UNIVERSIDADE NOVA DE LISBOA

Faculdade de Ciências e Tecnologia

Departamento de Conservação e Restauro

Part I

Comparing derivatization methods for amino acids – one and two-step procedures using Gas Chromatography – Flame Ion Detector (GC-FID)

Part II

STORY OF AN ICON
From its execution until its conservation

Por

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Dissertação apresentada na Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa para obtenção do grau de Mestre em Conservação e Restauro

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Refering to the first part of this thesis, I thank to the Chemistry Department of the New University of Lisbon, particularly to the Bio Organic Analytical group, where this work was inserted in. Thanks are extended to Constança Moctezuma, Pedro Sanchez (post-Doc) and Ana Rybka (PhD) for all the assistance, support and friendship during this stage of the work.

Concerning to the second part of this thesis the work was carried out in the Laboratory for Icons, oil paintings and wood carvings of the Conservation Department of the Benaki Museum in Athens, Greece. The analysis of μFT-IR and some photographs of the cross sections were made in the Department of Conservation and Restoration of the Faculty of Sciences and Technology of the New University of Lisbon.

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Єφγαριστω Πολγ.

Foreword

This master dissertation is organized in two parts. The first part describes the work developed during the first semester (from September 2007 to January 2008) made in the Chemistry Department of the Faculty of Sciences and Technology of the New University of Lisbon (DQ-FCT-UNL). The second part (from January to May 2008) accounts for the work developed is related to the work developed in the Laboratory for Icons – Oil Paintings and Wood Carvings of the Conservation Department of the Benaki Museum in Athens, Greece.

I chose the area of Paintings as the subject of my speciality and I calendarized the year as described above so I could be able to have a complete Master training from an academic point of view. The first part resumes a project started in the subject of Methods of Exam and Analysis II, during the second semester of last year and constitutes a study that deserves to be continued due to its relevancy to the Sciences of Conservation of Works of Art.

The choice of going to the Benaki Museum was made because of my great interest in panel painting and particularly in icon painting. Greece is a very good context to acquire further knowledge on the icon painting and restoration techniques, due to it being a country with a strong traditition in this kind of panel painting, as a consequence of the predominance of Orthodox church. The Benaki Museum is one of the most important museums in Athens. It has four buildings and several conservation departments (paper, textiles, photography, metals, ceramics, icons painting, canvas painting, wood works and laboratory). In so being, the interaction with the different conservators and experts on different areas is very useful and enriching. The Museum also works with the University of Athens, other museums - as the Byzantine and Christian Museum in Athens - and with the Ormylia Art Diagnosis Center in Tessaloniki. It was clear to me that the Benaki Museum, although focussing more clearly on the praxis of restoration and conservation interventions, felt the need to surround itself with the scientific and culturalsupport of other institutions.

The two parts of my work are not directly related, which is why I decided to divide the structure of this dissertation. However, both works have their own relevancy to a Master's degree in Conservation and Restoration and both are derived from my choice of specialisation: Painting.

During the first semester, my study approached the field of analytical chemistry applied to the diagnosis and conservation of paintings. As such, this part is more scientific and sintetic while the second part, in the field of conservation and restoration of icon paintings praxis, is more descriptive . This second part is a more profound study that combines history of the arts, production techniques, iconography, exams of analysis, conservation and intervention in the work of art made available to me by the Benaki Museum. I organized this part putting all the figures and detailed results in Appendices I, II, III and IV.

The Part II of the present work was submitted and accepted to the trimestral online magazine E_Conservation in the fourth of June 2008 to be published in the Issue No. 6, August 2008. (the website adress is www.e-conservationline.com)

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Part I

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Abstract – Two derivatization methods were tested in twenty-one standard amino acids (AAs) for further identification and quantification by the analytical technique of Gas Chromatography with Flame Ion Detector (GC-FID). For the one-step derivatization reaction N-methyl-N (*tert*.-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) was used and for the two-step reaction we used hydrochloridic acid (HCl) and trifluoroacetic anhydride (TFAA).

We obtained better results with the derivatization procedure in two-steps, although it takes longer, and we concluded that the reproducibility of these reactions is difficult to achieve.

1. Introduction

The identification of standard amino acids by GC-FID enables the elaboration of a database, since their derivatization is made by the same experimental conditions and analysed by the same equipment. This possibility can be useful for further studies in the conservation of art field, especially in researches about binders used in paintings

The analysis of pigments and binding media used in the creation of a work of art can be useful in the painting technique and also in provenance and authentication studies [1].

Binders are important parts of paintings. They primarily occur both in the supporting and painting layers and are differentiated, as a function of the major component, into protein, oil, resin and polysaccharides. Commonly used protein binders involve casein, bone or hide glue, gelatine, egg white and yolk [2].

The advantages of a gas chromatographic (GC) analysis of amino acids are the low cost, the high sensitivity and the low sample amount needed (<0.1 mg). The samples of paintings normally available for analysis are characterized by their small size to avoid further deterioration of the work [3-4]. Analyses by GC are preceded by protein decomposition into amino acids (AAs). A disadvantage of GC lies in the necessity of a sample pre-treatment, because only those substances that are sufficiently volatile and thermally stable can be analysed under the GC conditions [2].

In this paper we report the use of N-methyl-N (*tert*.-butyldimethylsilyl)trifluoroacetamide (MTBSTFA), as a donor of the *tert*.-butyldimethylsilyl group (TBDMS), in a one-step derivatization procedure and the use of hydrocloridic acid (HCl) and trifluoroacetic anhydride (TFAA) as derivatization agents that transform the amino acids into their trifluoroacetyl-O-2-propyl esters, in a two-step derivatization procedure [1,5]. MTBSTFA was proposed for silylation, whose derivatives were found to be low moisture-sensitive and required milder conditions to complete the derivatization [5]. Numerous publications have appeared on the application of MTBSTFA to gas chromatographic amino acid analysis [6-10].

The two methods have been applied to the twenty-one standard amino acids singularly in order to identify the best results with this equipment.

2. Experimental

2.1 *Solvents and reagents*

The amino acids used to prepare standard mixtures were obtained from kit 21- L-Amino acids + Glycine, Fluka Chemie (Switzerland).

2mL crimp vials and caps were obtained from Agilent Technologies (Germany).

The following reagents were used to treat the samples. Hydrochloridic acid (HCl) at 37% for analysis, Panreac Química SA (Barcelona, Spain). Acetonitrile (ACN) for HPLC-isocratic-preparative, Panreac, Química SA (Barcelona, Spain). N-methyl-N (*tert.*-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) was obtained from Sigma-Aldrich (Sintra, Portugal). 2-Propanol gradient grade for chromatographie, LiChrosolv, Merck (Germany). Trifluoroacetic anhydride (TFAA) for synthesis, Merck, (Munich, Germany). Dicloromethane (DCM), José Vaz Pereira (Lisbon, Portugal) n-Pentane analytical reagent, Riedel-de Haën. Phosphorus pentoxide, Riedel-de Haën. Hexadecane, Riedel-de Haën.

The internal standard (I.S) used was a solution of 5,2 µL of hexadecane in 50 mL of pentane.

2.2. *Derivatization procedures*

One-step reaction

A standard solution mixture was prepared at a concentration of 3500 ppm of each AA in HCl 0,1 M. 25µL of each solution was placed in a vial and the solvent was evaporated under a gentle stream of nitrogen and the residue was kept overnight over phosphorus pentoxide under vacuum. 50 µL of acetonitrile and MTBSTFA were added to the dry residue and the vials capsulated. The mixture was sonicated at room temperature for 30 min and then heated at 150ºC for 60 min to complete the TBDMS derivatization. After cooling to room temperature 15 µL of the I.S was added and 1µL of the solution was injected directly on to the GC column.

Two-step reaction

50 µL of each standard solution prepared before was placed in vials and evaporated to dryness under a stream of nitrogen. The dry residue was dissolved in 100 µL HCl 2M in 2-propanol, capsulated and heated at 90ºC for 1h. After evaporation of the solvent, the residue was dissolved in 100 µL dichloromethane and treated with 40 µL TFAA, capsulated and heated at 60ºC for 1h. After cooling, the vial was opened, and the solvent evaporated. The residue was dissolved in 100 µL DCM, 15 µL of I.S was added to the solution and 1 µL was injected directly on to the GC column.

2.3 *Instrumentation*

The GC–FID system used was a Trace *2000 Series* gas chromatograph equipped with a flame ionization detector (FID) and a Zebron (ZB-5 30m x 0.25mm) i.d. fused-silica capillary column with film thickness 0.25μm. Hidrogen was used as the carrier gas at a flow rate of 1,0 mL/min. Samples were injected in the split mode with a split flow of 15ml/min. The GC conditions were as follows: injector temperature,250 ◦C; detector temperature,250 ◦C; initial oven temperature,120 ◦C increased to 290 ◦C at 4◦C/min, hold for 10 min, to 290 ◦C increased to 295◦C at 2◦C/min, hold for 5min. The total program run was 60 min. Data was collected and integrated with a personal computer using the XCalibur software.

3. Results and discussion

In the one-step derivatization reaction with MTBSTFA, happens at the same time, two nucleofilic attacks both to the Si atom. One from the OH molecule and the other one from the NH resulting in the transformation of the amino acids in TBDMS ethers.The two-step derivatization method involves the esterification of the carboxylic groups with 2-propanol followed by the trifluoroacetylation of the amino groups with trifluoroacetic anhydride. In this way the amino acids were quantitatively transformed into N-trifluoroacetyl-O-2-propyl esters.

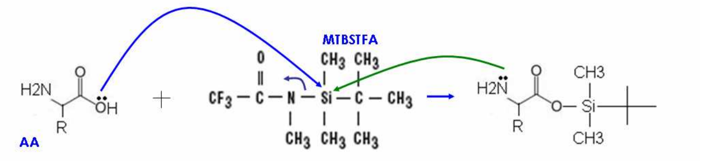


Figure 1. Derivatization reaction with MTBSTFA

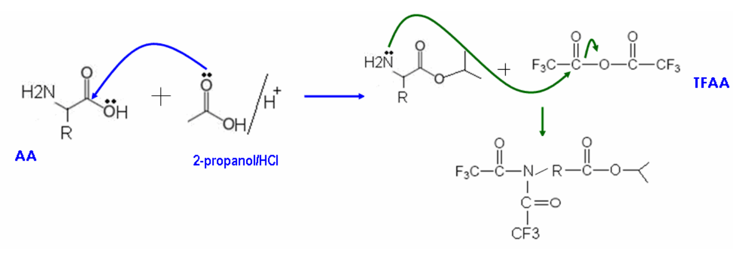


Figure 2. Derivatization reaction with 2-propanol/HCl and TFAA.

Table 1

Retention time and peak areas from the AAs succesfuly derivatizated with MTBSTFA and HCl/TFAA.

	MTBSTFA	HCl / TFAA
Amino acid	RT (min)	RT (min)
Alanine	7,5	1,70
Glycine	7,8	__
Valine	10,31	2,32
Leucine	11,63	2,95
Ileucine	13,77	2,98
Glutamine	13,95	__
Glutamic Acid	13,83	__
Proline	18,83	3,35
Phenelanine	25,4	8,93
Tyrosine	32,6	__
Arginine	42,92	__
Serine	__	3,03
Hidroxyproline	__	5,03
Methionine	__	5,33

RT for IS: 10, 8 min

There have been several different approaches to the characterisation of proteinaceous media based on the detection of amino acid ratios. Some of these works (Schilling and Khanjian [11] and Terlixi et al. [12] and Ioakimoglou and co-workers [13]) show that for identification and quantification of proteic mediums used in painting - egg white, egg yolk, collagen or casein – the relative amount of these seven amino acids – Alanine (Ala), Valine (Val), Leucine (Leu), Glycine (Gly), Proline (Pro), hydroxyproline (HPro) and Ileucine (Ile) - is enough. Since each proteinaceous material has a distinct amino acid composition the type of binding medium used can be identified from the relative abundances of selected amino acids, which can be obtained by measuring the relevant peak areas in the gas chromatogram.

