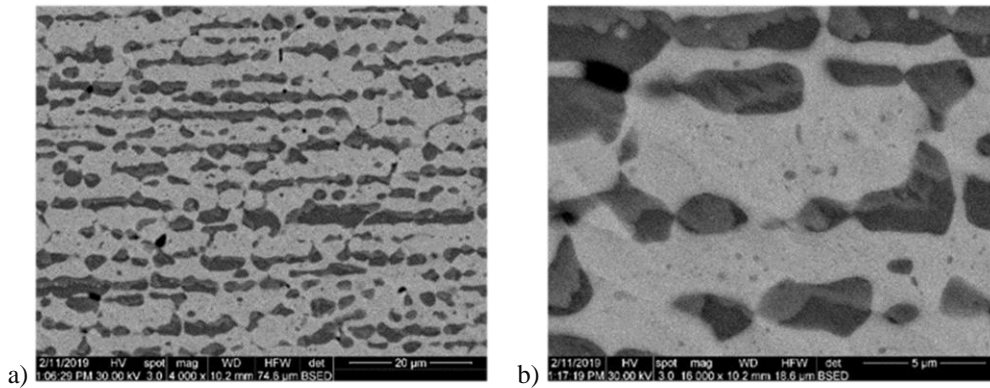
The main spectral lines of silver, copper, and zinc are visible in the EDX spectrum as a whole ( fig. 8.9 ). The tips of the silver spectral lines are pronounced.



**Figure 8.9.** Overall EDX spectrum

The structure of the silver-copper-zinc ternary alloy (Ag-Cu-Zn) is highlighted both in the electron microscopy micrography with scanning (SEM) 20 microns at a magnification power 4000: 1 ( fig. 8.10.a ), as well as in 5 microns at a magnification power of 16000: 1 ( fig. 8.10.b).





**Figure 8.10.** SEM micrographs highlighting the structure of the ternary alloy Ag-Cu-Zn: a ) 20 microns and magnification power 4000: 1 and b ) 5 microns and a magnification power 16000: 1.

Both in the general distribution folder of the elements on the sample analyzed after grinding and in the specific EDX spectrum ( fig. 8.11 ), the following constituent chemical elements have been identified: silver, copper, and zinc.

In the case of the silver alloy icon revetment "St. Andrew", based on the investigations carried out, the concordance between the brand of the silver title "12" silver lots ( equivalent to 750/1000 silver ), stamped on the window and test results indicating a silver alloy with concentrations ( expressed as a percentage by weight ) between 70.71% and 77.39% silver.

### 8.1.2. Silver alloy icon revetment "Saint Great Martyr George"

On the icon revetment "Saint Great Martyr George" ( fig. 8.12), two punches are stamped in the lower central area ("and "12"); at the same time, on the surface of the icon revetment "Saint Great Martyr George" was attached the halo of who does not present markings. In the upper central part is the inscription ( Cyrillic alphabet ) "Σ. ΓΕΟΡΓΙΕ" ( phonetic transcription St. Gheorghe ).



**Figure 8.12.** Overview of the icon revetment "Saint Great Martyr George": a ) front and b ) verso.

In the lower central part of the icon revetment "Saint Great Martyr George" ( fig. 8.13), two adjacent punches are stamped: KJI" (Cyrillic letters; phonetic transcription CL) -

silversmith monogram ( fig. 8.13.b ) and silver title mark "12" ( fig. 8.13.c ), specific to the loti system - 12 silver lots (equivalent to 750 ‰ or 75% Ag in alloy).



**Figure 8.13.** Bookmarking details: a ) marking positioning in the lower central area; b ) silversmith monogram "KJL" phonetic transcription ( "CL" ) and c ) standard silver mark "12" .

Concentration averages of the constituent chemical elements, expressed as a percentage by weight, recorded on the icon revetment "Saint Great Martyr George" (made of plastic deformed silver plate) ( table 8.10 ) are: 75% Ag and 20.59% Cu.

