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TITLE

"Characterization of technology from four (4) panel paintings of hieromonk Dionysius from Fourna, author of "Hermeneia of the Painting Art" and comparison with his manuscript"

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ABSTRACT

The contribution of hieromonk Dionysius of Fourna and his treatise: “Hermeneia of Painting Art” is decisive because it gathers all the previously scattered advices and information about the construction of portable icons –panel paintings-, which are mentioned in his text, in an autonomous chapter. In addition, his essay becomes a reference point for many years, both for the writing of various "Hermeneias" of painting in the wider Greek and Balkan space, as well as for the exploration of the construction technology and the study of the iconographic types of post-Byzantine orthodox painting.

In the construction technology section, the information quoted by hieromonk Dionysius is probably the only recorded source about the construction stages for post-Byzantine panel paintings and for the materials used during this process. Characteristic are the information about the construction concerning the gesso layer preparation, the gilding technique and process, the pigments that he uses, the varnish recipes, and so on.

In this context, four panel paintings signed by Dionysius, which are kept in the sacristy of the Transfiguration Church in his native village, in Fourna, were selected for scientific research. A research protocol of imaging techniques and physicochemical analysis was carried out, aiming to characterize the materials and the construction technology applied by Dionysius concerning the construction of the four panel paintings and compare the results with all the relative references mentioned in his work "Hermeneia of Art Painting" in order to ascertain moreover, by using scientific methods, if all that he mentions in his work, he also applies them in practice.

Initially, the research protocol was set up and then the relevant research procedures were carried out, which were digital microscopy (DM), X-ray fluorescence (XRF), optical microscopic observation (OM), microchemical tests, scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDX) and Infrared Spectroscopy (FTIR).

The microscopic observations and the physicochemical analyses were carried out in the Laboratory of Physical and Chemical Research of the National Gallery in Athens, in the Laboratory of Archaeometry of the University of Peloponnese in Kalamata, in the Laboratory of Physical and Chemical Techniques of the Technological

Educational Institute of Athens, Department of Conservation of Antiquities and works of Art and at NCSR Demokritos, Department of Materials Science.

The obtained results will help to study Dionysius painting technique and at the same time will perform an attempt to compare his technique with his earlier treatise "Hermeneia of Painting Art". It was the first time that an extensive physicochemical research on Dionysius selected panel paintings concerning his painting technique was applied.

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INTRODUCTION

The first references about Dionysius of Fourna (1670-1744/5) can be traced back in 1845, when the archaeologist Adolph-Napoleon Didron published a French translation of Dionysius's Hermeneia, a treatise on painting and iconography, which he had discovered in a Greek manuscript on Mt. Athos (Kakavas 2008, p. 23; Ferens 2015, pp. xv-xvi). Dionysius was a hieromonk who lived and operated on Mt. Athos and his native village of Fourna and was both a painter and an author.

His treatise "the Hermeneia of painting Art" is a compilation of post-byzantine artistic traditions and practices structured as a series of instructions for painters. It consists of three prologues and six sections. The first section provides technical instructions about hagiography technique; including, among others, recipes for colors, for gilding and for varnishes, and steps on how to prepare materials for painting. The following five sections deal with the iconographical treatment of different religious subjects.

Since his death, Dionysius has been viewed as the author of the most important post-Byzantine handbook on iconography, which earned him a solid reputation and great respect (Kakavas 2008, p. 23).

In 1737 Dionysius' painted four panel paintings in order to dedicate them at Zoodochos' Pigi monastery which he himself had founded. These panel paintings were constructed to adorn the catholicon –the central church of the monastery-, and more specifically the iconostasis of the church. Today, these four panel paintings are kept in the church of Transfiguration at Fourna due to the collapse of the Zoodochos Pigi monastery in 1906.

The main aim of this thesis is to evaluate Dionysius' painting technique in conjunction with his earlier text. The content of this thesis intends to identify the materials used by Dionysius for four (4) panel paintings, to recognize the construction technology of these artifacts, to study Dionysius' painting method and evaluate whether he applied everything described in his Hermeneia, taking into account that the studied panel paintings were constructed in 1737, a few years after he had completed the writing of his treatise (1729-1732). It is the first step towards confirming and verifying the technical information, about constructing panel paintings, presented in Dionysius' treatise. In this context, the connection between his painted works and the text of his Hermeneias will be investigated and evaluated.

The first chapter concerns historical data about Dionysius's life and the text of the Hermeneia. It is divided in four sections. The first one provides a historical briefing about the development of panel painting, attempting to trace its origins from the Fayum portraits up until the development of post-Byzantine painting in Mt. Athos by Dionysius. The second section deals with some historical data about Dionysius's vita as it can be found in the existing literature, as well as through information given by Dionysius himself in his literary and artistic works. Section three examines the text of the Hermeneia and the sources both of its technical and iconographic sections, the editions of Hermeneias' text starting from Didron's first publication (1845) and, finally, the content of Dionysius's treatise. The fourth sub-chapter of the last section focuses on the technical part of the Hermeneia, trying to discern the sources for this part, the content of the technical instructions provided by Dionysius and, finally, to record the recipes directly related to panel paintings construction as mentioned by him.

The second chapter involves the study of a basic panel painting's stratigraphy, which includes the substrate, the ground layer, the paint layers, and the layer of varnish (Kouloumpi, Moutsatsou & Terlixi 2012, p. 362). The use of science and technology for the determination of the chemical identity of art materials started in the early 20th century. However, it was not until the 1990s that an increasing interest of the scientific community focused on the study of the artist's materials, offering a vast amount of knowledge and understanding along with a number of new investigative techniques. This section outlines the most widely used non-invasive and invasive techniques for the characterization of panel paintings' construction materials and techniques (Kouloumpi, Moutsatsou & Terlixi 2012, pp. 366-367).

The third chapter deals with the main goal of the research in this thesis, which is a systematic and scientific examination and analysis of a group of panel paintings painted by Dionysius himself. For this purpose, the research protocol was set up to provide answers to a set of queries concerning Dionysius painting technique. The research protocol consisted of imaging techniques applied in situ, sampling from specific parts of the panel paintings, in situ microscopic observation by digital microscopy, and laboratory analysis by optical and scanning electron microscopy, microchemical tests for cross section samples-one for each panel painting-, elemental techniques performed in situ by XRF and while in the laboratory by EDX, and laboratory spectroscopic techniques such as infrared spectroscopy in the laboratory.

In the fourth chapter, the data obtained from each physicochemical technique for each panel painting is presented. Each panel painting was studied separately. At the end of the data presentation for each panel painting, a small section of discussion follows, while an effort is made to identify the construction technology of these artifacts and evaluate whether Dionysius eventually applied the instructions he had provided in his earlier treatise.

The fifth and final chapter presents the conclusions of this scientific research, and attempts to answer the main question of the research. During the construction of his panel paintings, did Dionysius follow the instructions that he had already written in his "Hermeneia of Byzantine Art?"

After the five main chapters of this thesis, four different Appendixes follow. In the first one, the sampling application and the permission for sampling from the Archaeological Service and from the Greek Ministry of Culture is provided. The second one lists all the obtained elemental data from the study of the samples by EDX. The third Appendix deals with the sampling positions for each panel painting and, finally, the fourth one includes all the spectra from elemental analysis by XRF performed in situ.

The aim of this thesis is to study Dionysius's painting technique and evaluate it in comparison with his text. One of the difficulties during the interpretation of data and writing the text of the thesis was that this effort was applied on Dionysius's panel paintings for the first time. Thus, it was difficult to collate the data of this scientific examination with previous research related to him. This being the first step concerning the recording of Dionysius's painting technique and the extension of this protocol, in order to obtained more in depth information, is the aim of a future research.

CHAPTER A - DIONYSIUS AND HIS TREATISE

1. The Byzantine Painting - Some Historical background

The painting art of the Orthodox Church was formed and developed in the early Christian years, until the fall of Constantinople as well as for centuries beyond. It expanded in various artistic forms of expression, such as wall paintings and panel paintings. It should be pointed out that Byzantine art is mainly distinguished by its remarkable conservatism. For example, a depiction of Saint Demetrius of the 6th c. AD is extremely similar to one in the 14th century (**Fig.1-2**) and a depiction of Christ Pantocrator in a dome mosaic is, despite the differences in size or material, virtually identical with one of an ivory triptych (**Fig.3-4**) or a gold coin (Vikan 1989, p. 47).

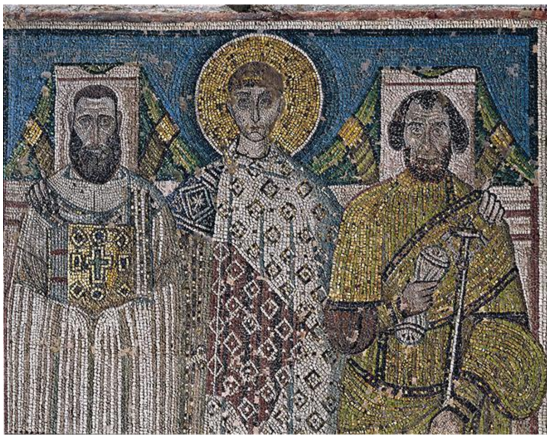


Fig.1 St. Demetrius among the two church's owners. Mosaic, Basilica St. Demetrius, Thessaloniki, 650 AD (*personal archive Th. Mafredas*)

Fig.2 St. Demetrius, mosaic in wooden substrate. Xenofontos monastery, Athos, second half 12th c. AD (*personal archive Th. Mafredas*)

Fig.3 The Deisis mosaic in St. Sophia. Constantinople, 7th c. AD (Shepard 2008, p. 826)

Fig.4 The Deisis. Ivory triptych. 10th c. AD. Louvre Museum (*personal archive Th. Mafredas*)

The beginning of this "novel" art seems to be the 4th c. AD with the transfer of the Empire's Capital from Rome to Constantinople and it continues until the occupation of Constantinople by the Ottomans in 1453 (**Fig.5**) (Kefalas 2011, p. 33).

Fig. 5 The siege of Constantinople by the Ottomans (1453). Fresco from Moldovita's monastery, Romania, Unknown 1537 (source: wikipedia.org)

Constantinople becomes a melting pot of various influences and artistic movements that manage to combine the religious traditions of the East with the Classical Greek culture and character. This fusion gave birth to a unique artistic style that is still easily recognizable today. With the prevalence of Christianity, the Byzantine style shifts from the quest about beauty and harmony, which was the object of classical antiquity. On the contrary, it places emphasis on the inner world of the forms that are being depicted, in the symbolism and the submission of religious emotion (Kalokiris 1972, p. 34; Kefalas 2011, p. 33; Antourakis 1997, pp. 438-439).

The first centuries of the development of the Byzantine art are characterized by the transition from the painting' monumental character, namely the coexistence of Roman tradition with the standards of late antiquity, to the picturesqueness of the figures which mainly characterize the Fayum portraits of the 3rd and 4th c. A.D (Kalokiris 1972, p. 54). It is widely accepted that the funerary portraits known as Fayum portraits (**Fig.6-8**), named after the homonymous oasis in Egypt where they were found, are the forerunners of icons (panel paintings).

Fig. 6-8 Fayum Portraits. Kunsthistorisches Museum, Vienna (*personal archive Th. Mafredas*)

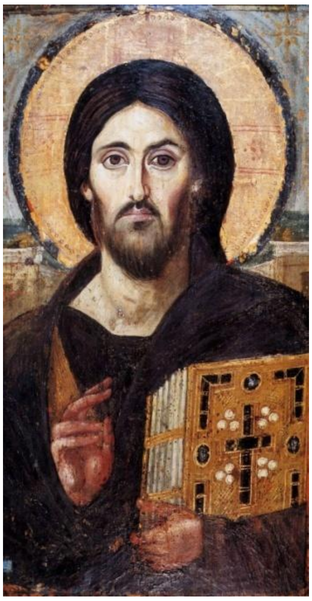


Fig. 9 The Christ-Pantocrator. St. Catherine's Monastery, Sina, 6th century AD. Encaustic technique. (*personal archive Th. Mafredas*)

This hypothesis is further supported by the fact that some of the earliest Byzantine icons were made using the same technique as the Fayum, known as encaustic[1] (**Fig.9**) (Vassilaki 2009, p. 759; Katsibri 2002, p. 27). These portraits focus mainly on the intensity of the gaze, while the body's glory becomes secondary (Papaioannou 2007, p. 19; Antourakis 1997, p. 439).

As the empire grows under the reign of Emperor Justinian, the Byzantine art once again moves its focus from being the art of mental representation to expressing spiritual presence. The worship of the figure represented becomes more important than the beauty of the portrait itself (Papaioannou 2007, pp. 45-46). With the exception of the Constantinian period, the Justinian era is the only time when the Mediterranean world comes so close to achieving unity. However, the lack of unity during the previous years had not been as influential as the iconoclastic controversy. In this context, the painting art will radically reshape its style (Papaioannou 2007, pp. 55-59).

The condemnation of the icons during the 120 years of the iconoclastic controversy (724-843) will stop the development of Byzantine painting. Decorative motifs become predominant while the Cross as the symbol of victory over death retains its place; it is the only remnant from the previous painting period that survives (Kalokiris 1972, pp. 59-60).

[1] The basic characteristic of an encaustic icon was that the color had to be mixed with beeswax. In order for the wax to be mixed with the color, it had to be heated and, for this, a tray with cavities heated from below was used. Each cavity contained a different color. The panel itself had to be hot as well, so it was heated once the colored wax was ready for application (Vassilaki 2009, p. 759)

The Seventh Ecumenical Council of Nicaea (787) summarizes the principles of icon veneration, restores the worship of the icons and declares their necessity in Church's life (Louth 2005, p. 148). Nevertheless, the final restoration of icons does not take place until 843 (**Fig.10**). From this time on, icons can be freely produced and honored (Vassilaki 2009, p. 759). The victory against the iconoclasts and the connection of Orthodox doctrines with the icons leads to a substantial reform in painting. From now on the decoration of the temples is dictated by functional and doctrinal reasons, while all iconographic themes are imposed by a hierarchical order (Şarlak & Onurel 2014, p. 323; Vassilaki 2009, p. 762).

Fig. 10 The Icons' restoration, 16th c. AD. Benaki Museum, Stathatos Collection (Delivorias 1997, p. 280)

In 867 a new dynasty arises in Constantinople with Basil I, the Macedonian Dynasty, which ruled the empire for almost two centuries. These centuries signal the peak of glory and culture of Byzantium (Grabar 1967, p. 15). There is a brilliant spiritual blossom that accompanies the economic and political revival of the Empire. This is the so-called "Macedonian Renaissance" (Kalokiris 1972, p. 65; Papaioannou 2007, p. 67; Antourakis 1993, pp. 14-15; Grabar 1967, p. 98).

The Macedonian Dynasty will give way to the Komnenos dynasty (1057-1185), whose presence on the throne will be accompanied, at the political level, by a series of disasters culminating in the conquest of Constantinople by the Latins in 1204 (Papaioannou 2007, pp. 75-77; Grabar 1967, p. 17). On the artistic level there is an exact pictorial perception of the subject that unifies the style of painting while at the same time, strict regulation dictate the iconographic program according to systematic theological thinking (Papaioannou 2007, p. 77). In the Orthodox doctrine, the themes and representations develop into a scientific discipline that produces standardized patterns and models. Since the representations in icons are carried out within the frame of a given protocol, icon painters are careful about following these rules (Papaioannou 2007, p. 77; Vassilaki 2009, p. 765). Dionysius of Fourna, who analyzed various manuscripts and codified the Orthodox Christian iconographic rules in 1700s, explains the rules that apply in the representations of saints in his guide book for icon painters. In his book Dionysius not only presents the rules of iconography, but also includes valuable information on the preparation and application of materials used in icon painting technique (Şarlak & Onurel 2014, p. 324; Zarra, Merantzas & Tsiodopoulos 2015, p. 120).

The liberation of Constantinople from the Latins in 1261 by Michael Palaeologos signals the revival of the Byzantine art (Grabar 1967, pp. 17-18). Thus, it can be supported that one of the brightest seasons of Byzantine culture starts in the 13th c. (Vassilaki 2009, p. 764; Kalokiris 1972, p. 81). This period, up until 1453, is the most flourishing era in icon painting (Grabar 1967, p. 23). The number of icons increased enormously and surpassed that of monumental painting in both fresco and mosaic. It was not only the quantity but also the quality of late Byzantine icons that reached the highest levels ever. Icons scattered all over the empire, many of which still survive to this day, indicate that it is not only Constantinople that is producing icons of great quality. Thessaloniki seems to play an equally important role in the icon production of the late 13th and the 14th century, receiving commissions not only from the wealthy monasteries of Mt. Athos but also from local governors of the area (Vassilaki 2009, p. 765; Grabar 1967, pp. 23-25, 101).

This Late Byzantine period, also known as “The Palaeologian Renaissance” is characterized by the co-existence of two major, diametrically opposed painting patterns (Kalokiris 1972, p. 81; Papaioannou 2007, pp. 39-99; Antourakis 1993, pp. 14-15). The Macedonian school, centered in Thessaloniki and Constantinople, draws its inspiration from traditional eastern sources and is characterized by realism, freedom and lively movements. The tones of the colors used are vibrant with a wide figuration and an impressionistic apposition (Kalokiris 1972, pp. 81-82). The main representative of the faculty was Manuel Panselinos -14th c. AD- (Kalokiris 1972, p. 82; Vasilaki 1999) (**Fig.11**). The so-called Cretan school is formed in the region of Crete during the second half of the 15th century. In the beginning of the 16th century, its principles are spread out to Meteora, Mt Athos and elsewhere by Theophanes (**Fig.12**) and other Cretan icon painters. Finally in the 17th century, the Cretan school spreads to the entire Orthodox world. It adheres to Byzantine idealism and is characterized mostly by restrained movements, austerity, and reverence, emanating a sense of strict conservatism (Kalokiris 1972, pp. 82-83; Kefalas 2011, p. 38; Grabar 1967, p. 101).

Fig.11 Anapeson. Manuel Panselinos. Protaton, Karyes Mt. Athos, 1290 (*personal archive Th. Mafredas)*

Fig.12 Holy Mandylion. Theophanis, Stavronikita Monastery Mt Athos, 1545-6 (*personal archive Th. Mafredas)*

The fall of Constantinople in 1453 by the Ottomans, interrupts the Palaeologean Renaissance, even though the painting art will continue to exist and develop based mostly on the Palaeologean standards (Gratsiou 2005, pp. 184-185). The conditions for the development of the ecclesiastical painting are defined by the dispersion of the painters in major urban centers and the emergence of artistic workshops in various regions as well as the easier contact with the West (Vassilaki 2009, pp. 765-766).

It should not be forgotten that, since about 1400 AD, Venetian Crete appears to have become the most important center of icon production. The island of Crete came under Venetian domination in 1211 and by the mid-fifteenth century its hybrid society, consisting of native Greek Orthodox Cretans and Catholic Venetians, was experiencing widespread and fertile cross-cultural interactions (Harrison et al. 2011, p. 35). The documented presence of Constantinopolitan painters on the island along with the flourishing economic conditions prevailing at the time must have played a decisive role in this (Vassilaki 2009, p. 766). This two-way relationship between Crete and Venice contributes to the widespread use of the Cretan painting style. The number of icon painters who sign their works increases enormously, promoting their icons beyond the narrow geographical boundaries of Crete. This results in the creation of new iconographic types that will be used as models and a gradual improvement of the social status of the painter and the role of icons in general. (Potamianou-Axeimastou 1992, p. 13; Vassilaki 2009, p. 766).

During the 16th and 17th c. AD, the painting art seems to still retain its cultural and monumental forms. These two centuries are marked by the great edge of Cretan icons and frescoes and constitute the turning point for the development of the so-called Post-Byzantine art. Under Theophane's directions, a group of talented Cretan painters created a new style of painting, even though they tried to maintain the Palaeologean standards (Paliouras 2000, pp. 208-209). These painters seemed to have the power and ability to take on new perceptions and express them in a different way by drawing ideas and forms from the Palaeologean art of the 14th century (Paliouras 2000, pp. 213-214). Thus, there is an imitation of specific iconographic types and ways of painting from the Palaeologean art, which certainly impressed the artists of the 16th and 17th century (**Fig.13-14**) (Siomkos 2008, p. 146; Tsilipakou 2007, p. 258).

What should be noted is that it is not the iconographic type that is being drawn from the Palaeologean standards, but the rendering of the forms and the wording of the garments. A lot of artifacts show that since the middle of the 16th century and despite the dominance of the so-called Cretan school, there has been a parallel flow towards returning to the iconographic and typological models of Palaeologean painting (Siomkos 2008, p. 147; Taylor 1980, pp. 63, 67).

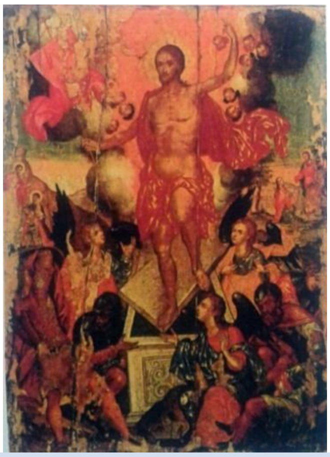


Fig. 13 Resurrection. Moskos 1679 *(Kakavas 2008)*

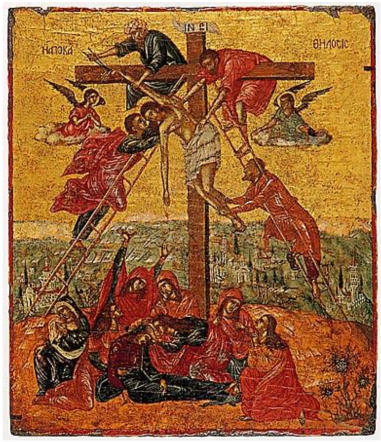


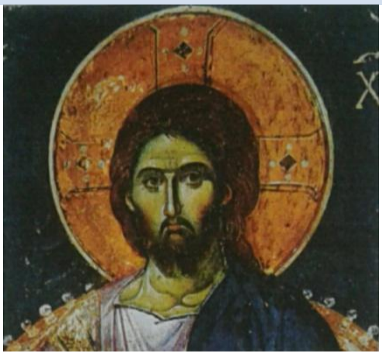
Fig. 14 Deposition of Christ. Byzantine Museum, end 16th- beginning of 17th century *(personal archive Th. Mafredas)*

During the 18th century there is a more powerful and more conscious artistic current of returning to the Palaeologean motifs especially in northern areas of Greece and the rest of the Balkan countries. For example the form of Christ in Protato, in Mt. Athos (**Fig.15-16**), by Dionysius of Fourna is painted in the exact same way as it had been portrayed by Panselinos (**Fig.17**) (Vasilaki 1999, pp. 49-50), because Dionysius had set the studentship in Manuel Panselinos' artifacts as his main aim (**Fig.18-19**) (Siomkos 2008, p. 147; Vassilaki 2012, p. 382). At the same time the Cretan art is still flourishing in central Greece, while in Dodecanese and the Ionian Islands there is a revival of western painting, which seeks naturalness in both icons and frescoes (Kalokiris 1972, pp. 98-99). Especially in Ionian Islands the theoretical and artistic work of Panagiotis Doxaras, a Greek painter and the main representative of the so-called Ionian faculty, signals the starting point of modern Greek art by detaching it from the Byzantine and post-Byzantine traditions and getting it to adopt the principles of western European painting, both on the level of technique and the level of style (Drakopoulou 1999, pp. 63-65; Moutafov 2006, p. 76; Ferens 2015, pp. 36-38).

Fig.15 The Church of Protaton, Karyes Mt Athos, W view *(personal archive Th. Mafredas)*

Fig.16 The interior of Protaton, Karyes, Mt Athos *(personal archive Th. Mafredas)*

Fig.17 Christ enthroned, Panselinos, Protaton, Karyes, Mt Athos, 1290 *(personal archive Th. Mafredas)*



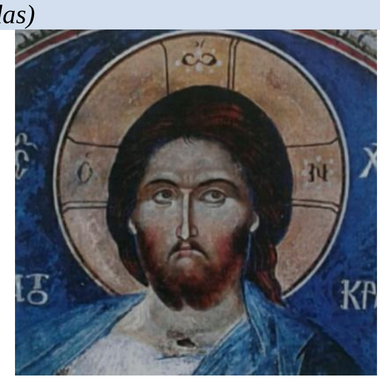


Fig.18 Pantokrator Protaton-Karyes Mt. Athos. Manuel Panselinos 1290 *(Kakavas 2008)*. **Fig.19** Pantokrator, Timios Prodromos cell, Karyes Mt Athos. Dionysius 1711 *(Kakavas 2008)*

In 19th century the establishment of a free Greek state creates a new situation. The academic style following the German's Nazarenes' paths and motifs, expressed by the so-called Athenian School of Munich, influenced ecclesiastical painting through the creation of new motifs, mostly in major urban centers of the new state (Stoufi-Poulimenou 2007). A characteristic example of the Nazarene movement can be found in the paintings of the Metropolitan Cathedral of Athens. On the contrary, the parts of Greece that are still enslaved by the Ottomans, such as Macedonia and Thessaly, continue to preserve the native tradition, uninfluenced by the principles of the "Athenian School of Munich" (Triantafyllopoulos 1996, pp. 47-52).

Finally the 20th century is characterized by an attempt to return to the previous iconographical standards of the Macedonian and Cretan schools. In this effort, the contribution of Fotis Kontoglou is indispensable. His contact with the Byzantine art during his first visit in Mt Athos (1923) led him to become a strict imitator of Byzantine style (**Fig.20)**. The result of this was the evaluation of Byzantine compositions in a way which testified that he essentially isolated the morphology from the technique. (Zarra, Merantzas & Tsiodopoulos 2015, p. 105). This was the reason why he preferred to follow the sophisticated techniques of the Cretan School in his icons, but chose Panselinos', Fragkos Katellanos' and Theophanes' standards for his wall and panel painting (Triantafyllopoulos 1996, pp. 52-54).

Fig.20 F. Kontoglou, Constantine Palaeologos 1953, Private collection, Athens (*Kakavas 2008*)

2. Dionysius Vita

The 18th century as discussed above is significant because during this period, a tendency towards returning to the Palaeologean painting develops, with Dionysius, a hieromonk from Fourna, being the main representative of this movement (Vasilaki 1999, p. 49). The main information about Dionysius' Vita is offered by his biographer, Theophanis of Agrapha, who was an apprentice and friend of Dionysius and succeeded him as hegoumenos of the Zoodochos Pigi monastery at Fourna (Kakavas 2008, pp. 77-78). Details about the life of Dionysius are located in the Codex 37 of the Benaki Museum, written by Theophanis (Kakavas 2008, pp. 79-85; Vassilaki 2012, pp. 380-381). It should be mentioned that Theophanis does not provide specific dates when mentioning the events in Dionysius' life, in fact even the date of Dionysius' death is not disclosed.

Fig.21 Hieromonk Dionysius of Fourna, 1996, Column outside of the Church of Fourna (*personal archive Th. Mafredas)*

Fig. 22 Map of Central Greece. In the frame the village of Fourna *(Kakavas 2008)*

Dionysius (**Fig.21**) was born at the village of Fourna in the district of Agrapha in Evrytania, Central Greece (**Fig.22)**. There is no evidence about the exact date of Dionysius birth but, according to some scholars the year of his birth is 1670 (Hetherington 1974, p. 2; Piompinos 1984, pp. 107-108; Kakavas 2008, p. 85; Markozanis 2017, p. 20). His father was Panagiotis Chalkias, the village priest who, according to an epigram in the Monastery codex seems to be already dead in 1733 (Dionysios 1938, p. 32). It's difficult to identify his mother name (Kakavas 2008, p. 87; Markozanis 2017, p. 21) and his secular first name before he became a monk in Mt Athos (Kakavas 2008, p. 87). It is speculated that his father died when he was still young and, at the age of twelve, Dionysius went to Constantinople, presumably to complete his education. He stayed there for four years and, at the age of sixteen, he went to Mt Athos to become a monk. From the early years of 18th century, he became established as a painter (Dionysios 1938, p. 7; Piompinos 1984, p. 107; Kakavas 2008, pp. 87-90; Vassilaki 2012, p. 381; Markozanis 2017, p. 21). In Mt Athos, Dionysius settled in Karyes, where he built a cell complex with its church dedicated to John the Baptist (**Fig.23-24**). According to its donor inscription, the church was decorated with wall paintings made by Dionysius himself (Kakavas 2000, p. 214). He stayed in Karyes until 1727, when he finally returned to his native village and remained there until the end of 1728 (Kakavas 2008, p. 90).

Fig.23 Mt Athos, Karyes, topographic plan (*Kakavas 2008*)

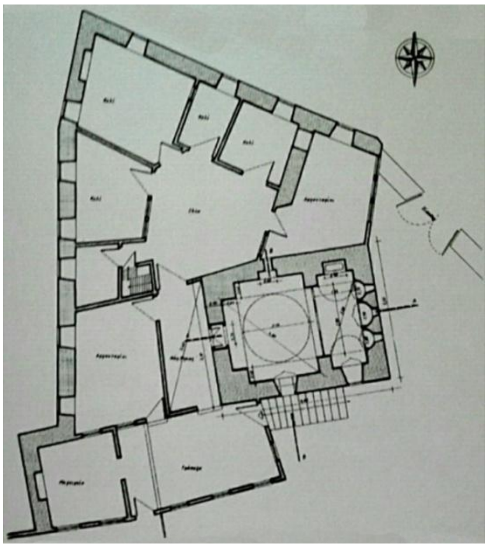


Fig.24 Mt. Athos, Karyes, Cell complex of Dionysius, topographic plan (*Kakavas 2008*)

During his presence in Fourna, probably accompanied by his pupil Kyrillos, he painted the murals that decorate the interior of the local church dedicated to the Metamorphosis of Christ. These wall paintings were destroyed in 1821 when the entire church of Metamorphosis burnt down (Kakavas 2008, pp. 93-94). At this point, it should be mentioned that, during his two years presence in Fourna, Dionysius had a frequent correspondence with the priest, teacher and author Anastasios Gordios. Four letters of Gordios written to Dionysius, all dated between October 24th, 1727 and October 28th, 1728, have survived (Kakavas 2008, pp. 94-100). In these letters, Dionysius seems to be looking for answers about dogmatic issues related to iconographic themes (Vassilaki 2012, p. 381). However, it is not clear whether Dionysius' queries regarding iconographical matters are connected to scenes to be depicted on the wall paintings in the Metamorphosis' church at Fourna or to the future compilation of his Hermeneia. It is more likely that he was interested in collecting materials for the writing of the Hermeneia and therefore, needed advice in theoretical matters, such as the canon he would include in the system of instructions of the hagiographic corpus he was composing (Kakavas 2008, p. 101).

In 1729 Dionysius returned to Karyes where he restored his Kellion in 1731 and stayed there until 1733 (Kakavas 2008, pp. 101-102; Vassilaki 2012, p. 381; Kakavas 2000, p. 214). Between these years, with the assistance of his apprentice Kyrillos, Dionysius wrote up his Hermeneia, which included iconographical and technical instructions both for his apprentices and future artists, after having spent at least twenty years familiarizing with the Athonite painting tradition (Hetherington 1974, p. 2; Piompinos 1984, p. 107; Kakavas 2008, p. 102; Vassilaki 2012, p. 381; Markozanis 2017, p. 22).

In 1733, Dionysius returned to Fourna, where under the permission of Patriarch Seraphim (Dionysios 1938, pp. 38-39), he founded a monastery (**Fig.25)** and an educational establishment with the help of his pupils Peter and Agapios. In 1734 he completed the construction of the school next to the monastery, where Theophanis, the author of Dionysius' Vita, taught for several years (Kakavas 2008, pp. 108, 110-111). In 1738, according to: "The homologia of the place in which this Divine and Holy Monastery was erected" (Dionysios 1938, pp. 41-43), it seems that the monastery was functioning properly and the first Abbot was Dionysius himself: "…the ruler of all things and the foreman…" (Dionysios 1938, p. 42). One year later Dionysius returned to Mt Athos where he stayed for one year and, in 1740, he moved in Constantinople (Kakavas 2008, pp. 112-114; Vassilaki 2012, p. 381). There, he presented to Patriarch Neophytos and asked for his support. In August 1740, the Ecumenical Patriarch issued him a Sigillion (**Fig.26**), a Patriarchal letter giving privileges (Kazhdan 1991, pp. 1893-1894), concerning the foundation of the Zoodochos Pigi monastery at Fourna which was honored with the Stavropigial rank (Dionysios 1938, pp. 52-57; Kakavas 2008, p. 114; Vassilaki 2012, p. 381).

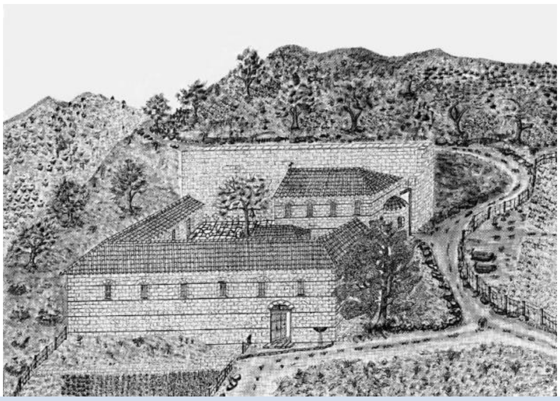


Fig.25 The Zoodochos Pigi monastery complex. Drawing after S. Chatzithanos (*Kakavas 2008*)

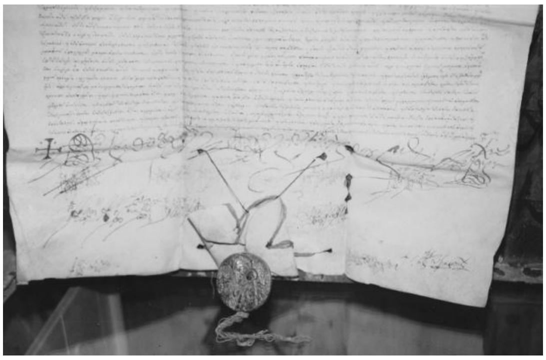


Fig.26 Sigilion of Ecumenical Patriarch Neophytos VI concerning the foundation of the Zoodochos Pigi monastery at Fourna, 1740.

Metamorphosis, Fourna (*personal archive Th. Mafredas*).