Analytically, for egg yolk, leucine makes up 30% of the amino acid content and there is a total absence of hydroxyproline. Animal glue (collagen), on the other hand, contains hydroxyproline, which is absent from egg and white yolk and casein, as well as high proportions of alanine, glycine and proline. Finally, the major amino acids in casein are leucine, proline and valine [14] (see comparative amounts of AAs in Table 2)

From these seven AAs, in this work, glycine and proline weren’t derivatized with HCl/TFAA but they were successfully derivatized with MTBSTFA, hydroxyproline wasn’t derivatized with MTBSTFA but it was with HCl/TFAA. As hydroxyproline is an essential amino acid for identification of proteic mediums and glycine and proline are not, it can be concluded that the derivatization method in two steps is a better choice to obtain results in the analysis of paintings.

All the other AAs from the group of seven were derivatized by both methods.

The unsuccessful results in the derivatization of some amino acids can be due to the sensitivity of these to acid hydrolysis conditions, the high volatility of some derivatives formed and to their incomplete derivatization.

Table 2 [2, 4, 11]

Relative amount of seven amino acids in four proteinaceous mediums used in paintings

Medium	Ala	Val	Leu	Gly	Pro	HPro	Ile
Egg white	+ +	+	+ +	+ -	+ -	0	+ -
Egg yolk	+ +	+	+ +	+ -	+ -	0	+ -
Casein	+ -	+	+ +	-	+ + +	0	+ -
Collagen	+	- -	- -	+ + + +	++	+	- -

Figure 3. Gas chromatogram obtained from the derivatization with MTBSTFA of standard AAs

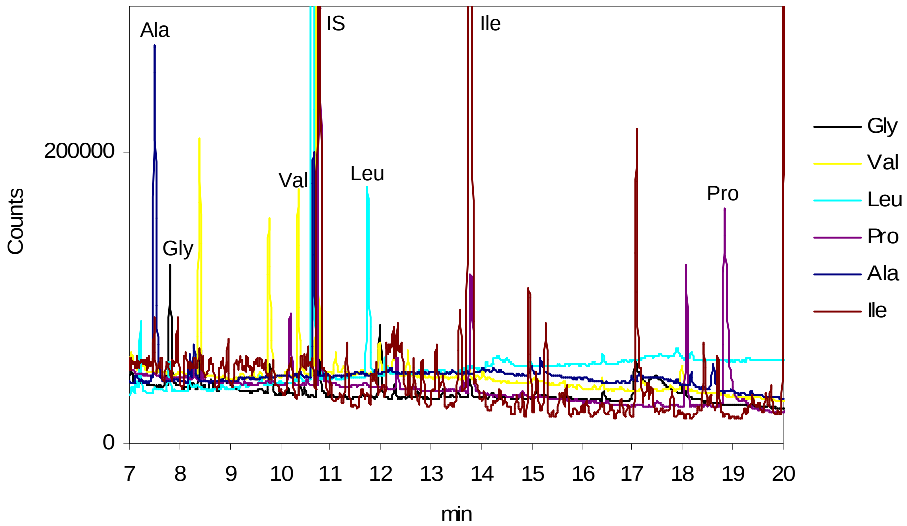
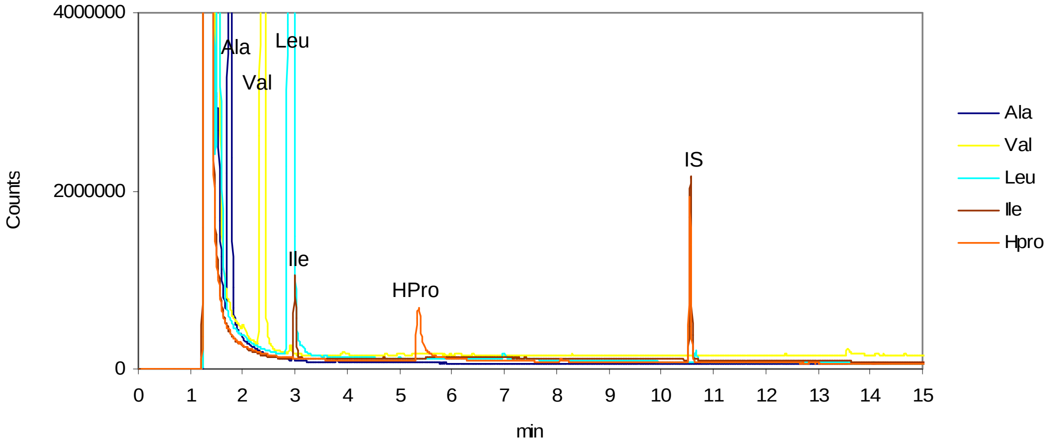


Figure 4. Gas chromatogram obtained from the derivatization with HCl/TFAA of standard AAs.



4. Conclusions

Derivatization of 22 AAs with two different silylation reagents have shown that optimum unified conditions for all AAs cannot be obtained.

The identification of amino-acids by this method is difficult because the need of pre-treatment of the samples takes a long time and the reproducibility of these procedures is not guaranteed.

However, the results obtained of the derivatization of the seven amino acids that constitute the proteic mediums used in painting as egg white, egg yolk, casein and collagen permit a further study in the field of conservation of works of art.

Appendice

Drying acetonitrile

To ensure the utmost dryness of this reagent, it was dried with molecular sieves type 4A (group of synthetic aluminosilicates of calcium and sodium dis-hidratated, adsorbents). After this, the reagent was partially dried with calcium hidryde part by part until the libertation of H_2 stops. The solvent was decanted and fraccionarily distilled with a high efficiency column at atmospheric pressure.

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Part II

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Abstract - This work describes the study and conservation of an icon from the late eighteenth century provenant from the private Valadorou collection, now belonging to the Benaki Museum of Athens.

The icon studied will be presented with a group of other icons from this collection in an itinerary route of exhibitions foreseen to start in October 2008 in Romania.

In this paper, the major concern was to understand the construction of the icon and to identify the various materials used by technical exams. The identification of the pigments was made by analytical methods of exam such as the observation of the cross-sections through the microscope, X-Ray fluorescence spectroscopy (XRF) and by phtography methods such as Infrared (IR) photography using also the IR false colour images. The micro Fourrier Transform Infrared (μFT-IR) was used to identify the varnish and the green glaze.

ID

Theme - Presentation of Jesus in the Temple

Provenance – Valadorou Collection, Benaki Museum, Athens.

Material – Egg tempera on wooden panel

Artist – Unknown

Dimensions (cm) – 72, 5 x 47 x 2, 3

Date – eighteenth century

State of preservation – B/Fair/3/C2[1]

Introduction

Derived from the Greek word *eikona*, an icon is in its broadest definition any image or portrait figure. Many early Christian icons were painted, but many others were also made of mosaics or metal by *repoussé* and chasing, casting, by stone or ivory carving. [1]. After the great iconoclastic controversy[2] in the eighth and ninth centuries, the Eastern Orthodox Church formulated a doctrine of veneration of icons and also a set of technical rules for their artistic production. [1]

[1] Scales of preservation state by the British Museum, English Heritage and Ancient Monuments Laboratory and Office of Arts and Libraries.

[2] In the Byzantine world, Iconoclasm refers to a theological debate involving both the Byzantine church and state. The controversy spanned roughly a century, during the years 726–87 and 815–43. In these decades, imperial legislation barred the production and use of figural images.. In certain regions of Byzantium, including Constantinople and Nicaea, existing icons were destroyed or plastered over. Very few early Byzantine icons survived the Iconoclastic period; notable exceptions are woven icons, painted icons preserved at the Monastery of Saint Catherine on Mount Sinai, Egypt, and the miniature icons found on Byzantine coins, including those of Justinian II (r. 685–95; 705–11). [2]

Making an icon

It is quite a complex task to create an icon. It can involve the skills of many craftsmen carpenters, gesso-workers, gilders, draughtsman and painters which explains why icon painting workshops have so often been attached to a princely court, a monastery, or a village specialized in the craft, so that these craftsmen could work as a team. Other times, a patron gathered the necessary number of artists to work on the icons of a specific church. However, it can also be the case, that only one artist creates the icon by himself, mostly in recent icons, as their production wasn't done in such a large scale as Byzantine and Post-Byzantine icons. [2]

Greek icons can be organized in three periods:

1. Byzantine, during this phase clearly defined in time and space, icons were produced in the territory of the Byzantine empire from the tenth century to the Fall of Constantinople in 1453. [3]
2. Post-Byzantine, a term applied to icons from areas or workshops that were artistically active after the second half of the fifteenth century. At this time, after the conquest of Constantinople by the Ottoman Turks, the production centers shifted away from Constantinople, mainly to Crete, the Ionian Islands, Mount Athos and the Balkans in general. [3]
3. Late icons, a concept referring to icons made after the seventeenth century up to now, where the icon studied in this paper belongs.

The icons that were made not for private devotions are pictorial references to the historical substrate of the Divine Liturgy. By John of Damascus, one of the theologians that most defended the use of icons in churches, the icon is a reminder.

Icons are placed in various parts of the church, on *proskynetaria* (icon-stands), walls, chapels, sacristies or other places. Since the twelfth century icons are put in *templon* or *iconostasis,* that is a screen of marble, wood or precious materials as ivory, parclosing the sanctuary from the *naos* (nave). [4]

Iconographic theme

The icon constituting the subject of my work in the Benaki Museum represents the biblical scene of the 'Presentation of Jesus in the Temple' (*Hypapanté* in greek) described by the evangelist Luke: "When the time of their purification according to the Law of Moses had been completed, Joseph and Mary took him to Jerusalem to present him to the Lord and also to offer in sacrifice a pair of doves or two pigeons. Now there was a man in Jerusalem called Simeon, who was righteous and devout. He was waiting for the consolation of Israel, and the Holy Spirit was upon him. It had been revealed to him by the Holy Spirit that he would not die before he had seen the Lord's Christ. Moved by the Spirit, he went into the temple courts. When the parents brought in the child Jesus to do for him what the custom of the Law required, Simeon took him in his arms. There was also a prophetess, Anna. She was very old. She never left the temple but worshiped night and day, fasting and praying. Coming up to them at that very moment, she gave thanks to God and spoke about the child to all who were looking forward to the redemption of Jerusalem." [5]

This description is useful to recognise all the figures present in the icon and their intentions. This episode appears only in the gospel of Luke. The other evangelists never make references to it. In order to understand the iconographic theme, it proves necessary to know not only the origin of the Scriptures, but also where the Christian art took the theme from and in adition be familiar with the rites of Purification in the Christian cult. [6]

The Law of Moses obliged all Jews to consecrate their first borns to the Lord in commemoration of the exodus from Egypt. The ritual described in the Leviticus[3] says that all women that gave birth were considered unclean during the seven days after the birth of a boy, which is why the entrance in the temple was refused to them for thirty days. [6]

It is presumed by theologians that the Virgin submitted herself to this law to show example of humility and obedience. In fact, she didn't need to be purified as she gave birth without sin. [6]

Simeon, due to not being a high priest has his hands covered in a sign of respect. This oriental rite can be found in the Baptism of Christ as well, where the angels also have their hands covered. [6]

Joseph, a secondary character, brings in his hands a basket with two pigeons that was the modest offer from the poor (while the rich offered a lamb). [6]

Anna the prophetess assists Simeon and handles of the law where a prophetic text is written. [6]

A. Icon structure

1. The Wooden Panel

The traditional drying process was the most important stage in the treatment of the wood. The trunks were stored for a very long time in a covered but well ventilated place, with the cut ends waxed. They lost their initial moisture, became lighter and harder, shrank and cracked. After the trunk had been cut into boards, there was a lengthy storage period until the wood was finally ready to be used. This traditional procedure was followed for centuries in the manufacture of the wooden supports for portable icons. The supports themselves were made either from a single piece of wood or from two or more pieces joined by wooden or metal nails dowels and held together by glued linen fabric in the panel. This had the purpose of reinforcing the cohesion and resistance of the paint layers to the retraction of the wood. [3]

The battens were placed to stop the retraction of the wood but most of the times their effect is negative to the panel because it limits the natural movements of the wood originating cracks.