**Table 8.10.** Table with mean of recorded chemical compositions (face and verso)

<i>Element</i>	<i>XRF 1 %wt</i>	<i>XRF 2 (verso) % wt</i>	<i>XRF 3 (verso) % wt</i>	<i>Average concentration % wt</i>
<i>Ag</i>	71,91	83,90	70,09	75,3
<i>Cu</i>	26,50	15,03	20,25	20,59
<i>Zn</i>	0,74	0,36	0,69	0,59

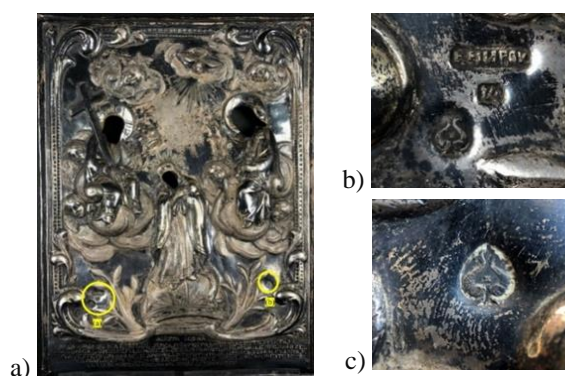
It has been confirmed that the icon revetment "Saint Great Martyr George" is made of a silver plate specific to the silver title brand "12" .

### 8.1.3. Silver alloy icon revetment "Coronation of the Virgin"



**Figure 8.18.** Icon painted on wood, with silver revetment "Coronation of the Virgin" overall images of a) front and b ) verso.

The icon revetment "Holy Trinity" or "Coronation of the Virgin" shows on the lower left three types of markings ( fig. 8.24.b ): silversmith mark "F. Filipov", silver title mark "4" and the Romanian control mark depicting two dolphins framed in a geometric figure in the middle of which the Latin figure "II" is observed. Control mark ( fig. 8.24.b, c ) is stamped in two distinct areas (next to the group of markings on the lower left and individual left, at the bottom right).

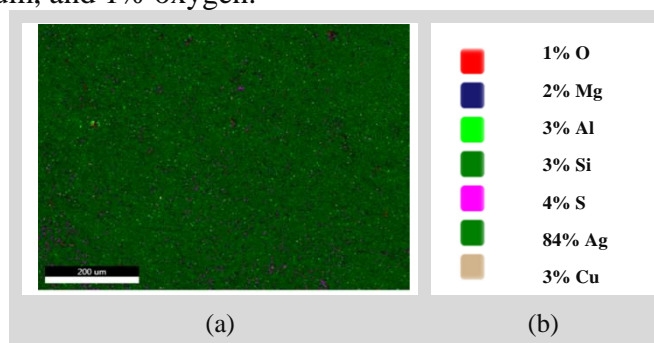


**Figure 8.24.** a ) Overview of the icon revetment "Coronation of the Virgin" in which the positioning of the punches is indicated; b ) details of the group of markings on the lower left side consisting of master mark silversmith "F Filipov", the punch of the silver title "14" and the control mark (two "dolphins" in the middle of which is the Roman figure "II") and c ) the control mark stamped at the bottom right.

Teodor / Theodor Filipov was a known silversmith of Russian origin who settled in Bucharest and married in 1860 Maria Ștefănescu [171].

According to "Law and Regulation establishing control over objects made of precious metals" ( since 1906 and March 27, 1924 ), on the Romanian territory, there were three types of control marks with "dolphins" in the period 1906-1926 [160]. The differentiation between the marks with "dolphins" consists of the different geometric classifications and the presence of a distinct Roman number (stamped in the frame) and by one of the Roman numerals - "I", "II" or "III" -stamped in the frame. The silver title correspondent for the Roman number "I" is 950/1000 silver, for "II" - 800/1000 silver, and for "III" - 750/1000 silver [174], [160].

In electron microscopy micrography with scanning (SEM) of 200 microns (fig. 8.28), the following concentrations of chemical elements on the surface of the sample expressed as a percentage by weight may be observed: 84% silver, 4% sulfur, 3% copper, 3% aluminum, 3% silicon, 2% magnesium, and 1% oxygen.



**Figure 8.28.** General distribution map of chemical elements on the sample's surface: a ) SEM micrography, 200 microns; b ) legend and concentrations of chemicals expressed as a percentage by weight.

**Table 8.19.** Average of the recorded chemical compositions ( face and verso).

Element	XRF 1 % wt	XRF 2 % wt	XRF 3 % wt	XRF 4 %wt	XRF 5 (verso) % wt	XRF 6 (verso) % wt	XRF 7 (verso) % wt	Average concentration % wt
Ag	94,22	91,56	93,56	91,52	97,51	98,18	98,13	94,95
Cu	3,95	5,49	6,37	4,31	1,65	1,70	1,76	3,60
Au	1,76	2,94	-	-	-	-	-	2,35

Following a large study, we concluded that the icon revetment "Coronation of the Virgin" was performed by the Russian-born silver craftsman Teodor Filipov who settled in Bucharest around 1860. Electron microscopy analyses (EDX) and X-ray fluorescence spectrometry confirmed the markings applied to the saw.