In 1741, Dionysius returned to Fourna and, until the May of 1744, it seems that he was still alive[2]. The exact date and place of Dionysius' death is unrecorded. According to Kakavas (Kakavas 2008), Dionysius died shortly after 1744 and was buried in the monastery, as was customary (Kakavas 2008, p. 121; Vassilaki 2012, p. 381). His greatest achievement, the monastery of Zoodochos Pigi was destroyed by earthquake in the early years of 20th century (Vassilaki 2012, p. 381), which makes searching for his tomb in order to identify the exact place of his burial impossible. As a result, Dionysius' exact date and place of death remains a mystery until further information comes to light (Kakavas 2008, pp. 120-121; Vassilaki 2012, p. 381).

[2] The last relevant document directed to him was dated May 18th 1744 (Dionysios 1938, p. 75)

3. The Hermeneia's text

3.1. The Sources

Whenever someone discusses Eastern Orthodox art and its theoretical and technical foundations, especially for panel and wall paintings, the first thing that comes to mind is the work of hieromonk Dionysius, who was both, a painter and an author[3] (**Fig.27-28**), who lived and operated in Mt Athos and his native village (Vassilaki 2012, p. 380), as already mentioned above.

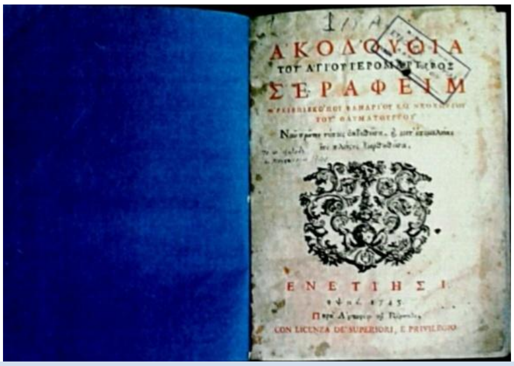


Fig. 27 Dionysius of Fourna, Akoloythia of St. Seraphim, Venice 1745, p.1 (*Kakavas 2008*)

Fig. 28 Dionysius of Fourna, Akoloythia of St. Seraphim, Venice 1745, p.3 (*Kakavas 2008*)

For the researchers and the scholars of Orthodox Church writings, the Greek term Hermeneia means much more than the interpretation, the explanation or even a guide and a glossary of religious art. According to Emmanuel Moutafov the term Hermeneia: "is an elucidation of Holy Scripture and other liturgical texts and this is why the term was borrowed from a strictly religious genre of medieval Byzantine literature" (Moutafov 2006, p. 69) So, the term Hermeneia consists not only of instructions on how to paint icons and wall paintings, rules concerning the composition of specific religious themes and general characteristics of personalities, but also an attempt to render these themes and personalities in the sacred pictorial language called Iconography. In other words this specific term, *Hermeneia*, has a deep theological meaning than merely the explanation of how an icon should be made, which makes the use of this term appropriate in this Thesis, rather than the English translation of Interpretation.

[3] Besides the Hermeneia, Dionysius has written the Holy ceremony of Saint Hieromartyr Seraphim Archbishop of Phanar and Neochorion (Eustratiadis 1926), printed in Venice in 1745 in 2nd version with additions; see AMerican British Online Search In Athens (AMBROSIA) book number 000277202. Also, (Eustratiadis 1932; Chrysostomou 1988), the Nomokanona for the Monastery of Zoodochos Pigi in 1741, which has saved the code EBE no. 4042 of the National Library of Athens (Nikolopoulos 1986), Epigrams and epistles in codex 37 of the Benaki Museum, and the Codex of the Zoodochos Pigi monastery at Fourna (Kakavas 2008) .

The sources of the Hermeneia vary widely and, so far, only a few instructions have definitively been linked to them. Dionysius would have had access to older manuals, to existing paintings in churches on Mt Athos, to liturgical books, as well as to oral tradition. For example, in one of the parts of his treatise, Dionysius mentions how a painter should depict the martyrdom of the saints for each day and month, of a full year, based on theirs Vitae stories, known as synaxaria (Ferens 2015, p. 81). Reading this particular part, of Dionysius' Hermeneia, it seems that Kakavas is right when states that: "We can assume that Dionysios was influenced[4] for these descriptions by the appropriate text of a "*Menologion"*[5], "*Synaxarion"*[6] or "*Martyrologion*"[7] (Kakavas 2008, p. 61).

While Dionysius integrated a wide range of sources into his manual, in the introduction of the Hermeneia, he is the one who mentions (Dionysius 1909, p. 4) that he gathered all the instructions and the information with a lot of difficulties[8], implying the idea of an assembly of courses of different kinds (Ferens 2015, pp. 3-5; Hetherington 1973, p. 320). According to Hetherington (Hetherington 1973) it is really difficult to locate all the sources that Dionysius used for his text, a lot of which are drawn from a wide variety of liturgical books, while it seems that the first section, the technical part, includes the earliest demonstrable traditions (Hetherington 1973, pp. 318, 321; Dionysius 1909; Muñoz Viñas 1998).

In 2010 three scholars, Georgi Parpulov, Irina Dolgish and Peter Cowe published a manuscript that displays many similarities in content with the text of Dionysius (Parpulov, Dolgikh & Cowe 2010). It is an early manual for the construction of panel paintings[9] found in manuscript Vaticanus Palatinus codex graecus 209

4 The same influence for Dionysius' text is subscribed by Paul Hetherington: "A suggested explanation for this is that the texts were taken from printed service books" (Hetherington 1973, p. 320). You can also see Alexander Kazhdan and Henry Maguire article, where it's possible to identify that the physiognomic characteristics of individual saints, which were listed in post-Byzantine painters' guides, such as the Hermineia of Dionysius of Fourna, were occasionally recorded by hagiographers which makes the icon not only beautiful but also useful (Kazhdan & Maguire 1991, pp. 8, 12).

5 Menologion: A catalog of brief biographies of Saints arranged in the order that they appear in the church calendar of fixed feasts, the Synaxarion (Kazhdan 1991, p. 1341)

6 Synaxarion: A compilation of hagiographies corresponding roughly to the martyrology of the East Orthodox Church (Kazhdan 1991, p. 1991)

7 Martyrologion: The book that containing the descriptions of the death of Christian witnesses (Kazhdan 1991, p. 1309)

8 "…άτινα και επιπόνως εσυνάθροισα μετά του ιερολογιωτάτου κυρί Κυρίλλω του εμού μαθητού του εν Χίου» (Dionysius 1909, p. 4)

9 The instructions in the codex refer almost certainly to panel rather than mural painting, since several operations that it describes make no sense on a plastered surface (Parpulov, Dolgikh & Cowe 2010, p. 204)

(**Fig.29**), and must have been bought in Venice or Padua at some point between 1550 and 1570 AD. Nothing is known about the earlier history of this manuscript. Written on watermarked paper datable on 1355, it contains an extensive collection of miscellaneous texts. Since many of these start on a recto, most of folio 284 verso remained at first blank, and was subsequently filled with a short set of instructions for painters. The vocabulary and the kind of syntax leave little doubt that the treatise is not a literary composition but reflects actual workshop practice. Being the oldest one of its kind (no other Greek text on iconographic technique predates the 17th century); it is, despite its brevity, an important source for studying late Byzantine painting (Parpulov, Dolgikh & Cowe 2010, pp. 201,204).

In this earlier text about constructing icons there are obvious similarities with the text of Dionysius. In the Vaticanus Palatinus graecus codex 209 there are instructions about the construction techniques about the figures' faces and garments[10], and the pigments' names[11] (Parpulov, Dolgikh & Cowe 2010). When the comparison comes to the technical part, the Palatinus codex is paralleled, almost identical to the corresponding sections of two post-Byzantine Greek painting manuals: the Hermeneia of Dionysios and another, anonymous text that must also date from the 18th century (Dionysius 1909, pp. κε-κζ). But according to Papadopoulos-Kerameus, the composition of this second anonymous text is assigned to the late 16th century on the sole ground that it mentions the Cretan painter Theophanes by the name (Dionysius 1909, pp. κς, 237-253).

[10] "…each painted on a separately laid and differently colored undercoat (*πρόπλασμα*). The actual painting process consists of layering varying shades of a single color or rarely, laying upon the principal color a different, complementary one. The modeling of garments is based on three principal shades: dark folds (*χάραγμα*), flat surface (*λάμα*), and highlights (*ἔγγυσμα*, also spelled *ἔγγισμα*)" (Parpulov, Dolgikh & Cowe 2010, p. 204).

[11] Among other indicative are mentioned: "…the white (*ψιμμύθιον*) is lead white, while the cinnabar (*κινναβάρι*), i.e., vermilion, is red mercuric sulphide. The ocher comes in two varieties, Constantinopolitan (*πολίτικη*) and plain, which are most probably reddish and yellowish earth. In spite of its name, the *ἀληθινή* may or may not be genuine purple. The words *μελάνη*, *πρασίνη*, *ὀξύν*, and *λαζούριον* give no clue about the chemical composition of the black, green, violet, and blue" (Parpulov, Dolgikh & Cowe 2010, p. 205).

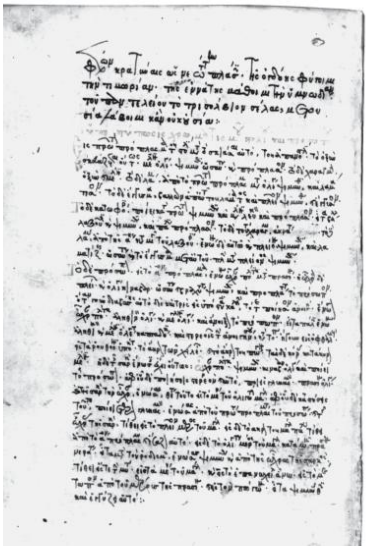


Fig.29 Vatican City, Biblioteca Apostolica Vaticana, MS Vaticanus Palatinus graecus 209, fol. 284 verso (*Parpulov, Dolgikh & Cowe 2010*)

It is really difficult to reconstruct the history of Dionysius' Hermeneia, based on his sources. For Papadopoulos-Kerameus the only thing that someone can be sure of, is that the text of Hermeneia, in its present form has been written by Dionysius. The first part, the technical[12] one, appears to be a unified transcription of two earlier texts. As far as the other sections are concerned, there seems to be no perceivable connection to any previous literary effort but, again in general terms, these parts rely on former texts, out of which Dionysius took the main and most basic instructions (Dionysius 1909).

3.2. The Editions

As defined above, it would be risky to identify the first sources of Dionysius' text because the original manuscript Dionysius wrote with the help of his pupil Kyrillos, has not survived. According to Kakavas, there is a vast number of manuscripts scattered among libraries and in private hands which vary in content and date. A large portion of them have been listed by Vasilie Grecu, Paul Hetherington and Panagiotis Nikolopoulos as listed in the literature cited in his work (Kakavas 2008).

Until 1839, the text of Dionysius' Hermeneia was unknown. The first notice that one of these copies had been discovered comes in a publication of 1845 by the French archaeologist Adolph-Napoleon Didron[13] and his companion Paul Durand, when the

[12] The basic division of the text into technical and non-technical subject matter was not adopted by V. Grecu in his considerable contributions to knowledge of the text (Hetherington 1973, p. 321).

[13] The Adolphe Napoléon (Ainé) Didron was an archeologist and professor of Byzantine iconography. Born in the village of Hautvillers, near the city of Reims, France, on March 13, 1806, he completed his studies at the Law School, and then attended Christian Archaeology courses at the University of Paris. In 1839-1840 he held a scientific trip to Greece and Turkey, seeking answers to issues related to Christian architecture and iconography. His research focused particularly in the monasteries of Mt Athos, where he discovered the manuscript of Dionysius' "Hermeneia" of Painting Art, which was published in Paris

two of them published a French translation made by the latter, including an introduction and numerous commentaries (Dionysios 1855). Although this publication introduced Hermeneia to a wider audience for the first time, and established it as the key to the medieval painting tradition, it was, unfortunately, incorrect. According to Papadopoulos-Kerameus, during the middle 19th century a forger named Konstantinos Simonidis, obtained a copy of Dionysius' Hermeneia from the monks of Mt Athos which he had recopied in 1840. It seems that when Simonidis discovered that Didron was looking for a copy of Dionysius' Hermeneia, he offered him a forged copy in 1842 (Kakavas 2008, pp. 33-35; Dionysius 1909). A few years later, in 1853, Simonidis published the first Greek edition of Dionysius' Hermeneia in Athens, based on another copy made by him in 1840. In 1855, a second printed edition of Simonidis' forgery appeared.

In 1867-1868, the Russian bishop Porphyrii Uspenskij published a Russian translation of a Greek manuscript Hermeneia that he had found and copied in Jerusalem, dated in 1674 (Hetherington 1973, p. 318; Gravgaard 1987, p. 79; Kakavas 2008, p. 34; Zografos 1926, pp. 49-50)

In 1909 Athanasios Papadopoulos-Kerameus published a critical edition of Dionysius' text using another copy of the manual. The Dionysius' manuscript on which Papadopoulos-Kerameus based his transcription and edition dates to the 18th century, and is kept in the Saltykov - Shchedrin State Public Library in Saint Petersburg as Codex Graecus 708. It is the same manuscript as the one Paul Hetherington used for his translation of the manual into English (Gravgaard 1987, p. 79). Papadopoulos-Kerameus incorporated five older and anonymous manuscript fragments relating to the Hermeneia as appendices into his edition, which he identified as Dionysius' primary sources.

In 1936 the Romanian scholar Vasilie Grecu, published a second critical edition, based on Romanian translations of Dionysius' Hermeneia made in 1863 from three Greek manuscripts written in 1805 by a certain bishop Makarios. In 1974, a new and authoritative English translation of Dionysius' Hermeneia was published by Paul

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shortly thereafter. For his trip in Greece he mentions among others: "I wanted in this way to observe closely the evolution of Christian art in Greek religion and to add knowledge on issues related to Christian archeology in former Latin and Turkish occupied areas. I like to locate the origin of Christianity visiting the Byzantine churches of the East and following closely the liturgy and the ritual that followed by Greek priests" (Gregoriou 2011, pp. 305-306).

Hetherington based upon the manuscript Codec graecus 708 in the Saltykov - Shchedrin State Public Library in Saint Petersburg. This codex is the one used by Papadopoulos-Kerameus in his publication of 1909, but Hetherington checked the original manuscript against Papadopoulos-Kerameus' edition for his own translation, without republishing the Greek text. He prefaced his work with an introduction and added an appendix in which he drew up a list of manuscripts containing material relating to the Hermeneia (Kakavas 2008, pp. 37-38).

During his research, Kakavas discovered an unpublished Hermeneia in the Benaki Museum, Codex no. 58, which is dated precisely to 1768 and is the oldest known copy of Hermeneia (**Fig.30-33**).

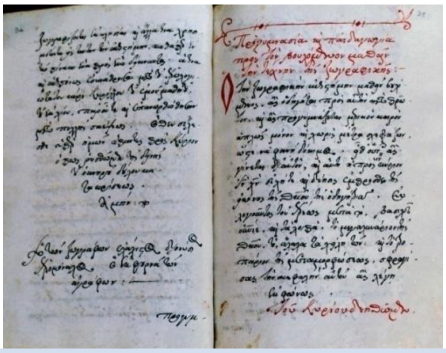

Fig.30 Part from Great Lavra Ms 126 *(Kakavas 2008)*

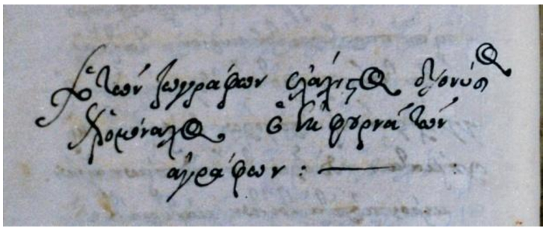

Fig.31 Dionysius sign. Great Lavra Ms 126 (*Kakavas 2008*)

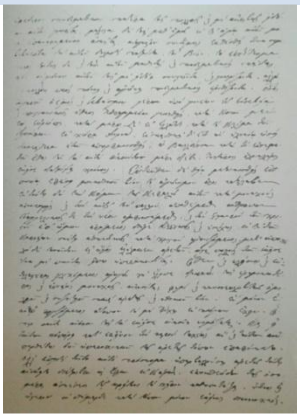

Fig.32 Athens, Benaki Museum, Codex 37, Vita p.74 (*Kakavas 2008)*

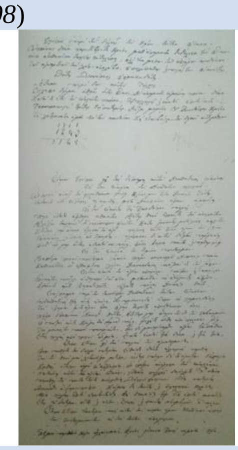

Fig.33 Athens, Benaki Museum, Codex 37, epigrams p.21-22 (*Kakavas 2008)*

It is significant that the text of the Hermeneia, published by Papadopoulos-Kerameus is almost identical to the text from Codex 58 in Benaki Museum. So according to Kakavas: "the text of the Hermeneia in the library of Saint Petersburg may well have been copied in the first decades after the second half of the 18th century in all probability from the same prototype as the Benaki codex" (Kakavas 2008, p. 40). The text of the sources shows that Dionysios in fact systematized and elaborated the tradition of these earlier manuals. None of the original manuscripts seems to date back further that the 16th century.

3.3. The contents of the Hermeneia

Ever since the 16th century, the growing trend of artists to the western painting, drawing elements and standards from Panselinos and Theofanis, the two representatives of the Macedonian and the Cretan art painting, led to the creation of a widespread reaction. This reaction manifested mainly by halting the stream of the introduction of foreign[14], relative to the orthodox tradition, standards. First, Dionysius, through his Hermeneia, gave instructions to apprentice painters for returning to Panselinos' painting standards. This tradition, established by Dionysius, followed a large number of artists from all regions as Epirus and Western Macedonia. At the same spirit, Saint Nicodemus the Hagioritis as a second proponent of the Orthodox hagiographic tradition, attempted to raise the doctrinal validity of orthodox art through foreign iconographic types[15] (Mponovas 2009, p. 20).

In this perspective, the writing of Hermeneia was considered a particularly important moment in the history of post-Byzantine art, as it defined the boundaries of Byzantine painting, by leaning on older models, yielding them a more refined and scholar character (Louth 2005, p. 151).

Before the early 18th century the iconographical and technical handbooks for painters existed independently, and Dionysius was the first to consolidate them in one volume. Since its appearance in Western scholarship in the late-19th century, the Hermeneia has been regarded as the key element to the general conformity of Byzantine art. The Hermeneia is an indispensable source of Orthodox Christian iconography and of Byzantine and post-Byzantine technical practices (Ferens 2015, pp. 6-7), it is a compilation of post-Byzantine artistic traditions and practices (Louth 2005, p. 151), structured as a series of instructions for painters and students. It contains three prologues and six sections (Dionysius 1909). The first section provides technical instructions; these include recipes for colors, steps on how to prepare materials for

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[14] For example you can see Zois Mylonas' article entitlied: "The Coronation of the Virgin and other western iconographic subjects in 17th and 18th century icons, in Zakynthos", where she indicatively states inter alia: "....The episode of Coronation of Mary is not mentioned in the written sources and are entirely foreign to the Orthodox iconographic tradition" (Mylona 2001, p. 249)

[15] The general climate of St. Nicodemus' notes betrays the replacement that has been made in the orthodox traditional painting language by the Roman Catholic Church painting language. For more see (Uspensjky 1998, pp. 531-532).

painting, some descriptions on the stylistic treatment of visual elements, and the proportions of the human body. The following four sections deal with the iconographical treatment of religious subjects[16] (Dionysius 1909; Kakavas 2008; Ferens 2015; Tsigaridas 2009; Papadopoulos 2006).

More specifically, Dionysius' Hermeneia starts with three prologues. The first prologue is a hymn and a pray to Virgin Mary in which he asks for Her legation about the work he has undertaken to perform. The second prologue is a prompt from Dionysius to those who want to learn the art of painting. Thus, he invites them to follow a capable teacher, while not failing to mention the necessity of maintaining the standards of Manuel Panselinos and Cretan painters. At the end, he informs the scholar that his effort of writing the Hermeneia was assisted by his student Cyrill from Chios. The third prologue, entitled: "Προγυμνασία και Παιδαγωγία»[17] begins with the prayer that the painter should say every time he is about to paint, and continues with encouragement for the student. The prayer that Dionysius records encompasses the whole theology of the icon. This means that the construction of an icon is not an autonomous and independent process, but entails a seamless, unified and indivisible link with the theology that rules the construction of an icon**.** Furthermore he does not forget to provide some information on how to take anthivola from icons[18], the procedure for taking a drawing from an existing prototype (Kakavas 2008, p. 99).

The first part, which is entitled "Technology" contains all the necessary information for the technical preparation for wall and panel painting. It gives specific

[16] According to Papadopoulos-Kersameus' edition (Dionysius 1909) of Dionysius Hermeneia, the other five sections include different iconographical instrumentation. So section two describes how to illustrate scenes from the Old Testament «Περί του πως ιστορούνται τα θαύματα της Παλαιάς», Section three covers the principal events from the New Testament «Πως ιστορούνται τα κατά το Ευαγγέλιον». The third section includes the iconography of the Passion of Christ and the facts after the Resurrection: «Τα πάθη και τα μετά την Ανάστασιν». The fourth section includes the parables, the description of the Divine Liturgy, psalms, and it ends with eschatological themes – the Apocalypse and Hypothesis of the prophets and the gospel about the Second Coming, and the Last Judgement: «Αι Παραβολαί, Λειτουργικά, Υποθέσεις εκ των ψαλμών, Η Αποκάλυψις του Θεολόγου, Υποθέσεις εκ των προφητών και *του Ευαγγελίου*». The fifth section describes how to illustrate different feast-days of the Theotokos, twenty-four stanzas of the akathistos: «Πως ιστορίζονται αι θεομητορικαί εορταί» and groups of holy figures including apostles and evangelists, holy bishops and ecclesiastics, holy martyrs and saints; «*Πως ιστορίζονται τα μαρτύρια του όλου ενιαυτού*», and the Seven Ecumenical Councils. The final section contains additional information on how to depict the life of the true monk, iconographical nomenclature, epithets, epigrams, and the appropriate allocation of scenes within the church: «*Πως ιστορίζονται αι εκκλησία και τα λοιπά*».

[17] Coaching and Pedagogy

[18] Antivolo is a paper with in purpose perforated lines, for transferring the painting drawn, through the traces coal dust or pigments on the surface of a new artifact (Mponovas 2010, p. 78).

guidelines for drawing, of how to make brushes and glue, how to make the gesso preparation for the icons, how to make halos, how to gild an icon, and much more.

From the second part to the end, Dionysius' Hermeneia deals with classical iconographic issues, namely, the ways that a painter should draw the presentations of the ecclesiastical themes. In this frame, the second part includes all the topics mentioned in the Old Testament, the third part[19] includes all the Despotic feasts and everything related to the New Testament.

The fourth part, entitled "Symbolic" is divided in four categories; the same applies to the fifth part, the Hagiographical. The final, sixth part contains various topics such as how the life of a monk is depicted, and which is the proper order for a church depiction, and much more.

19 (Dionysius 1909), Third part, §1-111

4. The Technical part of Dionysius’ Hermeneia

4.1. The sources of the Technical Part

The main interest of this Thesis focuses to the technical part of Dionysius’ Hermeneia, and not so much on the theoretical and iconographical parts. Thus, if someone wants to study the iconographical part, there are a plethora of works that have been established in the academic community, written by various scholars. Only a few of them worth mentioning include: Dr. Emmanuel Moutafov published book entitled: “*Europeanization on Paper”. Treatises on Painting in Greek during the First Half of the 18th century* (Moutafov 2001), Dr. George Kakavas’ Thesis, *Dionysios of Fourna (c. 1670-c. 1745). Artistic Creation and Literary Description* (Kakavas 2008) and Mateusz Jacek Ferens’ Thesis at the university of California *Dionysius of Fourna: Artistic Identity through Visual Rhetoric* (Ferens 2015).Thus in this Thesis, the main aim is to identify the technical part for constructing an icon according to what Dionysius records in his work. So, the first query is about the sources that Dionysius used during his writing of Hermeneia.

In his introduction about Dionysius’ Hermeneia, Papadopoulos-Kerameus notes that the Hermeneia, as it exists is a work of Dionysius, and the first part, the technical one, turns out to be a combination of two earlier texts (Dionysius 1909, p. κε'). This part deals with technical issues, such as how to make anthivola, colors and how to prepare the materials used in painting. It also includes recipes for mixing colors, for making glue, gesso and technical instructions for the gilding. Papadopoulos-Kerameus has identified and published five manuscripts, as the primary sources for Dionysius’ Hermeneia (Dionysius 1909).

The first anonymous Hermeneia of painting art, which is known as the First Jerusalem Codex, is attributed shortly after 1566 (Dionysius 1909, p. ια'; Moutafov 2001, p. 2 (summary)). The second manuscript dated in 1674 is the text: *A book on the Art of Icon-painting* by priest Daniel, also known as the second Jerusalem Codex which is unique in having an identified author and uncontestable date (Moutafov 2001). The text of this handbook, on account of the lack of a section on technical issues seems to underpin the notion that the sections on iconography and technique existed independently before the early 18th century, the time of Dionysius’ and his Hermeneia (Moutafov 2001, p. 2 (summary); Kakavas 2008, p. 52). In a discussion with Dr.

Moutafov[20] about whether there are relevant, if only scattered, records of the manufacturing technology of icons, he insists that the second Jerusalem Codex predates Dionysius, and the work of priest Daniel was merely copying a pre-existing manuscript, probably the first Jerusalem Codex. Thus, for Dr. Moutafov, priest Daniel was simply a transcriber of the text, and not the author of a new Hermeneia text, which bishop Porhyrij Uspensky copied in 1850 and Papadopoulos-Kerameus used it for his edition in 1909.

Another source that Dionysius used for his Hermeneia is a primary source from Codex graecus 255, in Saint Saltykov-Shchedrin State Public Library of Saint Petersburg, entitled *Hermeneia of the Painters' Art, containing the proportions and colors of Panselinos and of "Naturale" and the flesh tones of Theopanis and certain other masters useful for this Art* (Dionysius 1909, p. 238; Kakavas 2008, p. 52).

If someone wants to find traces from previous works in Dionysius' Hermeneia, with regards to the technical aspects, he will find numerous, such as the *Compositiones variae*[21], or the *De Diversis Artibus*, a 12th century handbook of the German Theophilos (Markozanis 2017, pp. 24-27), as well as the *Trattato della Pittura* composed by Cennino Cennini in 1390 (Kakavas 2008, p. 56; Partington 1934, pp. 136-138,140; Markozanis 2017, pp. 29-31). Dionysius' Hermeneia is related directly to eastern manuals, such as the second Jerusalem Codex. Furthermore, as Papadopoulos-Kerameus pointed out, the technical section of the Hermeneia partly derives from two anonymous painters' manuals dating to the 17th century and appended in his edition (Dionysius 1909, pp. κς'-κζ, 237-253, 255-260; Kakavas 2008, p. 57). Thus, it could be assumed that, before Dionysius, the technical handbooks for painters existed independently and he was the first who tried to incorporate them in one volume (Kakavas 2008, pp. 55-57). In the technical part of his Hermeneia, Dionysius used contemporary terms taken from the colloquial and technical language of his time. Hermeneia is the most comprehensive painters' manual on panel painting techniques and gives to the painters the opportunity to choose, besides the iconographical, the methods and the style for their work (Kakavas 2008, p. 55).

4.2. The content of the Technical part

[20] 28-02-2017

[21] For more see Rozelle Parker Johnson, *Compositiones Variae, from Codex 490,* Biblioteca Capitolare, Lucca, Italy. An introductory study. Illinois Studies in Language and Literature XXIII, no. 3. Urbana, Ill.: University of Illinois Press, I939.

As discussed above the technical part of Dionysius' Hermeneia contains all the necessary guidelines for the painter in order to construct wall and panel paintings. If someone tries to divide the technical part in subcategories, then he could identify two major categories, one for constructing wall paintings and one for the panel paintings.

About the wall painting, Dionysios provides all the necessary instructions for the construction, beginning from the preparation of the wall up until the drawing process, the colors, and even more, how to make halos for the saints.

About the panel paintings, this section could be divided in more than two or three categories. Actually, it is divided in six categories which are:

- Instructions for the gesso preparation of the icon (Dionysius 1909, pp. 11-15 §4-6),
- Instructions for making paint brushes (Dionysius 1909, pp. 10-11 §2-3),
- Instructions for drawing and how to use the colors (Dionysius 1909, pp. 9,20-23,33-36 §1,16-24,49-52),
- Recipes for making glue, colors, varnishes and how to make the gilding of the icon (Dionysius 1909, pp. 17-19,24-27,28-32,44 §10-13,27-34,36-39,41-47,72),
- Instructions of how to make the halos on the icons (Dionysius 1909, pp. 15, §7)
- How to repair an old and disintegrating icon (Dionysius 1909, pp. 27 43-44 §35,71).

As it could be observed Dionysius gives instructions for almost everything, especially for constructing panel paintings, (Markozanis 2017, pp. 35-52) but nowhere he mentions any information about the wooden substrate. For example, the type of wood that should be chosen, the factors that should be taken into account for the selection of the wood, the process of drying the wood, how it should be prepared to be appropriate for the icon, why the crosspieces are necessary for the icon and how they can be constructed and much more.

There are two reasons for such an omission. Initially, the manuscripts he had in mind when he wrote Hermeneias' text did not mention such instructions related to the wood. Second perhaps for him, the choice of the wooden substrate was not as significant as the pictorial part and how it will be presented. This can be proven partially by the fact that, when he refers to the way in which a rotten, old icon could be repaired, his interest focused mainly on preserving the painted surface. At the same time, when he refers to wood, he simply names it as a plank or a plain piece of wood, without giving further details or information about the type of wooden substrate (Dionysius 1909, pp. 43-44, §71).

The same information could be found if someone searched the sources of the Hermeneias' text, as Papadopoulos-Kerameus inform us (Dionysius 1909, pp. γ-δ). Furthermore, if someone studied manuscripts from different Hermeineiae of roughly the same period with Dionysius' Hermeneia, then he would find that all the manuscripts contemporary to Dionysius' text contain either part, or the sum of the guidelines from the technical part (Muñoz Viñas 1998, pp. 115-120), that was published by Papadopoulos-Kerameus[22].

4.3. Dionysius recipes

As discussed above, nowhere in his treatise does Dionysius mention something about the choice of the wooden substrate. But he is sufficiently detailed, about all the other stages that constitute the icon construction and technology. There are, among others, recipes pertinent to the preparation of wooden panels for painting purposes that exist in many medieval and post-medieval manuscripts (Muñoz Viñas 1998, p. 115). However, the most appreciated text in the case of post-byzantine icons is Dionysius' Hermeneia. Dionysius is very detailed in his description of the selection and preparation of raw materials; it is characteristic that he asks for the double firing and water-slaking of the gypsum. The material thus produced is mixed with animal glue and used throughout the preparation of the ground while, in the final coatings, a few drops of "peziri" (drying oil) and a very small amount of soap are added, which probably was used in order to reduce the ground's absorbency (Dionysius 1909, pp. 13-17, §5-6; Mastrotheodoros et al. 2016, p. 831).

4.3.1. Glue

Concerning the use of the glue, it should be noted that, the glue level can be affected by different workabilities of collagens coming from different sources, seasonal parameters and personal preferences and even the properties of the gesso (Mastrotheodoros et al. 2016, p. 839; Leonida 2014, p. 11). The need for material and condition-specific adjustments is exemplified by instructions given by Dionysius

[22] For example, compare the Hermeneia that was published by Papadopoulos-Kerameus with the manuscript MS 40726 from the British Library (Manual of Byzantine ecclesiastical painting MS 40726 1999, pp. 68r-77v), the Vaticanus Palatinus codex graecus 209 (Parpulov, Dolgikh & Cowe 2010, p. 203) and the Benaki Codex 58 (Kakavas 2008, p. 40)

following the description of the basic recipe (Dionysius 1909, pp. 11-12, §4). So, according to him, the glue is made by boiling limed and de-haired skins, or skins from the feet and ears of oxen after liming, with water in a copper pot, skimming, evaporating till it gelatinizes on cooling, cutting up, and drying in the air (Partington 1934, p. 147). Therefore, Dionysius gives basic instructions for making the gesso preparation and the use of glue, but he does not mention the place of origin of the raw materials (Dionysius 1909, pp. 13-15). During applying the gesso preparation, the most important points for Dionysius were the quality of the animal glue, the thin and sequential coatings on the surface and the initial impregnation of wood with the animal glue, in order to seal the pores of the wood and make the surface more stable (Markozanis 2017, p. 40).

4.3.2. Gilding

Recording the recipes that are provided by Dionysius, it can immediately be realized that, in his treatise, he mentions a few details about the metals, but he is preoccupied solely with the preparation of dyes derived from them (Partington 1934, p. 141). The gold color is created by mixing a piece of gold, such as a ducat with mercury and sal ammoniac, heating in a crucible till the mercury fumes away, then adding double the weight of sulfur, grinding on a porphyry and heating strongly in a large crucible till the sulfur has disappeared in fumes; it is then ground on a porphyry with water and a little salt till it looks like fine sand. It is then washed well and kept in a shell (Dionysius 1909, pp. 44, §74; Partington 1934, p. 141).

Gilt letters are painted with a liquid made by grinding white lead, mercury, tin, lead, silver and strong vinegar on a “marble” till it liquefies (Dionysius 1909, pp. 29, §38-39; Partington 1934, p. 141).

The bole, also known as ampoli, is a preparation which is laid over gold leaves (**Table 1**). It contains bole, ochre, lampezi (red lead), tallow, and mercury "killed" by rubbing with the fingers on the palm of the hand mixed with the ash of paper and saliva, or with soap or bile and egg white. The bole or Armenian bole (In Greek: *κιλερμενί*) for use in laying gold leaves etc. is best when it is not very red, and has white veins inside (Dionysius 1909, pp. 17-18, §10-12; Partington 1934, p. 142). Armenian bole is earth clay, usually red due to presence of F_2O_3. This clay may also contain hydrous silicates of aluminum and possibly magnesium (Markozanis 2017, p. 258; Robert & Etherington

1982). Silver is either made yellow by using a yellow varnish, or used to make amalgams for letters (Dionysius 1909, pp. 26, 29 §33, 38-39; Partington 1934, p. 142).

4.3.3. Pigments

In Dionysius' treatise, many pigments and colors are described. Some of them are mineral, while others are of vegetable origin.

Black includes lampblack from resinous woods and charcoal pencils are made either by charring sticks of nut-tree or myrtle wood in a covered pot, or by putting them, on a fire wrapped in paper, and then cooling in ashes (Dionysius 1909, pp. 10, §9; Partington 1934, pp. 142-143; Markozanis 2017, p. 43; Thompson 1997, p. 143). Tracing paper is made by impregnating paper with raw sesame oil, rubbing with pumice stone, and drying in the shade (Dionysius 1909, pp. 9-10, §1).