The problem and the damage that occur in the course of time, affecting both the paint film and the wooden support, are direct consequences of the choice of wood and the cutting, trimming and drying process. Hard and soft woods were used indiscriminately. The sole criterion was their availability.

The use of nails was very frequent. They were nailed onto the support, with the nails running either from back to front or from the painted surface towards the back. In either case both the wood and all the coatings of paint suffer considerably due to the swelling caused by rust in the nails. The nails restricted the movement of the wood and sometimes caused it to split irreparably. [3]

[3] Leviticus is a book from the Old Testament of the Holy Bible.

The support of this icon was made up of one board, a single piece produced from a radial cutting and the wood was originally missing along the grain (Figure 2 Appendicce). Two horizontal battens have been glued and nailed in the reverse of the panel. The battens are rectangular, cut to the width of the support and nailed from the back to the front with four nails each. The nails were placed in regular intervals and aligned.

The presence of the nails and the battens restricted the movement of the wood and originated a crack along the panel. Also the heads of the nails caused part of the paint losses in the surface because of the movements which were described aove. These were the main problems of the wooden support (Figure 3 in Appendicce).

It is worth noting that icons produced up to the end of the sixteenth century are in much better condition and present less deterioration from icons of the seventeenth, eighteenth and nineteenth centuries. This is due to the surge in demand for portable icons in this period, when the art of painting moved from the closed painter's guilds into the hands of small local ateliers and monastic centers. The need for a substantial speedy output meant that artists lost sight of the necessity of a properly constructed wooden support. [3]

In one side of the icon we notice marks made by the saw used to work the timber (Figure 4). The back and the side of the icon were covered with a thin layer of gesso ground, which was intended to protect the backside of the icon from the humidity of the environment, to reduce the risk of the support cracking and also to decrease the imperfections of the surface (Figure 4).

From the late seventeenth until the end of nineteenth century we notice methods of construction similar to those of the previous period except that the wood is mainly cypress, fir and pine. [3]

The type of wood used in this panel was identified as belonging to resinous trees. Most likely is pine. It was a common wood used in this time, and the color and smell exhibited indicate this tree. To help this identification, a small tangential sample of the wood panel was taken and observed in the microscope. Here one can see the veins of typically resinous trees (Figure 5).

2. The Canvas

The wooden panel is covered by a glued canvas of medium density. The use of canvas, between the panel and the ground had the purpose of reinforcing the cohesion and resistance of the paint layers to the retraction of the wood.

The canvas fiber was identified by the optical microscope as being linen (Figure 6).

3. The Ground

A mixture of glue and gesso was applied in layers of decreasing thickness and perpendicular to each other.

Sometimes, in the surface of the ground layers a thin layer of glue was applied to obtain the necessary capacity of absorption of the gesso. It also guarantees a high and durable cohesion of the upper layers.

The technique of the ground layer in icons is the same as the one described by Cenninni in *El Libro del Arte* relating to the preparation of wooden supports for tempera's paintings.

In cross-sections one can see that the ground layer included small amounts of carbon black pigment (see tables 3 and 4 in Appendice) which must have been added deliberately by the artist to decrease the intensely white hue of pure gypsum.

It is visible in some areas a type of craquelet with perpendicular cracks that seem to be due to the canvas (Figure 7). In the upper area of the icon, is also visible a particular type of craquelure in which diagonal cracks mark the area (figure 8). This may be due to the intentional scratches that were made in the wood so that the glue could penetrate better.

4. The Drawing

In Greece, from the late seventeenth, through nineteenth centuries, model working designs and drawing samples were reproduced by authors and their assistants. A great number of these designs, mostly the ones belonging to Athanasios survive today in the Benaki Museum. Most of them were drawn and coloured in paper and circulated for all the schools. [8]

The drawings were transferred to the ground layer by covering it with carbon and with an instrument marking the outlines, resulting in dark lines slightly engraved. The lines can be seen at naked eye when the paint layers are very transparent: lacks, ochres; or when these layers are very thin: cinnabar or lead white.

Normally the design was very detailed. The dark lines were used as shadows so there was no need to add any dark pigment to this effect.

In this icon lines of the drawing visible at naked eye are engraved, mostly the outlines of the figures, architectonic elements and also the lines of the margins of the icon (Figures 9, 10 and 11). Some details were then drawn with a fine brush (faces, hair, flesh).

In some places, the underdrawing can be seen through the paint film due to the carbon black used and to the thinness of the paint layers above. The infra-red photography helps to identify the underdrawing, because the thinness of the paint layers permits a good result.

5. The Gold leaf

The decoration techniques used were sgrafitto and simple decoration with brush over the paint layer.

The icon studied is made up of gold leaves applied just in the background area of the architectural elements (from the grey columns to the ceiling tiles) and the halos. Gold powder was also used, probably applied with a brush in the decorated surfaces with floral and geometric motives (ceiling area and altar).

The ground of the circular areas gilded (halos and the semi-circle dividing the representative area from the decorative part) were all engraved with a tool (Figure 13). The use of a different tool in these areas shows their higher importance.

When applying a gold leaf, a layer of *bole* is firstly was used, which can have a yellow or a reddish tone. In this case a thin layer of a reddish tone *bole* was used. (Figure 12)

6. The Paint layer

6.1 The Medium

The most common painting technique found on icons is egg tempera. The artists used the egg-yolk mixed with water. Some vinegar was added partly to conserve the egg longer and partly to offset the natural greasiness of the yolk and make it more agreeable under the brush when painting. [10]

6.2 The Painting Technique

The traditional Byzantine technique of icon painting consists in starting with darker shades as the background colour, which they maintain at the edges of an area and in the shadow areas. This is called *proplasmos* in Greek iconography, which is a dark toned underpaint. Over this undertone are superimposed layers of lighter tones that are called mid-tones and finally the highlights. This shows a painting technique going from the general to the specific.

In the face areas, hands and exposed parts of the body, the *proplasmos* is followed by the the flesh and at the end by *glykasmos*, which defines the facial features and lines of body parts. The existing underpaint is left exposed in areas to suggest shadows.

Icon painting strikes us by the frontality of the figures. This frontality brings the figures in direct relationship with the viewer and brings out the fullest expression to the characters' faces.

Icon painting deliberately disregards the principle of natural perspective in order to avoid the illusion of three-dimensionality. Instead, it gives the impression of complete flatness and lack of perspective. However, icon painting does use a perspective, called by scholars either reversed or inverted, to indicate that it is different from the illusive perspective of the Italian masters. Inverted perspective depends on multiple points of view. But these multiple points of view are placed in front of the painting, not behind it, which results in background objects often being larger than the foreground ones and in distortions in shapes of some of the objects (like the altar for example) [11]. The reverted perspective is used also to enable the viewer to get closer to the spiritual dimension, being the icon a window between the terrestre and the divine world.

Icon painting has the ability to represent several moments of the same action (story) on one panel. In this scene we can see not only the presentation of Jesus in the temple, but also the purification of Mary and Simeon's destiny being fulfilled in the temple. Some scholars call this the "continuous style". [12]

In the architectural elements one can see the type of brushstrokes made by the painter through the infra-red recorded image. These brushstrokes are characterized by freehand and fluid paint, varying in width and direction. Examples of the painting technique are visible in the grey area (Figure 14).

In faces and flesh parts the type of brushstrokes is recognizable at naked eye and it is quite impressive (ex. the detail of the contour of Simeon's hair in Figure 15).

Oftentimes, the colours used were the result of local availability of the pigments and their price, but there are some standard colours to each figure, that are respected in this icon. For example the red colour of the Virgin's mantle was common in the Byzantine tradition (figure 16). Red is the colour of clay, of matter. In the Incarnation, Our Lady contributed with her physical matter to the Spirit.

6.2.1 The painting of faces and flesh

Especially in the painting of the faces and visible flesh, the technique of applying several layers beginning with the dark tones progressing to the highlights is evidently used. These are the areas where the artist is more detailed.

In the *Hermeneia* or *Painters Manual*, written by a greek monk (from Month Athos) and icon painter, Dionysius of Fourna, the making of the flesh colour is explained, "Take drams of terraverte, drams of dark ochre, drams of lime-white for working on walls, and drams of black; grind them up well and use as *proplasmos* when you paint flesh colour. [13]

In the icon studied the following tones were used: red, yellow, white, black and possible blue or green. The underpaint ranges from light brown to dark brown, the result of combinations of yellow ochre, cinnabar, carbon black, lead white and copper blue or green (undistinguishable in the cross-sections).

The mid-tones seem to be two. They are salmon pink made up of lead white, cinnabar and yellow ochre applied in different hues in a way as to soften the transition between the brownish underpaint and this lighter layer and also to differentiate the flatter areas as the foreheads or the backs of the hands.(Figure 16)

The highlights are white and are the only touches painted in impasto. A very thin brush is used in quick and repeated movements of different shapes (Figure 18).

In some places, where the artist meant to create more volume, he applied a dilute red paint, like in the cheeks, necks and near the mouth (Figure 18). This layer is called *glyklasmos.*

The faces have large almond-shaped eyes, enlarged ears, long thin noses, and small mouths. All these elements, as well as hands and chins are delineated in thin brown brushstrokes (Figure 18).

It is interesting to notice the difference of the brushstrokes between the painting of a young face (Joseph and Mary) and an old face (Anna and Simeon). By the iconography we have the indication that Anna and Simeon are very old and the painter represents the faces with wrinkles from the age (Figure 17).

B. Methods for the examination and the analysis

The methods for the examination and the analysis used in this work can be divided in a) non-destructive and b) destructive methods. Both types of exams permit an interpretation of the work of art based in the results obtained regarding the characterization of the materials used and the painter’s technique.

The non-destructive methods for diagnosis used were visible (Vis), ultra-violet (UV) and infrared (IR) photography. For identification of the pigments false-color infrared photography (explanation in Appendicce) and XRF was used.

The destructive methods of analysis for the identification of the materials used were the optical microscope with transmitted and reflected light, the sampling of cross sections and the μFT-IR.

Results

Table 1. Data from spot X-Ray fluorescence spectroscopy for the characterization of the materials used. The "detected elements" are arranged in three rows following a semi-quantitative hierarchy to major (first row), minor (second row) and trace (third row) elements.