## 8. 2. Icon revetments of Russian origin

### 8.2.1. Silver alloy icon revetment "Mother of God with Baby"



Figure 8.31. Overview of the icon revetment "Mother of God with Baby": a ) face and b ) verso.

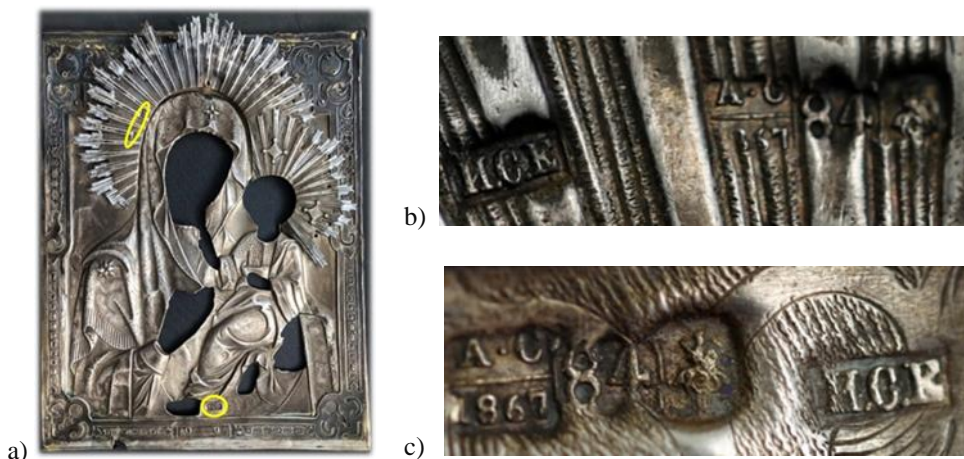


Figure 8.32. a ) Overview of the cover for the icon revetment "Mother of God with Baby" in which the positioning of the following punches is indicated: silversmith mark "И.С.К." (phonetic transcription I.S.K.), control mark " $\frac{A.C.}{1867}$ " (phonetic transcription A.S./1867), silver title mark "84" and city mark (Moscow coat of arms - "St. George killing the dragon"); b ) detail of markings stamped on the halo and c ) detail of markings applied in the lower central part.

The research carried out on the icon revetment "Mother of God with Baby" of Russian origin allowed me to identify four markings: silversmith "И.С.К." (phonetic transcription I.S.K.); verification mark " $\frac{A.C.}{1867}$ " (phonetic transcription A.S./1867); silver title mark "84" and the city brand (Moscow's coat of arms - St. George killing the dragon).

Analyzing the catalogs of Russian silversmiths from the 19th century, we managed to identify the silversmith and the control mark, as follows: monogram "И.С.К." (phonetic transcription I.S.K.) from the silversmith mark "И.С.К." may belong to the Russian silversmith Иван Семенов Комаров (phonetic transcription Ivan Semenov Komarov) which operated in 1808 in the Russian village Подольское (phonetic transcription Podol'skoye) [175], and the monogram of the control mark " $\frac{A.C.}{1867}$ " (phonetic transcription A.S./1867) probably belongs to the controller silversmith А. Свечин (phonetic transcription A. Svechin) who worked in Moscow between 1862-1875 [175].

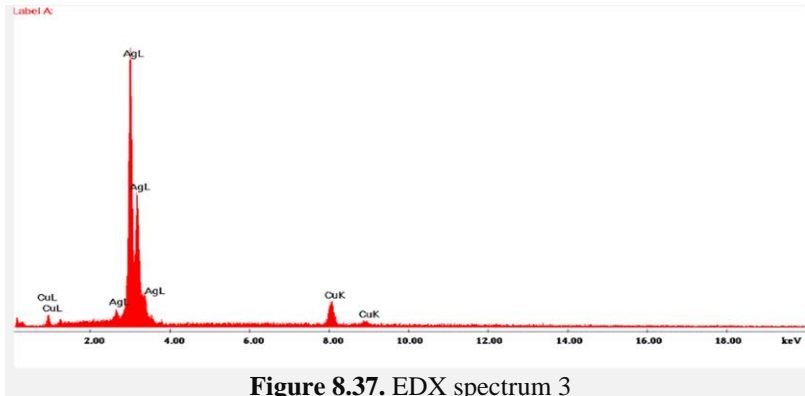


Figure 8.37. EDX spectrum 3

Table 8.22. EDX results 3

Element	% wt	% at
Ag	88,81	82,38
Cu	11,19	17,62
Total	100,00	100,00

Following the metallographic analysis, we found that the saw was made by lamination and mechanical stamping, techniques that developed in the 19th century, and electron microscopy analyses (SEM - EDX) confirmed the concentration ( expressed as a percentage by weight) of Ag from of alloy 87.88 - 90.73% of standard silver mark.