White lead, including Venetian white and French white in pastilles, is made by hanging pieces of lead over vinegar in a closed pot; white is made from chalk or from old lime (Dionysius 1909, pp. 20, §18; Partington 1934, p. 143; Thompson 1997, pp. 141-142) .

Cinnabar was known and used extensively by the iconographers of the middle Ages and by those who followed them. Although it is not very clear how the information about the synthesis of cinnabar came to Mt Athos, it is very likely that the rest of Orthodox Europe received it from Mt Athos either through the pages of Hermeneias or through the experience of painters trained there and was strongly influenced by Byzantium (Leonida 2014, pp. 16-17). Dionysius' Hermeneia presents recommendations concerning the synthesis of cinnabar separately, mentioning the use of cinnabar in the recipe of a red ink (Dionysius 1909, pp. 33, §48). The synthesis of cinnabar seems simple enough. Sulfur and mercury were heated together (Leonida 2014, p. 18). In more details, according to Dionysius cinnabar is made by heating 100 parts of mercury with 25 parts of sulfur and 8 parts of blood ground together in a vase (Dionysius 1909, pp. 31, §43; Partington 1934, p. 143).

Other reds and browns include umber and ochre (Thompson 1997, pp. 147-148) of various shades, including that of Constantinople and of Thasos, as well as burnt ochre (Dionysius 1909, pp. 20-23, §16-23). The color *proplasmos* appears to be a brownish-green; also there is a mixture of umber and bole. *Proplasmos* is the dark value tone that serves as background for faces and areas with visible skin tone. It represents the color over which the light tones and shade accents are overlaid and, after their settlement, it will become itself a shadow for the respective face or area (Grecu 2016, p. 689). The flesh color consists of Venetian white lead, ochre and cinnabar, made in the same way. *Glykasmos* is made of 2 parts of flesh color and 1 part or less of *proplasmos*. *Glykasmos* is the light, red-whitish tone that serves as the drawing for faces details. (Dionysius 1909, pp. 20,21 §16,18, 20; Partington 1934, pp. 143-144).

A crimson lake is made by a red dye extracted from the Cochineal insect, while adding water, ammonia or soda is necessary. The liquid is stirred and powdered alum is added. It is then filtered the lake is allowed to settle out, the liquid is taken out with a spoon and then a moist cloth is dipped in (Markozanis 2017, pp. 41-42), which "sucks off the liquid wonderfully". Then it has to dry it in the shade (Dionysius 1909, pp. 29-30, §41; Partington 1934, p. 144).

An azure (perhaps a blue) is a natural blue pigment which is derived from the mineral, azurite, a basic copper carbonate $2CuCO_3{\bullet}Cu(OH)_2$ (Gettens & Stout 1966, pp. 95-96). For use as a pigment, it is made by boiling caustic lye with ***τζιμάρισμα***, alum and white of egg. (Dionysius 1909, pp. 31-32, §45-46; Partington 1934, p. 144; Markozanis 2017, pp. 42-43; Thompson 1997, p. 149).

The green colors were malachite—basic copper carbonate $CuCO_3{\bullet}Cu(OH)_2$, verdigris—$CuO{\bullet}2Cu(CH_3CO_2)_2$, synthetic chrysocolla—hydrated copper silicate $CuSiO_3{\bullet}2H_2O$, and terre verte—glauconite, a mixed silicate of potassium aluminum and iron, $KMg(Fe, Al)(SiO_3)_6{\bullet}3H_2O$. Chemically, the green pigment mostly used by these artisans was hydrated copper acetate $Cu(CH_3COO)_2{\bullet}H_2O$, having clinorhombic (monoclinic) crystals of a dark bluish-green color. Very close chemically to verdigris, it is not affected by light, but it is toxic and not very reliable in paintings because, under the aggressive action of internal (other pigments) and external factors (gases, moisture) it is unstable and is converted to other chemical compounds with different hues (Leonida 2014, pp. 25-26; Thompson 1997, p. 150). Most of the green pigments used by ancient artisans were copper-based although some green earths and green plant juices were used as well. In Dionysius' Hermeneia, the green mentioned is the "Brass green", which was known, prepared, and used in Europe and the Middle East since Antiquity. This is the period when the pigment started to be used extensively in painting and for miniatures and letters at the beginning of chapters in some illuminated manuscripts. While in painting it was used without being mixed with other pigments, in inks and colors used in manuscripts it was sometimes mixed with vegetable saps. In a copper pot, concentrated vinegar was put in contact with small pieces of metallic copper (Markozanis 2017, p. 42). Covered, to prevent mechanical contamination by insects or suspensions from the air, the reaction vessel was left in a place with adequate exposure to the sun light. In his treatise, Dionysius states that this process was preferably done during days when the air temperature was high. The concentration of the solution was continued in a vessel with a large diameter, by evaporation. However, nowhere in Hermeneias' text was it stated for how long this had to be done. Still, the recommendation concerning the shape of the vessel is proof that the advantage offered by a large surface in evaporation was noticed during the centuries-old technical experience, recorded and transmitted correctly through the popular tradition. The copper acetate solution obtained using this procedure was generally kept and used as such, in water-based colors for painting on wood panels, on textiles, paper, parchment, and mother-of-pearl (Dionysius 1909, pp. 30, §42; Partington 1934, p. 145; Leonida 2014, pp. 27-33; Markozanis 2017, p. 42; Mayer 1985, pp. 135, 137-138).

4.3.4. Acids

The only acid mentioned is vinegar, including black vinegar. A solution of quicklime in strong vinegar is boiled and then heated in hot dung for 36 days to make a solution (calcium acetate) for preparing azure (Dionysius 1909, pp. 32, §46). One the other hand, an aqua fortis (in Greek: *δυνατή καταςταλακτή*) is not nitric acid, but a filtered clear solution of caustic potash used for cleaning the painting surface of old icons; although Dionysius had successfully managed to restore icons in this way, another technician, as mentioned by Dionysius, had removed all the color, leaving a bare canvas, thus ruining the icon (Dionysius 1909, pp. 27-28, §35; Partington 1934, p. 145).

4.3.5. Medium

Concerning the binding medium for colors, Dionysius mentions one that can provide gold with brilliance, which is made by melting equal quantities of glue, white wax and potash solution (Dionysius 1909, pp. 28, §36; Partington 1934, p. 146). In his instructions of how to make gold capital letters, he describes another medium, which is a mixture of snail slime (the preparation of which, by toasting the snail with a candle, is described), gum and alum. This forms a medium for gold (Dionysius 1909, pp. 29, §39; Partington 1934, p. 146). Besides these, he furthermore mentions the use of egg medium, more precisely the use of the white part of the egg, while the yolk is not mentioned. The egg white was used for the construction of the bole (Dionysius 1909, pp. 17-18, §10-12). Apart from egg, garlic or onion juices (for black and gilding) are also used, for transfers and for making the antivolon (Dionysius 1909, pp. 9-10,§1; Partington 1934, pp. 146-147).

4.3.6. Varnishes

Varnish is a solution of a resin in a volatile solvent. Brushed on a painted surface, it dries leaving a glossy, transparent, protective film. There are two types of varnishes: simple solution varnish (resin is dissolved directly in the solvent) and oil varnish (resin is melted together with a drying oil and a drier, and then thinned with a solvent). Once applied and dried to form a film, varnishes have a protective role, they brighten the colors and they maintain the chromatic scheme. At the same time, they strengthen the paint layer, increasing its resistance to mechanic shocks, friction, and other accidental mechanical, physical or chemical strains. The raw materials used for varnish preparations were obtained either from local sources (linseed oil, colophony-pegula, chemical siccatives like $ZnSO_4$) or from import (sandarac, aloe, santalon, colophony) (Leonida 2014, pp. 61-62).

Pezeri, which is raw unboiled linseed oil[23] is used (Dionysius 1909, pp. 24, §28) to make a ground for painting and pegula (Dionysius 1909, pp. 24-25, §29; Leonida 2014, p. 62), it is a fir resin (turpentine) which has been heated in a copper pot till it ceases to froth, and is used for varnish (Partington 1934, p. 147). Several types of varnish are described by Dionysius (Dionysius 1909, pp. 25-27, §30-34), from pezeri,

[23] Linseed oil was obtained from clean flax seeds, without other oleaginous seeds present, by cold pressing. Sometimes the oil was siccativated prior to using it in a recipe, usually by prolonged exposure to the sun (Leonida 2014, p. 62)

pegula[24], sandalwood[25], sandarach resin[26], aloes[27] dissolved in alcohol or naphtha and sometimes filtered through a cloth (Partington 1934, p. 147). A thicker varnish is made from pegula and mastic (Dionysius 1909, pp. 25, §30; Partington 1934, p. 148). Alcohol used for laying on gold leaf and making varnish is sometimes "four or five times distilled" (Dionysius 1909, pp. 24, §34; Partington 1934, p. 148). The varnish is made by heating 10 drachm of powdered sandarach and 5 drachms of pine resin with 10 drachms of raki in a closed vessel on an ash-bath. Two coats of this varnish may be put on with only a small interval between layers (for drying). Naphtha is used as a medium for varnishes which dry in the shade (Dionysius 1909, pp. 26, §32; Partington 1934, p. 148), for thinning boiled or thickened oil and for colors. Although the original meaning of Naphtha is petroleum, according to Partington (Partington 1934, p. 148) this means turpentine oil instead of petroleum. Naphtha in Modern Greek means Turpentine, except in Zante, where it is the natural petroleum. This use of turpentine has a 16th century Venetian origin, since the distillation of turpentine was probably discovered in Italy (Partington 1934, pp. 147-148) (**Table 2**).

4.3.7. Mixing pigments

Dionysius does not fail to mention the combination of pigments that should be used by the painters to construct the icon (**Table 3**). So he begins by describing how to construct the *proplasmos* (Dionysius 1909, pp. 20, §16).

For *proplasmos* the most important recipe is the one formulated by the painter Manuel Panselinos, which Dionysios preserved and transmitted in Hermeneias' treatise as follows: "Put lead white, ocher, green earth that is used to work on the wall [and

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[24] Rosin (colophony, pegula) from autochthonous sources was produced in a brass vessel filled to one third only with resin from local conifer species. The resin was heated until it became clear and no froth was produced anymore. Frothing was controlled either by removing the heating source or by blowing air. Finally, the melted resin was poured into a vessel with cold water. Pegula was obtained as pieces (of variable sizes) of transparent material, with a light yellow tint (Leonida 2014, p. 62).

[25] Santalon was a hard resin extracted from the wood of several tropical trees from the species Santalum, the best known of which is the Indian sandalwood tree. In Dionysius' Hermeneia this resin is mentioned under the name "sugar of santalon" (Leonida 2014, p. 64)

[26] Sandarac, a hard resin extracted from Thuja occidentalis, Tetraclinis articulata, Cypress conifers, and Calitris quadrivalvis, was imported. As the European West, icon painters in Southeastern Europe used it in hard and glassy oil varnishes, which were transparent, with a light yellow tint. In the oil varnish recipes used in this geographical area and which contained sandarac, very seldom a plasticizer (such as camphor) was used in spite of the resin's hardness, as was the case when other solvents were used (Leonida 2014, p. 64)

[27] The aloe resin was obtained from imports as well. It was extracted from plants from the Liliaceae family (Aloe africana, Aloe vera/vulgaris). Oil varnishes containing it also contained sandarac and sometimes neft. They were sometime used to imitate gold when applied on sections of icons covered in silver. In the Romanian area this resin was used in popular medicine as well (Leonida 2014, p. 64).

black] and powder them all together. Then apply this background or *proplasmos*, wherever you have to paint flesh color (Dionysius 1909, pp. 20, §16; Grecu 2016, p. 689).

After *proplasmos,* the skin colors follows. Skin color represents the tone to be used when rendering the color of the human skin. It is, in a practical sense, the tone that gives the natural color of the character in question. Given that the *proplasmos* does not remain in large areas, the skin color represents the basic color of faces or other body parts that are visible (Grecu 2016, pp. 689-690). All descriptions from Byzantine painting manuals lead to the idea that this tone should be close to warm ochre (Grecu 2016, p. 690). Yellow ocher is the main pigment that is included in the composition of the skin tone, a "mixture called sankir" (Grecu 2016, p. 690). Dionysius preserved the main recipe in which the color of the skin was prepared by Panselinos: "*Take lead white - Venetian or French, which is in pieces in papers - and yellow Venetian ochre and, if you don't have Venetian, take another one that resembles, and a little cinnabar. And if you want it to be more extinguished, do as follows: grind some cinnabar and add a little of it to the mixture, then leave it to settle down. When it settled down on the bottom of the dish, pour the water into another dish and let the cinnabar dry. Then mix it a little and paint the flesh color*". (Dionysius 1909, pp. 20-21, §18) Dionysus also used a red skin tone, borrowed from the Cretan school. He lists it as a recipe, calling it another skin color and describing it as follows: "*Take lead white and reddish ochre, and powder them together and prepare the skin color. If you do not take the reddish ochre, take the other one, the yellow ocher, and mix it with little boles, to make the mixture reddish. Then, as we wrote above, prepare the skin color; only take heed, not to make it too red*" (Dionysius 1909, pp. 21, §19).

The rosiness of the faces is the next step after adding the skin tone, especially in the case of the young characters (Grecu 2016, p. 690). In this sense, Dionysius stated that: "*For the faces of Blessed Virgin and the young saints, you ought to put blush in the middle of the face, too thin, mixing cinnabar with the flesh color. And for the shadows and lines with which you draw the hands, put a very thin layer of boles. Also, for the elderly, in the deepest wrinkles, put some thin boles. And the others (skin wrinkles), as many as there are above the eyes (forehead), make them stand out with semi flesh color*" (Dionysius 1909, pp. 22, §22; Grecu 2016, p. 690).

The face in Byzantine painting is represented in its entirety and from a technical standpoint, is achieved by overlapping the color tones, starting with proplasmos, skin color, lights. An exception from this technique is embodied by Theophanes, who substitutes the flesh color in some works by applying the lights directly over the proplasma (Grecu 2016, p. 692). In aesthetic terms, two clear directions at the level of the *proplasmos* are traced: the Panselinos painting (Dionysius 1909, pp. 20, §16), which uses green *proplasmos*, and the Cretan painting (Dionysius 1909, pp. 34, §50), which uses red *proplasmos* (**Fig.34**) (Grecu 2016, p. 692).

Fig.34 The Macedonian's School and the Cretan's School proplasma (*Grecu 2016, p. 689*)

In addition to some isolated exceptions in time, the technique has remained unchanged without deviating from the canons of Byzantine painting, transmitted from master to apprentice with ultimate authenticity (Grecu 2016, p. 693), as it could be identified by Dionysius and his apprentice's paintings (Tsigaridas 2009; Bonovas 2009).

Table 1 Dionysius' recipes for bole (Dionysius 1909, pp. 17-19)		
1st recipe for red bole	**2nd recipe for bole**	**3rd recipe for bole**
Bole (=clay), not so red	Bole (=clay), not so red	Bole (=clay), not so red
Ochre	Ochre	Ochre
Red Lead	Soap	Red lead
Wax	Egg white	Cinnabar
Burned paper		Egg White
Mercury		Gall
		Wax
		Mercury

Table 2. Dionysius' recipes for Varnishes (Dionysius 1909, pp. 24-27)		
1) Varnish from Linseed oil	**2) Sandalwood Varnish**	**3) Naphtha Varnish**
Linseed oil	Sandalwood	Sandalwood
Fir resin (=turpentine)	Linseed oil **OR**	Linseed oil
Naphtha	Naphtha	Naphtha
Unboiled linseed oil	Boiled linseed oil	
Mastic		
4) Yellow Varnish	**5) Alcohol Varnish**	
Sandalwood	Alcohol	
Aloe	Sandalwood	
Boiled linseed oil	Fir resin (=turpentine)	
Naphtha, as a solvent		
Notes:	**Peziri =**	raw unboiled linseed oil
	Pegoula =	fir resin (=turpentine)

Table 3. The main pigments mentioned by Dionysius for panel painting (Dionysius 1909, pp. 20-23, 31-34, 41)				
Proplasmos	**Flesh (skin color)**	**Red skin tone**	**Rosiness of face**	**Optionally**
Lead white	Lead white	White lead	Flesh color	Blue
Ochre	Yellow venetian Ochre	Reddish ochre	Cinnabar	Red lake
Green	Cinnabar	Reddish ochre	Boles (for shadows and lines)	Orpiment (yellow)
Black		a) yellow ochre		Green
		b) bolos		

CHAPTER B - STUDYING A PANEL PAINTING

1. Icon's Stratigraphy

Panel paintings have been constructed in a particular way for about fifteen hundred years. They are considered sacred in more than one sense. Not only they represent persons and events of religious significance, but their composition is also a statement about the relationship between the created world and to its Creator (Kenna 1985, p. 348). An icon, besides being an artificial artwork, conveys a crucial theological meaning. In this context, the complexity of its construction is bestowed with a theological meaning as well. According to Kenna (Kenna 1985, p. 348) an icon is constructed of substances derived from all parts of the created world: animal, vegetable, and earth resources. The icon, then, is a microcosm of the relationship between the material world, human beings, and the divine power believed to have created them all.

With regards to the thematology, the representation of the human forms and the landscape, it can be assumed that the development of religious themes follows strict rules and patterns which are described in various consulting books (Markozanis 2017, pp. 66, 87-88, 105-107; Leonida 2014, pp. 2-4) such as the Dionysius' treatise "Hermeneia of the Painting Art" (Kenna 1985, p. 347; Louth 2005, p. 147),

At the same time considering the technological context of panel painting a multilayered object, it's obvious that its stratigraphy consists of the composition of different layers, from the wooden substrate to the final coating layer, the varnish (**Fig.35**). Panel paintings are generally made up of the same fixed fundamental components:

1) Pigments, which are most typically fine powders of inorganic or organic colored materials, and a fluid binder which enables pigments to be dispersed and applied with a brush (Colombini et al. 2010, p. 716; Colombini & Modugno 2004, p. 147).
2) The binder or binding agent which is any organic material or substance that holds or draws particles together to form a cohesive whole mechanically, chemically, by adhesion or cohesion (Gettens & Stout 1966, p. 35). The binder may be a proteinaceous material such as egg or casein, a vegetable gum, a drying oil, a natural wax, or a mixture of two or more of these materials. After drying or curing, a solid paint film is produced (Colombini et al. 2010, p. 716; Colombini & Modugno 2004, p. 147).

3) In the background of panel paintings and haloes of the figures, gold leaves are applied most of the times. Gold has always been an integral part of Byzantine iconography, with its main role being to detach the depicted scenes and figures from the material world and confer a sense of divine provenance upon them (Katsibiri 2002, p. 49). The standard modern gold leaf is 0.1 μm thick and 8.3 cm^2 wide. Although its size has remained more or less the same as in medieval times, its thickness would vary substantially depending on the contemporary technology available (Katsibiri 2002, p. 39). The background and haloes are water gilded on bole, a generic term used for a velvety-smooth reddish earth composed of clay and red iron oxide (Fe_2O_3) (Leonida 2014, p. 43; Katsibiri 2002, p. 44). This method was widely introduced to panel painting during the Post-Byzantine period, despite the existence of much earlier examples of paintings with bole-gilded backgrounds (Katsibiri 2002, pp. 49,51)

4) The substrate on which the paint is applied is a wood panel. Such substrates generally need to be prepared with a ground layer in order to isolate the surface and enhance the stability of pigments solution. For instance, a mixture of animal glue and gypsum was used for centuries as a ground for wooden panels (Colombini et al. 2010, p. 716; Colombini & Modugno 2004, p. 147).

5) The paintings are often varnished, which means that a transparent layer containing natural resins and sometimes drying oil and/or a solvent has been applied to the paint surface to protect and create depth by saturating the colors (Colombini et al. 2010, p. 716; Colombini & Modugno 2004, p. 147).

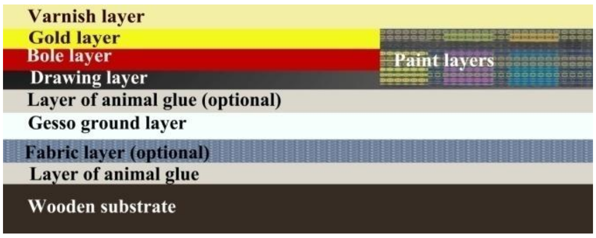


Fig.35 Schematic cross section of a panel painting *(personal archive Th. Mafredas)*

Byzantinists scholars agree that two main techniques for panel paintings construction were developed (Katsibiri 2002, p. 27). The first technique, known as "encaustic", is the older of the two and the predecessor of the egg tempera. For this technique the medium is wax mixed with various pigments and then applied by means of a hot metal tool (Vassilaki 2009, p. 759; Katsibiri 2002, p. 27), as discussed in the previous chapter. The other technique was adopted by Byzantines, which became the traditional painting technique for panel painting is "egg-tempera" (Katsibiri 2002, p. 27). In his text, Dionysius only refers to this one. In this technique the binding medium consists of egg yolk diluted with water, into which a couple of drops of vinegar are added for balancing the greasiness of the yolk, thus preserving the mixture and making it easier for use (Thompson 1997, pp. 167-169; Katsibiri 2002, p. 28; Louth 2005, p. 147).

The first step for constructing a panel painting was the choice of the substrate. For panel paintings, the appropriate substrate was a piece of wood whose natural properties made it an adequate substrate for painting (Kenna 1985, p. 347). For example, it could be easily cut and shaped into a flat board which was strong and, therefore, resistant to impact (Thompson 1997, pp. 27-33; Katsibiri 2002, p. 28). Lime, pine, spruce, and larch were the most commonly used woods for the construction of historical panel paintings; however, the substrate was usually native to the place of the work's creation (Thompson 1997, pp. 29-31; Kouloumpi 2016, p. 29). Limewood was chosen for high quality panel paintings because of its stability and resistance to deformation, splitting, and insect attack (Beaver & Espinola 1992, p. 18). Boards were often joined by mortise and tenon joints in order to avoid warping (Katsibiri 2002, p. 28), and adhered with animal glue. After the late 19th century, casein glue was used instead (Thompson 1997, pp. 32-33). After this process the wood panel had to be planed and polished to produce an even surface, ready to accept the gesso ground (Beaver & Espinola 1992, p. 18; Kenna 1985, p. 347).

The ground layer was a heterogeneous intermediate layer of a few hundreds of mm between the substrate and the paint layers whose role was to produce a fine surface ready to accept the consequent layers. There is a variety of grounds (white or subwhite and colored grounds) depending on the technique used and the historical period the artwork was created in (Thompson 1997, pp. 72-76; Dionysius 1909, pp. 14-15 §6; Kontoglou 1979; Kouloumpi 2016, p. 31). This layer comprised of an inert material and an organic binder. The inert material could be gypsum, chalk[28] or a pigment[29] of a high hiding power (Kouloumpi 2016, p. 31).

The gesso mixture, which was made of gypsum and animal glue (Kenna 1985, p. 347; Beaver & Espinola 1992, p. 18; Katsibiri 2002, p. 28; Thompson 1997, pp. 52-55),

[28] Chalk is one of the many mineral forms of calcium carbonate (CaCO3), while gypsum can be used as ground material in three forms: unburned (CaSO4. 2H2O), anhydrous (CaSO4) or burned (CaSO4. ½H2O) (Kouloumpi 2016, p. 31; Mastrotheodoros et al. 2016, pp. 37-39)

[29] Typical pigments used as inert materials of the ground were lead white (Pb(CO3)2.2Pb(OH)2) and zinc white (ZnO) both of mineral and synthetic origin (Kouloumpi 2016, p. 31; Milanou et al. 2008, p. 29)

was applied to the wood in several coats in order to form a thick and smooth surface upon which the painting and gilding would be performed (Mastrotheodoros et al. 2016, p. 38). Usually one or two coats of glue size were applied first to reduce the absorbency of the wood, while a piece of fine, open-weave linen canvas could optionally be placed between the wood and the ground (Katsibiri 2002, pp. 28-29). The main binding media for ground layers, depending on the historical period and location, were proteinaceous media such as animal glue from different types of gelatinous tissues, casein and egg yolk. There were sometimes mixed with lipid binders such as drying oils or terpenoid media such as natural resins (Kouloumpi 2016, p. 31; Kouloumpi et al. 2013, p. 4; Milanou et al. 2008, p. 29). When the gesso dried, the panel was thoroughly sanded to create a smooth surface of uniform color and matte texture. Then it was ready for the beginning of the drawing process (Dionysius 1909, p. 14 §6; Thompson 1997, pp. 56-57, 59-65; Katsibiri 2002, pp. 28-29).

Dionysius notes how important the drawing of the theme to be depicted was, and this is why he was so insistent on knowing how to make anthivola (Dionysius 1909, pp. 9, §1). The term antivolon, is used to characterize a painting or drawing, the production of which can be done in different ways, and is typically used by painters as a mean of reproducing homogeneous works (Mponovas 2010, p. 45). In his treatise, Dionysius gives a very detailed account of the procedure followed for the production of a drawing from the prototype, which could be an icon, a wall painting or another drawing (Dionysius 1909, pp. 9-10; Hetherington 1974, p. 5). Dionysius refers to the procedure of making the so-called imprinted anthivola, usually in black and red, sometimes accompanied by abbreviated indications of the colors to be employed (Vassilaki 2009, p. 320). From these, it was possible to obtain further copies of the drawing by pricking or pinning the black and red lines, which is why they are known as pinned or pricked anthivola. Such pinned anthivola were employed by panel painters in order to produce a pounced drawing over the gesso ground preparation of the panel by rubbing chalk or charcoal dust on the reverse side of the anthivolon. The dotted outlines thus produced on the surface of the panel were then incised, and the painter proceeded by adding the gold leaf and successive layers of egg tempera without any fear of losing tack of the incised outlines (Vassilaki 2009, p. 320). After the drawing, most icon painters used a gold layer for the background which diffused light that symbolized the light of God (Kenna 1985, p. 352). Gold with a greenish tone (mixed with silver) is seen on very early panel paintings of the 11th century. On later paintings, the gold was usually bright yellow with a slightly reddish tint (Beaver & Espinola 1992, p. 18). A pale gold, almost electrum, provided a light background with a silvery sheen. In the beginning of the 16th century, icon painters used a thin sheet of silver with a thinner layer of gold beaten into it so that one side became silver, while the other was a very pale, whitish-looking gold. After the 18th century, the silver leaf was sometimes covered with a reddish shellac to produce a tint that looked like gold (Beaver & Espinola 1992, p. 18; Katsibiri 2002, p. 52).

The pigments used were mostly natural materials including mineral compounds and vegetable extracts (Kenna 1985, p. 347) such as yellows and red ochre, white lead, bone black etc., while a few manufactured pigments were also used such as verdigris and cinnabar (Thompson 1997, pp. 134-152; Dionysius 1909, pp. 29-33 §41-46). The main binding media used during the Byzantine period was egg-yolk, while, in post-Byzantine period, the binding media depended on the historical period and location. For example, in panel paintings taken from the same historical period, for instance the 18th c. but from different location, we are able to identify proteinaceous media such as egg yolk, drying oils and natural resins or combinations of these groups, such as egg-oil emulsions (Kouloumpi et al. 2007, pp. 169, 175).

The pigments first were grounded with water to form a wet paste and then mixed together with the medium as they were applied. The first step was the painting of the background, which was often gilded (Beaver & Espinola 1992, pp. 18-19). The background colors that constituted the deepest shadows of the landscape, architecture, furnishing, garments, and figures were the first to be applied on the surface. These dark pigments were followed by other pigment layers, gradually building up the lights and moving from the cooler and darker tones to the warmer and lighter ones. During the final phase, the details of the faces, hands, hair, and clothing were painted, as well as the various details of the composition, such as halos, letters, golden decorative patterns and panel borders (Dionysius 1909, pp. 20-23 §16-24; Katsibiri 2002, pp. 29-30; Thompson 1997, pp. 193-196) After finishing this process, a layer of a varnish was implemented to protect the painted surface (Dionysius 1909, pp. 24-27 §29-34; Beaver & Espinola 1992, p. 19; Thompson 1997, pp. 206-212)

2. Technical review - Review of analytical methods

Panel paintings, as discussed above, are multilevel objects consisting of many different layers which are joined together. In order to examine a panel painting in its entirety, there is a set of applications that concern either its structural elements such as the support body or assess the elements directly related to the materials used in composition and the construction techniques implemented (Sotiropoulou & Daniilia 2010, p. 787). In the case of materials and construction techniques identification, the bibliography is abundant and covers a fairly wide range of applications (Surowiec 2008; Romani et al. 2010; Casali, Palla & Tavlaridis 1998; Valianou et al. 2011; Prati et al. 2010).

The first attempts for physical-chemical analysis of materials for panel paintings were recorded as early as the 18^{th}century. For Johann Winckelmann (1717-1768) a German art historian, it was crucial that the history of art should be extracting from the surviving works of antiquity, rather than from the ancient texts (Nadolny 2003, p. 39). Thus, apart from historical texts, the only available source of information for those who were interesting in the ancient techniques and materials was the examination of artifacts through chemical experimentation (Nadolny 2003, p. 39). The first to implement a chemical analysis of historical paint samples was a German pharmacist, Johan Friedrich Gmelin (1748-1804) in 1781. Through the addition of various reagents, the application of heat and flame, and the observation of reactions, smells, etc., he attempted to identify the pigments from an Egyptian sarcophagus (Nadolny 2003, p. 40).

Before 1880, the analysis of the inorganic components of paintings was generally performed by applying a series of chemical reagents, observing reactions to heat and testing for solubility (Nadolny 2003, pp. 41-42). In comparison to inorganic analytical techniques, those used for the analysis of organic material were significantly less accurate. The solubility of a sample in various liquids and whether or not it would burn were the main empirical criteria, while factors such as melting point, smell and taste were also taken into consideration (Nadolny 2003, p. 41). The main tools available to technical researchers of the time were magnifying lenses. It is certain that microscopes were also utilized, although evidence for the use of microscopes occurs somewhat later. In fact, the earliest reference regarding microscopic analysis is found in Semper’s investigation of 1834. Semper (1803-1879) was a German architect, art critic and professor of architecture (Nadolny 2003, p. 42). By the mid-19thcentury, a substantial number of analyses had been published, and a thorough examination of contemporary sources could indicate that they had made a considerable impact on the study of art and technical history. By the 1880s, the scientific analysis of paintings was no longer a novelty (Nadolny 2003, p. 43). Undoubtedly, this early period of technical studies produced some solid accomplishments. For example, the basic palettes used by various schools of painting were characterized, the nature of pigments was defined, and analytical methodologies were developed. As a result, research that was undertaken during the 18th and 19th century served to establish the belief that the application of chemistry and scientific methodology to the study of historical artifacts was in itself a worthwhile endeavor (Nadolny 2003, p. 43).

From that time on, the development of the physicochemical methodology and instrumentations has been rapidly evolving. There is an extensive range of scientific techniques that can be applied to panel paintings concerning the identification of materials and construction techniques, and they could be divided into two categories: those which could be carried out in situ, where the object is, without involving sampling, and those for which sampling is necessary and the examination process is being implemented in the laboratory (Stuart 2007, p. xvii; Tsairis 2001, pp. 16-17). Furthermore, the analysis methods could be distinguished into those relating to the structure of the object and those relating to its materials. Information regarding the elemental composition, molecular structure, and physical properties can be obtained and used to characterize a material (Stuart 2007, p. 1).

The combination of Science and Technology through instumental analytical techniques to determine the chemical identity -chemical element or chemical compound- of cultural heritage construction materials began in the early 20th century (Derrick, Stulik & Landry 1999, pp. 1-3; Striegel & Hill 1996, pp. 5-13; Grasselli 1983; Casadio & Toniolo 2001; Lahanier 1991; Clark 2002; van Asperen de Boer 1968; Katon 1996). Nevertheless, it wasn’t until the 1990s that the interest in the study and recording of materials and constructing techniques began to increase among the scientific community (Mahnke 2014; Fotakis et al. 2006; Janssens 2004, pp. 194-214; Calligaro, Dran & Salomon 2004, p. 268; Hubin & Terryn 2004, pp. 308-310; Jeffries 2004, p. 343) (Howell & de Faria 2004, pp. 359-366; Darque-Cerett & Aucouturier 2004, pp. 440-457). The identification of the constituents materials of an artifact (Harkins, Harris

& Shreve 1959; Marinach, Papillon & Pepe 2004; Karapanagiotis et al. 2005) as well as the recording of the ratio –quantity- (Casali, Palla & Tavlaridis 1998; Kouloumpi et al. 2007; Romani et al. 2010; Kouloumpi 2016, p. 160) is achieved through scientific analysis techniques (Chiavari & Prati 2002; Colombini et al. 2010; Cartechini et al. 2010; Sotiropoulou & Daniilia 2010). Today, the application of scientific methods to the study and conservation of works of art is a genuinely interdisciplinary process in itself, mainly because of the multiplicity of the variety of problems, approaches, materials, and technical and scientific means (Lahanier 1991, p. 245).

There is no single analytical method that will provide all the answers needed. Depending on the object and the problem to be studied, different techniques need to be used. In many cases, two or more techniques have to be used to confirm the data obtained (Van der Snickt et al. 2012; Miguel et al. 2012). It is also important to remember that scientific analysis techniques have varying degrees of sensitivity when it comes to detecting the presence of an element or compound. Thus, not finding a particular element may not necessarily mean that this element is not present in the sample, rather it may be that the technique used does not have the required sensitivity to detect it at a low concentration. The sensitivity of a method depends both on the method itself and element or compound to be detected (Charola & Koestler 2006, p. 15). Types of information that could be derived from scientific techniques are, among others:

- The identification of inorganic constituents of an artifact.
- The identification of organic constituents of an artifact.
- The determination of the degree of decomposition and aging of organic material.

Generally speaking, every research project can be differentiated from others, by the type of questions it seek to answer such as the constituent materials of an artifact, the historical period of an artifact etc. This differentiation means that, depending on the case study or the research goals, the use of specific scientific analyses techniques may vary widely. The available means can be classified in three main groups: methods of examination, analysis and dating.

Methods of examination are based on the recording of images from different zones of the electromagnetic (e/m) spectrum [visible (Vis), ultra-violet (UV), infra-red (IR), X-rays, beta, gamma, electrons, etc.] in adequate experimental conditions for revealing information that is typically invisible to the naked eye. The second group involves methods of analysis and of microanalysis (atomic or nuclear, isotopic, vibrational and structural, surface or bulk, panoramic or sequential, directly on the work itself or on a sample, destructive or non-destructive). Finally, the third category consists of absolute dating methods. All these very different and often complementary techniques sometimes call for major co-operations, making it necessary to work with inter-disciplinary teams (Lahanier 1991, p. 246).