Point	Colour	Detected Elements	Characterization *Identified pigments*
1	Anna's green garment	Ca, Cu, Pb S, Fe, Sr K, Ti, Zn	Major pigment based on copper. Major amounts of calcium and lead. Minor amounts of iron based pigments. - Copper Green (malachite or verdigris), ochre, lead white, gypsum
2	Mary's red garment (light red shade)	Hg, Ca, Pb S, Fe, K, Sr Al, Cu, P, Cl	Major amounts of mercury based pigment. Main constituent based on calcium and lead. Minor amounts of iron based pigments. - Cinnabar, ochre, lead white, gypsum
3	Mary's red garment (deep red shade)	Hg, Pb S, Ca, Ti, Fe, Sr Al, Cu, P, Cl, Si	Major amounts of mercury and lead based pigments. Minor amounts of iron based pigments, calcium and sulphur. - Cinnabar, ochre, lead white, gypsum
4	Joseph's brown garment	Fe, Pb, Ca Hg, S, Mn, Cl, Sr Si, Ti, Cu	Main constituents based on lead and calcium. Major amounts of iron based pigment. Minor amounts of mercury based pigment, manganese and sulphur. - Umber, ochre, cinnabar, lead white, gypsum
5	Red frame (lower left side of the icon)	Pb, Hg, S, Ca, Cl, Sr Si	Main constituents based on lead, and mercury. Minor amounts of sulphur and calcium. - Cinnabar, lead white, gypsum
6	Mary's green garment	Cu, Pb, Sr, Ca, Fe, Zn, S, Cl, Sr	Major pigment based on copper. Major amounts of calcium and lead. - Copper Green (malachite or verdigris),ochre, lead white, gypsum
7	Grey ceiling	Pb, Ca, S, Cl Sr	Major constituent based on lead. Minor amounts of calcium, sulphur and chlorine. - Organic black (?), lead white, gypsum
8	Red frame (upper left side of the icon)	Hg Pb, S, Ca, K Cl	Main pigment based on mercury. Minor amounts of calcium, lead and sulphur. - Cinnabar, lead white, gypsum
9	Green column base	Pb, Cu, Cl, Ca, Fe Zn, Sr, Ti	Major constituents based on lead and copper. Minor amounts of calcium, iron and chlorine. - Copper Green (malachite or verdigris),ochre, lead white, gypsum
10	Anna's red garment	Pb, Ca Sr, S Cu, Fe	Major amounts of lead and calcium. Minor amounts of strontium and sulphur. Traces of iron. - Red lake (?), ochre, lead white, gypsum
11	Joseph's blue garment	Cu, Pb, Ca, Fe, Cl, Sr S, K, Si, P	Main constituent based on lead. Main pigment based on copper. Minor amounts of iron, calcium and strontium. - Azurite, lead white, gypsum
12	Joseph's flesh (left foot)	Fe, Hg, Pb Ca, S, Cl Cu, Sr	Main pigments based on iron, lead and mercury. Presence of calcium and sulphur. Traces of copper. - Cinnabar, lead white, ochre, gypsum
13	Yellow decoration (upper left side of the icon)	Pb, As Co, Ni, Sr Fe, Zn	Arsenic-based main pigment. Major amounts of lead. Minor amounts of cobalt and nickel. Traces of iron. - Orpiment or realgar, lead white, ochre gypsum

1. Pigments

1.1 Reds

The red pigments are used in a range of tones from light red to dark red (Figure 20). The major pigment found in red areas is cinnabar mixed, more or less according to the tone required, with lead white.

An exception to this technique can be found on Anna and Simeon's red garments. Here, as suspected and then confirmed with XRF and false color IR, a red lake mixed with lead white was used on the cross-section that presented a pink tone and a rather different aspect from the other red samples. The underpaint in this area is of a dark pink tone, the mid-tone is light pink and the highlights are white.

In the cinnabar red areas, the underpaint has a dark red tone (cinnabar whit black particles), the mid-tone is a strong red tone (cinnabar with lead white) and the highlights are light red in the Virgin's mantle and yellow ochre in the curtains.

The red colour is also used to delineate the yellow floral motifs and the mouths of all figures.

1.2 Blues (Figure 21)

In figures using green-blue garments, one can distinguish blue, green and white particles in the cross sections through the optical microscope.

By the XRF it was possible to see that these cross sections contain copper, which indicates the pigments possibly used – azurite, malachite, verdigris, copper resinate.

We can state that azurite is the copper pigment mixed with this green pigment in this areas by observation and comparison to the literature. The particles distribution and the colour in the paint film and the confirmation of the presence of copper gives this information.

From the literature we also know that azurite (basic copper carbonate, $2CuCO_3.Cu(OH)_2$) was the most important pigment in European painting during the Middle Ages, the Renaissance and later despite the more exotic and costly ultramarine. Kuhn (1973) gives a terminal date of c.1800 for natural azurite in European easel painting, with the majority of occurrences before the last quarter of the seventeenth century. [14]

The blue underpaint from the upper part of the icon presents a grayish tone and its false color is reddish, different from the other blue tones present in the garments.

From the cross section one can see that the blue particles were mixed very litle with white and what seemed at first, black particles. From the false color IR image recorded, the reddish tone emitted could be ultramarine, cobalt or smalt blue. Ultramarine and cobalt were expensive pigments so it is more likely that smalt was the chosen pigment.

Through XRF the presence of cobalt, arsenic and niquel was detected and according to the literature I concluded that the blue pigment used in this area was smalt.

The principle source of cobalt used in the preparation of smalt in Europe since Middle Ages appears to have been the mineral smaltite ($[Co,Ni]As_{3}$-$_{2}$). In the seventeenth and eighteenth centuries the associated cobalt minerals erythite ($[Co,Ni]3[AsO_4]2.8H_2O$) and cobaltite (Co,Fe)AsS were probably also used. [14]

Smalt is considered an inferior pigment relatively to azurite and ultramarine, but in the seventeenth century when those pigments became scarce, smalt was employed as a substitute, particularly in the skies and backgrounds of paintings where a an intense blue was not needed.[14] A coarse grade of smalt was frequently used for strewing as a blue background.

Potassium glasses are chemically less stable than sodium or lithium glasses. Stability also decreases with an increase in K_2O content. This may explain why several samples of smalt, on exposure to atmospheric conditions, have been seen to become pale and grayish. This is why in the sample taken I could only see few blue particles and much more grayish and dark ones.

1.3 Greens (Figure 21)

The green copper pigments are more difficult to distinguish. We need more techniques besides XRF identification to be sure of what copper pigments are present in the painting.

Although it was common to find azurite and malachite mixed together because of the close association of these minerals nature (both copper carbonates), we also have to consider the use of verdigris and copper resinate.

Malachite was more satisfactory in tempera than in oil-medium. The early examples of artificial malachite, which have been found on easel paintings, have generally been in an egg tempera medium. On the other hand, artificial copper greens, like verdigris and copper resinate made from malachite or other copper minerals, were more satisfactory greens, especially in oil or oil-resin media [14]

Rees Jones (1965) stated that in European paintings a common device for obtaining a green of increased saturation was to glaze with transparent copper resinate over malachite. Malachite was produced in various grades, but principally coarse, medium and fine which correspond to dark, medium and light tones of green paint when used with an aqueous medium. [14]

Because the pigment is produced by crushing and grinding, all particles have a fractured appearance. With transmitted light particles are pale green and have high birefringence. [14]

By comparing optical characteristics (colour, shape size and appearance) of the green particles of the samples with the literature ([15] and [16]) everything indicates that the pigment is malachite. The presence of copper identified by the XRF and the history of the pigment lead us to the conclusion that is in fact malachite (see Table 1).

However, when we observed the sample from Anna's mantle consisting of green type of glaze new doubts arose. Most particles are very similar to malachite but there are others similar to verdigris regarding their optical properties. Through XRF technology this distinction is not possible since it only detects copper, but it doesn't give us any information on whether it is copper acetate (verdigris) or copper carbonate (malachite).

In colour lists and literature on the technique of painting through the Middle Age, Renaissance and baroque periods, verdigris is often mentioned. It was used by European painters from the thirteenth to the nineteenth centuries and is often found on easel paintings of the fifteenth to seventeenth centuries. [14]

A common technique was to glaze over an opaque body color of lead white combined with verdigris, or sometimes verdigris mixed with lead-tin yellow, with a copper resinate layer to produce a deep saturated green. [15]

Typical characteristics under the microscope are the blue-green color, non crystalline characteristics and its pleochroism from light pale green to full dark blue. [14]

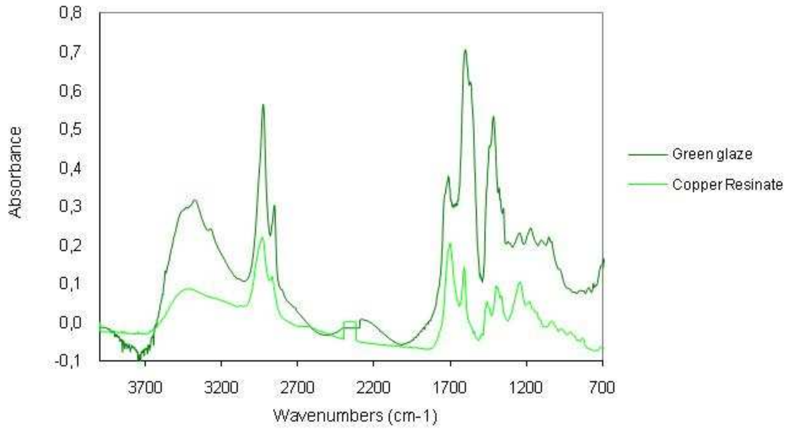

Figure 2. FT-IR spectrum of Anna's mantle green glaze comparing with a spectrum of a copper resinate made from an old recepie.

To identify the green pigment, we needed further exams and we chose to analyse the green glaze with µFT-IR. With this analysis, by comparison of standard spectrums of malachite and verdigris we concluded that the glaze was made with verdigris.

We can assume it is copper resinate and not a transparent layer of resinate applied on a layer of green pigment by stereoscope and optical microscope observation and further confirmation with comparison with the µFT-IR spectrum showed in Figure 2. (see also Figure 24 in Appendice I)

According to literature copper resinate is normally found as being made of verdigris, the corrosion product of copper vapors of acetic acid. This is dissolved in melted resin. [15]

1.4 Yellow

The floral motifs have been filled with transparent yellow paint. This thin paint layer was applied over the blue underpaint. The XRF analysis detected iron and lead white but the major compounds on this area were the ones related to the blue layer due to the thinness of the yellow layer.

1.5 Greys

A range of grey tones have been used in the columns of the temple following the principle of superimposing layers. The back columns have only two layers: the underpaint is dark grey and the mid-tone is grey. The front columns have three tones: the underpaint is grey, the mid-tone is light grey and the highlights are white. All the lines are delineated with fine brush and black paint.
The grey tone is a mixture of organic black with lead white.

1.6 Browns

The brown areas (Figure 22) are a mixture of umber, ochre, cinnabar and lead white. The altar has a brown-reddish tone because the highlights are of a reddish color, probably constituted by the same mixture of pigments but with a higher content of cinnabar. The mantle has three tones: the underpaint is dark brown, the mid-tone is light brown and the highlights are very light brown.

2. Varnish

A sample of the varnish removed from the icon's surface was analysed by contact with a diamond cell in µFT-IR. The spectrum obtained was compared with several standard natural resins spectrums. The sample contains the main peaks relating to these resins but it seems to be a mixture with other components possibly oils or maybe these other peaks correspond to degradation products of the aged resin.

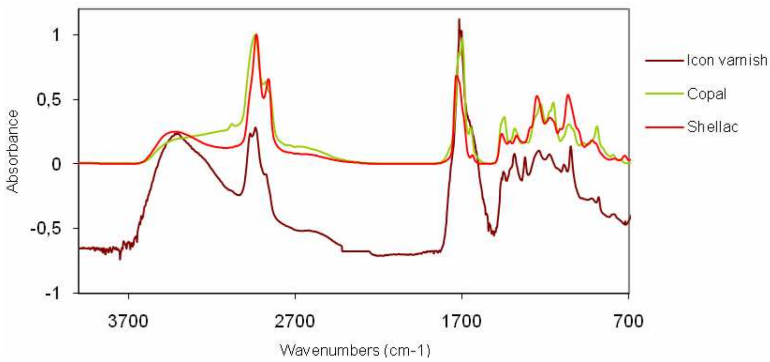

Figure 3. FT-IR spectrum of the varnish of the icon comparing to standard spectrums of copal and shellac resin

C.