### 8.2.2. Silver alloy icon revetment "Madonna and Child"



a)

b)

Figure 8.40. Overview of the "Virgin with Baby "icon: a ) front and b ) verso.

Icon revetment "Madonna and Child" (fig. 8.40) does not show markings. According to the metallographic analysis, the microstructure of the analyzed sample is specific to the Ag-Cu-Zn type eutectic alloys.

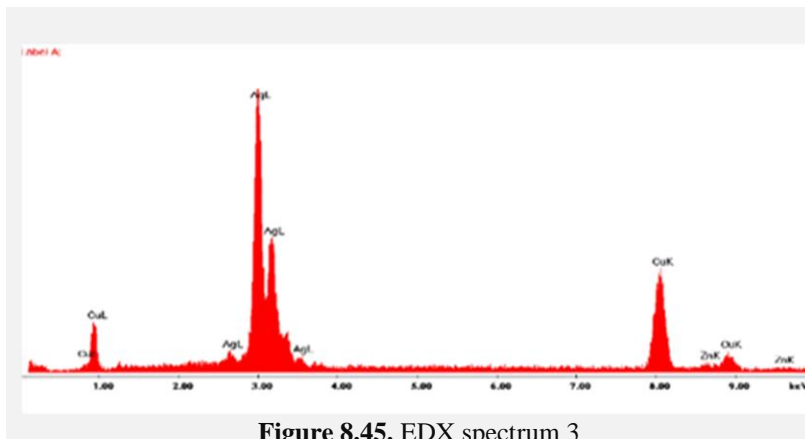


Figure 8.45. EDX spectrum 3

Table 8.27. EDX results 3

Element	% gr (wt)	% at
Ag	66,85	54,34
Cu	30,73	42,41
Zn	2,42	3,24
Total	100,00	100,00

Analysis of electron scanning microscopy coupled with energy-dispersed X-ray spectroscopy (SEM - EDX) performed at three points on the surface of the sample taken from the cast indicates that the iconic screw is made of a silver-ternary alloy Ag - Cu - Zn, rich in silver (between 66.85 - 83.76%), with copper-rich phases (14.7 - 30.73% Cu) and zinc (1.54 - 2.42%).

### 8.3. Icon revetments with counterfeit markings

#### 8.3.1. Non-ferrous alloy icon revetment "Sf. Martyr George"

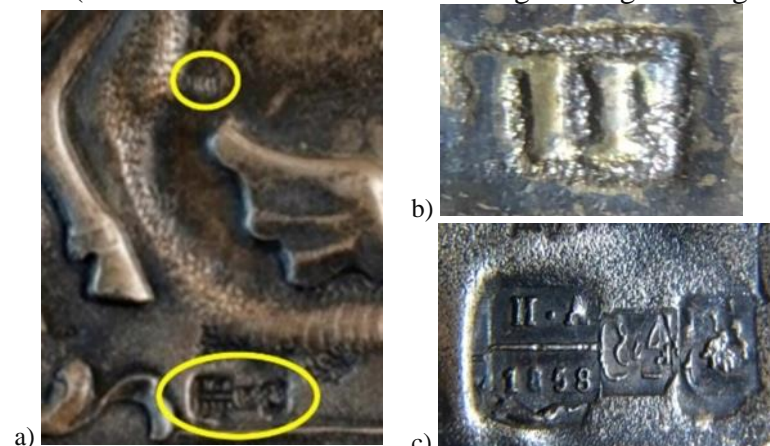
In the lower central part of the fern for the icon revetment "Sf. Martyr George" (fig. 8.46), four types of marks specific to silverware works of Russian origin (fig.8.47) are visible. The halo is unmarked and removable.