The development of physicochemical techniques in study and analyses of works of art had resulted in a wide range of means for a variety of analyses. According to bibliography, there are numerous techniques for the identification of constuction techniques and materials, especially for panel paintings, a representative sample of them are discussing below. In general, it could be argued that, for scientific analyses in panel paintings the most common techniques in use can be distinguished in three categories, the imaging techniques, the microscopy techniques and finally the analytical techniques.

But before embarking on more sophisticated methods an initial visual examination of a panel painting is always the first appropriate step because it could provide useful information. Apart from important identifying marks on an object, an examination with a magnifying glass can provide information regarding colour, surface finish, degradation and production method, while different types of lighting can also assist a visual examination (Ianna 2001). Standard lighting from the front of an object provides information regarding colour, opacity and gloss. Light from the side (raking light) reveals information about texture, cracking and planar distortion (Stuart 2007, pp. 43-44; Lazidou et al. 2006, pp. 3-13).

2.1. Imaging Techniques

Imaging techniques have already played a very important role in the study and protection of works of art for decades. They provide a significant piece of information in image format, in contrast with the spectroscopic techniques that respectively provide spectra. A key advantage of these techniques is that the study of the project can be carried out without the researcher touching it and without taking a small sample while they could be implemented in situ. These techniques allow the visualization of the forms or mapping of the distribution of the materials not only on the surface, but also in the underlying layers (Alexopoulou & Kaminari 2008, pp. 154-158). Another important feature is that these techniques exploit radiation from a wide range of the e/m spectrum (**Fig.36**), such as from Vis, IR, UV and X-rays (Mairinger 2004, pp. 15-16; Liang 2012, pp. 313-314,). For this reason, they can record information that is not perceived by the human eye.

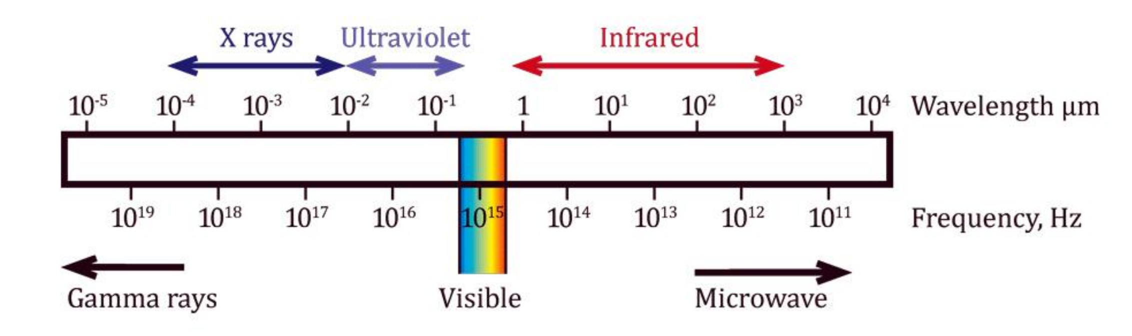


Fig.36 e/m wave spectrum (Sakai & Hanzawa 1994)

Imaging techniques can provide information on the construction technique of a work, on underlying layers of paint that are not visible to the naked eye, on areas of the work that have undergone interventions in the past, etc. Multispectral and hyper-spectral imaging technology allows the visualization of underdrawings as well as the under-modeling and colored grounds that could be significant for the attribution of paintings (Fischer & Kakoulli 2006, pp. 6-7; Sotiropoulou & Daniilia 2010, p. 879). Furthermore, the use of Multi Spectral Imaging system is able to provide imaging spectroscopy. In this way the system capture images at a large number of spectral bands and can identify materials with unique spectral signatures (Fischer & Kakoulli 2006, p. 7; Liang 2012, pp. 8-10,11). These techniques can be implemented in situ and are non-destructive for the artifacts, and they could provide some significant results about the first drawing of the painter and variation in the drawing, and investigate areas with over paintings.

2.1.1. UV fluorescence imaging

The UV range of the e/m spectrum extends over the wavelength range of 10-400 nm. In particular, the ultra-violet regions UVA (280-315 nm) and UVB (315-400 nm) are the areas that are applied in the study of artworks (Mairinger 2000 (2), pp. 56-57; Hain, Bartl & Jacko 2003, pp. 11-12). UV lighting causes the emission of fluorescence in the visible spectrum of a work’s surface elements, while this emission’s heterogeneity reveals changes that often arise from occasional restorations (Lahanier 1991, p. 247).

The property of certain substances to fluoresce in the visible range of the spectrum when receiving ultraviolet radiation between 300-400nm differentiates these substances from others that lack this property. Thus, the surface areas of artwork that have been damaged or repaired over a layer of varnish are readily and quickly detected, as varnishes, older or newer, fluoresce. In contrast, varnish losses due to wear or subsequent interventions are presented as dark areas with zero fluorescence (Stuart 2007, p. 76; Ianna 2001; Franceschi, Nole & Vassallo 2013, pp. 21, 22-24; Liang 2012, p. 319; Lazidou et al. 2006, pp. 13-17). In addition, it is one of the most interesting techniques for the study of some organic, mainly pigments and binders (Daniilia et al. 2002; Liang 2012, p. 11; Franceschi et al. 2011, pp. 347, 351-352). The image obtained during the application of this technique is a colorful visible image (Mairinger 2000 (2), pp. 63, 65), although the light sources used are emitting ultraviolet radiation (Stuart 2007, p. 76; Ianna 2001; Mairinger 2004, pp. 25-26, 45).

2.1.2. Infrared Reflectography

IR radiation is invisible radiation, with wavelengths ranging from the deep red spectrum to the limits of the microwave region (Ianna 2001). Areas of interest in scientific conservation applications are limited to the area known as near IR (NIR: 700 - 1000 nm) and in the short wave IR (SWIR: 1000 - 2500 nm) (Mairinger 2000 (1), p. 41). IR radiation is characterized by its high penetrating capacity (Alexopoulou & Chrysoulakis 1993, pp. 147, 153). This property, combined with the fact that many materials reflect IR radiation or allow it to pass through their mass in a different way than they do with visible radiation, allows for "reading" underlying paintings (Liang 2012, pp. 313-314) or other elements that are invisible to the naked eye (Ianna 2001; Stuart 2007, p. 73; Mairinger 2004, pp. 50-53).

The imaging of the reflected IR radiation or IR reflectography is a non-invasive technique (van Asperen de Boer 1968, pp. 1711-1714) that has been widely applied in the field of art study and conservation for decades (Alexopoulou & Chrysoulakis 1993, pp. 171-185; Daniilia et al. 2000, pp. 92, 94; Faries 2005, pp. 87-104; Mairinger 2000 (1), p. 48; Hain, Bartl & Jacko 2003, pp. 9-11) (Mairinger 2004, pp. 53-54; Daffara & Fontana 2011).

The penetrating capability of IR radiation, in conjunction with other parameters such as the camera's functional characteristics or the geometric characteristics of the observation layout, makes it possible to uncover underlying paintings that are not perceptible to the naked eye, such as drawings or changes to the drawing during painting (Hain, Bartl & Jacko 2003, p. 9; Mairinger 2004, pp. 53-54; Mairinger 2000 (1), pp. 52-53; Liang 2012, pp. 5-6; Marras et al. 2002, pp. 5-7), and over-painted areas. It could also reveal unreadable inscriptions or paintings masked by natural patina (Lahanier 1991, p. 247; Stuart 2007, p. 73; Fischer & Kakoulli 2006, pp. 6-7). Depth imaging investigation, which is applicable with IR reflectography, reveals the internal structure of opaque objects (Alexopoulou & Kaminari 2008, pp. 152-161; Lazidou et al. 2006, pp. 17-22) or of complex strata under an opaque surface layer (Liang 2012, pp. 316-319), in a non-destructive manner ,while it could be used to test the structural integrity of components and assemblies (Mairinger 2004, pp. 49, 50; Stuart 2007, p. 73). This technique is able to provide also initial indications concerning the nature of certain materials (Alexopoulou & Chrysoulakis 1993, pp. 171-185; Daniilia et al. 2000, pp. 92, 94; Stuart 2007, pp. 73-74; Liang 2012, pp. 8-10; Cosentino 2014).

2.1.3. X-Radiography

X-ray radiography is a non-destructive technique in which an object is irradiated with X-rays of a wavelength of 10^{-7}–10^{-11} m (Stuart 2007, p. 77). As X-rays are of a shorter wavelength than visible and UV light, they are able to penetrate materials that are opaque to such radiation (Mairinger 2004, p. 49). X-rays will either be absorbed or pass through a material, depending on the composition of the material. When X-ray photons interact with a material, some of the photons are transmitted, some absorbed and some scattered from their path of incidence (Mairinger 2004, p. 55). As a result, the incident beam is attenuated and a shadow image is generated behind the object being studied (Stuart 2007, p. 78).

Radiographs of paintings provide information about the selected materials (e.g., support, pigments), the techniques employed, including peculiarities of specific artists and their workshops, compositional and dimensional changes, temporal changes and damages such as the effects of aging processes, cracks, paint losses, later additions by restorers, etc. Furthermore the structure and construction of wooden supports, like growth rings, number of boards, textures (puttied knots, cracks), tool marks, joining techniques, worm tunnelling and later accretions can be seen quite clearly even on panel paintings that bear paint layers on both sides. In gilded panels the gold foil is invisible in a radiograph because the thickness of the gold leaf is around 1 mm. The same holds true for silver foils as well (Mairinger 2004, pp. 63-64).

X-ray radiography has been widely used to study panel paintings (Sotiropoulou & Daniilia 2010, p. 879; Milanou et al. 2008, pp. 26-28; Mairinger 2004, p. 64). Radiographs can provide information about the pigments which will absorb X-rays differently depending on their atomic weight and density (Sotiropoulou & Daniilia 2010, p. 879). For instance, a pigment containing lead or mercury will absorb more X-rays than a pigment containing chromium or cobalt (Ianna 2001; Stuart 2007, p. 78; Alexopoulou & Chrysoulakis 1993, pp. 212-213).

X-ray radiography can, significantly, provide information regarding the painting technique and layer structure. Radiographs will present details that cannot visually be observed, since they provide a summation of all the absorbing layers (Lazidou et al. 2006, pp. 28-43). Variations in paint thickness will also affect the radiograph produced. X-ray radiography may be employed to determine various changes (Daniilia et al. 2002) that have occurred to a painting, such as compositional, dimensional, ageing, damage or later additions. For example, cracks in a paint layer appear black in a radiograph, so if they appear white the cracks must have been over painted (Stuart 2007, p. 78; Mairinger 2004, p. 64; Alexopoulou & Chrysoulakis 1993, pp. 222-224; Sotiropoulou & Daniilia 2010, p. 879).

As discussed above, imaging techniques can provide significant information about the painting technique, and a preliminary identification concerning the nature of ceratin materials, e.g. pigments. Furthermore the penetration depths of different types of radiation (**Fig.37**) is an important feature that allows the combination of these techniques in order to achieve material mapping images from both the upper layer and the existing under-layers.

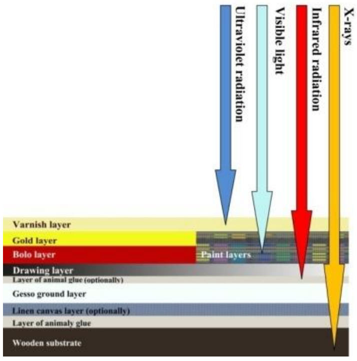


Fig. 37 Structure of a panel painting and penetration depths of different types of radiation *(personal archive Th. Mafredas)*

2.2. Microscopy Techniques

Microscopic observation and characterization techniques have been applied in the field of cultural heritage since the early 20th century (Benedetti-Pichler 1964; McCrone 1994; Weerd van der et al. 2003, pp. 716-717; Stuart 2007, pp. 84-85; Sotiropoulou & Daniilia 2010, p. 879). These techniques provide useful information on how various works of art have been constructed, as well as the type and the morphology, of their construction materials (Milanou et al. 2008; Hochleitner et al. 2002, pp. 2-3; Lazidou et al. 2006, p. 48).

Depending on the type of microscopic technique applied and the work of art being considered, various information can be obtained such as:

- Observation and recording of the intersection of the layers of construction called the stratigraphic structure (Milanou et al. 2008, pp. 102-113; Sandu et al. 2010)
- Detection and recording of subsequent operations such as over-paintings, or the deposition of new varnish materials used to stabilize loose layers (Daniilia et al. 2002, pp. 808-810)
- Recording the size, shape and color of the grains of pigments and how they are distributed within the color layer (Demertzi et al. 2012, pp. 108-109)
- Detection of wood, textile fibres, pigments and inorganic materials (Banik et al. 1981, pp. 95-96; Abdel-Maksoud, Issa & Magdy 2015, p. 491)
- Determination of the organic material used as a carrier (binder) of pigments such as, linseed oil, egg or animal glue (Daniilia et al. 2008, pp. 116-149; Daniilia et al. 2002, pp. 812-813)

There are many types of microscopic methods and techniques among which are Optical Microscopy and Electronic Scanning Microscopy. With the exception of digital stereomicroscopy, all other methods involve the study of samples taken from the objects to be examined. The samples are obtained either in the form of small particles such as pigment granules, wood fibers, or in the form of cross-sectional sections. In the case of multilayer sections, the sample is obtained by making a small vertical cut with a scalpel at the edges of the work or at other selected points in such a way that the sample contains all layers of construction from the bottom, e.g. the gesso preparation, up to the top layer, which is usually a varnish (Sandu et al. 2012, p. 860).

Microscopy techniques are the oldest basic, most readily available methods that give insight into the stratigraphic structure and composition of a polychrome or paint sample. Particulacly, the use of methods based on a cross section observing and analyzing organic materials presents several advantages, such as spatial resolution versus bulk methods, the possibility of mapping the organic materials in each layer of the stratigraphic structure, and distinguishing different materials according to their intrinsic fluorescence (Sandu et al. 2012, p. 860; Weilhammer 2007, p. 50).

2.2.1. Optical Microscopy

Optical or light microscopy (OM, LM) is used to magnify small objects and can provide information about the structure and characteristics of a sample (Karapanagiotis et al. 2009, p. 234; Mazzeo, Prati & Sandu 2009, pp. 179-183). OM involves the interaction of light with a sample, and a magnification of the sample from 20x to 2000x is attainable (Mazzeo, Prati & Sandu 2009, p. 180). A resolution of about 0.5 μm is possible, depending on the limits of the instrument and the nature of the sample being examined. OM is a quick method for identifying a broad range of materials (Lazidou et al. 2006, p. 48) including minerals, wood and paint (Stuart 2007, pp. 80-81; Wheeler & Wilson 2008; Kouloumpi et al. 2013, p. 3; Cristache et al. 2013, pp. 74-75; Katsibiri, Lazidou & Howe 2006, p. 2) and validate the painter's technique (Terlixi, Doulgeridis & Ioakimoglou 2006, p. 1). There is a variety of LM techniques that may be used to examine materials (Stuart 2007, p. 81; Terlixi, Doulgeridis & Ioakimoglou 2006, p. 2). Samples may be examined with transmitted light, reflected light and via stereomicroscopy, where a three-dimensional image is obtained. There are also different imaging modes that may be used. Bright field is the normal mode of operation in OM. In the case of transmitted light, the contrast is based on variations of colour and optical density in the material to be examined (Wheeler & Wilson 2008; Artioli 2010, pp. 64-66; Stuart 2007, pp. 81-82).

2.2.2. Fluorescence Microscopy

Fluoresence microscopy (FM) as a technique, uses a UV light source in addition to filters for samples examination (Terlixi, Doulgeridis & Ioakimoglou 2006, p. 3; Ioakimoglou 2010, p. 186). It is able to observe and record the fluoresence in the sample, which is visible to the naked eye. FM technique could characterised as extrimely useful for observation and study of multi-layer samples. while it could provide a first impression of the distribution of fat and protein binding media in paint layers (Ioakimoglou 2010, p. 186). For example, using this specific technique for observing samples from artifacts scientists are able to discern coating varnishes (Katsibiri, Lazidou & Howe 2006, pp. 5-6) which are not detectible in visible light microscopy or better distingush the painting layers (Sotiropoulou & Daniilia 2010, p. 879; Katsibiri & Howe 2010, p. 16; Hochleitner et al. 2002, p. 3). In some cases, ultraviolet FM could provide thenidentification of pigments (Franceschi et al. 2011, pp. 348-349, 352-354), while, in others, it is able to achieve the distingushing of the painting layers which, when observed under visible light appear as a single layer (Sotiropoulou & Daniilia 2010, pp. 882-883; Karapanagiotis et al. 2009, p. 234).

2.2.3. Scanning Electron Microscopy - Energy Dispersive X-ray spectroscopy

Scanning Electron Microscopy (SEM) is applied in the field of scientific research of artifacts as an imaging tool for a detailed study of the surface of a sample or even a cross-section and analyzes its entire stratigraphy in much larger scale than that achieved by OM (Lahanier 1991, p. 250; Sotiropoulou & Daniilia 2010, pp. 880-881; Albrecht et al. 2016, pp. 42-43; Joosten & Spring 2009, pp. 191-192). Samples from artworks examined with SEM, can be magnified significantle more than usual, up to 40.000x, while there is the possibility of even larger magnification. It is also used to observe grain size (Burnstock, Jones & Ball 2002), and shape (Hochleitner et al. 2002, pp. 1, 3-4), parameters associated with the manufacturing technology and construction techniques implemented (Stuart 2007, pp. 91-92; Artioli 2010, pp. 66-68).

The combination of SEM with Energy Dispersive X-ray (EDX) spectroscopy can provide elemental information about the identity of inorganic materials present in a sample, such as pigments (Genestar & Pons 2005, pp. 270-274; Iordanidis et al. 2013; Cristache et al. 2013, pp. 75-78; Franceschi et al. 2011, pp. 353-354; Katsibiri, Lazidou & Howe 2006, p. 7) and gesso preparation materials (Genestar 2002, pp. 385-388; Kouloumpi et al. 2013, p. 3; Mastrotheodoros et al. 2016). This method is based on capturing the characteristic energy of atoms (Stuart 2007, p. 92; Charola & Koestler 2006, pp. 21-22) .

SEM has proved to be a popular means of examining the materials that make up paintings (Burnstock & Jones 2000; Athene 1993; Feller 1986; Roy 1993; West FitzHugh 1997). The surface characteristics of paintings may be investigated using scattered (SE) and back-scattered (BSE) electron imaging in SEM (Stuart 2007, p. 94). SE images of paintings can provide information about surface texture, such as fine cracking, the nature of the relationship between the pigment and the binding medium at the surface, paint drying defects and surface pores. BSE images provide information regarding the atomic number contrast in the sample and can be used prior to EDX analysis. (Stuart 2007, pp. 94-95; Charola & Koestler 2006, p. 20; Katsibiri, Lazidou & Howe 2006, pp. 5, 7-8; Groen 1997; Doehne & Stulik 1990).

2.2.4. Microchemical Tests

Around 1905 Oswald, a Canadian-American physician and medical researcher, performed analyses on cross sections using biological stains for the first time (Sandu et al. 2012, p. 863). Since then, a variety of stains with visible or fluorescent emission range, have been suggested in the conservation literature (Johnson & Packard 1971, pp. 150-152; Byrne 1991, pp. 5-6; Magrini, Bracci & Sandu 2013; Sandu et al. 2012, pp. 864-866, 867-868; Terlixi, Doulgeridis & Ioakimoglou 2006). The staining technique is mainly based on the use of dyes able to form colored compounds with organic materials, such as proteins, polysaccharides, resins, and oils (Sandu et al. 2012, p. 863). Limitations in the formation of the staining color may apply due to dye absorption by porous matrices -such as calcium carbonate grounds- or to the degree of aging of the materials to be identified (Sandu et al. 2012, p. 864; Martin 1977; Mazzeo 2009, p. 195).

There are techniques used to identify pigments and dyes (drop tests) and organic binders (selective coloring) (Stuart 2007, pp. 44-48; Sciutto et al. 2016, pp. 214-215). The medium used to dissolve and bind the dyed grains in a painting work is in liquid form, and the paint practicles disperse into it. In Chemistry terminology when the medium solidifies and holds the particles together, it is called a binder, and it can be identified with the use of some reagents (Banik et al. 1981, pp. 93-94; Masschelein-Kleiner 1986, pp. 186-189; Sciutto et al. 2016, p. 214). The identification of proteinaceous compounds through histochemical staining tests is based on the interaction with specific functional groups, such as carbonyl, carboxyl, hydroxyl, etc., and/or on the characterization of specific properties of chemical functions of these materials: redox, acid-basic, or metachromatic properties (Sandu et al. 2012, p. 864; Feigl & Anger 1966). The detection of the binder which is not visible by OM is similarly exploited through the properties of some chemicals to bind to the painting binders, thus coloring them and making them visible during observation by OM (Banik et al. 1981, pp. 95-96; Stuart 2007, pp. 82, 85; Cartechini et al. 2010; Daniilia et al. 2002, pp. 812-813; Cartechini et al. 2016, pp. 241-246; Terlixi, Doulgeridis & Ioakimoglou 2006, pp. 11-18).

The identification of pigment layers is done by applying a suitable reagent to the sample. The reagent chosen for each test has the property of reacting chemically with a particular coloring agent in the painting, causing some kind of visibly detectable change (Cartechini et al. 2010, pp. 868-874; Mazzeo 2009, pp. 193-195). The interaction of the dye with proteinaceous paint materials will depend on the pH of the stain solution, as this determines the protein's net charge. The presence of dark or colored pigments can complicate the identification of a positive stain, especially if it is of similar color as the pigmented layer (Cartechini et al. 2010, pp. 869-870; Ioakimoglou 2010, p. 186). Some of the dyes, particularly the acidic ones, may also dissolve salts or inert charges, as in the case of calcium carbonate (Sandu et al. 2012, p. 864). The histochemical dyeing of lipids (triglycerides, phospholipids, cerides) in panel paintings samples is based on reactions with formation of chromophore groups using lysochromic dyes capable of dissolving the lipids and/or specific reactions for some radicals (such as carbonyl from the ketone and aldehyde groups) or reactions to prove the unsaturated state of an acid. The staining tests for lipids are more difficult to evaluate, as they are less homogenous, less intense, and/or less stable than the protein stains (Sandu et al. 2012, p. 864).

2.3. Analytical Techniques

There are many kinds of analytical techniques, which can be divided in two major categories, spectroscopic techniques and chromatographic techniques. Another category may also be identified, which includes techniques that provide structural diagnosis information such as the holographic interferometry (Tornari 2007).

Spectroscopic techniques are the methods where the spectrum of a substance, i.e. the intensity of radiation in terms of with the wavelength, is measured. These are in turn divided into molecular techniques and elemental techniques (Anglos, Georgiou & Fotakis 2009).

Chromatographic methods of analysis are those which separate organic mixtures into their constituents through the differences in behavior of their component in given analytical conditions (Fotakis et al. 2006, p. 98).

2.3.1. Spectroscopic Techniques

Spectroscopic techniques are a large group of optical analytical techniques based on the interaction of e/m radiation with the atoms or molecules of a sample (Anglos, Georgiou & Fotakis 2009). These techniques are divided into two categories: molecular techniques (Nevin, Spoto & Anglos 2012, pp. 346-356) and elemental techniques (Nevin, Spoto & Anglos 2012, pp. 340-346).

2.3.1.1. Molecular Techniques

Through molecular techniques (**Table 4**) it is possible to characterize and identify materials by identifying the molecules that comprise the sample material which is analyzed.

Table 4. Indicative Molecular Analysis Techniques in Cultural Heritage (Fotakis et al. 2006, p. 97)

Analytical method	Applications
UV-visible Absorbance/Reflectance Spectroscopy	Analysis of inorganic materials
Fluorescence Emission Spectroscopy	Pigment analysis
Infrared spectroscopy (FTIR)	Paint analysis (pigments, binders, gesso preparation)
Raman spectroscopy/microscopy	Inorganic and organic pigments, binder and varnish analysis
X-ray diffraction (XRD)	Pigment analysis
Gas chromatography (GC), Gas Chromatography–Mass Spectrometry	Analysis of organic components such as binders, varnishes, etc.
Mass spectrometry (MALDI-TOF, DTMS, SIMS)	Pigments, minerals, organic components such as binders, varnishes, etc.
High-Performance Liquid Chromatography (HPLC)	Analysis of organic components such as binders, varnishes, dyes etc.
Nuclear Magnetic Resonance (NMR) Spectrometry	Analysis of organic binding media and varnishes

2.3.1.1.1. Fourier Transformer Infrared Spectroscopy

The infrared Spectroscopy has been applied in the analysis of diverse types of specimens of art and ancient objects for more than 50 years (Casadio & Toniolo 2001, pp. 71-72). The emergence and spread of instruments that implemented Fourier transform in 1977 (Derrick, Stulik & Landry 1999, p. 43; Casadio & Toniolo 2001, p. 72) equipped scientists with high sensitivity and spectral resolution which turned the infrared spectroscopy it into a highly reliable tool in the field of Cultural Heritage (Sarmiento et al. 2011, p. 3602).

Many publications (Harkins, Harris & Shreve 1959, p. 541; Daniilia et al. 2004, pp. 880-881; Daniilia et al. 2004; Sotiropoulou, Papliaka & Vaccari 2016; Miliani et al. 2012; Casadio & Toniolo 2001, pp. 72-75; Wilhelm 1996, pp. 189-192) can be found concerning Fourier-transform infrared spectroscopy (FTIR) in the characterization of constituent materials (organic and inorganic) of panel paintings (Grasselli 1983), from support to outer layers of varnish (Poliskie & Clevenger 2008, p. 47; Miguel et al. 2012; Almeida, Balmayore & Santos 2002; Souza & Derrick 1995; Genestar & Pons 2005, pp.

270-274; Meilunas, Bentsen & Steinberg 1990; Katsibiri, Lazidou & Howe 2006, pp. 19-20). In fact, this technique offers a quick analysis of micro samples -less than 0.5 mg- and is able to identify the different molecular groups typical of the materials used by the artist (Bitossi et al. 2005, p. 189). Some FTIR databases containing the spectra of pigments and artists' materials are also available, and are commonly adopted as a reference[30].

Infrared spectroscopy is based on molecular vibrations (Stuart 2007, p. 110) and provides molecular structural information useful in the identification of constituent materials, both organic and inorganic (Meilunas, Bentsen & Steinberg 1990, p. 33; Joseph et al. 2009, p. 900; Wilfried & Manfred 2001, p. 10; Prati et al. 2016, p. 130; Joseph et al. 2009, pp. 903-905) (Protopappas et al. 2001; Daniilia et al. 2004, p. 595) from the support to the outer layers of varnish. Chemical bonds undergo various forms of vibrations such as stretching, twisting and rotating (Derrick, Stulik & Landry 1999, pp. 8-10). The energy of most molecular vibrations corresponds to that of the infrared region of electromagnetic spectrum (Parvez & Feride 1999, p. 208; Stuart 2007, p. 112; Prati et al. 2010, p. 130). Thus, an infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed in a particular energy. The energy at which a peak in the absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule (Stuart 2007, p. 111; Prati et al. 2016, p. 130). Many of the vibrations can be localized to specific bonds or groupings, such as the C=O and O-H groups. This led to the concept of characteristic group frequencies which are of interest to conservators' scientists (Parvez & Feride 1999, p. 208). By comparing the different vibration frequencies, classification of the sample becomes possible (Genestar 2002, pp. 382, 385; Bitossi et al. 2005, p. 190).

The identification of natural materials containing proteins, such as animal glues, casein, or egg, is aided by the characteristic bands due to the protein (Stuart 2007, p. 120). For example some typical proteinaceous peaks in the obtained spectra indicated the presence of natural glue (Souza & Derrick 1995, pp. 573, 576, 578; Bitossi et al. 2005, p. 190).

[30] Infrared and Raman User Group (http://www.irug.org/search-spectral-database) and e-VIBRATIONAL SPECTROSCOPIC DATABASES (http://www.ehu.eus/udps/database).

There are several studies about the identification of natural resins used as coating formulations for paintings. Feller (Feller 1954; Bitossi et al. 2005, p. 190) was one of the first to use infrared spectroscopy for the analysis of painting varnishes from Dammar and Mastic. A little bit later, in 1977 Low and Baer (Low & Baer 1977) published their study about distinguishing Dammar from Mastic using a Fourier Transformation spectrometer. Furthermore Newman (Newman 1998) used IR spectrometry analysis, thus receiving more specific information, which permitted the identification of specific resins (Newman 1998, pp. 47-48). Besides natural resins, as demonstrated by Bruni and Guglielmi in their recent work (Bruni & Guglielmi 2014), FTIR spectrometry is able to identify synthetic resins (Derrick, Stulik & Landry 1999, pp. 130-132) used as coating formulations, as was proven by Domenech-Carbo et all published in 2001 (Domenech-Carbo et al. 2001)

To sum up, infrared spectroscopy has been used for decades in the analysis of the constituents of panel paintings but it has not always been conclusive due to the extreme complexity of the mixtures and the limited sample size. As a result of the enhanced sensitivity and spectral resolution associated with the technique, FTIR has appears promising for the analysis of art objects and ancient artifacts (Meilunas, Bentsen & Steinberg 1990, p. 33) and has been established as a powerful analytical technique to study of organic materials (Sarmiento et al. 2011, p. 3601), used for constructing panel paintings.

2.3.1.1.2. RAMAN Spectroscopy

Raman microscopy has been established as a reliable tool for the noninvasive analysis of a wide spectrum of both inorganic and organic materials in art (Casadio, Daher & Bellot-Gurlet 2016, pp. 161-162) and archaeological objects (Edwards 2004, pp. 871-878) presenting unique advantages over other molecular analysis techniques (Vandenabeele 2004). Its high sensitivity and specificity enables the analysis of a wide variety of materials in situ, noninvasively, at relatively short times, and with excellent spatial resolution (Fotakis et al. 2006, p. 95; Casadio, Daher & Bellot-Gurlet 2016, p. 161). As a technique it is similar to FTIR and involves the study of the way in which radiation is scattered by a sample (Stuart 2007, p. 136). Raman spectroscopy probes vibrational transitions within materials. These transitions represent distinct and well-defined ways -vibrational modes- that atoms oscillate within a molecule or crystal lattice and, as such, are very specific to chemical bonds, molecular species, and lattice structure (Best et al. 1995, pp. 31-32). As a result, the Raman spectrum is essentially a fingerprint, which can be used for the identification of the material probed (Fotakis et al. 2006, p. 95; Stuart 2007, p. 136; Best et al. 1995, pp. 32, 38; Smith & Clark 2004, p. 1139).

The source of radiation used may be in the near-UV, visible or near-infrared regions of the spectrum. When radiation falling on a molecule does not correspond to that of an absorption process, it is scattered. Most of the scattered radiation remains unchanged in wavelength and is known as Rayleigh scattering. A small proportion of the scattered light slightly increases or decreases in wavelength and this is known as Raman scattering (Stuart 2007, p. 136). The effect relies on the inelastic scattering of light from a molecule. The spectrum of this inelastically scattered radiation called the Raman spectrum reveals the molecule's structure and identity based on characteristic spectral bands corresponding to various vibrational modes of the molecule (Fotakis et al. 2006, p. 95)

Raman microscopy is an important analytical technique for a range of conservation analyses (Wise & Wise 2004, pp. 716-719; Casadio, Daher & Bellot-Gurlet 2016, pp. 180-187) as Raman spectra with 1 μm spatial resolution enables samples in the picogram range to be investigated (Stuart 2007, p. 137; Smith & Clark 2004, pp. 1138-1139; Fotakis et al. 2006, p. 102). There are several special Raman techniques that are available to aid in the recording of spectra (Stuart 2007, pp. 138-139; Fotakis et al. 2006, pp. 102-105; Vandenabeele et al. 2007).

Raman spectroscopy is an excellent tool for the characterization of paintings (Clark 1995; Clark 1999; Best et al. 1995) and has been used to examine, panel paintings from a range of periods (Clark 2006, pp. 2987-2988; Fotakis et al. 2006, pp. 106-111; Casadio et al. 2010; Vandenabeele, Verpoort & Moens 2001; Burgio, Clark & Theodoraki 2003; Daniilia et al. 2004; Daniilia et al. 2002, pp. 807, 809, 813) (Sotiropoulou & Daniilia 2010, p. 879). Raman spectroscopy is highly applicable when identifying pigments in paintings and many related studies have been published (Bell, Clark & Gibbs 1997; Burgio & Clark 2001; Otieno-Alego 2000; Perardi, Zoppi & Castellucci 2000; Casadio, Daher & Bellot-Gurlet 2016, pp. 187-190). Collections of the Raman spectra of commonly encountered pigments have been published and an assembly of the spectra may be accessed online (Bell, Clark & Gibbs 1997; Burgio &

Clark 2001; Burrafato et al. 2004; Castro et al. 2005; Edwards 2000, pp. 2-17; Casadio, Daher & Bellot-Gurlet 2016, p. 180).

MicroRaman spectroscopy can be also used to obtain information about the nature of organic binding media and varnishes used in paintings (Casadio, Daher & Bellot-Gurlet 2016, pp. 191-192). According to their chemical structure, natural binders and varnishes can be classified into four major categories: proteinaceous, polysaccharide, fatty acid, and resinous media (Fotakis et al. 2006, pp. 111-112; Burgio & Clark 2001; Nevin et al. 2007; Nevin et al. 2008; Vandenabeele et al. 2000). However, as the composition of a number of these organic compounds varies due to their biological nature, care must be taken when identifying such compounds by comparison with "reference" spectra (Burgio & Clark 2001; Stuart 2007, pp. 139-140).

2.3.1.1.3. X-Ray Diffraction

X-ray diffraction (XRD) is a technique used to determine the arrangement of atoms in solids (Janssens 2004, p. 130). When monochromatic X-rays (Janssens 2004, p. 147) impinge on a crystalline material in which the crystal lattice dimensions are in the order of the wavelength of the X-rays, diffraction of the beam occurs. As the wavelengths of some X-rays are about equal to the distance between the planes of atoms in crystalline solids, reinforced diffraction peaks of radiation with varying intensity are produced when a beam of X-rays strikes a crystalline solid (Stuart 2007, pp. 230-231) which is the result of the physical phenomenon of constructive (or destructive) interference (Janssens 2004, pp. 137-143). Then a diffraction pattern emerges where some beams are reinforced and other cancelled (Charola & Koestler 2006, p. 17).