Conservation

The construction of the support of Greek icons implies many dangers for the painting, which suffers considerably due to the nature of the materials and construction. Small cracks all over the paintings, blisters due to nails, flaking, large areas of lost paint and ground layer are but some of the problems.

1) Consolidation

For the consolidation ethanol (from Fluka) was at first injected with a microsyringe to turn the surface more absorbent for the consolidant agent. A polymeric acrylic consolidant was used, Primal® in water (1:3) and applied with a fine brush. In order to help the penetration of the consolidant agent and also its adhesion weights have been put in areas of higher losses.

2) Cleaning

The icon had a thick layer of varnish that was darkened obscuring the true colours used by the artist (Figure 25). According to the literature, most varnishes used in icon paintings are natural resins or mixtures of natural resins with oil. Using the UV light is visible that there were no interventions in the varnish layer because there were no fluorescent areas.

The solvents used were chosen in reference to the Teas Triangle (see Appendix IV) and then tested with a small cotton swab in the multi-coloured area. All the cleaning process was made with the assistance of the stereoscope.

The solvents used were acetone (from Fluka) in cotton patches in the borders (pink columns and red borders); acetone:white spirit (W.S) (1:1) applied in cotton patches on the floor, altar, all garments (not on reds and green from Anna's mantle), flesh parts and ceiling tiles; ethanol in cotton patches and with cotton swab in the upper floral motifs and grey areas; ethanol:W.S (1:1) in red garments (Virgin and Simeon), in the curtains and with cotton swab in the green of Anna's garment.

In some areas the scalpel was used to help the removal of the varnish. It's important to underline that this procedure was always assisted with a stereoscope, which permits a great control of the cleaning methods and their interference with the icon's surface.

Anna's garment was made of a green glaze making it more sensitive to the cleaning solvents because the medium used is more similar to the varnish than with tempera. In this the cotton swab impregnated with the solvent was strictly used to dissolve the varnish layer a bit and then carefully removing it with the scalpel. Although it may seem more aggressive, the use of the scalpel in this area is safer because there's a better control of the layer we wish to remove. If we use a cotton patch with cleaning solvent or insist with the cotton swab, the solvent penetrates more deeply and starts to dissolve the glaze layer as well.

The use of the scalpel was also necessary in the upper floral motifs. In this area the surface was more irregular than on the rest of the icon. It seemed that a lesser quantity of medium was used and that part of it was absorbed by the ground layer originating a rugged surface. This is merely an hypothesis.

Either way, it was concluded that in this area it was better to apply a patch with the solvent during only a few seconds, in order to dissolve the varnish layer and then remove it with a cotton swab. In this stage, the scalpel was used to remove all varnish residues without removing the paint film. As it was an irregular surface, the scalpel reached all the zones obtaining a satisfactory result.

The use of patches is justifiable when we are dealing with a thick layer of varnish. In icons, most of the times, this layer is very thick and very dirty not only with dust but also from the smoke of candles used to illuminate and pray to the image. The patches permit softening the varnish making this layer easily and more efficiently removable, since it leaves almost no residues and isn't more aggressive mechanically to the paint layer.

After cleaning the icon (Figure 26), it was reconsolidated in the areas where needed (mostly in the crack and nails spots) and a facing was applied (Figure 27): small leaves of Japanese paper were placed over the front side of the icon with SodiumCarboxyMethylCellulose (SCMC). SCMC is a polymer derived from cellulose, highly soluble in water and capable of forming solutions and gels.

For facings it is used in gel form and applied with a fine brush over the paper leafs. Before application, it was tested in all color areas the solubility to water with a cotton swab. None of the pigments was soluble so it was safe to use this gel as an adhesive between the icon surface and the Japanese paper.

3) Stabilization of the wooden support

The main conservation problem present with this icon was the condition of the wooden support. Five of the eight nails of the battens were creating a tension between the canvas and the paint film, starting to show on the surface of the painting while one of them (together with the battens' tension) destroyed the surface and originated a crack along the panel.

Regarding the battens, one should assess whether they are necessary. Under certain circumstances, they may not be used at all, as in the case of museum icons whose display or storage conditions are ideal and where problems arise only when these icons have to be moved. Nevertheless, even in the case of museum icons the use of battens is obligatory when their dimensions are large and their construction complex. The use of battens is also absolutely necessary for icons placed in churches and in places where environmental conditions cannot be controlled.

In this case, it was decided to remove all nails because of their negative effect in the condition of the painting. The nails were hammered strongly inside the wood so the removal was made by opening the area around each nail (in the batten) and then taking them off with a hammer and a plier.

After this, it had to be decided whether to remove the battens or leave them and fill the nails space with wooden sticks. It was decided that it would be best to remove the battens, in order to stop the restraining forces induced by them. Moreover, since this icon is going to be part of an itinerary collection, it will be susceptive to handling hazards (packing, handling, trips) very often and should be stabilized in a way as to become resistant to such procedures. At the same time this is a museum object, therefore its conservation will be constantly controlled, making the use of battens unnecessary.

With the battens removal, we discovered that although the panel showed very few insect holes, the area underneath the battens was full of dead insects and dust. (Figure 29)

Treatment of the cracks

When cracks become threatening, it’s usual to deal with this by removing part of the wood along the crack and filling the gap with small laths 1 x 1 cm laid in the gap, like bricks in a wall. The laths are of a softer wood than that of the icon, but their grain is solid and uniform. The shape of the cut in the wood varies, being sometimes square shaped and sometimes triangular shaped. Under such conditions the following questions arise:

1. How deep should the cut be and in what cases should this intervention take place?
2. What size and shape should the cut have?
3. Could the lack of uniformity in the material possibly produce forces in the area which, on the one hand, hinder the even course of the movement in the wood or, on the other hand, cause damage to the area close to the crack?
4. Ultimately, in view of the fact that in this construction, part of the wooden support is ruined and its original form altered, how successful can this system be in repairing wood?

After discussing these questions with the museum conservators, we thought the best solution for the case was to treat the cracks as described above dealing first with the questions mentioned. This type of intervention can be considered more aggressive to the work of art, but it proves necessary when understanding the needs of the use this icon will have after the treatment.

As mentioned before, this icon will be part of an itinerary collection and so it has to be in a conservation condition allowing for constant traveling, handling and assembling. In these conditions, it’s crucial that the icon structure is stable and resistant.

The profound crack along the height of the icon needed to be treated immediately and the option of filling it as described was considered safer than to follow the principle of minor intervention. This way, the tension forces that the progression of the crack was creating on the above layers (canvas, ground and paint film) were reduced and the surface of the icon could be flattened creating a better adherence of all the layers to the support.

It's important to underline that this intervention would also enable a better reading of the icon in its whole.

After making the case to proceed with this intervention it was still necessary to answer the questions previously raised. The thickness of the panel was 2,3cm so it was decided to make a cut[4] 1,2cm deep x 1,2cm wide and apply 1cm x 1cm laths of softer pine wood. As the crack is more open on the front side of the icon than on the back this cut will reach it in a point where the panel can be joined without originating great tension.

To avoid the introduction of new tension forces, as much as possible, four laths were made with heights ranging from 10 to 30 cm instead of only one lath along the crack. Each lath was semi-cut perpendicularly (with a japanese saw) to its vein in both sides and in regular intervals to permit its natural retraction. For the same reason, the laths are smaller than the cut area. The laths were then glued with polyurethane glue[5] (10%) that occupies the free space left between the lath and the panel and creates a stronger composite.

The lack of uniformity in the material may produce forces in the area of connection between the laths and the panel, but laths applied as described above, enable the wood retraction behavior. The retraction movements of the different woods won't interfere with each other.

In conclusion, although part of the wooden support is ruined and its original form is altered we considered this system successful in repairing the existing cracks and more importantly, in the stabilization of the wooden support making it suitable for its current and future function.

Being in a controlled temperature and humidity environment and being a highly itinerant work of art this structure will render it more stable. There are fewer tensions this way than if we leave the support without intervention.

In the nails areas a more profound hole was made inside which a small cylinder of less dense pine wood was glued. After the intervention on the panel structure, the surface of the icon was finally flattened with the hot spatula with the facing paper still protecting the icon. The facing paper was removed easily with a fine brush with water.

4) Fillings and retouching

Some areas needed fillings that were made with a mixture of gesso, Primal® and water applied and flattened with a thin spatula.

Two layers of varnish – Paraloid B72 in toluene (10%) from stock solution 40% - were sprayed (at P=3,5 bar) to cover the icon. Above this layer, the retouchings were made. Beva inpainting® was used as a medium and ethanol as a solvent together with the pigments. In the gilded areas acrylic paint with water was used (Figure 31). The final varnish was also PB72 in toluene (10%) from stock solution 40% sprayed and eight layers were applied perpendicularly to each other.

[5] Wood glue of polyurethane Bison® (consummation of 200g/m^2). Mechanically removable.

Conclusions

The work one is able to develop in an University or in a Museum comprehends very different areas. The University environment allows for a more scientific work, with more access to expertise, possibly conducive to new discoveries. The Museum environment allows for acquiring technical experience conservating, restoring and observing the restoration of works of art. Both places connect to histpry and Literature, as well as to the different experiences of local experts. As such, this year as a student was enriched by the learning of different subjects and techniques that will be useful to my future as a professional. More importantly, my work during this year made me understand that a conservator and restorator in practice needs to be scientifically inovative, trying to develop researches and studies, particularly in the area he decides to specialise on.

Ideally, the goal of the museum is education and research as well as the preservation and protection of objects. For the icon, these objectives can be reached through conservation by detailed examination to collect information about condition, materials, technology, history, and ethnographic use, physical stabilization, cleaning, and restoration for stabilization. These main objectives were achieved with this work in the Benaki Museum.

The painting technique and the quality of the materials which were used in this icon are not show us that the artist knew the basic tchnique of the iconography but he was not an expert icon maker. The low quality of the materials, perhaps indicates the low price order f the icon.

In the field of conservation and restoration of works of art, this is one of the research studies that shows the importance of interdisciplinary to a successful approach to the work of art. The exchange of opinions between museum conservators, art historians and chemical engineers allows for a reliable study and safe intervention. It's important to say that the use of technical exams are essential for a correct identification of the original materials, but also that consulting literature is as important as science since many times in the extensive experience of others lie the answers to our doubts.

The particular study of this icon and the whole experience in the Museum contributed greatly to my training and experience, but also to a profound knowledge of the technology of panel painting, specifically understanding the place icon painting occupies inside this technique. At first, icons can look the same as any other panel painting, but during my research and work I realised this is not true. Icons require a careful interpretation, starting with the period they're inserted, proceeding to the iconography of the representation, the materials and techniques used by the artist and finally the function they were made for and their future role in the society. Meaning whether they are meant for private collections, churches or museums.