**Figure 8.46.** Overview of the icon revetment "Sf. Martyr George": a ) front and b ) verso.

Marking types ( Fig. 8.47 ) present on the "St. Martyr George":

- silversmith mark „ΠΠ” (phonetic transcription PG);
- control mark " $\frac{И·А}{1858}$ " (phonetic transcription I·A/1858);
- silver title mark „84”;
- city mark ( Moscow coat of arms - "St. George killing the dragon").



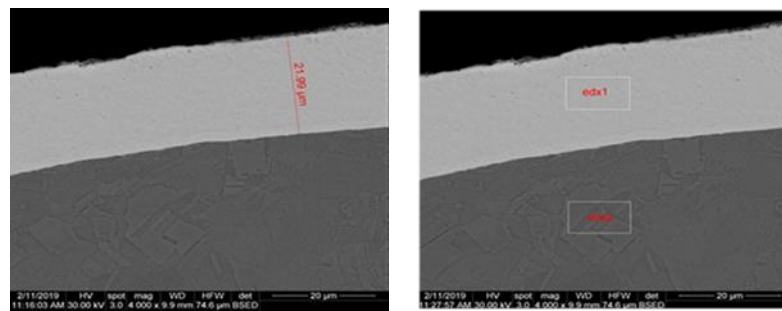
**Figure 8.47.** a ) Details of the markings positioned on the lower edge and in the lower center; b ) silversmith mark "ΠΠ" ( phonetic transcription PG), control mark " $\frac{И·А}{1858}$ " (phonetic transcription I·A), silver title mark "84" and city mark ( Moscow coat of arms - "St. George killing the dragon").



These carefully correlated markings, which give the impression of authenticity, could only be applied by criminals specializing in art counterfeiting. Only after the chemical-metallurgical analyses to which the piece was subjected I noticed uneven galvanic silver deposits on a copper plate ( fig. 8.48 ).

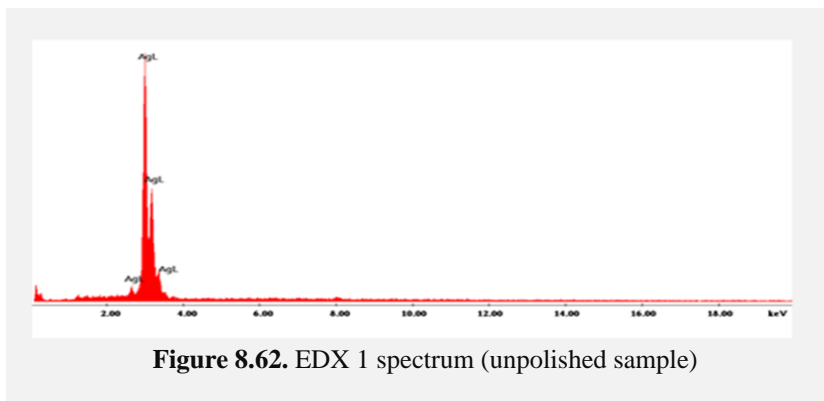


**Figure 8.48.** Technical details (reverse) in which the pure silver layer is electrolytically deposited (colloidal silver) is observed on the copper matrix.



**Figure 8.61.** a ) SEM micrographs of silver layer thickness (21.99 microns) deposited on the copper matrix: a ) 20 microns, magnification power 4000: 1; b ) 20 microns, magnification power 4000: 1 and indication of EDX analysis points (EDX 1 / microzone 1 - located on the silver layer deposited on the copper matrix and EDX 2 / microzone 2 - positioned on the copper matrix).

At the X-ray spectroscopy analysis point with energy dispersion EDX 1 (microzone 1 - layer deposited on the copper matrix) (table 8.32), a concentration expressed as a percentage of 100% silver was identified. EDX 1 analysis identified the deposition of a pure silver layer on the copper matrix. The main silver spectral lines are visible in the spectrum of X-ray spectroscopy with energy dispersion (EDX - microzone 1) ( fig. 8.62).



**Figure 8.62.** EDX 1 spectrum (unpolished sample)

**Table 8.32.** EDX 1 results ( microzone 1 ) - layer deposited on the copper matrix

Element	% gr (wt)	% at
Ag	100,00	100,00
<b>Total</b>	100,00	100,00

At the X-ray spectroscopy analysis point with energy dispersion (EDX 2 - microzone 2, where the base material is copper) (table 8.33), a concentration expressed as a percentage of 100% copper was identified. EDX 2 analysis allows the identification of the primary material - copper. The main copper spectral lines are visible in the spectrum of X-ray spectroscopy with energy dispersion (EDX 2 / microzone 2) (fig. 8.63).