XRD is used for the identification of crystalline materials such as pigments, metal powders, organic materials and salts, while non-crystalline materials lacking a regular crystal lattice, such as glass, do not produce a clear pattern (Charola & Koestler 2006, p. 18; Hochleitner et al. 2003, pp. 644-648; Stuart 2007, p. 232; Ajò et al. 2004, pp. 337-347; Corbeil 2004, pp. 19-28) (Crina et al. 2013, pp. 736, 737-741; Blanton et al. 2004; Janssens et al. 2016, p. 89; Mastrotheodoros et al. 2016). This is a powerful technique that enables not only determination of the molecular structure, but also the discrimination among different crystal phases, for example, in minerals. Sampling of a small quantity of powder is normally required, although in situ analysis has become possible with modern instruments or at synchrotron radiation facilities (Creagh 2005, p.

430; Van der Snickt et al. 2012). The latter offer high-brilliance X-rays that also permit routine X-ray microbeam diffraction measurements with spatial resolution down to 1 μm (Fotakis et al. 2006, p. 98).

2.3.1.2. Elemental Techniques

Through elemental techniques (**Table 5**) scientists achieve the qualitative and quantitative determination of the elements from which a material is composed.

Table 5. Indicative Elemental Analysis Techniques in Cultural Heritage (Fotakis et al. 2006, p. 54)

Analytical method	Applications
Atomic absorption / emission spectroscopy	Elemental analysis of pottery, metal, and glass
Inductively coupled plasma-optical emission spectrometry (ICP-OES)	Major and trace element analysis of metals and minerals
Inductively coupled plasma-mass spectrometry (ICP-MS)	Trace element and isotope analysis of metals and minerals
Secondary ion mass spectrometry (SIMS)	Elemental analysis of pigments, pottery, metals, alloys, and minerals
Scanning electron microscopy (SEM, energy dispersive x-ray (EDX) analysis)	Mapping and elemental analysis of pigments, pottery, metals, and minerals
X-ray fluorescence spectrometry (XRF)	Elemental analysis of pigments, metals, and minerals
Particle-induced x-ray emission (PIXE)	Major and trace element analysis of pigments, pottery, metals, and minerals
Neutron activation analysis (NAA)	Analysis of major and trace elements in pigments, pottery, and minerals. Provenance
Isotope analysis	Isotope analysis Dating and provenance

2.3.1.2.1. Laser Induced Breakdown Spectroscopy

Laser Induced Breakdown Spectroscopy (LIBS) has emerged in recent years as a new emission technique which is applicable in situ. It is able to provide information about the elemental composition of a sample based on the spectral analysis of the radiation emitted by plasma generated through focusing an intense laser pulse on the sample surface (Anglos 2001, p. 187; Stuart 2007, p. 216; Bruder, Detalle & Coupry 2007; Borgia et al. 2000, p. S281). Thus, the analysis is carried out directly on the object, without the need of special preparation of the object and sampling. It can provide qualitative and semi-quantitative analysis (Borgia et al. 2000, p. S282; Gaudiuso et al. 2010, pp. 7438-7441) on the elemental composition of materials, and it has been successfully applied to the analysis of materials in works of art and archaeological objects (Anglos 2001, p. 188; Nevin, Spoto & Anglos 2012; Borgia et al. 2000, p. S283). Furthermore the technique has the capability of providing depth profiling information if spectra from successive laser pulses delivered at the same point are recorded individually (Anglos 2001, p. 188; Anglos, Couris & Fotakis 1997, pp. 1028-

1029). All the analytical information arises from the recognition of the spectral lines recorded in the emission spectrum, and only a single pulse from the laser is sufficient for analysis (Tognoni et al. 2002, pp. 1118-1120, 1124-1126; Anglos, Couris & Fotakis 1997, pp. 1025-1026)

A number of recent studies have shown that LIBS can be an efficient technique for the rapid identification of the elemental composition of pigments in the study of painted works of art (Anglos 2001, pp. 190-199; Aloupi et al. 2006, pp. 7-8; Duchêne et al. 2010, pp. 62-65; Nevin, Spoto & Anglos 2012, p. 344; Giakoumaki, Melessanaki & Anglos 2007, pp. 756-757) (Castillejo et al. 2000; Bicchieri et al. 2001; Anglos, Couris & Fotakis 1997, pp. 1026-1028), because focusing the laser beam on the sample provides a very good spatial resolution (Burgio et al. 2001, pp. 906, 907-908; Burgio et al. 2000; Alberghina et al. 2015; Melessanaki et al. 2001).

Research efforts have shown that LIBS has several analytical advantages and, as such, it can be a potential alternative to other spectroscopic, mass spectrometric, or X-ray techniques used in art conservation (Alberghina et al. 2015; Burgio et al. 2001; Burgio et al. 2000; Melessanaki et al. 2001; Duchêne et al. 2010). It has been used as an analytic research tool for the analysis of pigments in panel paintings and other artifacts, and the results clearly demonstrate the prospects of the technique as a useful analytical tool in art and archaeology (Fotakis et al. 2006).

2.3.1.2.2. X-Ray Fluorescence

X-ray fluorescence analysis (XRF) is a well-established non-destructive technique (Romani et al. 2010, pp. 837-841; Mass et al. 2016, pp. 57, 63-64) for the measurements of the elemental composition of materials. It is based on the ionization of the atoms of the material being irradiated by an energetic beam of primary X-rays (Janssens et al. 2010, p. 83; Mantler & Schreiner 2000, pp. 3-4; Stuart 2007, pp. 234-235; Feretti 2000, pp. 285-286; Janssens 2004, pp. 129-130) (Streli, Wobrauschek & Kregsamer 2000, p. 2478; Milazzo 2004; Janssens 2003, pp. 365-367).

The physical principles of X-ray fluorescence are simple and well known (Janssens 2003, pp. 367-380): electronic transitions can be induced in the inner shells of the atoms by electromagnetic radiation – or charged particles - of suitable energy. Such transitions result in the emission of X-rays whose energy and intensity are related to the type and abundance of the atoms concerned. Due to the attenuation of the matter, only the X-rays emitted in the first layers under the surface can reach the detector (Feretti 2000, p. 286).

The determination of the energy or wavelength of the emitted photon allows qualitative analysis and the determination of the number of emitted characteristic photons allows quantitative analysis (Streli, Wobrauschek & Kregsamer 2000, p. 2478). The energy of the fluorescent photons is the difference in energy between the vacancy that results from the ionization process and the electronic state of the electron filling the vacancy. In this manner, the characteristic radiation emitted by the ionized atoms contains information on the nature and abundance of the elemental constituents present. The technique is particularly efficient for studying high atomic number (high-Z) elements in low-Z matrices (Janssens et al. 2016, p. 83; Kramar 2000, p. 2467).

The XRF technique is very important in the study of materials, especially in art (Feretti 2000; Mastrotheodoros et al. 2016; Artioli 2010, pp. 423-424). It offers an initial examination of the artwork, without touching it or damaging it in any way. Thanks to portable equipments, tests can be run in situ, without a necessity to move the peace of art from its original place. It is one of the gentlest ways to obtain information about the materials (Alfeld & Broekaert 2013, pp. 219-220; Aloupi et al. 2006) and technique applied by the artist. It also serves to discover possible later interventions, revealing modern materials where there should only be traditional ones (Křižnar et al. 2008, p. 2).

XRF can provide simple qualitative analyses (Janssens 2003, pp. 417-418) to identify inorganic pigments, since many of them are characterized by the presence of one or two detectable elements (Mantler & Schreiner 2000, p. 5; Stuart 2007, pp. 240-241; Moioli & Seccaroni 2002a; Franceschi, Nole & Vassallo 2013, pp. 21, 24-28; Moioli & Seccaroni 2002b; Hochleitner et al. 2003; Sotiropoulou & Daniilia 2010, p. 881) (Andrikopoulos et al. 2006; Křižnar et al. 2008; Civici 2006; Mass et al. 2016; Neelmeijer et al. 2000, pp. 104-106; Bitossi et al. 2005, pp. 194, 201-202). Since it is impossible to distinguish among signals coming from the ground and from the different painted layers, the correct interpretation of spectra may require considerable experience and knowledge of painting techniques (Feretti 2000, p. 294). Thus, in case of a multilayered paint sample, element identification might be hampered by the absorption of X-Rays through different layers that affects the intensity ratio between the different characteristic lines (Alberghina et al. 2015, p. 571). XRF furnishes an indirect identification of pigments through evidence of key elements. For example, the simultaneous presence of Hg and S, found by XRF analysis on a red pigment, indicates the use of cinnabar (HgS). On the other hand, being an element-specific technique, insensitive to the chemical state and/or the molecular environment in which the elements are present, XRF is often not specific enough to identify the pigments with certainty. For instance, the detection of Cu can indicate the presence of several pigments (azurite, malachite, etc.). Hence, it is not always possible to identify the nature of the pigment, but only its class (Bardelli et al. 2011, p. 3148).

Varnish and binding media consist of organic compounds (such as vegetable oils, egg yolk, egg white and resins) and are therefore composed predominantly of light elements, which can only modest absorption for the fluorescent radiation compared to heavier elements (Feretti 2000, p. 294; Mantler & Schreiner 2000, p. 5) which is why elements are not detectable by XRF (Alberghina et al. 2015, p. 271).

The XRF technique as discussed above, allows researchers to obtain the elemental composition of the specimen under study and to identify its key elements (Bardelli et al. 2011, p. 3152; Janssens 2003, p. 419), without sampling from the artifacts, while applying the technique in situ (Alberghina et al. 2015, p. 270).

2.3.2. Separation Techniques

Chromatography is a group of techniques used to separate complex mixtures (Harris 2010, p. 562), such as paint. They can be used to detect very small amounts of a component, making them excellent tools for characterizing small samples of heritage material (Colombini & Modugno 2004, pp. 147-148). Even though they are invasive and destructive, they have always been the preferred methods for organic material identification (Masschelein-Kleiner 1986, pp. 192-203; Colombini & Modugno 2004, pp. 147-148; Bonaduce et al. 2016, p. 299; Schilling 2005, p. 186), because the complex mixture of organic components can be separated and subsequently identified and quantified (Kouloumpi 2016, p. 160). All separation methods require the natural polymeric materials, such as proteins, oils, resins and gums to break down to yield the amino acids, fatty acids, sugars, etc., which are subsequently derivatized to render them amenable to chromatographic analysis. The analysis employs the passing of the mixture in a "mobile phase" through a stationary phase, which separates the analyte from other molecules in the mixture based on differential partitioning between the mobile and stationary phases (Harris 2010, p. 562). Chromatography records the differential retention on the stationary phase and, hence, the changing of the separation, which depends on the partition coefficient (Kouloumpi 2016, p. 160; Casoli, Musini & Palla 1996, p. 238; Stuart 2007, pp. 296-297).

There is a variety of chromatographic approaches to characterize organic substances (Kouloumpi, Lawson & Pavlidis 2007, p. 804; Colombini & Modugno 2004, p. 148). Among them, we can distinguish paper chromatography which is the simplest chromatographic technique and uses paper as the separation medium (Stuart 2007, p. 297), and thin layer chromatography (TLC), another simple chromatographic method in which the stationary phase (e.g. silica, alumina or cellulose) is coated as a thin layer onto a glass or plastic plate (Striegel & Hill 1996, pp. 13-15; Stuart 2007, p. 298; Masschelein-Kleiner 1986, pp. 192-194). The most common separation methods currently in use are (Kouloumpi, Lawson & Pavlidis 2007, p. 804; Colombini & Modugno 2004, p. 148) Gas Chromatography (GC) which involves the introduction of gaseous or vaporized samples into a long column when the sample components are separated (Stuart 2007, pp. 300-304; Harris 2010, p. 565; Miller 2005, pp. 141-148) and High-Pressure Liquid Chromatography (HPLC) in which the mobile phase is a liquid and proves useful when the compounds under investigation are not sufficiently volatile for GC. Furthermore, the use of high pressure forces the solvent through columns containing fine particles that produce a high-resolution separation (Stuart 2007, pp. 315-317; Harris 2010, p. 596; Miller 2005, pp. 183-194).

2.3.2.1. Gas Chromatography

The choice of GC for characterizing the natural organic substances of a panel painting is driven by the fact that these are complex mixtures of many chemical species that are very similar to each other. In other words, the resolution and determination of the molecular profile is essential in order to identify the materials present and the aging pathways (Colombini et al. 2010, p. 716).

Characterization of organic painting materials, such as binding media, glues, adhesives and varnishes from panel paintings of post-Byzantine period would enable researchers to investigate the validity of common assumptions about the influences in Greek panel painting techniques (Kouloumpi et al. 2007, pp. 169-170, 178; Sotiropoulou & Daniilia 2010, p. 881; Kouloumpi, Lawson & Pavlidis 2007). For example, the proteinaceous binders used by artists in the technique known as tempera are mainly collagen glues derived from animal skins or bones, egg and milk or casein. These binders can be used either on their own mixed together, or in a mixture with siccative oils in the technique known as tempera grassa (Casoli, Musini & Palla 1996, p. 147; Kouloumpi et al. 2007, p. 169).

For quantitative GC analysis, a mass spectrometer (MS) can be used to identify components. Coupling a MS with a GC combines the degree of separation of GC with the analytical ability of MS (Stuart 2007, p. 302; Masschelein-Kleiner 1986, pp. 200-201; Sotiropoulou & Daniilia 2010, p. 881; Lahanier 1991, p. 252). Applying GC-MS analysis to paint layers is widely recognized as the best approach for identifying organic materials, such as proteins, drying oils, waxes, terpenic resins, and polysaccharide gums, because it requires a sample of small size, and provides a diagnostic fingerprint of the material (Casoli, Musini & Palla 1996, p. 246). The method provides essential information for reconstructing artistic techniques, assessing the best conditions for long-term preservation, and planning restoration (Colombini et al. 2010, p. 715).

Consequently, in this specific field, the coupling of GC with MS is necessary due to the high number of compounds with similar retention times. In addition, most significant compounds are not available as commercial standards, and identification cannot be based only on retention times and requires the confirmation by mass spectra (Colombini et al. 2010, p. 716). GC-MS allows the compounds from the analysis to be uniquely identified by a combination of retention time and mass spectral fragmentation pattern (Kouloumpi 2007, p. 42).

There are a few analytical works carried out with GC-MS methods on derivatives of samples taken from the paint layers of Byzantine iconographic artworks (Kouloumpi et al. 2007; Casali, Palla & Tavlaridis 1998; Valianou et al. 2011; Harrison et al. 2011; Chiavari & Prati 2003) providing information about the best restoration operations to be employed, or about the authentication of the work under examination (Surowiec 2008, p. 294; Bocchini & Traldi 1998, pp. 1054-1059; Chiavari & Prati 2003, p. 544; van der Doelen, van den Berg & Boon 1998). Egg (Chiavari & Prati 2003, pp. 545-546; Chiavari et al. 1993, pp. 233-234), casein (Chiavari & Prati 2003, p. 547; Chiavari et al. 1993, p. 234) and animal glues (Chiavari & Prati 2003, p. 546; Chiavari et al. 1993, p. 231), lipid binders, such as oils (Chiavari & Prati 2003, p. 546; Kouloumpi et al. 2007) and waxes (Chiavari & Prati 2003, pp. 547-548), have also been analyzed using GC and GC–MS.

Throughout history, artists have experimented with a variety of organic-based natural materials, using them as paint binders, varnishes, and ingredients for mordants in gildings. The chemical characterization of these organic substances in paint materials is of great importance for artwork conservation because the organic components of the paint layers allows us to differentiate between the painting techniques that have been used over history (Colombini et al. 2010, p. 715; Kouloumpi et al. 2007, pp. 169-170; Surowiec 2008, p. 289). In other words, depending on the results from the applied chromatographic technique, scientists could obtain important information concerning the construction techniques and the materials used by the artists.

2.3.2.2. High Performance Liquid Chromatography

HPLC is mainly used for the characterization of proteins by quantification of the amino acids or for the analysis of organic colorants (Chiavari & Prati 2003, p. 543; Lahanier 1991, p. 252; Masschelein-Kleiner 1986, pp. 201-202) and employs high pressure to force the solvent through columns containing fine particles that produce a high resolution separation (Stuart 2007, p. 316; Harris 2010, p. 596; Degano & La Nasa 2016, p. 264). The HPLC system consists of a solvent delivery system, a sample injection valve, a high pressure column, a detector, a computer and often an oven for temperature control of the column (Stuart 2007, pp. 315-316). There are various detectors that may be used for HPLC. UV detectors are common, and provide qualitative information about each analyte by means of a photodiode array detector. Fluorescence and electrochemical detectors are very sensitive, but also high selective (Harris 2010, pp. 612-613). MS provides both qualitative and quantitative detection of the substance eluted from the column (Stuart 2007, p. 317; Harris 2010, pp. 616-617).

An analysis of natural and synthetic dyes, binding media (drying oils, proteins and gums) together with resins and other organic material can be obtained via HPLC analysis (Degano & La Nasa 2016, p. 266; Surowiec 2008, p. 290). Proteinaceous binding media can be analyzed quantitatively using amino acid analysis (Colombini & Modugno 2004, p. 148; Peris-Vicente et al. 2006, p. 1649) and samples in quantities of the order of some μg can be examined (Peris-Vicente et al. 2006, p. 1649).

HPLC methodology, combined with UV-Vis Diode Array Detection, is also developed for the separation and identification of organic dyes found in paintings (Sotiropoulou & Daniilia 2010, p. 881; Surowiec 2008, pp. 290-291). The method is used for the identification of organic dyes in extracts originating from panel paintings, and is a powerful tool in detecting the components of such natural organic compounds even when they are present in tiny quantities (Karapanagiotis et al. 2005; Karapanagiotis et al. 2006; Valianou et al. 2011; Pauk, Bartak & Lemr 2014; Karapanagiotis et al. 2009). Furthermore oils used in paintings have also been studied using HPLC, which is able to measure the fatty acid content of the oils, as the amount of each fatty acid is characteristic of the type of oil (Surowiec 2008, pp. 294-295). A part from that, HPLC has also been applied to study of resin mixtures used for varnish coatings (Vieillescazes, Archier & Pistre 2005; van der Doelen et al. 1998)

The procedures for the characterization of organic substances of panel paintings appear to be quite complex since they consist of several analytical steps, including solvent extractions, column chromatography clean up, hydrolysis, derivatization reactions, measurement and data analysis; thus, the uncertainty of the final result is analogous to the uncertainty of each step (Colombini & Modugno 2004, p. 153). In addition, the chosen techniques must provide specific information that prevents ambiguities or misinterpretations. To achieve this requirement, the most prudent option is to apply, if it is possible, more than one procedure to the sample (Bitossi et al. 2005, pp. 189-191). It must be emphasized however that in each case, the choice of separation technique and detector is mostly dependent on the questions being asked in the study. Another important characteristic of the analysis of historical samples is the limitations of that apply in sample availability. These limitations often call for a ‘one-off’ analysis which leads to a necessary selection of method which will enable obtaining as much information as possible within a single analysis (Surowiec 2008, p. 298). Chromatographic techniques are the most effective ones for this type of analysis.

As discussed above, there are a many scientific techniques for the identification and characterization of construction techniques and materials for panel paintings. It should be noted, though, that the final choice for the appropriate means of analysis depends on the questions that need to be answered. Only then could the obtained data be useful for the purposes of scientific research.

CHAPTER 3 – METHODOLOGY & RESEARCH PROTOCOL

3. The main goal of the research

Beyond any doubt, Dionysius' contribution to the development of the Post-Byzantine painting was extremely significant and influential. He strengthened the current of returning to Palaeolegean motives, as formed by Manuel Panselinos (Dionysius 1909, p. 6; Kakavas 2008, pp. 44-45; Vassilaki 2012, p. 382). Especially with regards to following traditions, Dionysius's desire for adhering to origins was exceptionally strong, according to his frequently references to Manuel Panselinos (Vassilaki 2012, p. 382), in his treatise, "Hermeneia of Byzantine Art" (Dionysius 1909).

Dionysius' contribution was significant and for one more reason: he was, a pioneer, especially in East orthodox areas (Moutafov 2006, p. 70; Kakavas 2008, p. 219) who, along with Panagiotis Doxaras, tried to wrote a complete treatise concerning the way and the rules by which icon painters should construct and paint their panel paintings (Moutafov 2006, pp. 70, 76; Kakavas 2008, pp. 217,218).

In chapter A, the sources of the Hermeneia were discussed extensively. Dionysius manages to collect all the sources that were dispersed among Mt Athos' different areas (Kakavas 2008, p. 52; Dionysius 1909, pp. 3-4), and, using his experience as an icon painter, wrote the text of the Hermeneia, addressing two distinct fields: the iconographical and the technological (Moutafov 2006, p. 76). The Hermeneia's text, according to Didron's narration, -the French archaeologist who published it in 1845-, was already in common use when he visited Mt Athos in 1839. During his visit, he noticed that the religious paintings in the various churches had been executed according to the same formula, as though "one thought had inspired a hundred brushes" (Partington 1934, p. 136). The source of this traditional painting style was uncovered during a visit at the Esphigmenou monastery, where Didron saw Joasaph, a monk-painter, who used a painter's manual entitled: "Hermeneia of art painting, a guide to painting" (Partington 1934, p. 136; Kakavas 2008, pp. 32-33; Dionysios 1855, pp. xx-xxii). This incident that Didron describes shows clearly that Dionysius's treatise, almost one century after he wrote it, had been accepted and was in common use, especially in Mt. Athos's artistic circle, thus demonstrating its value (Moutafov 2006, p. 76).

Several essays and publications have been made about Dionysius' artistic work, in combination with the iconographic part of his treatise. Perhaps more worthwhile, among others, mainly because of his pioneer survey, is the PhD Thesis of G. Kakavas', director of the Numismatic Museum of Athens (Kakavas 2008).

Some others publications, which are equally as worthy as Kakavas's Thesis, include Ferens's Thesis, an art historian scholar (Ferens 2015), Vasilaki's article, a Greek professor in University of Athens in the field of the history of Byzantine and Post-Byzantine art, (Vassilaki 2012) and Paul Hetherigton's (Hetherington 1973; Hetherington 1974) English translation of the initial book of Dionysius's Hermeneia.

About the construction technology and materials identification of panel paintings, even though there are a lot of publications in relevant literature (Alexopoulou, Theodoropoulou & Tsairis 1997; Kouloumpi et al. 2007; Milanou et al. 2008; Valianou et al. 2011), not one of them deals directly with Dionysius' work. A lot of published works can be found concerning the identification of materials (Clark 2006; Demertzi et al. 2012; Kouloumpi 2016) and construction techniques (Daffara & Fontana 2011; Groves et al. 2009; Janssens et al. 2010) from various painters (Alexopoulou & Kaminari 2008; Alexopoulou, Theodoropoulou & Tsairis 1997; Tsairis 2001) over the centuries (Karapanagiotis et al. 2009; Daniilia et al. 2002; Iordanidis et al. 2013), but until nowadays, not a single work has been published about the materials and the techniques that Dionysius used.

One significant effort is Markozanis's publication (Markozanis 2017), a conservator of artifacts, who carries out a comparative study of Dionysius's Hermeneia in relation to three European technical manuals about painting, which are also considered to be the most important manuals of middle Ages. These are, the Strasburg manuscript (Markozanis 2017, pp. 27-29), Theopanis's work (Markozanis 2017, pp. 24-27) and Cenninis's work (Markozanis 2017, pp. 29-31; Cennini 1990) concerning the construction techniques of panel and fresco paintings (Markozanis 2017, pp. 65-82, 87-102, 105-141).

However, no dedicated work has been published so far concerning the study of the Hermeneia with the concurrent use of physicochemical methods and techniques, in order to ascertain the convergence or not of what is mentioned in Dionysius' treatise. An exception may be a first effort took place in 2012 by the author (Kakavas, Mafredas

& Giannoulopoulos 2013), together with Dr. Kakavas and Ch. Giannoulopoulos, during which lateral tangential lighting was used to extract information about Dionysius' painting modes and habits through the peculiarities of his paint and in order to gain a more in-depth knowledge of the artist's personal painting style (Kakavas, Mafredas & Giannoulopoulos 2013, pp. 318-320). At the same time, black and white infrared reflection photography was applied to collect information on the structure of the chromatic layers below the painting surface of the artifacts, while focusing on the detection of the original drawing as well as the initial stages of the manufacturing process (Kakavas, Mafredas & Giannoulopoulos 2013, p. 322).

Through a framework of non destructive techniques as described previously, the implementation of a series of optical diagnostic and physicochemical analytical methods was decided in the context of a two-directional study:

- The systematic investigation of the materials used for the construction of his panel paintings during the various stages of his creation, and
- The study of the internal construction technology, the identification of methodology, and the determination of the specific way that materials were selected and combined by Dionysius in order to construct these specific artifacts (Alexopoulou, Theodoropoulou & Tsairis 1997, p. 151).

The main aim of this Thesis is, initially, a systematic and scientific examination and analysis of a group of panel paintings representative of a particular period and of a specific icon-painter, Hieromonk Dionysius. There is a historical document (Dionysius 1909) that provides descriptions of the materials and techniques used in the creation of panel paintings, in general. However, concerns about the accuracy of the technical information contained in it have currently arisen. This may be due to either certain vagueness or insufficiency in technical details, or more often, to difficulties in the interpretation of these early quotations. So, there is a clear need to verify the technical information in order to further explore the importance of this text for the identification of panel paintings (Sotiropoulou & Daniilia 2010, p. 878).

The content of this Thesis intend to identify the materials used by Dionysius for four (4) panel paintings, to recognize the construction technology of these artifacts, to study Dionysius's painting method and evaluate whether he eventually applied everything described in his Hermeneia, taking into account that the investigated panel paintings were constructed in 1737, a few years after he completed his treatise (1729-1732). The first step will be to confirm and verify the technical information about constructing panel paintings, as they are presented in Dionysius' treatise.

3.1. The methodology - The research protocol

The identification by physicochemical analysis of the materials used in the production of four 18th century panel paintings of Dionysius would provide significant new information about him, as an icon painter, which is otherwise unobtainable from the sparse literature. The availability of such analytical results, as discussed in the previous chapter, would be extremely helpful for better understanding of his painting technique and the substances that he used, including, pigments, binders and varnishes (Daniilia et al. 2002, p. 807). The aim of this research was to determine the characteristics of the structural materials and his painting technique.

The first crucial step was to set the questions about Dionysius' painting technique that needed to be answered, as followed:

- Which were the constituents of the ground layer?
- Did he use bole for the gilding? If so, which were the ingredients of the bole?
- Which were the pigments that he used for each panel painting? Identify of the color palette of the painter.
- Which was the binding media for the pigments?
- Which was the binding media for the ground layer?
- Was there any combination of pigments with the varnish layer?
- Which kind of varnish did he use?
- Were any changes identified in Dionysius' drawning?
- Were any painting details incomprehensible because of the current state of preservation?

Before deciding on the analytical techniques to start providing answer to these questions it was necessary to set an analytical scheme (**Table 6**) for the resynthesis of the construction technique of Dionysius's panel paintings.

Table 6. Analytical scheme for the resynthesis of the construction technique of paintings (Kouloumpi 2016, p. 54)		
Imaging Techniques & X-Rays	→	Detection of visible & invisible elements
Cross Sections & Microchemical Tests	→	Stratigraphy & indication of materials
Elemental Techniques	→	Inorganic materials (i.e. pigments)
Molecular Techniques	→	Organic & inorganic Materials (pigments, binder, varnish)
Separation Methods	→	Organic materials (binder, glues, varnish)

The second step of setting the research protocol was to determine which of the techniques were able to be implemented in situ for these four panel paintings, and for which techniques the sampling was a necessity. It was decided that Multi-Spectral imaging techniques and X-radiography could not be performed in situ. Instead, Visible, IR and UV photography and micro-photography, digital microscopy and portable XRF were all viable options for in situ analysis. Furthermore it was decided to take some samples in order to examine the stratigraphy, and to identify inorganic and organic materials (**Fig.38**).

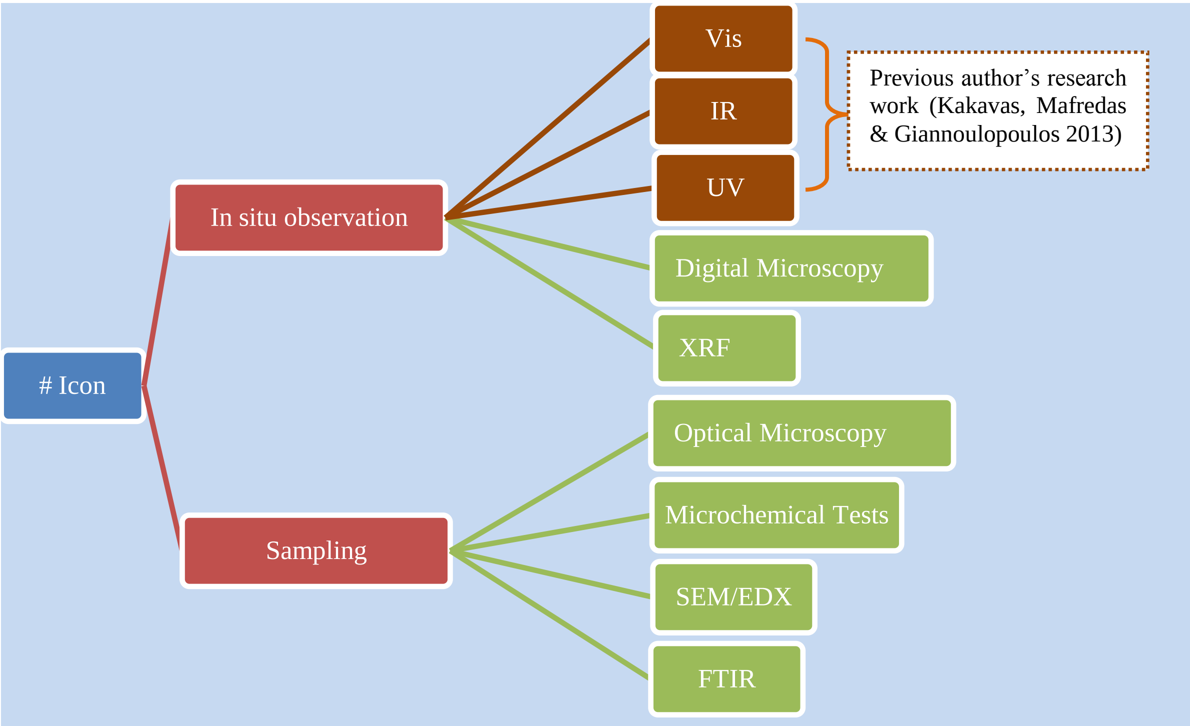


Fig. 38 The research protocol about Dionysius' panel paintings *(personal archive Th. Mafredas)*

A crucial step, concerning the sampling procedure was to check the availability of various research institutes and physicochemical laboratories that would undertake the arduous task of preparing the samples and examine them.

After the research protocol was set up, it was necessary to start the procedure by receiving the appropriate permission for sampling from the Ministry of Culture (***Appendix 1***). Sampling is defined as the process of selecting and collecting the sample for analysis (Derrick, Stulik & Landry 1999, p. 16), and consists of two steps: the sampling design and the implementation. The purpose of the first step is to determine how to obtain a representative sample or set of samples related directly to the analysis question. The second step involves the actual removal and preparation of the samples with the goal of avoiding sample loss and contamination (Derrick, Stulik & Landry 1999, p. 16).

The permission process is quite difficult and time consuming because of the ethical parameters and the bureaucracy, all related to the procedure, the obligations restrictions on sampling from artifacts for research and educational purposes. As can be understood, removing material from an artwork can be a complicated process since the integrity of the project may be jeopardized, so the questions, for such a process to be accepted, must be important and contribute to the history of art. In this case, sampling is allowed exclusively from areas which are already damaged, in order to avoid disfiguring of the painting, and not from entire areas of the artifacts (Johnson & Packard 1971, p. 148). The procedure includes an application form including the relevant questions to the various departments of the Ministry of Culture, an application to the institutions that hold the artifacts in their possession and, finally, the consent or not of all the involved services. All this bureaucracy results in a time-consuming process, and approval or denial of the sampling can take as much as six months –or even more- to be granted.

3.2. Digital Microscopy and macro-photography

Photographic methods in the spectrum of visible light were applied; more specifically, macro-photography with tangential incident radiation was used, and at magnifications up to 10x in order to identify some special features (Alexopoulou & Chrysoulakis 1993, pp. 127-128) which characterized Dionysius’s painting method. Consequently, the efforts focused on areas where particularities appeared (Mairinger 2004, pp. 15-16) regarding to Dionysius’s painting method. Strong radiation was used in the visible range of the spectrum that hit the surface almost in a parallel manner, forming a 5-10° angle (Kakavas, Mafredas & Giannoulopoulos 2013, p. 318; Alexopoulou & Chrysoulakis 1993, p. 127).

Digital visible microscopy was performed in specific points of the painting surfaces using a portable digital microscope, which provided information about the technical characteristics of the panel paintings, while the areas of sampling were recorded. 57 points were examined (some of which had already been included in the author's previous research work on the same panel paintings in 2012) on the four (4) panel paintings, regarding the decoration, the gilding and the painting technique, while traces from the initial drawing also identified (Kakavas, Mafredas & Giannoulopoulos 2013, pp. 320-321).

Instrumentation

Optical observation and photographic documentation was achieved using a digital camera Nikon Coolpix L120 equipped with a Nikon R21x wide optical zoom lens 4.5-94.5mm. Digital microscopic observation was achieved using a portable digital microscope DinoLite AM 413T in two magnification categories.

3.3. Infrared Reflectography

The penetrating ability of infrared radiation captured details that were invisible in the visible spectrum, as they were covered by translucent varnish due to deterioration in time, helping at the same time to identify earlier interventions. The varnish of the panel paintings, which has been polymerized due to aging, appeared in the infrared radiation as colorless and transparent. Thus, information on the structure of the underlying layers of color layers was collected. Furthermore the application of IR photography focused on detecting the original drawing as well as the initial stages of the manufacturing process (Kakavas, Mafredas & Giannoulopoulos 2013, p. 322).

Instrumentation

IR and UV photography was achieved using a digital camera EOS 50/50E with a Canon Zoom Lens EF-S 28-80 mm with Hoya Infrared R72 (52mm) filter in 720nm (NIR zone) and B+W (37mm) UV (403) Black filter. At this point, it should be noted that UV and IR photography has been performed during the authors' previous research work on the same panel paintings in 2012 (Kakavas, Mafredas & Giannoulopoulos 2013).