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Appendice I

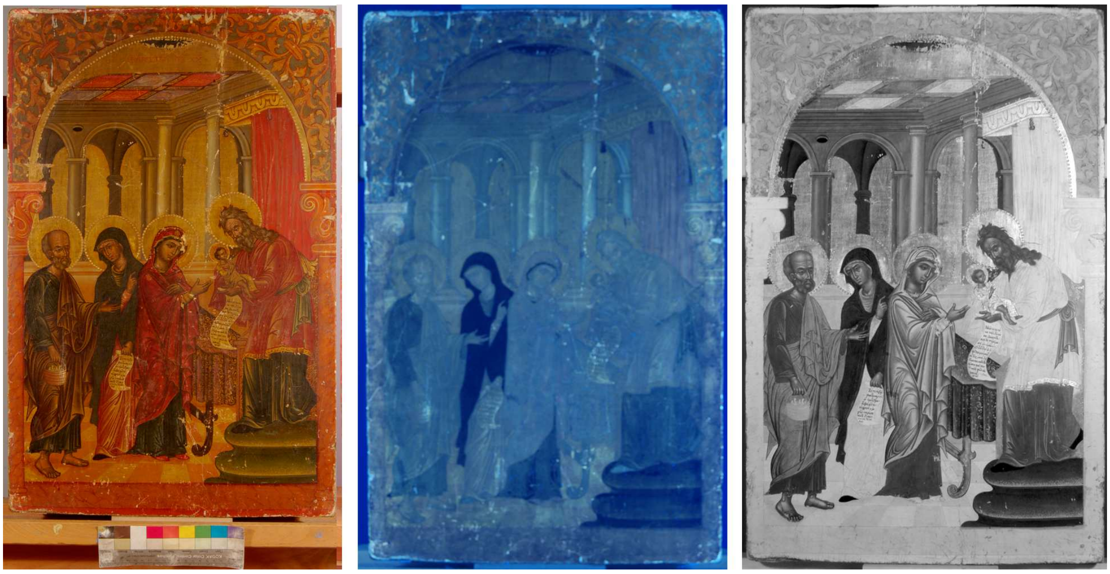


Figure 1. Visible, UV and IR photographs of the icons conservation state

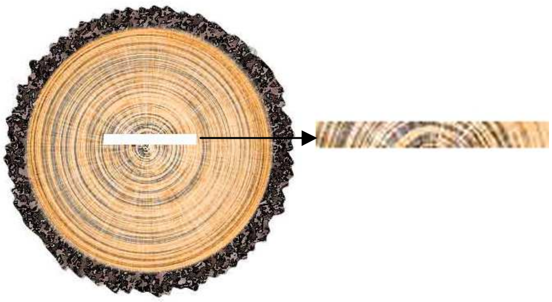


Figure 2. Example of the radial cut of the wooden panel

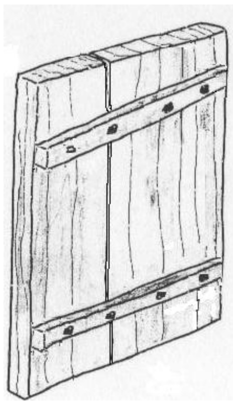


Figure 3. Scheme of the crack in the panel.

Figure 4. Detail of the saw mark in the right side of the icon (raking light).

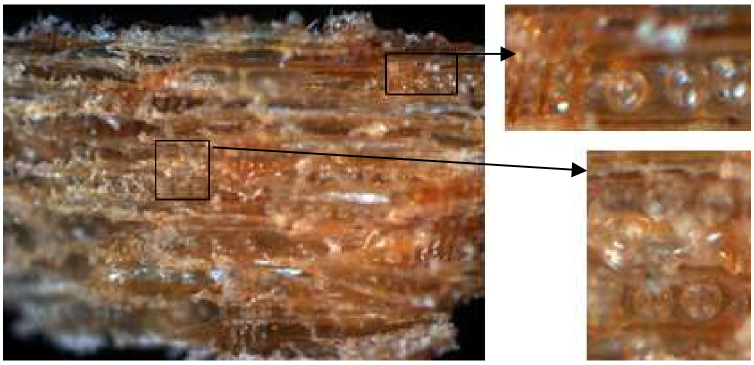


Figure 5.Longitudinal sample of the wood (20x): Details from the veins

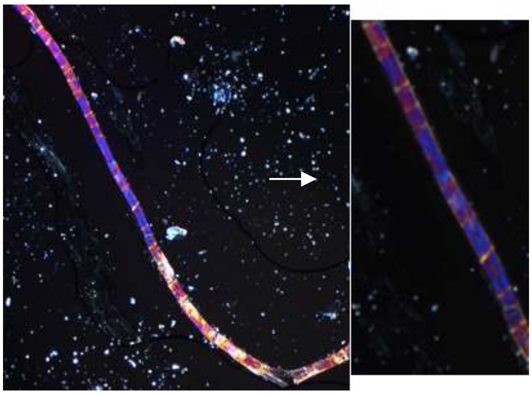


Figure 6. Linen fibre (20x amplified)

Figures 7 and 8. Types of cracking: the first one is due to the canvas and the second type is due to carved lines in the ground layer.

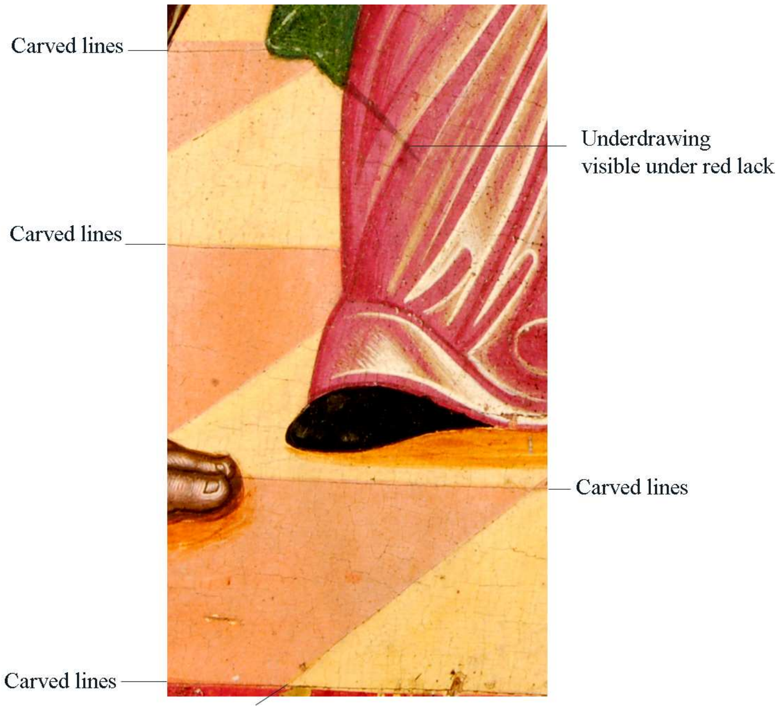


Figure 9. Details where is visible the carved lines of the floor tiles and the underdrawing of Anna’s mantle.

Figure 10. Details of the underdrawing visible by infrared photography.

Figure 11. Carved margins of the drawing and underdrawing of the figures (IR).

Figure 12. Reddish bolus

Figure 13. Carved detail.

Figure 14. Type of brushstrokes in the grey columns area visible by IR photography

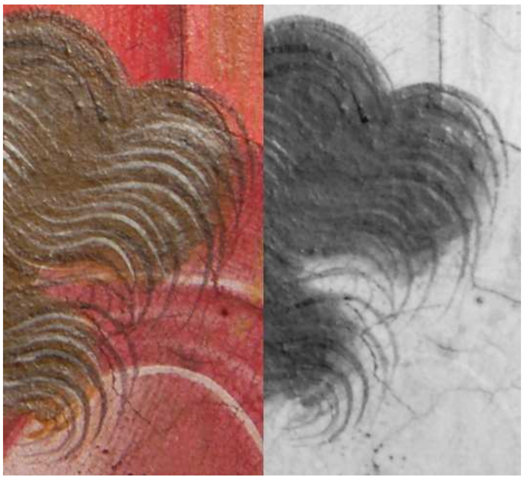


Figure 15. Detail of S. Simeon’s hair with fine brush

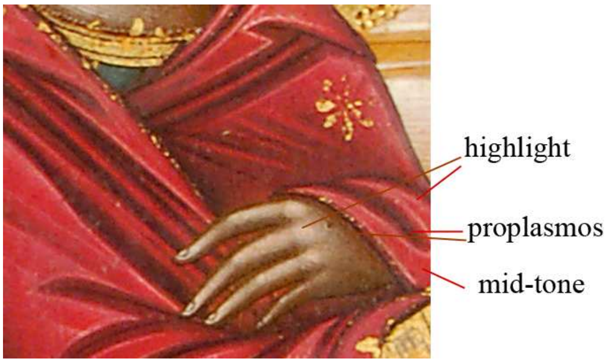


Figure 16. Painting technique

Figure 17. Comparing painting details of a young and an old woman

Figure 18. Painting of the faces technique: 1-proplasmos, 2-mid-tone of the mouth, 2.1-mid-tone of the face 3-highlight tone of the lips, 3.1-highlight of the face, 4-delineating line of the lips, 5-reddish tone as glyklasmos;

Figure 19. Detail of the pigeons basket

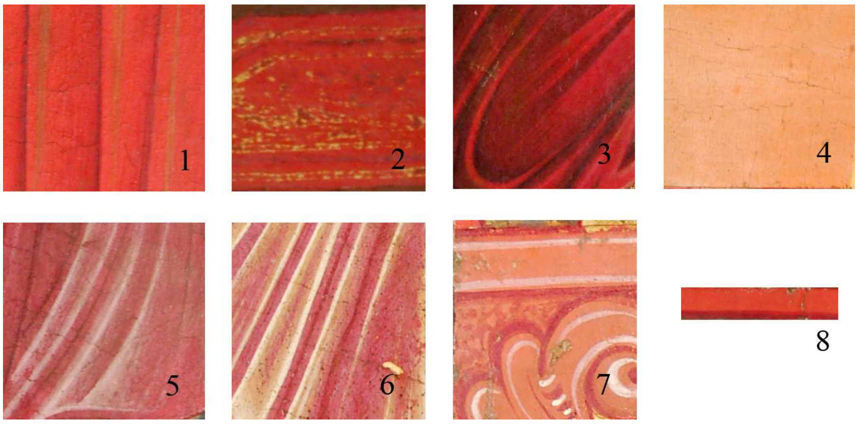


Figure 20. Details of red areas: 1-courtains, 2-ceiling tiles, 3-Virgin's garment, 4- floor tiles, 5-Simeon's garment, 6-Anna's garment, 7-left side column, 8- margins.

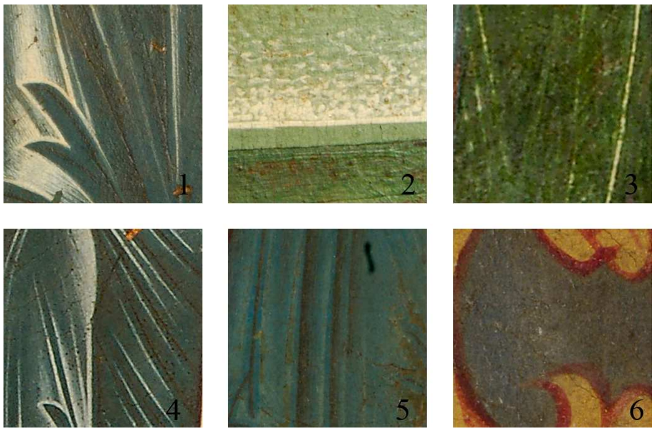


Figure 21. Details of green and blue areas: 1-Simeon's belt, 2-column under Simeon, 3- Anna's mantle, 4-Joseph's mantle, 5-Virgin's garment, 6- upper backround.