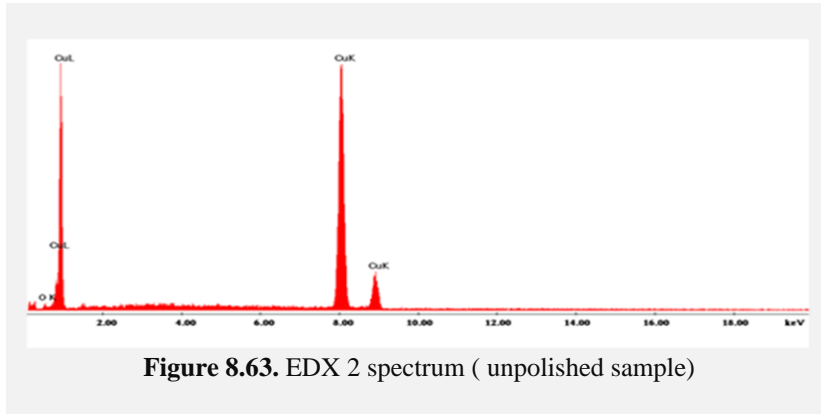


Figure 8.63. EDX 2 spectrum ( unpolished sample)

**Table 8.33.** EDX 2 results (microzone 2 ) - the basic material is copper

Element	% gr (wt)	% at
Cu	100,00	100,00
Total	100,00	100,00

### 8.3.2. Non-ferrous alloy icon revetment "Sorrowful Mother"

On the surface of the icon revetment "Sorrowful Mother" (fig. 8.68 ) two markings are applied. (fig 8.69). The halo is unmarked and removable.



Figure 8.68. Overview of the icon revetment "Sorrowful Mother": a) face and b) verso.

The icon revetment "Sorrowful Mother" has two markings ( fig. 8.69.b ): "MH" (with the letter "M" partially superimposed over the letter "H") - silversmith mark and silver title mark "13".

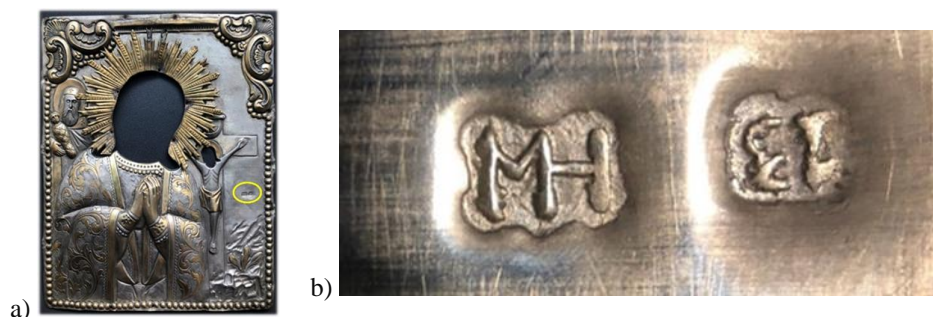
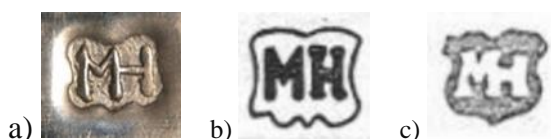


Figure 8.69. a ) Overview indicating the area where the markings are positioned; b ) detail in which you can view the group of markings formed (from left to right) from the silversmith mark "MH" and the silver title "13".

There were doubts as to the authenticity of the markings in the first stage of the visual examination. Both the silver title mark (overturned) and the silversmith mark "MH" ( with the letter "M" partially superimposed over the letter "H") (Fig. 8.70.a) seemed to be false. Probably the forger was "inspired" by the authentic marks of the Merten Herbert (1610) [157] (in the

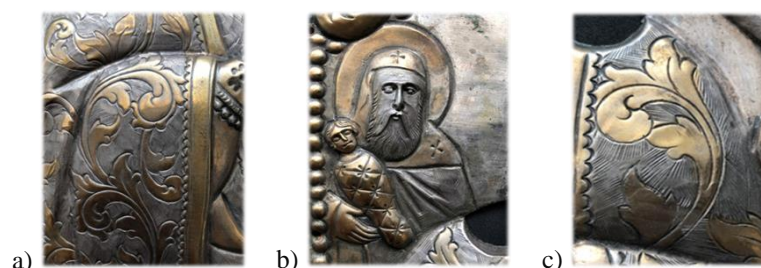


contour of the mark) and Merten Herman[n] [Stuckart] (II) (1671-1691) [157] (for overlapping letters „M” and „H”).