3.4. X-Ray Fluorescence (XRF)

The XRF technique, as discussed above, is very important in the study of materials, as it is a powerful analytical tool for the spectro-chemical determination of almost all the elements present in a sample (Janssens 2003, p. 365). With the use of portable equipment, tests can be run in situ without a necessity to move the artifact from its original place (Križnar et al. 2008, p. 1). The four (4) panel paintings were analyzed in 56 points, trying to examine different colours and tonalities, shadows and lights in order to record Dionysius's colour palette. The pigments used by Dionysius were recognized on the basis of characteristic chemical elements from the XRF spectra of analyzed points. The elements were identified by the energies of their characteristic X-ray peaks. Furthermore the XRF technique does not serve to identify organic materials, because it does not detect elements with Z lower than 13 or 14 (Mantler & Schreiner 2000, pp. 3-4).

Instrumentation

In situ elemental analysis was performed, by the author and his supervisor Dr. Eleni Kouloumpi using a Brucker Tracer III SD set up portable X-ray fluorescence spectrometry system, with a beam diameter of 3mm; data quantification was made using S1PXRF software by Dr. Eleni Palamara. The apparatus consists of an unfiltered low-energy excitation mode (high voltage set at 15 kV and current of 24 μA) for the analysis of major and minor elements with an atomic number (Z) between 11 and 26, and an Al/Ti filtered (0.012 inches Al plus 0.001 inches Ti) high-energy excitation mode (high voltage set at 40 kV and current of 12 μA) for the analysis of minor and trace elements with an atomic number Z>26. The collection time of each measurement was 60 seconds.

3.5. Sampling

Samples were taken, by the supervisor Dr. Eleni Kouloumpi from damaged areas of the four (4) panel paintings, as it was previously noted, and were divided in two categories for three kinds of analysis techniques: those which could be examined by microscopy (OM and SEM/EDX), those which could be examined by spectroscopic techniques (FTIR) and those could be examined by separating methods (GC-MS, HPLC).

The samples for microscopy were in the form of cross-section from two different points of each panel painting in order to investigate their stratigraphy i.e. the paintings layers and the gilding techniques.

The samples for spectroscopic technique were powder samples from the gesso preparation layer and from the varnish layer in order to identify the kind of gypsum used for preparation, the proteinaceous media, and the kind of the resins that were used for varnish coating respectively. Thus, one (1) powder sample from gesso preparation and one (1) powder sample from varnish layer were taken from each panel painting. From one specific point in panel painting #2 a varnish removed with acetone swab was obtained. A dilution process was then performed to obtain the varnish and enable its characterization.

The samples for separating methods were also powders from the gesso preparation and from paint layers in order to investigate the type of organic substances used in each layers. From each panel painting, one (1) powder sample from the gesso preparation and one (1) powder sample from varnish layer were taken.

At this point, it should be noted that, during the sampling process, it was found that the painting layers were very thin, with the exception of panel painting #3 where the paint layer was much thicker compared to the other three (3) panel paintings.

The sample for the cross-section was removed under the digital microscope, gradually cutting down into the gesso layer below the paint. The sample was lifted out with little tongs and spatulas, and transferred to a microscope cup. On this cup, identification of the sample was written (Johnson & Packard 1971, p. 149). The sampling area was recorded and photographed before and after the sampling, while a documentation spreadsheet, contained the number of the sample, the number of the panel painting, the description of sampling area, the purpose of the analysis, the chosen technique, and comments, was created.

3.6. Optical Microscopy and Microchemical Tests

OM often defined LM as well, refers to the observation under visible and ultraviolet light. A plethora of information can be acquired regarding both the stratigraphy and the composition of panel paintings through OM applications on particles (powders, pigments) or multi-layered samples. The identification is based on observations regarding the color, size, shape, opacity, refractive index measurements, extinction, optic sign, interference figures etc (Kouloumpi 2016, p. 128).

Prior to OM observation, samples in the form of particles are usually mounted on a microscopic slide using one of the suitable, commercially available, permanent mounting mediums. Multi-layered samples are usually cast into small polyester blocks and ground to reveal a cross-sectional presentation. These cross sectional samples may be then cut off with microtomes to produce thin cross sections, usually varying between 1-20μm depending on the microscopic technique to be applied and the nature of the sample (Kouloumpi 2016, p. 129).

Samples from Dionysius's panel paintings were taken either from the edges of the painting or from damaged areas; these would appear to be logical areas to sample in order to avoid disfiguring the painting (Johnson & Packard 1971, p. 148). The samples were mounted on plastic, and a polyester resin, Nosordyne, with its catalyst made by Neotex Company, was chosen because it was inexpensive and readily available locally. This may not be the only or best resin for this type of work, but it does have some definite advantages. It sets fairly rapidly from the bottom up, which makes it easy to position samples for cross-sections, and it is not necessary to cure this resin with heat. The polishing was done by hand at first, then on a wheel, using silicon carbonate 3M 'wet-or-dry' papers of various grades (Johnson & Packard 1971, pp. 149-150; Magrini, Bracci & Sandu 2013, p. 195; Derrick et al. 1994, pp. 231-240; Weilhammer 2007, pp. 50-52).

During OM were applied microchemical tests in order to have a first perception about the type of binding medium. Staining methods constitute a promising approach to the study of organic materials in panel paintings, like proteinaceous binding media, drying oils, waxes and resins. Their main advantage is that they allow the visual localization of analytical information on the layered structure of a paint section and they are a relatively low – cost method. The staining of cross-sections methods takes advantage of the proteins property to bind selectively to some organic colorants, like Noir amide. The dyes are directly applied on paint cross sections and their observation is done with reflectance light microscopy (Terlixi, Doulgeridis & Ioakimoglou 2006, pp. 1-2).

Micro chemical tests indicate the reaction between the materials, shown by the changes in colour, shape or by precipitation of particles, which can be observed by the microscope. Although it can be characterized as a destructive technique, a quick result can be obtained and it can be useful for the identification of the materials without expensive instrumentation. Spot tests are very important for primary examination. They can be in acid and alkaline environment. These kinds of tests can be used to detect the presence of organic substances, and through it to have a first perception of the artist's painting technique (Abd El Salam 2011, pp. 209-210).

Instrumentation

The technique was performed in the National Gallery of Athens' Laboratory of Physicochemical Research by Agni-Vasileia Terlixi. The apparatus for Optical microscopy consists of a Leica DM/LM Microscope with a double source of visible and UV light and integrated DC 300F infrared camera (Terlixi, Doulgeridis & Ioakimoglou 2006, p. 2). For grinding, a Stuers Labopol 5 stringing wheel was used with 3M sandpaper of various grades, n. 200, 500, 1200, 2000 and 4000. The sample was photographed examined in reflected Vis and UV light for the following: colour, particle size, shape, pigment/binding medium ratio, as well as for the thickness of paint layers, admixtures of pigments and paint layer stratigraphy. This offers a useful 'pictorial' guide when interpreting data from elemental analyses (Westlake et al. 2012, p. 1417).

For microchemical tests it was used Naphthol Blue-Black 10B, known also as Amido Black or Noir Amide (NA), in solutions of varying pH (ph2 and ph3), which introduce by Martin in 1975 (Martin 1977, pp. 63-64). It is one of the common stains currently used in conservation for distinguishing different proteinaceous materials. The blue positive staining is due to an acid-basic reaction with a protein's functional groups. It can be formulated in three different solutions according to the pH AB1, acidic; AB2, moderate acidity; AB3, neutral (Sandu et al. 2012, p. 864), and can be used to obtain some differentiation between various proteins (Martin 1977, pp. 65-66). The reagent applied on the sample using a micro-pipette. The waiting time for the reaction was about 10 minutes. After that, the sample was then rinsed out with acetic acid (5%) to remove reagent residues and finally the samples' observation was done with reflectance light microscopy.

3.7. Scanning Electron Microscopy/Energy Dispersive X-rays spectroscopy

Scanning Electron Microscopy is used in the field of panel painting investigation as an imaging tool for the topographical study of a sample, facilitating magnifications of 10^5 or even higher. SEM is basically used combined with EDX for the stratigraphic elemental analysis of the various inorganic materials (Kouloumpi 2016, p. 137).

The samples are usually covered with carbon powder to avoid energy charging by electrons. Furthermore, applying SEM/EDX technique made it easy to investigate the layers of the samples, to recognize the quality of the work -especially for gesso preparation, and to identify the ingredients constituting the bole layer and the different pigment layers, as well as the gold leaf, used for the gilding technique.

The technique was performed at the National Center for Scientific Research (NCSR) "Demokritos" by Dr. Ioannis Karatasios, researcher at NCSR Demokritos, Departmnet of Materials Science, and at Archaeometry Laboratory of the Department of History, Archaeology and Cultural Resources Management in Kalamata by the author, with the assistance of Dr. Eleni Palamara.

Instrumentation

The samples were pre-coated with a thin layer of conductive carbon powder deposited on their surface using an appropriate apparatus manufactured by Balzers Company (model CED 030, INN-NCSR "D"), for the ionization the sample with carbon powder (Mastrotheodoros 2016, p. 34).

The apparatus for scanning electron microscopy with Energy Dispersive X-ray (SEM/EDX), performed in the University of Peloponesse, at Department of History, Archaeology and Cultural Resources Management in Kalamata, consists of a Scanning Electron Microscope (SEM) by JEOL (JSM-6510LV) coupled with EDX (Oxford Systems). The analytical data were obtained by INCA software; the analysis were conducted at 20 kV accelerating voltage (Palamara et al. 2016, p. 139), under different magnifications.

The same samples were also examined at NCSR "Demokritos" using a SEM/EDX device of FEI Company, model Quanta Insppect D8334, INN –NCSR "D", integrated with super ultra thin window (sutw) EDX detector. The apparatus was operating under voltage conditions of 25kV, so that small pieces of data could be detected, while sample surfaces were examined using backscatter electrones (BSE-Backscattered electron mode) (Mastrotheodoros 2016, p. 34).

At this point it should be noted that BSE energy depends from the atomic number of the elements causing their scattering. This is the reason that BSE images contain relevant information to the composition of the investigated surfaces (Mastrotheodoros 2016, p. 34).

Finally, it is noted that quantitative elemental recommendations have been received from different layers of the samples, such as pigment layers, bolo, and gold leaf layer, gesso preparations, varnish and other organic layers. Data was obtained in the form of normalized (100%) elemental weight (elements, wt%) (Mastrotheodoros 2016, p. 35) (***Appendix 2***).

3.8. Fourier Transformer Infrared Spectroscopy

FTIR spectroscopy, as discussed above, is an analytical technique that utilizes the infrared radiation of the electromagnetic spectrum to excite molecular motions (Derrick, Stulik & Landry 1999, p. 8), which are unique for each molecule. Thus, as all compounds absorb radiation in multiple regions of the spectrum, the information on molecular activity in each region provides complementary data for material characterization (Derrick, Stulik & Landry 1999, p. 4).

Each of the samples was powdered together with potassium bromide (KBr) which is an IR transparent material, and pressed into a clear pellet for analysis (Derrick, Stulik & Landry 1999, p. 52). To prepare the pellet, a small amount of the sample was first placed in a clean agate mortar and grounded with a pestle to produce particles that are smaller than the wavelength of IR radiation. To determine when the sample was grounded finely enough, a pestle used to form a smear on the mortar. The sample should feel slippery, should have no grit and should spread out in a waxy film. After the sample was grounded, it was uniformly mixed with a powdered matrix that has a broad window for transparency in the mid-IR region, such as KBr (Derrick, Stulik & Landry 1999, p. 54).

The sample from a specific point in panel painting #2, which was obtained through dilution, was examined on gold plate. The sample was placed in a micro test tube covered with a few drops of solvent, namely acetone. The test tube was agitated in an ultrasonic bath for about 30 min. A micro drop of the extracted solution was removed with a micropipette. The micro drops of the extracted solutions were examined in two different ways. A first micro drop was placed on an inert IR window, such as a gold plate. A second micro drop was dripped onto KBr powder for pressing a salt pellet. In both cases, after this process the solvent was allowed to evaporate (Derrick, Stulik & Landry 1999, p. 29). When the solvent had evaporated the two micro drops were examined by FTIR, recording the respective spectra.

At this point, it should be noted that during the process of preparing the samples, all grinding containers, such as the mortar and pestle were thoroughly cleaned with methanol, in-between samples to prevent cross-contamination (Derrick, Stulik & Landry 1999, p. 54).

The implementation of the FTIR technique and the obtained spectra from the samples allowed identifying of the kind of gypsum that was used for the gesso preparation, the resins used for varnish coating, as well as the binding medium for the paint layer. The technique was performed in the Technological Educational Institute of Athens, Department of Conservation Antiquities and works of art by Dr. Stamatis Boyatzis, an assistant professor at the Conservation Department.

Instrumentation

For spectroscopic techniques the samples were examined in Fourier Transformed Infrared Spectroscopy (FTIR). The apparatus consists of a Perkin-Elmer, Spectrum gx-FTIR system, with the appropriate software of Spectrum 5.1.

3.9. Analytical Techniques

Due to time limitation and instrument availability, specific techniques, as GC and HPLC could not be performed at this stage of research but samples have been stored for future analysis, possibly under another research framework to accommodate the specific research protocol concerning Dionysius's panel paintings.

CHAPTER 4 – RESULTS AND DISCUSSION

The four (4) Dionysius's panel paintings created by were physicochemically studied following the research protocol which developed during the current research project, as discussed above. So for all the panel paintings Imaging Techniques were applied (Kakavas, Mafredas & Giannoulopoulos 2013), 57 hit points using digital microscopy (DM), 56 hit points with XRF, 34 points for sampling for different analysis procedures and one (1) varnish sample from cotton swap.

As it has been previously mentioned, a crucial step for the developed research protocol was the sampling process. The samples were divided into two (2) main categories, cross section and powders from different constituents in order to achieve a quite big range of data. Cross sections from different areas were selected, in order to examine the stratigraphy of the paint layer and for examining the gilding technique. For material analysis two (2) powder samples were selected from gesso preparation, for GC and FTIR examination respectively, two (2) from the paint layer for chromatographic determination, and one (1) from the layer of varnish in order to identify the kind of varnish that Dionysius had used. All the samples were taken from already damaged areas (**Fig.39-42**), and depending on the examination technique, were prepared respectively, as discussed in previous chapter.

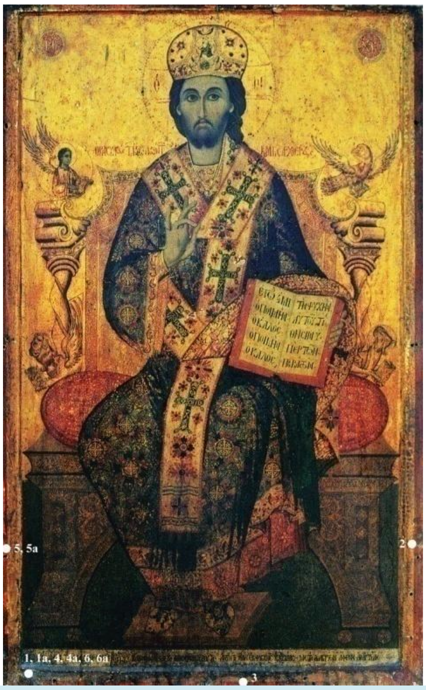


Fig. 39 Panel #1 Sampling positions *(personal archive Th. Mafredas)*

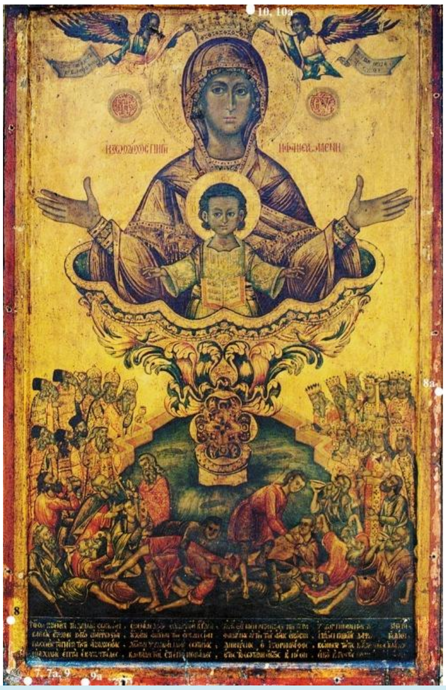


Fig.40 Panel #2 Sampling positions *(personal archive Th. Mafredas)*

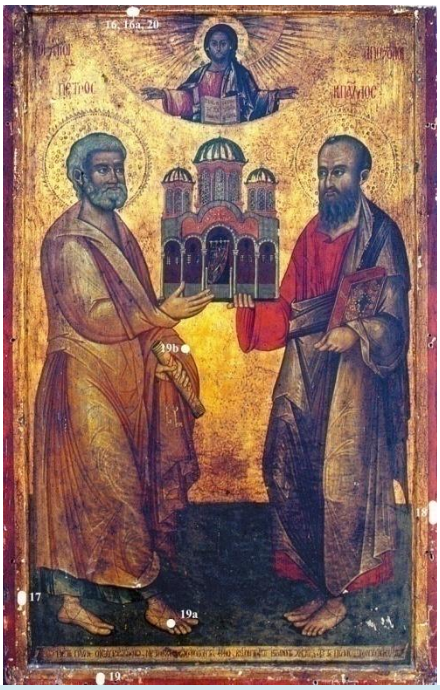


Fig. 41 Panel #3 Sampling positions *(personal archive Th. Mafredas)*

Fig. 42 Panel #4 Sampling positions *(personal archive Th. Mafredas)*

The samples were prepared for OM and SEM/EDX and for FTIR analyses, while the samples for GC and HPLC analyses were stored for future analysis (***Appendix 3***).

The investigation of the edges of the panel paintings and the cracks in wooden planks showed that no intermediate fabric was used beneath the painted surface (Franceschi, Nole & Vassallo 2013, p. 22), a feature that was verified by the microscopic techniques. IR photography contributed to the detection of some specific features of the drawing and data that were not readable and easily distinguishable by Vis imaging. The application of DM provided data about decoration and micro-decoration, painting layers, construction and gilding techniques. The XRF results were helpful in identifying the inorganic pigments by the intense edges of hit points' spectra. OM provided data about stratigraphy, painting and gilding techniques SEM provided detailed data about the layers and the techniques, used by Dionysius while the use of EDX achieved an elemental analysis of the various inorganic materials, which existed in the various layers. Finally the FTIR application helped to identify the kind of varnish and gesso preparation applied by Dionysius, while the identification of proteinaceous materials and lipids, through FTIR in combination with the microchemical tests from the samples led to a first perception about the kind of binding medium utilized.

All these results provided data in order to identify and record the painting technique of these four (4) artworks and compare Dionysius's work with his treatise: "The Hermeneia of Byzantine Art".

1. Christ as King of Kings and Great High Priest

1.1.Description

Fig.43 Christ as King of Kings and Great High Priest 1737, Dionysius, Church of Tranfiguration, Fournas *(perconal archive Th. Mafredas*

The iconography of Christ as King of Kings and Great High Priest (**Fig.43**), as painted around 1737 by Dionysius’, generally follows in general all the relevant instructions on this subject found in his earlier treatise text. Christ is portrayed seated on the throne in an upright, frontal pose, in the traditional gold-embellished prelatic vestments, a sticharion (an internal liturgical garment which covers the entire body) with maniples (garments surrounding the sleeves of sticharion) and epitrachelion (a long narrow garment which is worn around the neck), a patriarchal sakkos (the external garmnet of the Bishop’s liturgical costume) and an omophorion with crosses (a wide strip of fabric which is the distinguished vestment of the Archbishop), a royal mitre (an emblem of the Episcopal degree in the Orthodox Church), and gold shoes (Asfentagakis 2014, p. 27; Kakavas 2008, p. 205). He blesses with the right hand and his left holds an open Gospel book with text from John’s Gospel: “I am the god shepherd; the good shepherd gives his life for the sheep” (John 10:11). He is enthroned on a wooden throne bearing the four symbols of the Evangelists, the angel, the eagle, the lion and the calf, all holding Gospels, on each side of the dorsal (Kakavas 2008, p. 204; Kakavas, Mafredas & Giannoulopoulos 2013, p. 316). Finally in the gold background, over Christ’s shoulder, there is the epigram of the panel painting: “The King of Kings and Great High Priest” (Kakavas, Mafredas & Giannoulopoulos 2013, p. 316), while, at the lower part of the panel there is the dedicatory epigram written by Dionysius (**Fig.44**):

Fig.44 Christ as Great High Priest. Detail. Dedicatory inscription-Vis *(personal archive Th. Mafredas)*

“O Lord Christ, your Philanthropic by nature ears turn them to me, the priest Dionysius, who has already requested from the soul and heart, with tears forgiveness for sin”[31] (Dionysios 1938, p. 31; Kakavas 2008, p. 204).

The back side of the panel is also depicted bearing a Cross with letters forming the name of Christ and the word of victory (in Greek): IC//XC//NI/KA) (**Fig.45**).

Fig. 45 The back side of panel #1 *(perconal archive Th. Mafredas)*

[31] «Ω Χριστέ άναξ, τα φιλάνθρωπα φύσει κλίνον μοι ωτα Διονυσίω θύτη, αιτούντι ήδη εκ ψυχής και καρδίας μετά δακρύων, άφεσιν αμαρτίας» (Dionysios 1938, p. 31)

1.2. Imaging Techniques

Imaging techniques can provide information on the construction technique of a work, for underlying layers of paint that are not visible to the naked eye, while they could also ensure some significant and crucial results about the under drawing of the painter (anthivolon), as well as variation from the initial drawing.

1.2.1. IR photography

The IR photography provided detailed features of painting concerning Dionysius's under drawing. It was able to identify the intense drawing line in Christ's garments and in the Throne, along with details of the general presence of the under-drawing (**Fig.46**). The features of IR radiation allowed the identification of some details that were not easily recognizable because of the deterioration of the varnish, such as the decoration of the Sticharion, Epitrachilion and Sakkos, and the perimetric decoration of the pedestal at Christ's feet (**Fig.47**). Because of the ageing of the varnish, a discoloration through a yellow film appeared on the surface of the painting. With IR radiation we were able to identify some details in the drawing of the symbols of the evangelists, as well as the names of the Evangelists which were not visible in the Vis (**Fig.48-51**). In the same framework with IR photography, the panel painting's inscriptions and epigrams were easily read (**Fig.52**) while, at the same time, this kind of photography provided details of the drawing which were not easily distinguishable in the Vis (**Fig.53-56**).

Fig.46 Panel #1 IR photography *(personal archive Th. Mafredas)*

Fig.47 Decoration of the garments and from the pedestal *(personal archive Th. Mafredas)*

Fig.48 Evangelist .Matthew. Symbol and name
(personal archive Th. Mafredas)

Fig.49 Evangelist John. Symbol and name
(personal archive Th. Mafredas)

Fig.50 Evangelist Luce. Symbol and name
(personal archive Th. Mafredas)

Fig.51 Evangelist Marc. Symbol
(personal archive Th. Mafredas)

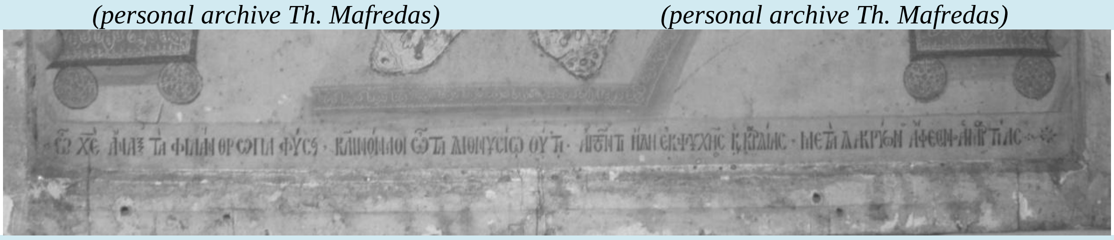


Fig.52 Dedicatory epigram of panel #1 in IR *(personal archive Th. Mafredas)*

Fig.53 Decoration of the throne
(personal archive Th. Mafredas)

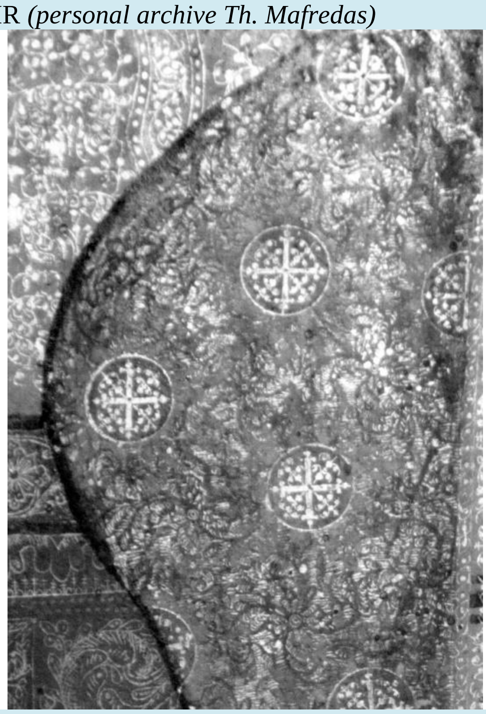


Fig.54 Decoration of Sakkos
(personal archive Th. Mafredas)

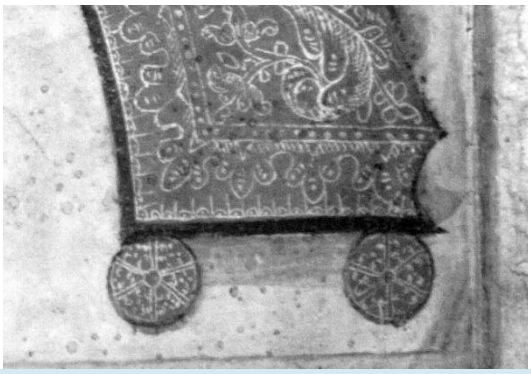


Fig.55 Traces from the drawing. Decoration to the lower part of the throne *(personal archive Th. Mafredas)*

Fig.56 Decoration of Christ's hoes and drawing traces *(personal archive Th. Mafredas)*

1.3. Microscopic Techniques

As discussed in a previous chapter (***Chapter 2.2***), microscopic techniques provide useful information on how various works of art have been constructed, as well as the type and morphology of their construction materials (Milanou et al. 2008; Hochleitner et al. 2002, pp. 2-3; Lazidou et al. 2006, p. 48).

1.3.1. Digital Microscopy (DM)

DM was applied two different times, -the first one with code DM and the second one with code St- in order to identify details about the painting and gilding technique. It was applied in 19 different points of the painting surface (**Fig.57**) using different magnifications, and the results helped to understand Dionysius's painting technology.

Fig.57 Panel #1 Digital Microscopy spots *(perconal archive Th. Mafredas)*

The DM1-3 hit points concerned a gold area with micro decoration. The investigated area was Christ's royal mitre (**Fig.58**). A dark pigment was identified over the gold layer in order to achieve the micro-decoration of the Holy Father's face (**Fig.59**) and the epigram (in Greek): "Ω Πατήρ" (**Fig.60-61**). Furthermore, with digital microscopy it was easy to identify a dark pigment for drawing the Father's fingers (**Fig.62**). The same pigment and decoration technique were also documented in St3, which was in the upper right side of Christ's throne (**Fig.63**) and in St4 in the eagle's eye (**Fig.64**). Besides the dark pigment, the use of red line for drawing and shaping was also found in this hit point. A high magnification level allowed the identification of traces from the dotted decoration of the eagle's halo in St5 spot (**Fig.65-66**) and the excellent drawing for micro-decoration, such as the Father's face in Christ's mitre in DM3spot (**Fig.67**).

Fig.58 Detail. Christ's head and Mitre *(personal archive Th. Mafredas)*

Fig.59 Details of Father's face. Magnification 60X *(personal archive Th. Mafredas)*

Fig.60 Left part from Father's epigram Detail magnification 60X *(personal archive Th. Mafredas)*

Fig.61 Right part from Father's epigram Detail magnification 60X *(personal archive Th. Mafredas)*

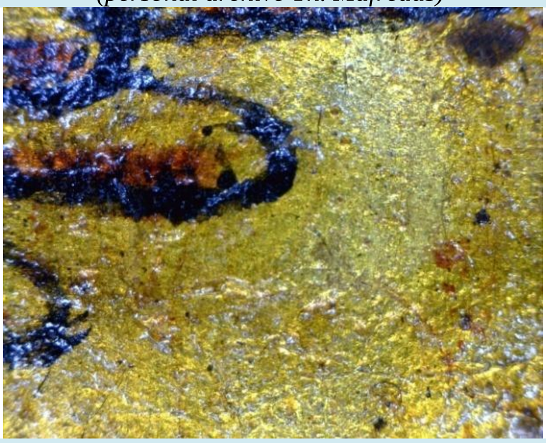


Fig.62 Detail from Father's finger. Magnification 65X *(personal archive Th. Mafredas)*

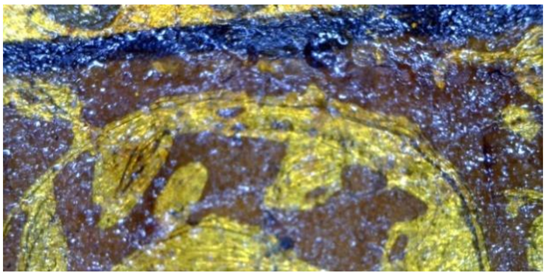


Fig.63 Upper right place of Christ's throne. Dark Pigment. Magnification 60X *(personal archive Th. Mafredas)*

Fig.64 Eagle's eye. Dark pigment. Magnification

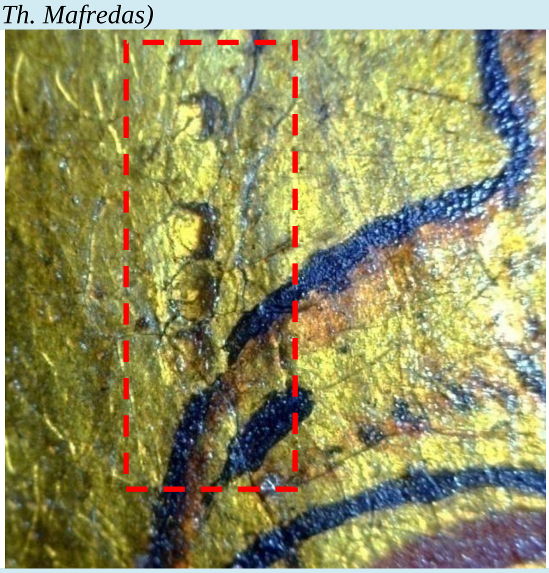


Fig.65 Detail from Eagle's dotted halo.

60X *(personal archive Th. Mafredas)*	Magnification 65X *(personal archive Th. Mafredas)*

Fig.66 Detail from Eagle's dotted halo. Magnification 65X *(personal archive Th. Mafredas)*

Fig.67 Detail from Father's face in Christ's mitre. Magnification 200X *(personal archive Th. Mafredas)*

The DM4 hit point was in the left part (**Fig.68**) of Christ's halo concerning a detail of the font and, more specifically, at the edge of the letter O which is open, giving the impression of the letter C, while it became apparent that the letter was painted over the gold layer (**Fig.69-70**). The next hit point, DM5, was in the left eye of Christ and it was significant in order to understand how Dionysius forms the eye. But, during the microscopic study in this area, a lot of varnish degradation was found, which made the eye rather unclear (**Fig.71**). The DM6 point concerned a part of the epigram "the King of the Kings" (in Greek): «Ο Βασιλεύς των Βασιλευόντων», and it was found that Dionysius has used red pigment for the letters over the gold layer (**Fig.72-73**)

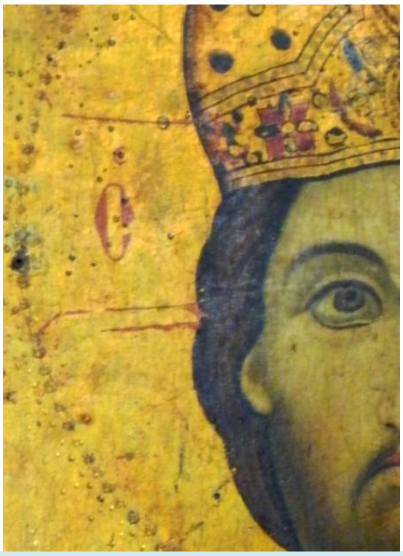
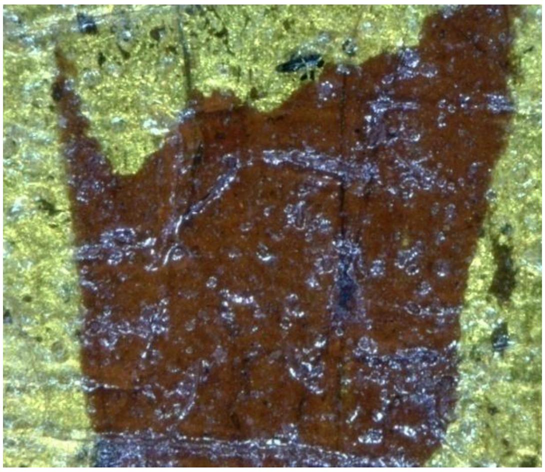


Fig.68 Detail. The left part of Christ's head *(personal archive Th. Mafredas)*

Fig.69 Detail from the letter O. Magnification 65X *(personal archive Th. Mafredas)*



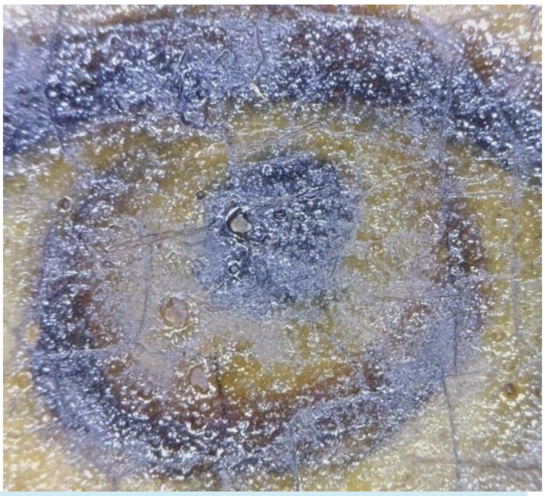


Fig.70 Detail from the letter O. Magnification 210X *(personal archive Th. Mafredas)*

Fig.71 Detail from Christ's left eye. Magnification 65X *(personal archive Th. Mafredas)*

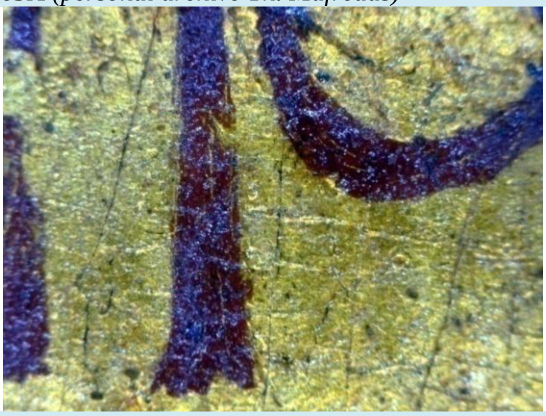


Fig.72 Part of the epigram of the Panel “King of the Kings” *(personal archive Th. Mafredas)*

Fig.73 Detail from the epigram. Magnification 60X *(personal archive Th. Mafredas)*

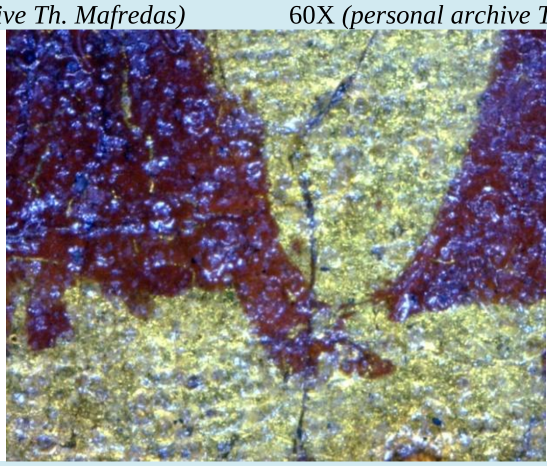


Fig.74 Detail from the epigram. Magnification 200X *(personal archive Th. Mafredas)*

The DM7-11 hit points were in Christ’s omophorion and, more specifically, in the letters on the decorated cross (**Fig.75-79**). It was observed that the dark (black?) perimetric pigment was applied over the gold layer and, this way, formed the decoration and the letters in Christ’s omophorion.