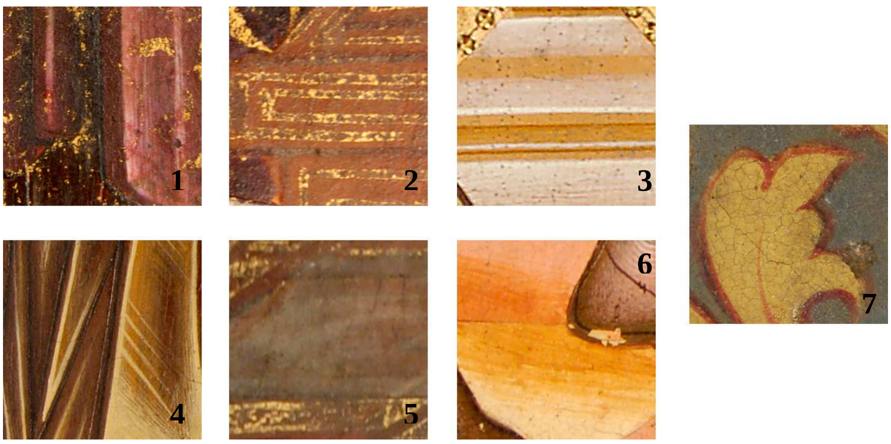
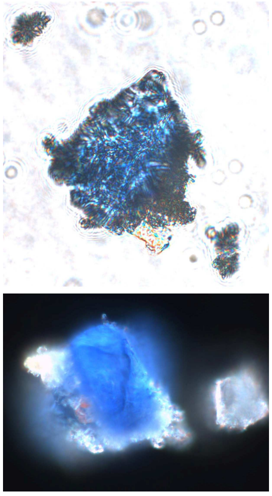
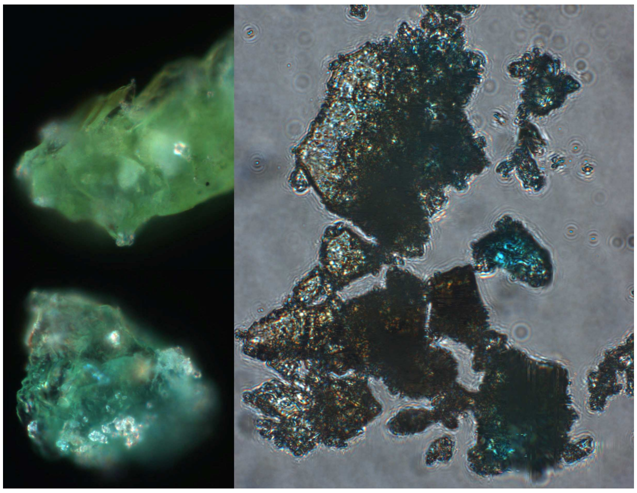


Figure 22. Details of ochres areas: 1-altar, 2-Simeon's chair, 3-backround of the figures, 4-Joseph's garment, 5-ceiling tiles, 6-ochre light aside Joseph's feet, 7- yellow decoration.





Figures 23 and 24 – Smalt and verdigris pigments particles by transmitted and reflected light.

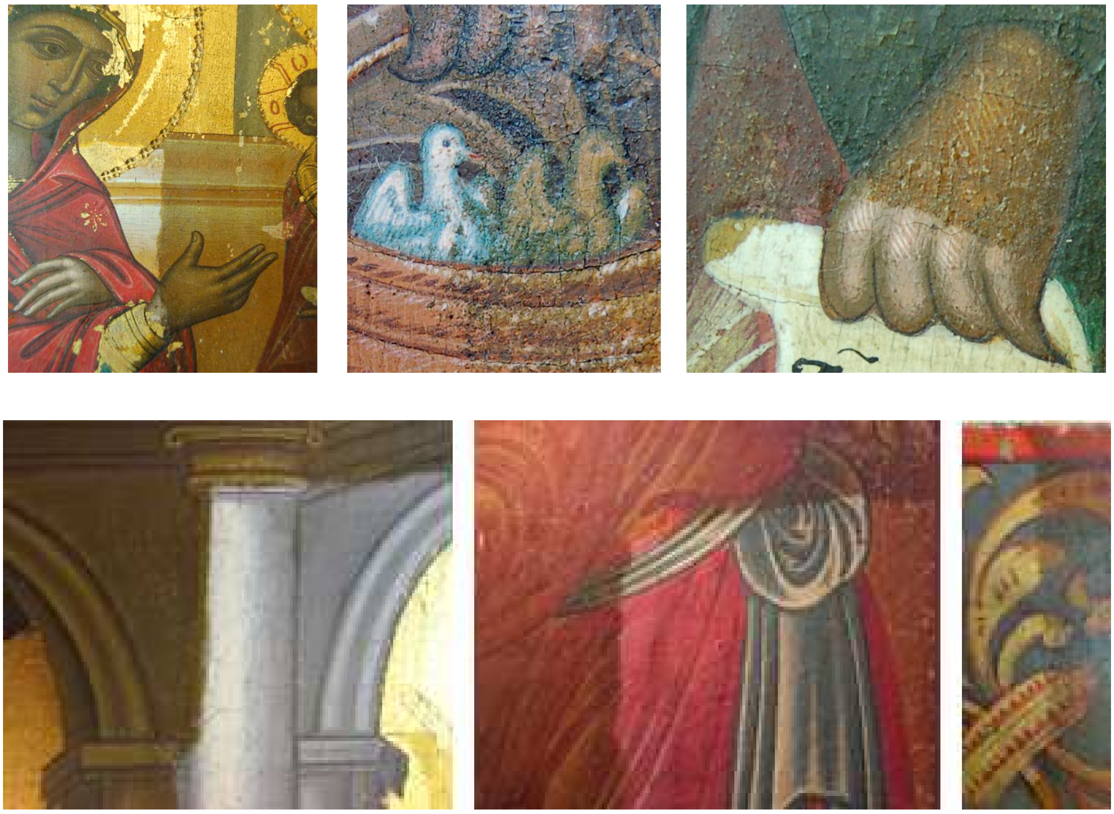


Figure 25. Details of the cleaninig proceduce

Figure 26. Icon cleaned

Figure 27. Facing of the icon

Figure 28. Detail of Joseph and Anna by raking light and visible light photography.

Figure 29. Wood interventions and crack detail

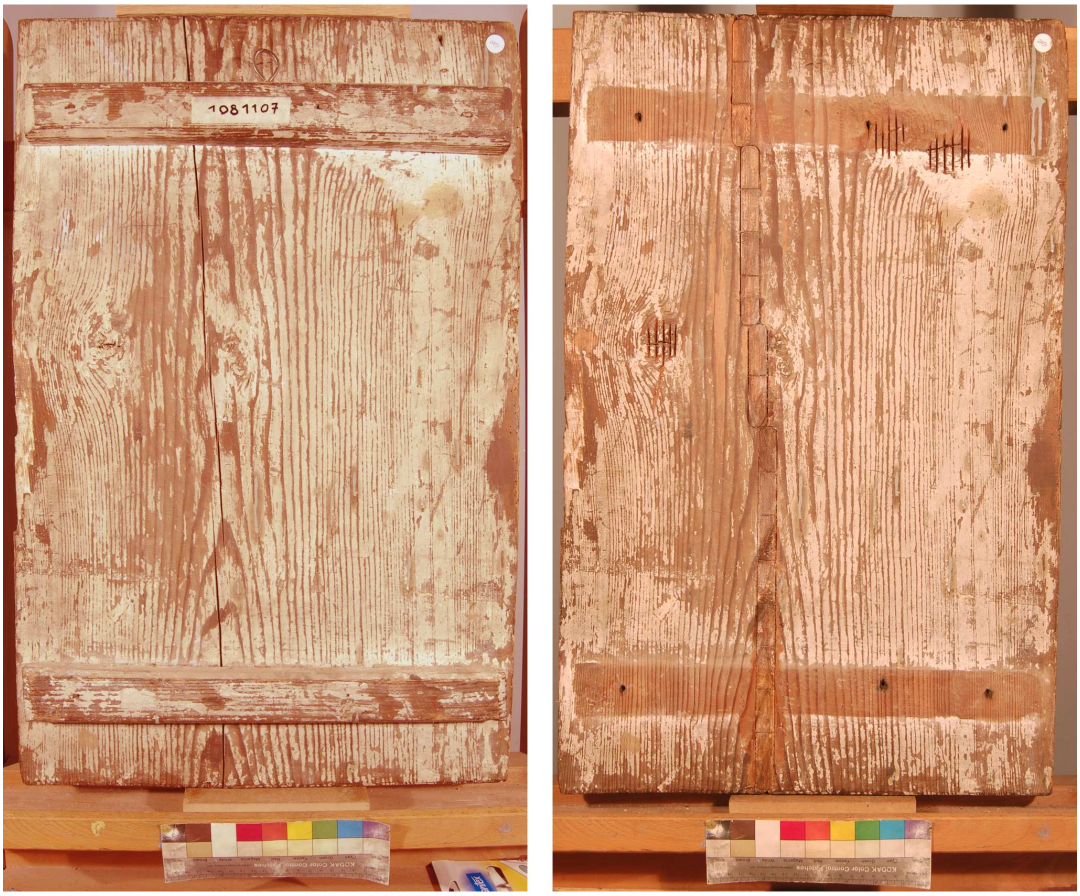


Figure 30. Wooden panel before and after the treatment.

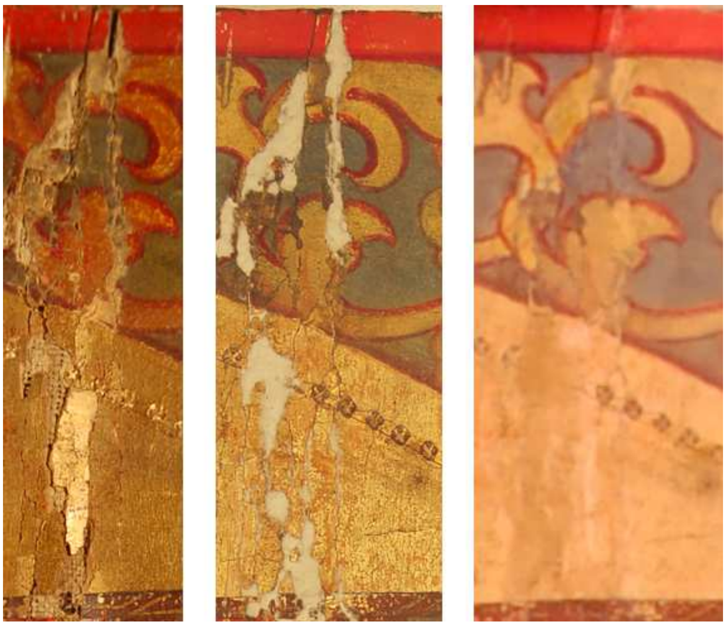
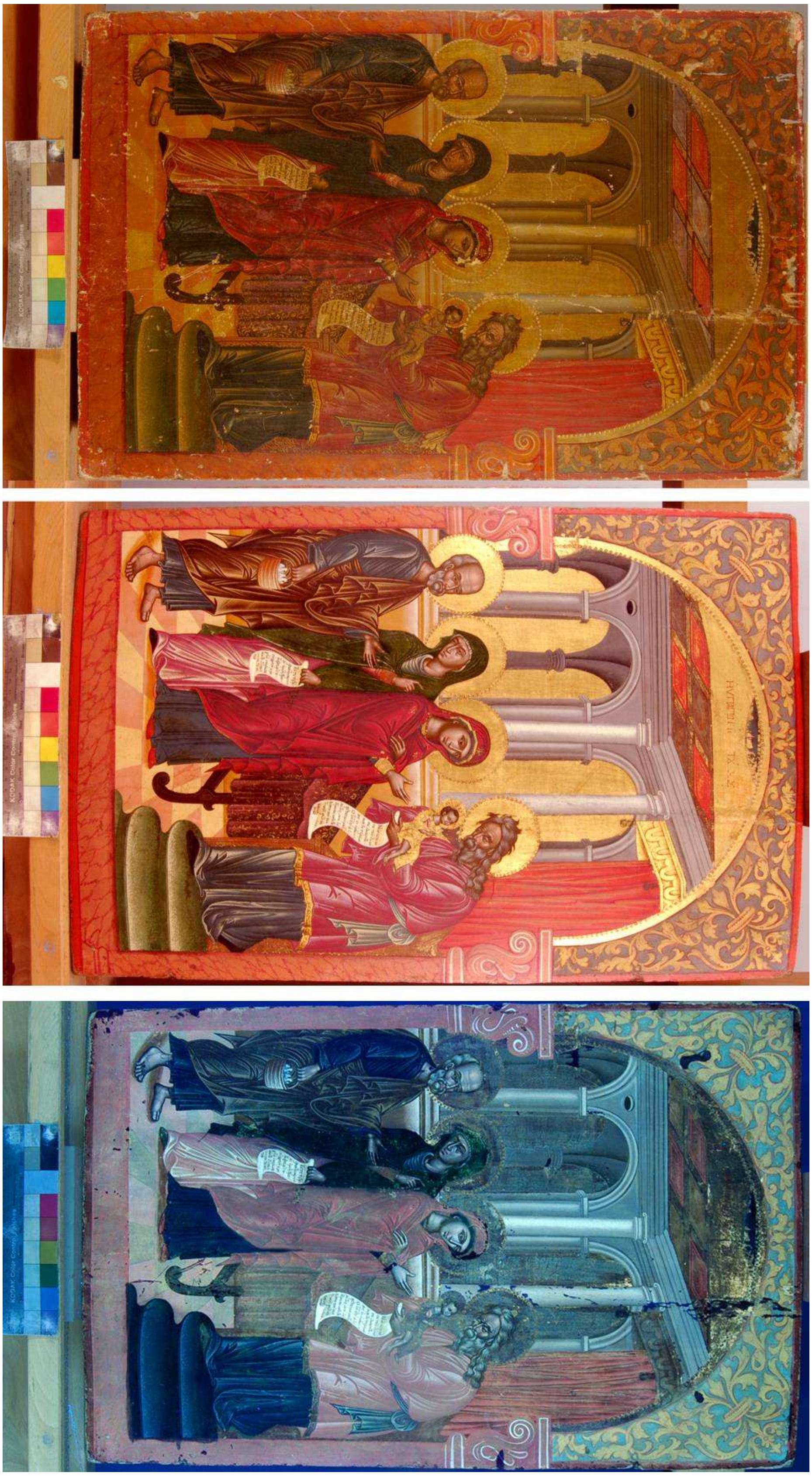