**Figure 8.70.** Similarities between graphism: a ) mark applied to icon revetment "Sorrowful Mother" and that of the original markings of the bodies b ) Merten Herbert (1610) [ 157 ] and c ) Merten Herman [ n] Stuckart [II ] (1671-m.1691) [157].

To highlight certain decorative elements, the icon cover was partially gilded ( fig. 8.71 ).



**Figure 8.71.** a-c ) Technical details in which partially gilded areas are observed



**Figure 8.73.** Details in which the technical deficiency in the execution of hands whose position is unnatural in relation to the body posture is visible: a ) direct light and b ) radiographic image.

Both in direct light (fig. 8.73.a), as well as in X-ray radiography (performed at a voltage of 100 kV and current of 100 microamperes) (fig. 8.73.b), the technical deficiency in the relief of the feet in the area of the hands is visible, where their unnatural position relative to the body posture is observed.

**Table 8.43.** Average of the recorded chemical compositions (face and verso)

<i>Element</i>	<i>XRF 1</i> % wt	<i>XRF 2</i> % wt	<i>XRF 3</i> % wt	<i>XRF 4</i> % wt	<i>XRF 5</i> (verso) % wt	<i>Average concentration</i> % wt
<i>Cu</i>	68,13	66,75	65,68	64,38	68,90	66,76
<i>Zn</i>	17,47	18,99	17,45	18,17	16,90	17,79
<i>Ni</i>	14,35	14,21	14,26	13,80	14,02	14,12
<i>Au</i>	-	-	1,93	2,83	-	2,38

Following performing X-ray fluorescence spectrometry analyses ( XRF ) in five points ( double-sided ), it was confirmed that the material that was intended to be silver "13" ( equivalent to 812.5 % Ag in alloy ) is an alpaca-type Cu-Zn-Ni alloy, which in some areas has been gilded.

## **9. Conclusions, personal contributions, and directions for further research**

### ***9.2. Personal contributions***

I have thoroughly analyzed data from various literature sources about metal easel painting and icon revetments.

Easel painting on metal support "Religious procession "is made in oil colors on iron and not copper plate, as erroneously indicated on the authentication label on the verso of the painting. Based on the electron microscopy analysis ( SEM-EDX ) performed on the sample taken from the metal support, we identified the critical chemical elements such as Fe, Pb, and Cu. The painter utilized a selection of inorganic pigments including lead white, barium white, vermilion red, arsenic-based yellow, as well as iron oxide-based pigments like yellow ochre, reddish brown, and green earth. This information is indispensable for the elaboration of the restoration documentation.

In the research performed on the easel painting on metal support "St. Antony", I identified the false signature applied to the painting based on an extensive study. Also, according to the results of the measurements, we established that the support is made of wrought iron and is covered with tin. The tin layer deposited on the wrought iron support has thicknesses between 7.61 and 16.74 micrometers. The narrow color palette used by the painter consists of pigments based on iron oxides, possibly asphalt, and lead white. As lead white has been identified in high concentrations in most XRF analysis points in the pictorial layer (even in the dark color area), I concluded that the preparation is on a white lead base, helpful information in the restoration process.

Regarding the seven icons for the icons analyzed, based on data from the literature and chemical-metallurgical analyses performed, we could give a clear and documented verdict on the authenticity of 5 icon droppings analyzed (3 Romanians, 2 Russians).

Thus, in the case of the silver alloy icon revetment "St. Andrew", based on the investigations, we confirmed the concordance between the brand of the silver title "12" silver lotions (the equivalent of 750/1000 silver) stamped on the fern and the results of analyzes indicating a silver alloy with concentrations (expressed as a percentage by weight) between 70.71% and 77.39% silver. The same thing happened with the icon revetment "Saint Great Martyr George", a saw made of a plastic deformed silver plate at which the value of the standard of the silver title, "12" was confirmed following the analyzes performed (75% Ag and 20.59 % Cu).

Following a large study, I came to the conclusion that the "Coronation of the Virgin" icon revetment was made by the silversmith of Russian origin, Teodor Filipov who settled in Bucharest around 1860.