Fig.75 The Cross from Christ's omophorion. The decoration of the cross with letters *(personal archive Th. Mafredas)*

Fig.76 The letter Φ from the Cross decoration. 60X *(personal archive Th. Mafredas)*

Fig.77 The letter X from the Cross decoration. 60X *(personal archive Th. Mafredas)*

Fig.78 The letter Φ from the Cross decoration. 60X *(personal archive Th. Mafredas)*

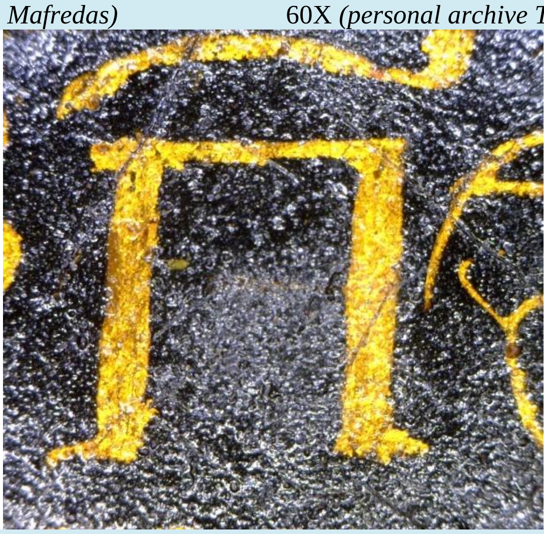


Fig.79 The letter Π from the Cross decoration. 60X *(personal archive Th. Mafredas)*

From DM12 up to DM14, the use of microscopy helped to identify features of the construction technique. Thus, the DM12 (**Fig.80**), in the middle of Christ's omophorion, below his right hand, gave a first impression about the thickness of the layers, which were very thin (**Fig.81-82**). This impression was verified during the sampling process and the examination of the cross section by OM and SEM. The same hit point gave the impression that the pigment has been applied over the gold layer

Fig.80 Detail from DM12. In the middle of Christ's omophorion, under his left hand *(personal archive Th. Mafredas)*

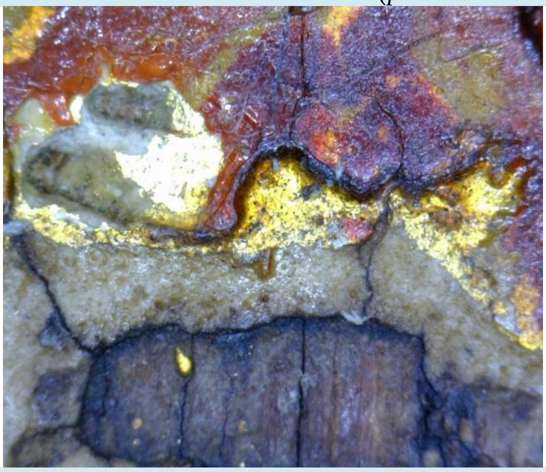


Fig.81 The thickness of the layers in DM12. Magnification 60X *(personal archive Th. Mafredas)*

Fig.82 The thickness of the layers in DM12. Magnification 200X *(personal archive Th. Mafredas)*

Furthermore in DM13 (**Fig.83**) and St1 (**Fig.84**), in the left vertical frame of the panel, it was found that there was a very thin layer of bolo (**Fig.85-87**).

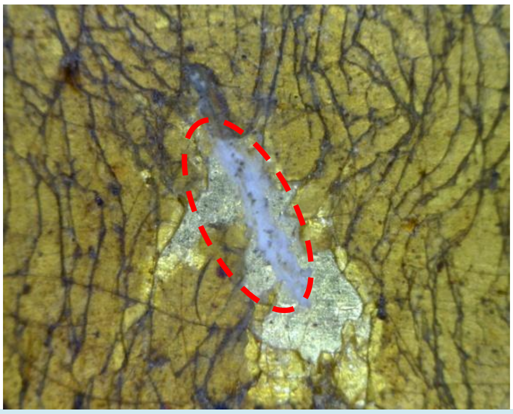


Fig.83 DM13. Magnification 60X. suspicion of bole layer *(personal archive Th. Mafredas)*

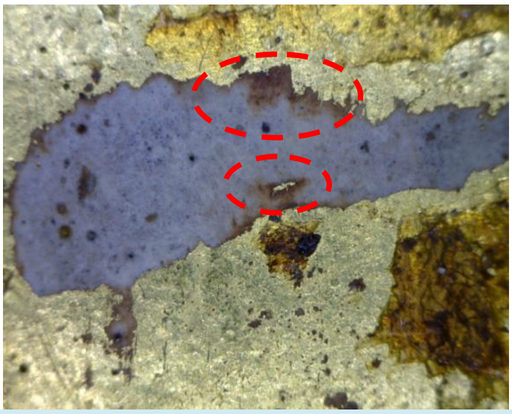
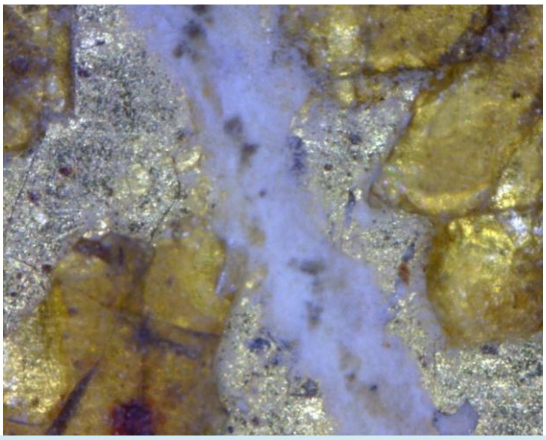


Fig.84 St1. Magnification 60X. Thin gold layer with a dark yellow substrate. Suspicion for bole layer *(personal archive Th. Mafredas)*



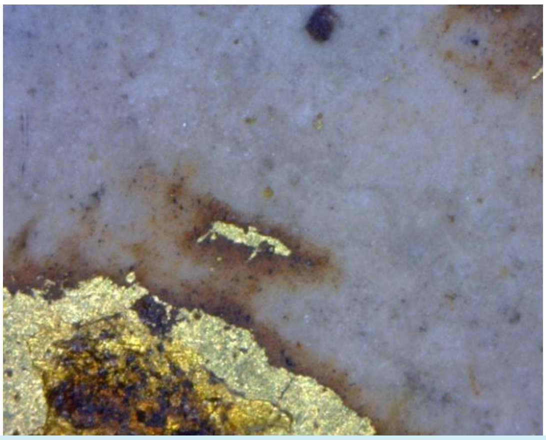


Fig.85 DM13 detail. Magnification 200X. Presence of some pigment grains. Suspicion for bole layer *(personal archive Th. Mafredas)*

Fig.86 St1 detail. Magnification 200X. Substrate below the gold leaf and presence of some pigments grains. Suspicion for bole layer *(personal archive Th. Mafredas)*

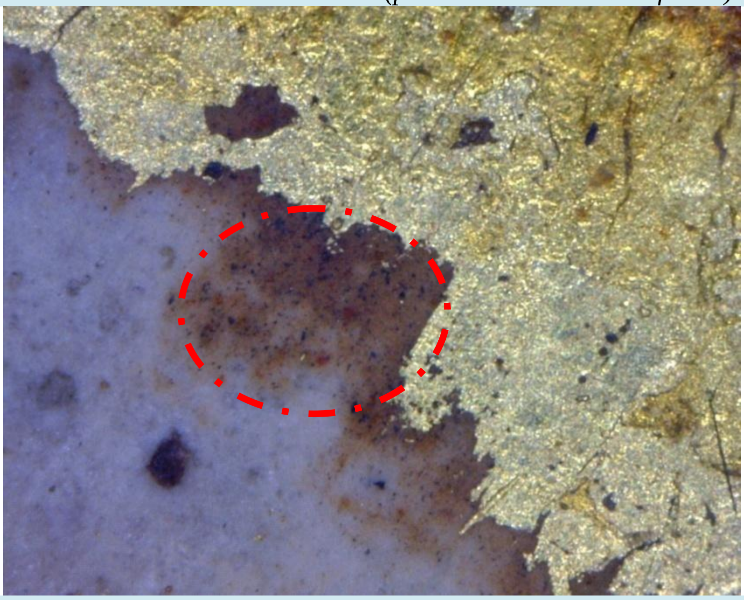


Fig.87 St1 detail. Magnification 200X. Substrate below the gold leaf and presence of some pigments grains (among them some red grains). Suspicion for bole layer *(personal archive Th. Mafredas)*

Furthermore, the DM14 (**Fig.88**), in the upper middle, in the horizontal side of the panel, examined an area with red pigment and found that there was a very thin layer of red pigment and gesso preparation (**Fig.89-90**).

Fig.88 The DM14 *(personal archive Th. Mafredas)*

Fig.89 Detail DM14, the gesso and the pigment layer, magnification 60X *(personal archive Th. Mafredas)*

Fig.90 Detail DM14, the gesso and the pigment layer, magnification 200X *(personal archive Th. Mafredas)*

Finally, the construction technique was also identified also with St2 (**Fig.91**), in the lower part of Christ's patriarchical sakkos, which documented the painted surface which consisted of gold and green painting. A thick layer of varnish was observed, as well as a thin gold layer and green pigment over the gold layer (**Fig.92-94**).

Fig.91 The St2 *(personal archive Th. Mafredas)*

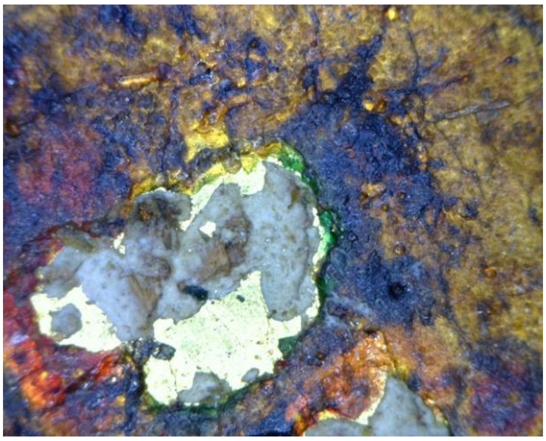


Fig.92 Detail, the St2. Magnification 60X *(personal archive Th. Mafredas)*

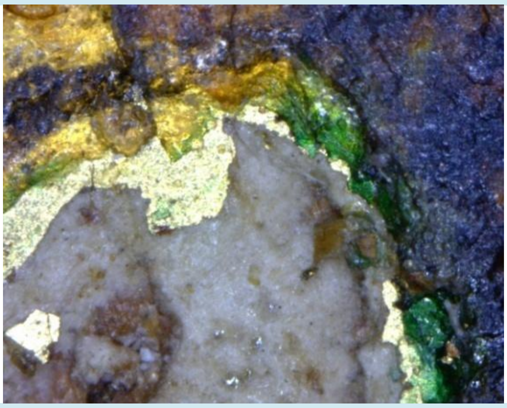


Fig.93 Detail, the St2. Magnification 200X *(personal archive Th. Mafredas)*

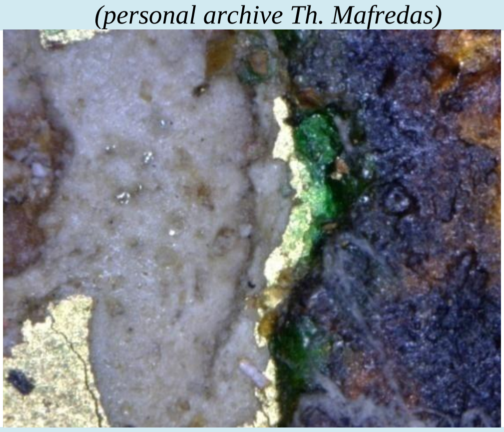


Fig.94 Detail, the St2. Magnification 200X *(personal archive Th. Mafredas)*

1.3.2. Optical and Fluorescence Microscopy

For applying OM, five (5) different samples in cross section from were detached from the panel (***Appendix 2***); three (3) of them were taken for studying the painting layer and two (2) of them for studying the gilding technique. During the sampling process, it was found that all the layers were very thin so, out of all the samples, only three (3) of them managed to be examined in OM: samples 3 and 4 for painting layer, and sample 6a for gilding technique. All of the samples were examined both in Vis and in UV.

The first sample (#3) which was examined using OM was taken from the lower part of the panel and, more specifically, from the horizontal frame of the painting in order to examine the painting layer (**Fig.95-96**).

Fig.95 Sampling area for sample #3
(personal archive Th. Mafredas)

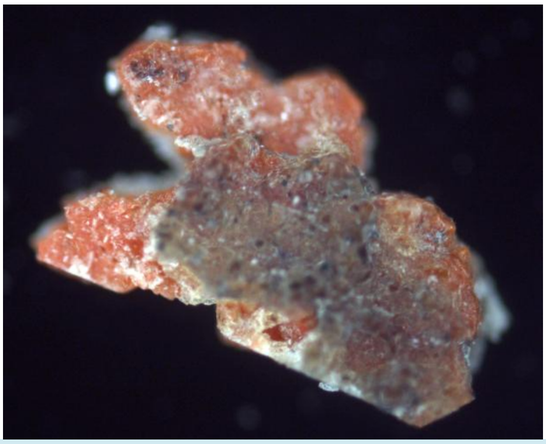


Fig.96 Sample #3 before preparation for OM
(personal archive Th. Mafredas)

The sample examined with OM, and it was found to consist of three (3) different layers (**Fig.97**). The first layer was an orange painting layer with some white grains, and the thickness of this layer was about 40μm. Over this layer, another layer was found, whose thickness was measured at about 6μm and its color was red with the presence of some red pigment grains. The third layer was organic, and its thickness was 4-10 μm. The sample was also examined under UV light in 50x magnification, and the two painting layers, the orange and the red, could clearly be distinguished (**Fig.98**).

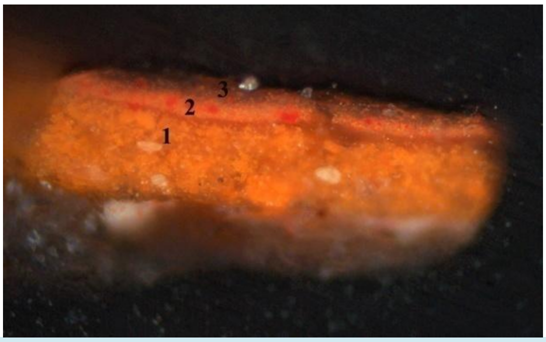


Fig.97 The layers of the sample. Magnification 50X *(personal archive Th. Mafredas)*

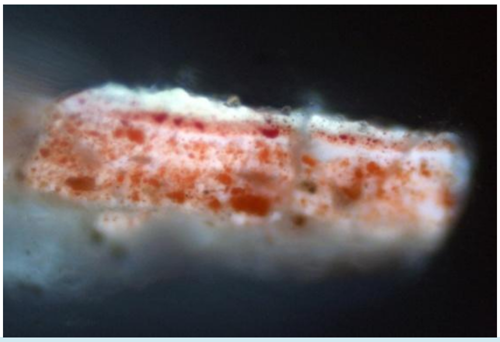


Fig.98 The sample under UV radiation *(personal archive Th. Mafredas)*

The grains of the pigments were also discerned, as well as the differentiation in grain size. Between the two painting layers a thin dark layer was detected, which distinguishes the two painting layers. When examining the sample under UV light, this thin dark layer appears as a thin white line between the two painting layers (**Fig.99-100**).

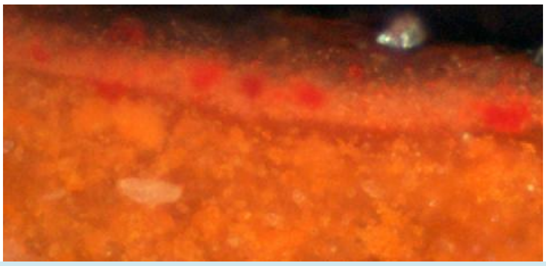


Fig.99 Detail the dark line between the two pigment layers *(personal archive Th. Mafredas)*

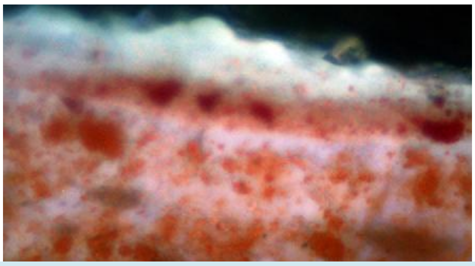


Fig.100 The same dark line of previous photo under UV radiation. Appears as a white thin line is in the middle of the two pigment layers *(personal archive Th. Mafredas)*

During the stratigraphy study of the sample, the presence of gesso is not recorded preparation.

The second sample, (#4), which examined by OM, was from another spot of the same horizontal frame of the panel (**Fig.101-102**), as sample 3, in order to examine also the painting layer.

Fig.101 Sampling area for sample #4

Fig.102 Sample #4 before preparation for OM

(*personal archive Th. Mafredas*) (*personal archive Th. Mafredas*)

During the microscopic examination, it was found that this sample consisted of eight (8) different layers (**Fig.103**). The first one (1) could be characterized as a layer of unspecified composition and texture, which could correspond to the preparation layer. While in OM, it was not easy to determine whether this layer came from gesso preparation, during SEM/EDX analysis, it was confirmed that this layer was the preparation layer. Over the first layer, a very thin organic layer was found which could be a kind of glue or binding medium for the pigments. Over the organic layer, two different painting layers were recorded: the first consisted of orange and white translucent pigment grains, with a thickness of up to 35μm, and the second one of red and white translucent pigment grains, with a thickness of about 5 up to 6 μm. Over the pigment layers, an organic layer whose thickness was about 30μm was found, as well as a non-continuous layer of particles, another organic layer whose thickness was about 10μm and, finally, anon-continuous layer of unspecified composition. Examining the sample under UV excitation (**Fig.104**), enabled the further classification of the micro-stratigraphic structure, especially of the upper layers which were found over the painting layers. Old varnishes were clearly revealed through their aging–increasing blue –white color fluorescence.

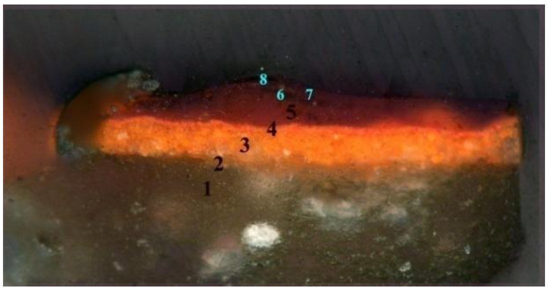


Fig.103 The layers of the sample. Magnification 50X (*personal archive Th. Mafredas*)

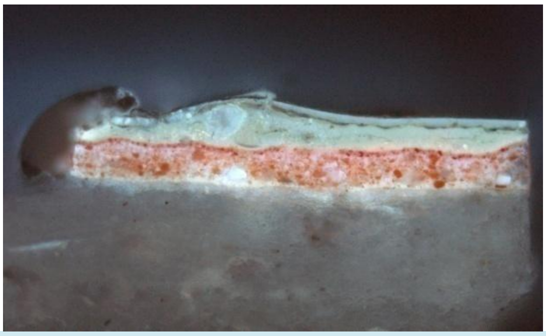


Fig.104 The sample under UV radiation (*personal archive Th. Mafredas*)

The third sample (#6a) which was also examined by OM was taken from another spot in the same area as the previous sample (4) in order to examine the gilding technique (**Fig.105-106**).

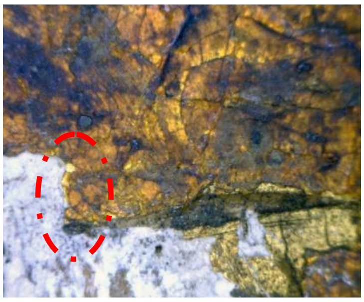
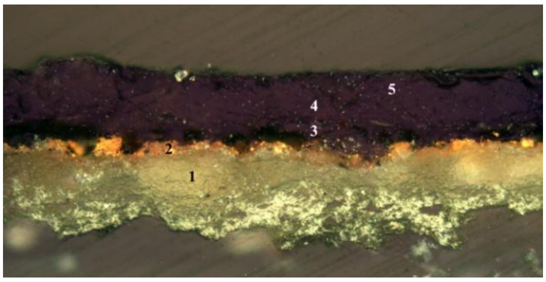


Fig.105 Sampling area for sample #6a *(personal archive Th. Mafredas)*

Fig.106 Sample #6a before preparation for OM *(personal archive Th. Mafredas)*

During the microscopic examination five (5) different layers were identified (**Fig.107**). The first (1) was an opaque layer of unspecified composition that could be part of the gesso preparation. Over it, a non-continuous, intermittent gold layer was found. In certain spots underneath the gold leaf, a few pigment grains were observed which could be assumed as the presence of some kind of bole layer. More specifically, these pigment grains from red and ochre pigment were observed in a 50x magnification during exanimation under Vis light (**Fig.108**)



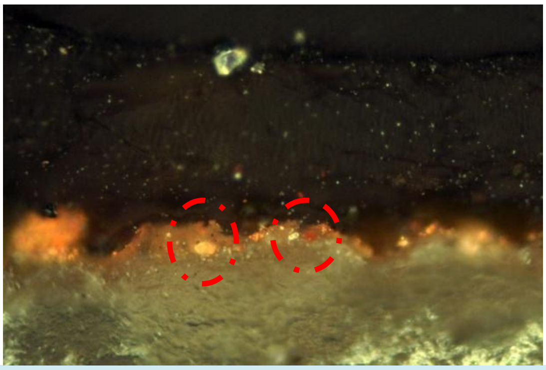


Fig.107 The layers of the sample. Magnification 20X *(personal archive Th. Mafredas)*

Fig.108 Pigments grain under magnification 50X *(personal archive Th. Mafredas)*

Over the gold layer, three different layers were observed: the first was organic, the second was a pollutant layer, and the third was also organic. The sample was examined under UV excitation; (**Fig.109-110**) the layers over the gold leaf were more easily observed and identified because of the increase in blue-white fluorescence. Furthermore, it was observed that these three organic layers presented some kind of cracks in-between, which made them easily distinguishable.

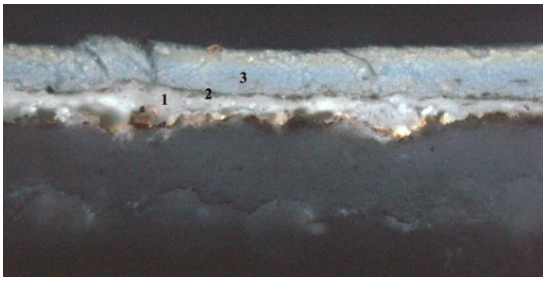


Fig.109 Three different organic layers over the gold leaf. OM under UV radiation, magnification 20X *(personal archive Th. Mafredas)*

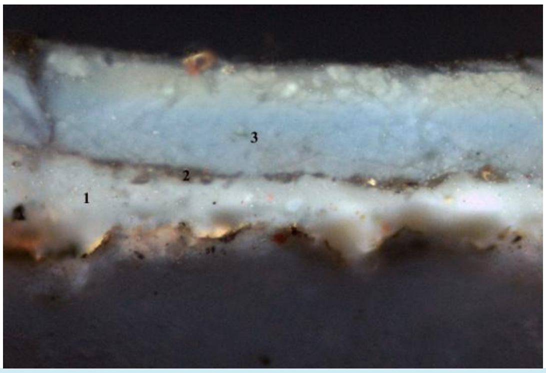


Fig.110 Detail. OM under UV radiation, magnification 50X *(personal archive Th. Mafredas)*

This feature supports the hypothesis that there could have been a previous attempt at conserving the panel painting by applying a new varnish layer over the initial one. This could also justify the layer of entrapped pollutant particles between the two organic varnish layers. In general, the sample displays a disturbed stratigraphic structure.

1.3.3. Microchemical tests

Out of the 3 samples studied by OM, only sample #4 was suitable for a microchemical test because of the thin thickness of the other samples. A specific reagent was used (Noir Amide (NA2)) in order to observe the presence of proteinaceous materials. The reagent reacted with the proteinaceous materials, and the staining of the layers may signify the presence of proteinaceous materials (**Fig.111-113**).

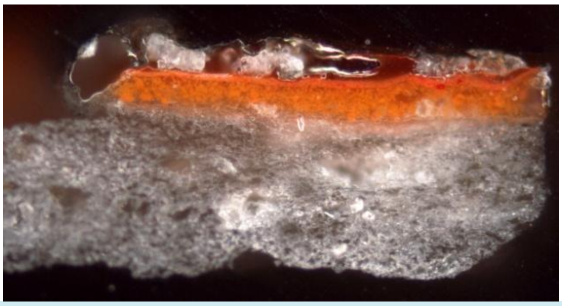


Fig.111 Sample #4 before NA2 *(personal archive Th. Mafredas)*

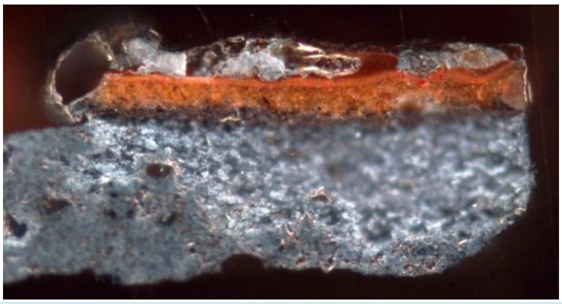


Fig.112 Sample #4 after NA2 *(personal archive Th. Mafredas)*

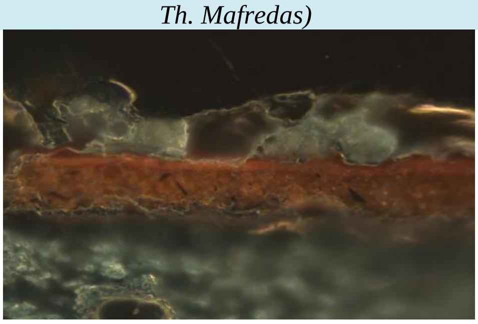


Fig.113 Detail Sample #4 after NA2 *(personal archive Th. Mafredas)*

Furthermore, it was observed that the first pigment layer displays a small quantity of proteinaceous materials concentration, in addition to what had already been observed during OM, where the presence of a fairly large concentration of binding medium was found (**Fig.114-115)**.

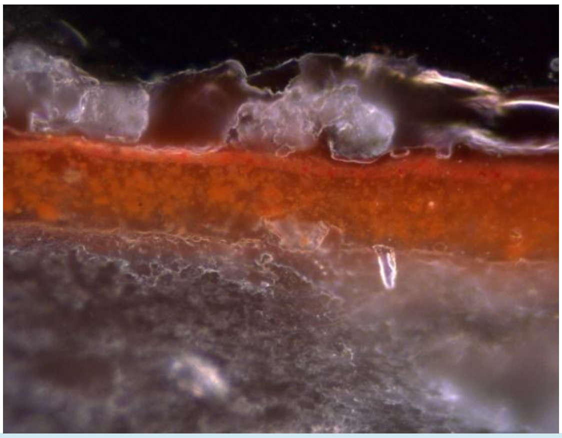


Fig.114 Detail. Sample #4 before NA2 *(personal archive Th. Mafredas)*

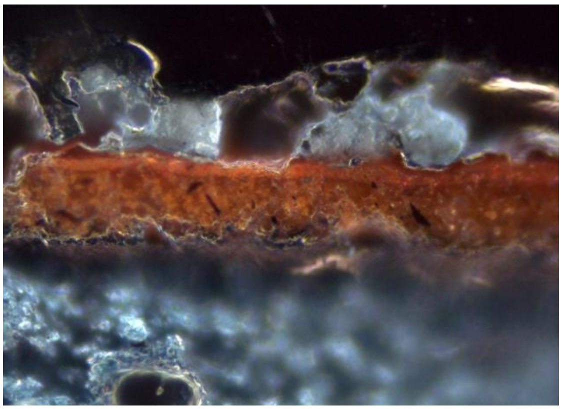


Fig.115 Detail. Sample #4 After NA2 *(personal archive Th. Mafredas)*

1.3.4. Scanning Electron Microscopy (SEM)

A magnification of 10^5, or even higher, was able to achieve a topographical study of the sample materials (Kouloumpi 2016, p. 137). Backscattered electron (BSE) images served a first hint for the identification of pigments used in different layers (Kouloumpi 2016, p. 137; Stuart 2007, p. 94; Mastrotheodoros 2016, pp. 34-35).

Upon examining sample #3 with SEM (**Fig.116**) through the BSE images, it was possible to measure the thickness of each layer (**Fig.117**) and observe the pigment grain size, to distinguish the pigment layer, and identify a tiny layer over the preparation, both of which were not detectable by OM.

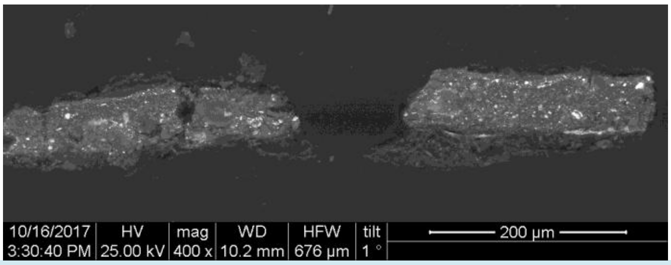


Fig.116 Sample #3. SEM *(personal archive Th. Mafredas)*

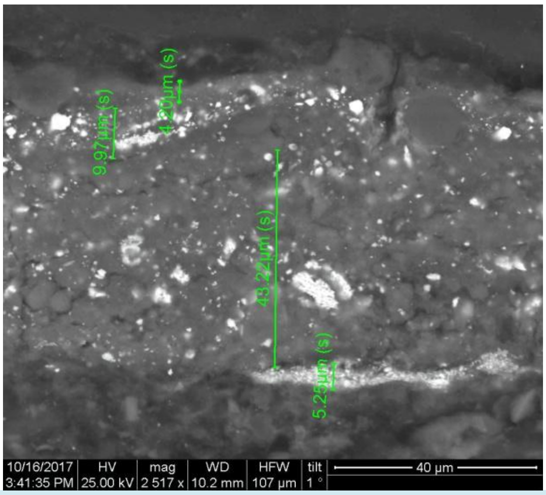
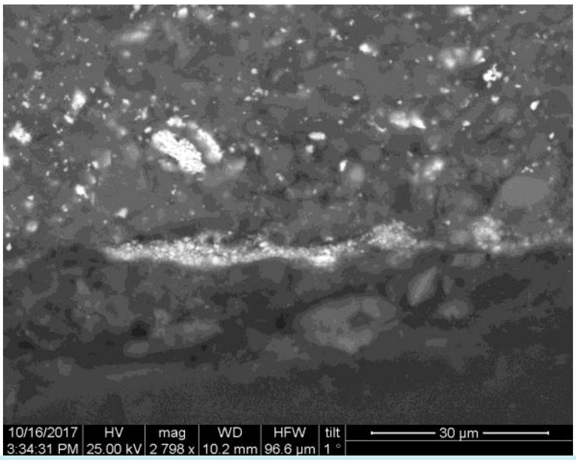


Fig.117 Sample #3. SEM. Measurements of layers' thickness *(personal archive Th. Mafredas)*

Over the gesso layer, a thin, white, non-continuous layer which consisted exclusively of Pb was observed (**Fig.118**) whose thickness was up to 5.25μm. Over it, the two different painting layers were observed, as seen in OM; the thickness of the first layer was up to 43,22μm and of the second one up to 10μm. The final, upper layer which appeared totally black and seemed to be organic was probably the varnish layer. It should be noted that this upper layer shows areas of micro-detachment from the painting layer (**Fig.119**).



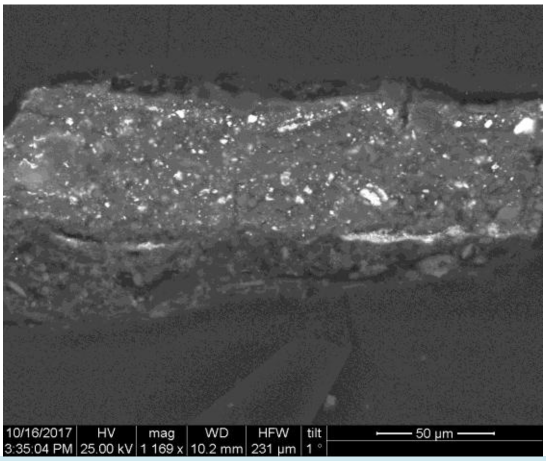
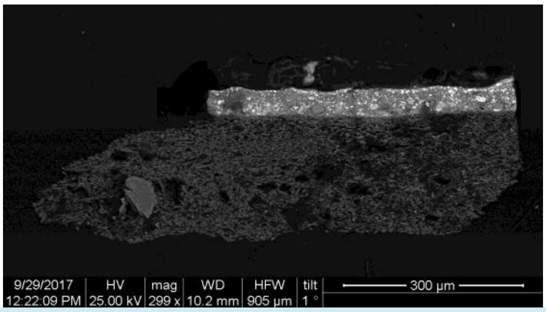


Fig.118 Details from a non-continuous pigment layer and the pigment grains *(personal archive Th. Mafredas)*

Fig.119 Details of sample's stratigraphy *(personal archive Th. Mafredas)*

During the stratigraphic examination of sample #4 (**Fig.120**), besides the measurement of the thickness of each layer (**Fig.121**), it was possible to observe the preparation layer and identify two different layers which had been worked and applied without diligence. The first painting layer seemed to contain large grains of pigment (**Fig.122**). Furthermore, through SEM observation of this layer, some grains were found which looked like small wax balls (**Fig.123**) This pointed to the hypothesis that there was a possibility that Dionysius used small quantities of wax in combination with the pigments. The second painting layer and the upper organic layer, which was probably the varnish layer, were also distinguished and observed.