Figure 31. Detail of filled up and retouched area.

Figure 32. Icon before and after treatment and UV photograph after treatment where is visible the retouched areas.



Appendice II

Infrared false colour photography

False-color infrared photography is a useful supplementary technique for the examination and characterization of objects, especially pigment identification. [1]

Because many paint layers are partly transparent to the near infrared radiation (IR) in many cases underdrawings can be detected along with artists brushstrokes and alterations due to later restorations [2]

Infrared images will be reproducible and capable of showing the subtleties required in order to make accurate judgments about the objects being photographed. Although there will always be slight differences between the results of every photographic session. [1]

This happens because image colour was found to vary with degree of exposure and by pigment concentration. Binding medium was found to have little or no effect on the observed coloration in the photographs [1]

As a method of identification of pigments for itself it's not enough, but it helps a lot to construct possible compositions of each color area.

The equipment used was a digital camera Nikon D50 with capacity to record photographs in the infra-red spectrum at a wavelength range between 900-950nm. To make IR photographs a filter was applied (Kodak Wratten, No.87 C) and the images recorded with an exposure time of + 1, 00 seconds, an aperture of 22 and the white balance (WB) defined for day light.

The images in visible light were recorded with an exposition time of +0,0 seconds, an aperture of 16 and the WB was defined for interior light.

The images were treated in Photoshop CS2©.The pallet of infrared false color used for comparison is recognized by the International Institute for Conservation (IIC) [1] and the pallet for infrared in greyscale is recognized by the University of Athens. [3]

The results were helpful and enrich the study (figures), but this technique is never conclusive.

True color	False IR Color
Black	Black
White	White
Cinnabar	Yellow
Azurite	Blue
Ultramarine	Reddish purple or dark blue
Indigo	Red or dark brown
Cobalt	Reddish
Yellow with Fe	Greenish
Other yellows	White
Copper greens	Blue
Green earth	Blue, light
Umber	Black

Table 1. Correspondence between true and false IR colour of the pigments.[6]

[6] Moon, T., Schilling, M.R., Thirkettle, S., 'A Note on the Use of False-Color Infrared Photography in Conservation', *Studies in Conservation* **37** (Feb. 1992) 42-52.

Pigments	TiO2	Copper Green	Yellow ochre	Cobalt blue	Indigo	Green earth	Malachite	Verdigris	Ivory black
Grey level	174,3	171,8	132,4	131,1	101,6	74,2	59,8	47,9	57,5

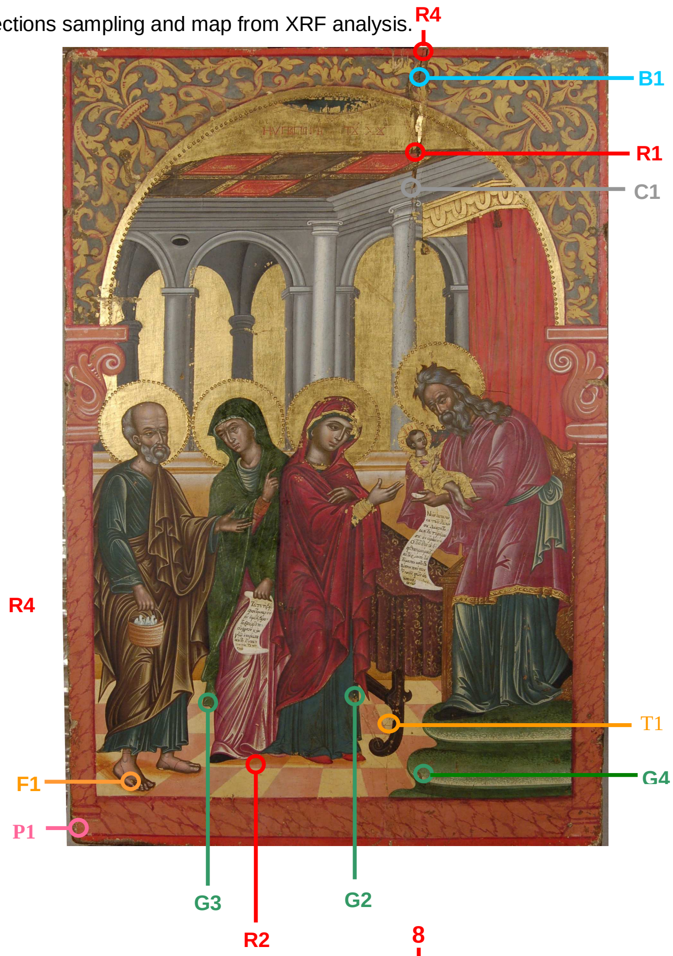
Table 2. Values of the grey level in IR photographs.[7]

Details of some areas photographed:

[7] Perdicary, J., Vourvopoulou, C., *The identification of inorganic pigments in the infrared spectrum by using the optical microscope,* Athens, (1997)

Appendice III

Figure 33 e 34. Map of cross-sections sampling and map from XRF analysis.



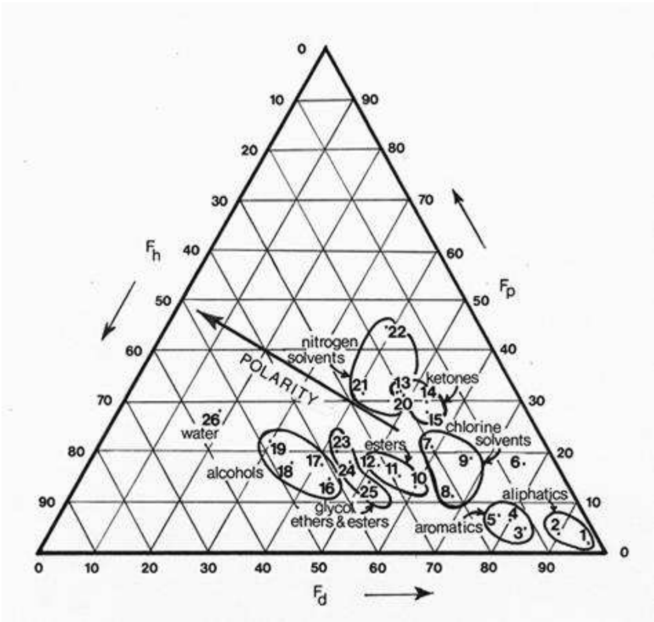
Appendice IV

Table 5. Solubility parameters and evaporation rate of the solvents used for cleaning the icon [20].

Solvents	Solubilty parameters f_p	f_h	f_d	Evaporation rate*
Acetone	47	32	17	5,6
Ethanol	36	18	12	1,4
White Spirit	3	3	94	0,1

* The relative evaporation rate of butyl acetate is 1.0. Other materials are then classified as fast (>3,0), medium (0,8 to 3,0) and slow (<=0,8)

The Teas Triangle



1 hexane
2 white spirits
3 xylene (dimethylbenzene)
4 toluene (methylbenzene)
5 benzene
6 spirits of turpentine
7 dichloromethane (methylene chloride)
8 trichloethane (chloroform)
9 1,2, dichloroethane
10 n- butyl acetate
11 propyl acetate
12 ethyl acetate
13 acetone (propanone)
14 butanone (methane ethyl ketone)
15 cyclohexanone
16 butan- 1 -ol (n-butanol)
17 propan-2-ol (iso-propyl alcohol)
18 ethanol (ethyl alcohol)
19 mathanol (methyl alcohol)
20 N-Methylpyrrolidone
21 Dimethylformamide
22 acetonitrile
23 2-ethoxyethynol (cellosolve)
24 2-butoxyethanol (butyl collosolve)
25 collosolve acetate
26 water

Figure 35. Teas fractional solubility diagram showing solubility parameters of common solvents and families of solvents with similar properties [21]

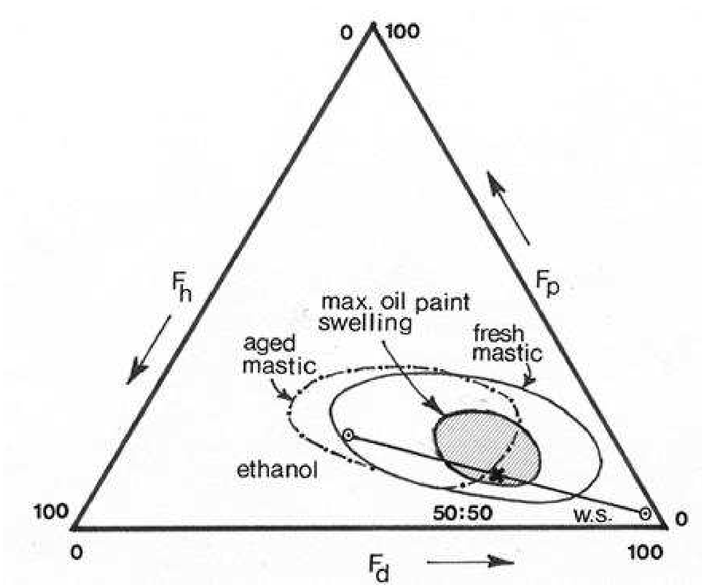


Figure 36. Teas fractional solubility diagram showing change in solubility region of mastic due to ageing, the area of maximal swelling of young oil paint and the solubility parameter position of a 50:50 mixture of ethanol and white spirits [21]