The silver alloy icon revetment "Coronation of the Virgin" shows three types of marks on the bottom left: the silversmith mark "F. Filipov" , the punch of the silver title "14" and the Romanian control mark with "dolphins" (depicting two dolphins) framed in a geometric

figure in the middle of which the Latin figure "II" (corresponding to silver title 800/1000). The electron microscopy results confirmed the markings stamped on the icon revetment analyses (EDX) and the fluorescence X-ray spectrometry.

The research on the icon revetment "Mother of God with Baby" of Russian origin allowed me to identify four markings: the silversmith mark "И.С.К" ( phonetic transcription I.S.K.); verification mark " (A.C.) / 1867" ( phonetic transcription A.S./1867 ); silver title mark "84" and city mark ( Moscow coat of arms - St. Mc. George killing the dragon ). Analyzing from the catalogs of Russian silver craftsmen from the 19th century, we managed to identify the silversmith and the control craft, as follows: the monogram "И.С.К" (phonetic transcription I.S.K.) from the silver silversmith marking "И.С.К" it is possible to belong to the Russian silversmith Иван Семенов Комаров (phonetic transcription Ivan Semenov Komarov) who worked in 1808 in the Russian village of Подольское (phonetic transcription Podol'skoye, and the monogram of the control silversmith "A.C. "from the verification mark" (A.C. ) / 1867" phonetic transcription A.S./1867) probably belongs to the controller А. Свечин ( phonetic transcription A. Svechin ) which operated in Moscow between 1862-1875 [175]. Following the metallographic analysis, we found that the saw was made by lamination and mechanical stamping, techniques that developed in the 19th century, and electron microscopy analyses (SEM - EDX) confirmed the concentration (expressed as a percentage by weight ) of Ag of alloy 87.88 - 90.73%, the same as the silver title mark "84" punching on the revetment.

In the case of the icon revetment "Madonna and Child" icon revetment of Russian origin, although I did not meet any markings, analysis of electron scanning microscopy coupled with energy-dispersed X-ray spectroscopy (SEM - EDX) performed at three points on the surface of the sample taken from the cast indicates that the icon revetment is made of a ternary silver alloy Ag - Cu - Zn, rich in silver (between 66.85 - 83.76%), with copper-rich phases (14.7 - 30.73% Cu) and zinc (1.54 - 2.42% ).

Unfortunately, in Romania, as everywhere in the world, counterfeit works of art are circulating. There is also the case of two icon revetments with false markings: the icon revetment "Sf. Martyr George" which in the lower central part presents four types of marks specific to the works of silverware of Russian origin, as follows: the mark of a silversmith "ПГ" (phonetic transcription PG); verification mark "И · А" ( phonetic transcription I · A / 1858 ); silver title mark "84"; city mark (Moscow coat of arms - Saint Martyr George killing the dragon). These carefully correlated markings, which give the impression of authenticity, could only be applied by criminals specializing in art counterfeiting. Only after the chemical-metallurgical analyses to which the piece was subjected, I noticed that it is the non-uniform galvanic deposit of silver on a copper plate.

The second counterfeit piece, the icon revetment "Sorrowful Mother" has two markings: the craft mark - "MH" ( with the letter "M" partially superimposed over the letter "H") and the brand of the silver standard "13". The quality of the technique of performing the fern is questionable as proof that the position of the hands is unnaturally related to the position of the body, but only based on electron microscopy analysis did we identify concentrations of chemical elements typical of an alpaca-type Cu-Zn-Ni alloy that in some areas was gilded.

The methodology used to investigate the artifacts listed above may be a standard procedure.

The results of the research carried out on the analyzed mobile cultural goods and the laboratory experiments performed on the aforementioned artifacts, were translated into 6 articles published as the first author - two of which in journals (1 with impact factor) and participation with papers at 4 international conferences, of which 3 with published articles (in Proceeding).

In order to address the doctoral research topic, we went through the master's program "Synthesis and Processing of Special Metallic Materials "within the Faculty of Metals Science and Engineering, Polytechnic University of Bucharest.

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### 9.3. Research follow-up directions

Future research perspectives will consist of complementing the database by adding an increasing number of data on both easel paintings on metal media, as well as information on icon revtments to complete the results of physico-chemical investigations conducted in this paper. The higher the number of artifacts investigated, the more conclusive the results of physico-chemical investigations will be for the characterization of execution materials and techniques, establishing the authenticity and state of conservation, and developing the restoration documentation. The methodology used to investigate the artifacts listed above may be a standard procedure.

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