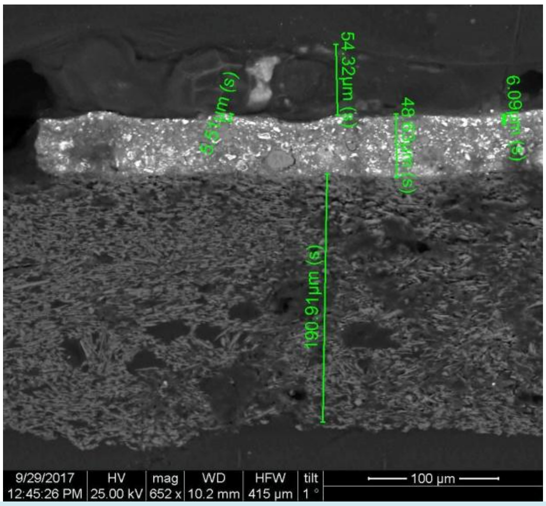
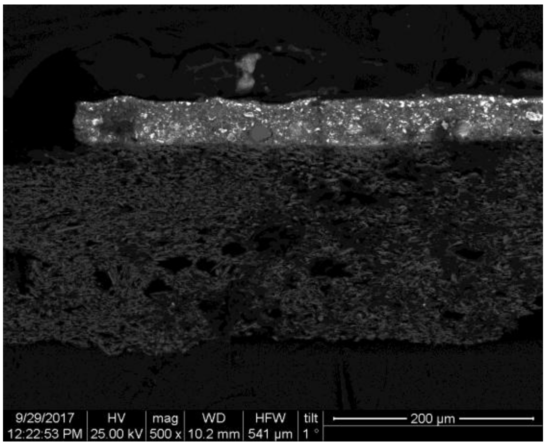


Fig.120 Sample #4. SEM *(personal archive Th. Mafredas)*

Fig.121 Sample #4. The layers dimensions *(personal archive Th. Mafredas)*



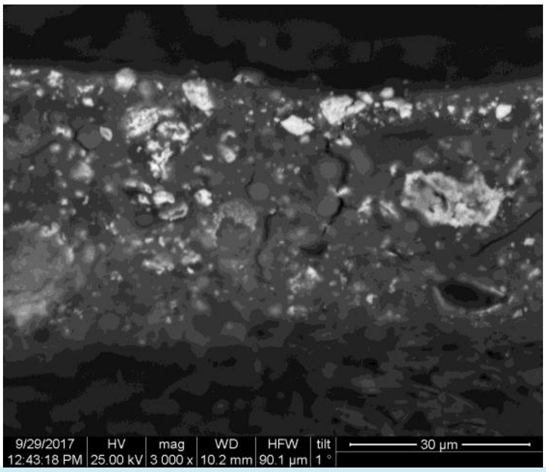


Fig.122 The stratigraphy of sample #4 *(personal archive Th. Mafredas)*

Fig.123 Grains, in pigment layer, which look like small wax balls *(personal archive Th. Mafredas)*

The observation of sample 6a (**Fig.124**) helped to distinguish the layer from each other, something that it was not possible during OM. In addition the thickness of the layers of the sample could be measured (**Fig.125**) and a more detailed observation of the layers became possible, including the bole layer (**Fig.126**), which was not detectable in OM.

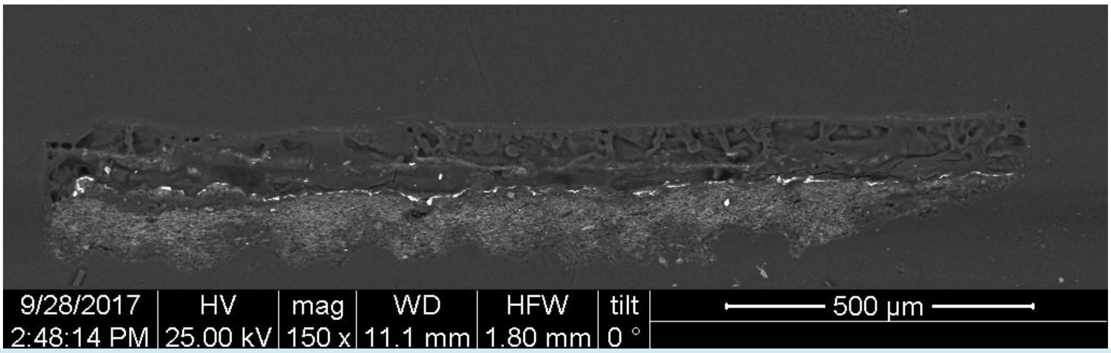
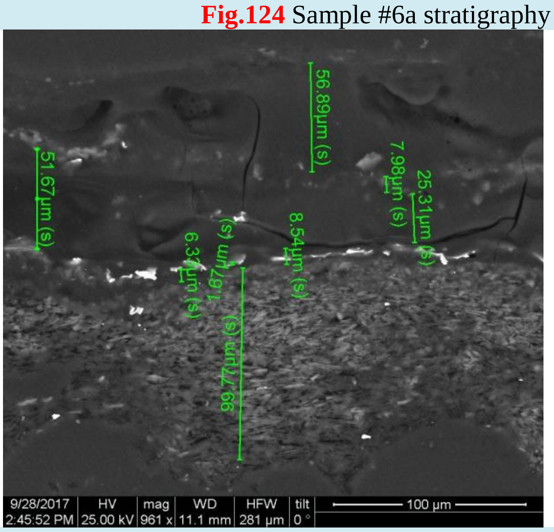


Fig.124 Sample #6a stratigraphy *(personal archive Th. Mafredas)*



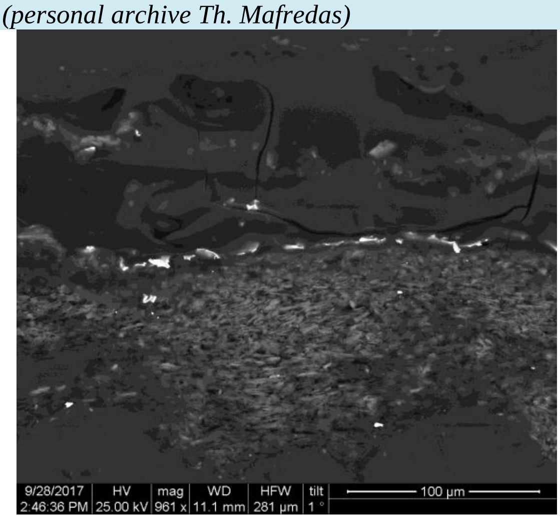


Fig.125 Sample #6a. The layers dimensions *(personal archive Th. Mafredas)*

Fig.126 Identification of gold layer which was not detectable by OM *(personal archive Th. Mafredas)*

Concerning the preparation layer it was found that it had been applied and worked without diligence (**Fig.127**), a common feature with sample 4 (**Fig.128**). The gold leaf layer seems to be non-continuous (**Fig.129**), while over it was found that there were two different layers of organic substances with a continuous line of clacks (**Fig.130**), which means that the panel painting has been re-varnished without previous cleaning of the painting surface.

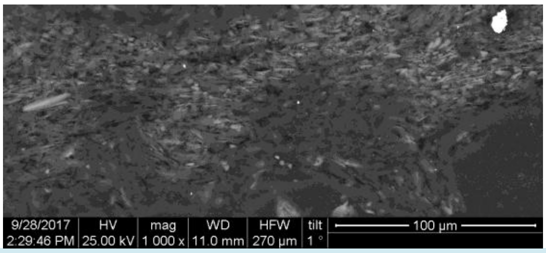


Fig.127 The gesso preparation from sample #6a *(personal archive Th. Mafredas)*

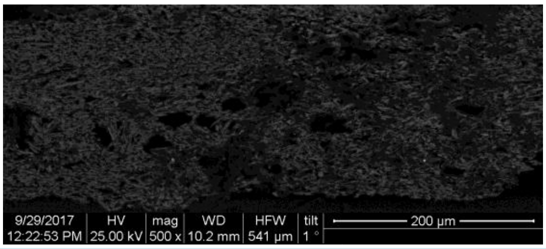


Fig.128 The gesso preparation from sample #4 *(personal archive Th. Mafredas)*

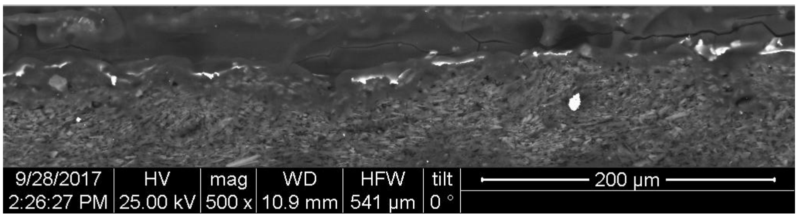


Fig.129 The gold layer of sample #6a which is non-continuous *(personal archive Th. Mafredas)*

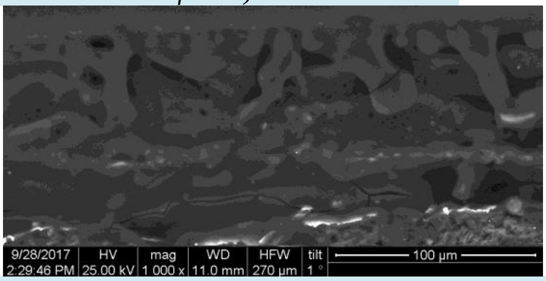


Fig.130 Two different layers of organic substances *(personal archive Th. Mafredas)*

1.4. Analytical Techniques

As discussed in a previous chapter (**Chapter 2.3**), there are many kinds of analytical techniques, such as spectroscopic techniques which are a large group of optical analytical techniques based on the interaction of e/m radiation with the atoms or molecules of a sample (Anglos, Georgiou & Fotakis 2009). These techniques are divided into two categories: molecular techniques (Nevin, Spoto & Anglos 2012, pp. 346-356) and elemental techniques (Nevin, Spoto & Anglos 2012, pp. 340-346).

1.4.1. Elemental Techniques

Through elemental techniques, the qualitative and quantitative determination of the elements from which a material is composed can be achieved.

1.4.1.1. X-Ray Fluorescence

XRF was applied in the painting surface of panel painting in 16 different points (**Fig.131**) in order to obtain data from a variety of areas concerning Dionysius's color pallet, and identify pigments in areas where the varnish layer had lost its transparency and had become opaque, compromising the painting's purity. Furthermore, the use of XRF in gold areas provided data that helped to conclude about the use of a bole layer, the kind of it, and the type of metal used.

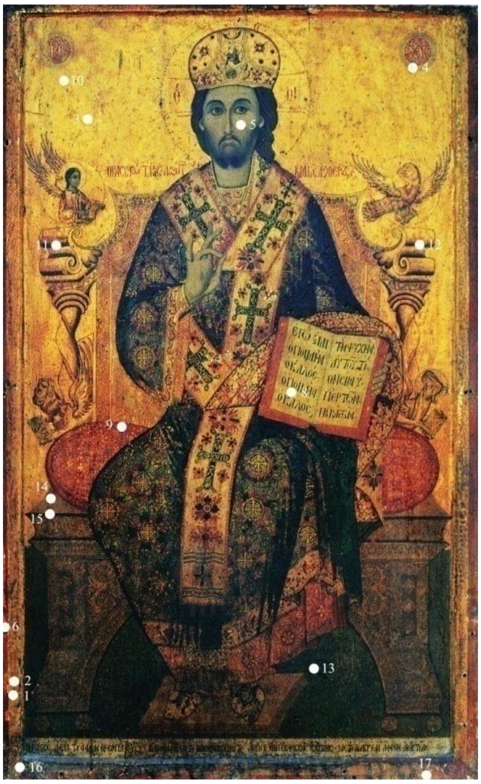


Fig.131 Christ High Priest. XRF spots *(personal archive Th. Mafredas)*

For hit points 1-4 and 10, the XRF data provided an elemental analysis of the ingredients of the bole layer (**Table 7**). Besides the Au, (***Appendix 4***), according to the spectra, Cu, Fe, Pb, and Ca were also identified.

The XRF analysis of the flesh in hit point 5 detected the presence of Pb and Fe, possibly deriving from the use of lead white ($2PbCO_3{\bullet}Pb(OH)_2$) and the presence of a yellow/red ochre. This data helped identify that, in this point, Dionysius had used his second recipe for flesh, consisting of white lead and yellow red ochre (Dionysius 1909, pp. 20-21). Additionally to Dionysius's recipe for flesh, it was found that, in hit point 8 on the whitish background of the open gospel, Pb, Cu, and Fe were detected according to the obtained spectrum data, possibly due to the use of white lead mixed with a small quantity of green and ochre, pigments that correspond to Dionysius's recipe for proplasmos (Dionysius 1909, p. 20).

Concerning the red pigment, the presence of Pb and Hg and S was detected according to hit points 6 and 9 (**Table 7**) and the obtained spectra (***Appendix 4***). Another attempt was made to characterize the dark pigment that Dionysius had used over the gold layer in the upper edges of the throne. So, according to hit points 11 and 12 (**Table 7**) and the obtained spectra (***Appendix 4***), the detected elements were Cu, Au, Fe, Ca, and Pb. The intense bands for Au and Ca could be assumed to have originated from the gold layer and gesso preparation respectively. Because of the limitations of XRF measurements, carbon or lampblack were not able to be identified. As a result, it could be assumed that he used some type of dark pigment or a mixture of different pigments with the possibility of including some quantity of black.

One of the most noteworthy points was hit point 13, which corresponds to the background below the throne (**Fig.131**). During the visual examination, this area was characterized as a very dark area due to the degradation of the varnish that has lost its transparency and has made the pigments appear opaque. It was really necessary to further examine the area in order to find the exact painting of the background. According to the obtained spectrum (***Appendix 4***) from this area, the trace elements were Orpiment (Sulfur arsenic: As_2S_3) in the same intensity as Pb, Fe, Ca and Cu. With the exception of Ca, whose intense band originated from the gesso preparation, all other intense bands came from the pigment layer.

The same framework was used to examine another point, the #14th (**Fig.131**), which gave the impression of using a quite dark pigment in Vis. According to the obtained spectrum (***Appendix 4*)** from this area, and from the trace elements, Pb, Fe, Au, Zn, Cu, Ca which were found, (**Table 7**) it could be assumed that Dionysius useda mixture of different pigments in order to achieve the right tone of brown. The spectrum bands for Au and Ca can easily be justified by the gold layer present in the neighboring area, and from gesso preparation. The same trace elements, Pb, Fe, Cu, were found in hit point 15 as well (**Fig.131**), which is the dark decoration line of the throne. According to the obtained spectrum (***Appendix 4***), the mixture of different pigments in order to achieve to right tone of brown paint is, again, a very likely possibility. At this point, it should be noted that, because of the limitations of XRF measurements, it was not possible to identify whether he used carbon or lampblack in the mixture of the pigments.

The last two hit points, 16-17, were located in the perimetric gold layer (**Fig.129**) of the panel, and the effort was to identify trace elements consisting of the ground preparation and the bole layer. More specifically, the detected elements were Pb, Ca, Hg, Au, Fe, S, and Cu for spot 16, and the same elements in different intensities, for spot 17 (**Table 7**). The obtained spectra of these two areas were almost identical (***Appendix 4***); with the only difference being in the intensity bands of the elements for each spectrum, which results in the differentiation of the tracing order of the elements. Thus, according to the spectra, the same elements were used as in hit points 1-3 with the addition of some quantity of HgS. The use of two different kinds of red pigment; HgS – Cinnabar and Pb_3O_4 –red lead, is a feature that has been verified not only through XRF in multiple hit points in this panel, but also during the EDX elemental analysis of the samples, as it will be discussed below. The very low intensity of Cu could be explained as part of the mixture with the gold leaf.

Finally, trace elements, such as Zn and Ti, are detected, which appear to be impurities of the raw materials without their presence interfering with the presence of raw materials as they are recorded by the intensity bands of the spectra.

After applying XRF in 16 different spots on the painting surface and obtaining the respective spectra, the interpretation of the data assisted in drawing a first conclusion about Dionysius's color palette (**Table 7**). So, according to the data as presented above, it would be safe to assume that he used a variety of pigments, all of which are mentioned in his treatise. Due to the limitations of this technique, quantification analysis could not be provided; only qualification. Furthermore, elements below Al could not be traced because the XRF device used does not allow the detection of elements with an atomic number less than 13, which excluded the detection of C (Mastrotheodoros 2016, p. 163). Thus, this panel painting, as well as the other three (3), was examined preliminarily with XRF, and then some of the pigments were identified by further study of the samples with SEM/EDX, as it will be discussed below.

Table 7. *Panel #1- Elemental Analysis – XRF*

Spot	# of Spectrum	Color	Trace elements
1	1825	Gold	Au, Fe, Ca, Pb, Cu
2	1826	Gold	Au, Fe, Ca, Pb, Cu
3	1827	Gold	Au, Fe, Ca, Pb, Cu
4	1828	Gold	Au, Hg, Pb, Ca, Fe, Cu
5	1829	Whitish (Flesh)	Pb, Fe
6	1830	Red	Pb, Hg, Ca, Fe
8	1832	Whitish	Pb, Cu, Fe
9	1833	Red	Hg, Fe, Cu, Ca
10	1834	Gold	Au, Fe, Ca, Pb, Cu
11	1835	Black	Cu, Au, Fe, Ca, Pb, Ti
12	1836	Black	Cu, Au, Fe, Ca, Pb, Ti
13	1837	Green (background)	As, Pb, Fe, Ca, Cu, Zn
14	1838	Brown	Pb, Fe, Au, Zn, Cu, Ca
15	1839	Brown (Dark line)	Pb, Fe, Cu
16	1840	Red with gold leaf	Pb, Ca, Au, Fe, Hg, S, Zn, Cu, Ti
17	1841	Red with gold leaf	Pb, Ca, Hg, Au, Fe, Zn, S, Cu

1.4.1.2. Energy Dispersive X-ray Analysis

The Energy Dispersive X-ray (EDX) spectroscopy can provide elemental information about the identity of inorganic materials present in a sample, such as pigments (Genestar & Pons 2005, pp. 270-274; Iordanidis et al. 2013; Cristache et al. 2013, pp. 75-78; Franceschi et al. 2011, pp. 353-354; Katsibiri, Lazidou & Howe 2006, p. 7) and gesso preparation materials (Genestar 2002, pp. 385-388; Kouloumpi et al. 2013, p. 3; Mastrotheodoros et al. 2016). The method is based on capturing the characteristic energy of atoms (Stuart 2007, p. 92; Charola & Koestler 2006, pp. 21-22) and is combined with SEM.

Upon examining sample #3 with EDX, it was found that this thin layer of preparation consisted Ca (Calcium) and S (Sulfur) (**Fig.132**). As a result, it could be assumed that the preparation layer was Calcium Sulfate ($CaSO_4$).

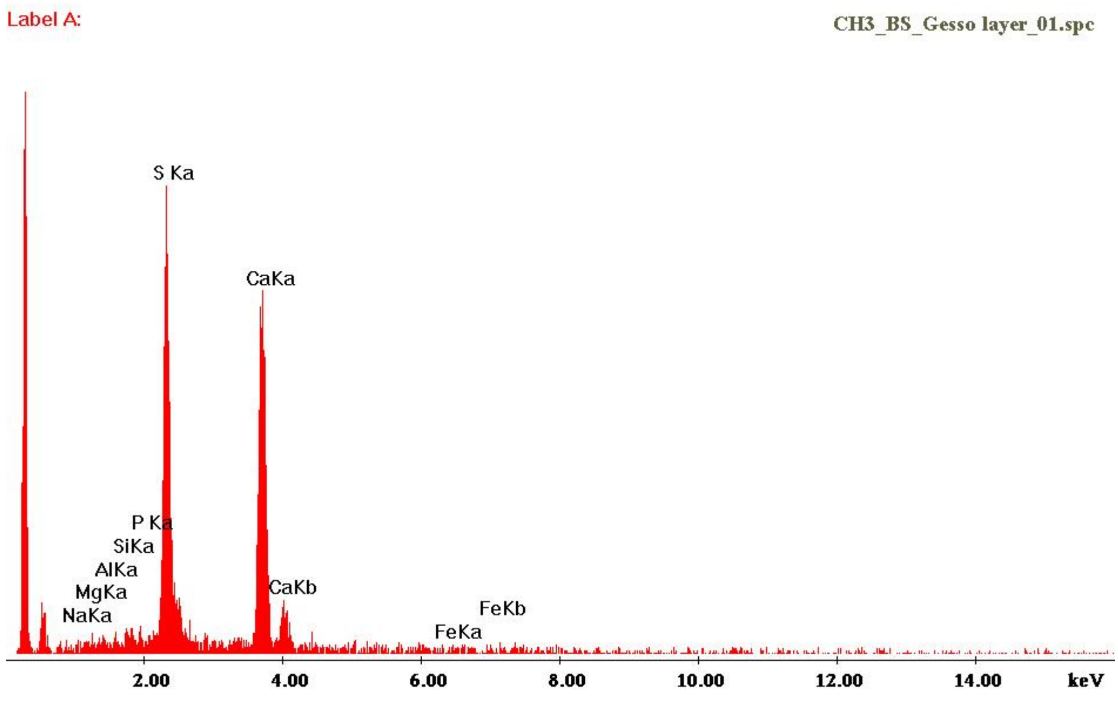


Fig.132 EDX spectrum, from gesso layer (sample #3) *(personal archive Th. Mafredas)*

Over the gesso layer a thin, white, non-continuous layer was observed, which consisted exclusively of Pb (**Fig.133)**.

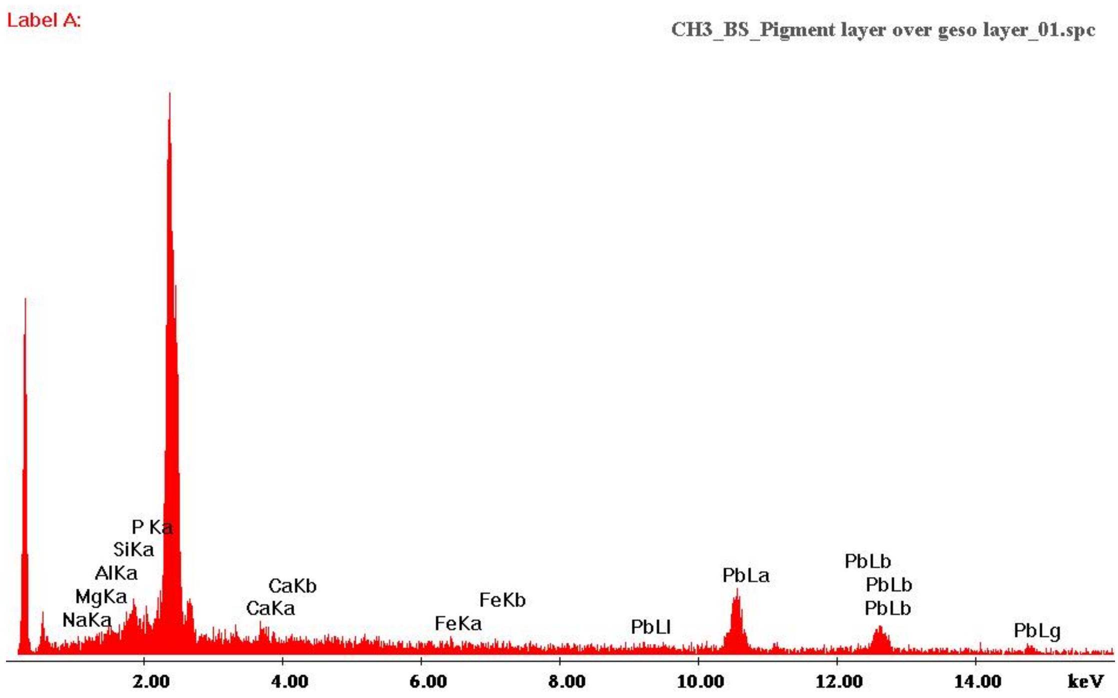


Fig.133 EDX spectrum from pigment layer over the gesso layer (sample #3)
(personal archive Th. Mafredas)

Over that, two different painting layers were observed, confirming the findings observed in OM and SEM. The first layer in OM appeared to be an orange color and the second one a red color. The EDX elemental analysis for the first layer detected the presence of Pb (red lead: Pb_3O_4), while the second layer consisted of HgS (cinnabar) and Pb in mixture (**Fig.134-135**).

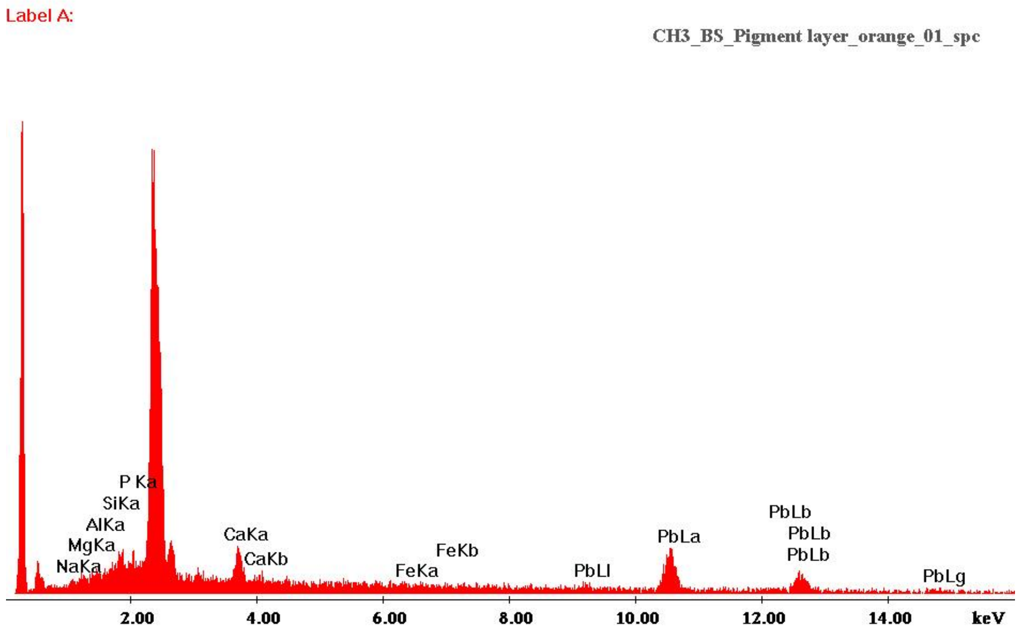


Fig.134 EDX spectrum from pigment layer with orange color (sample #3) *(personal archive Th. Mafredas)*

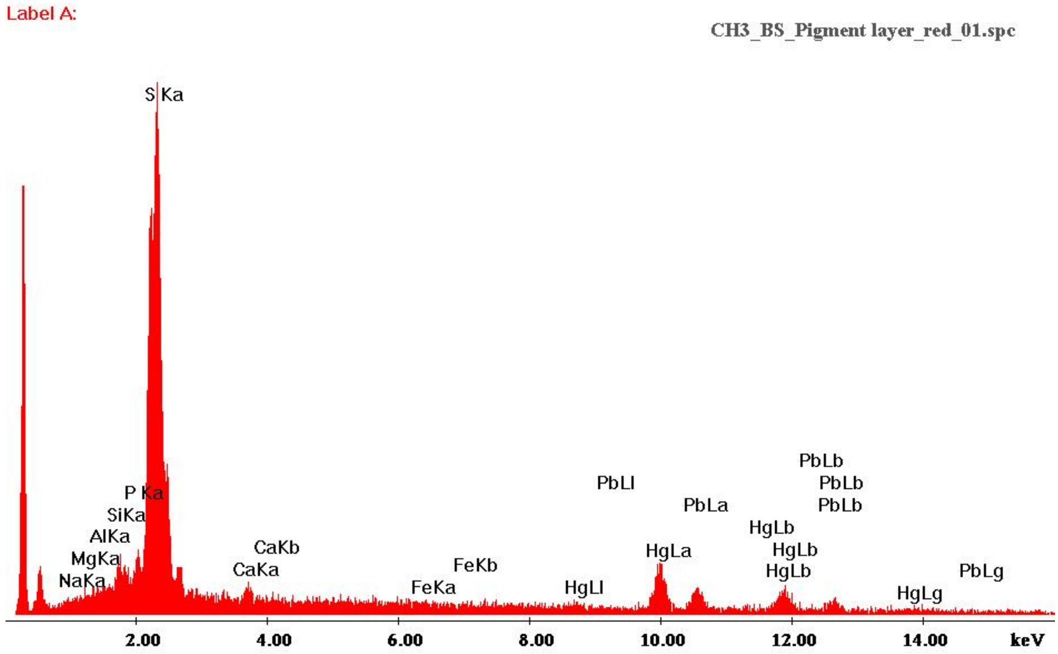


Fig.135 EDX spectrum from pigment layer with red color (sample #3) *(personal archive Th. Mafredas)*

During the study of sample #4, the EDX analysis showed that the preparation layer was $CaSO_4$ (**Fig.136**), and the first painting layer consisted of red lead (**Fig.137**). In the same layer were observed in which S was also identified besides Pb (**Fig.138**). The combination of these trace elements could point to the hypothesis that this might be a mixture of organic pigment.

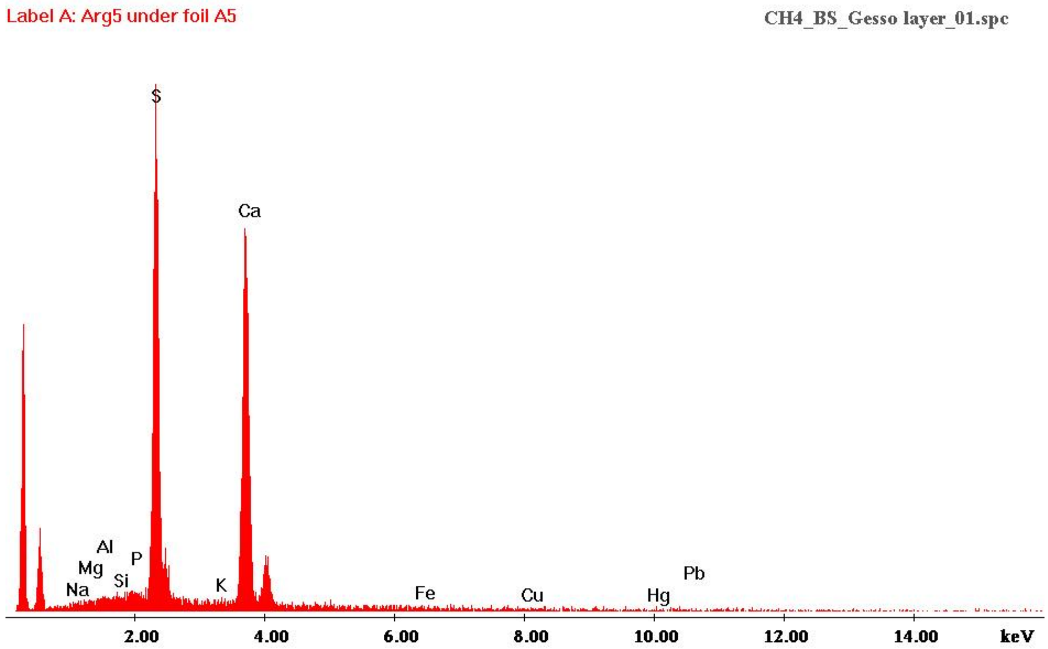


Fig.136 EDX spectrum from gesso layer (sample #4) *(personal archive Th. Mafredas)*

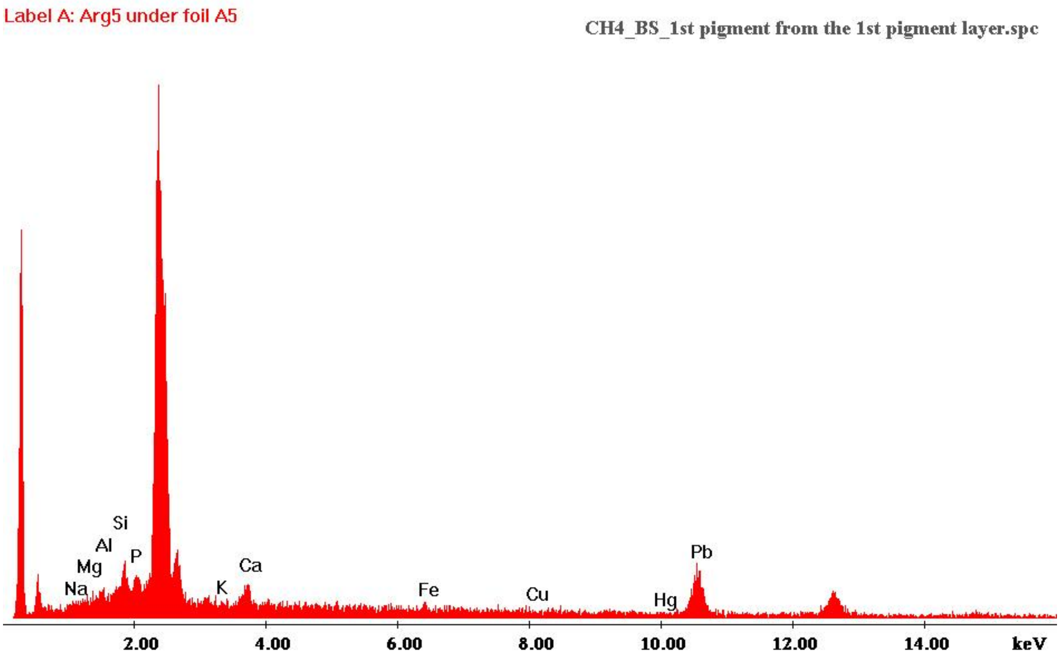


Fig.137 EDX spectrum from 1st pigment from the 1st pigment layer (sample #4)
(personal archive Th. Mafredas)

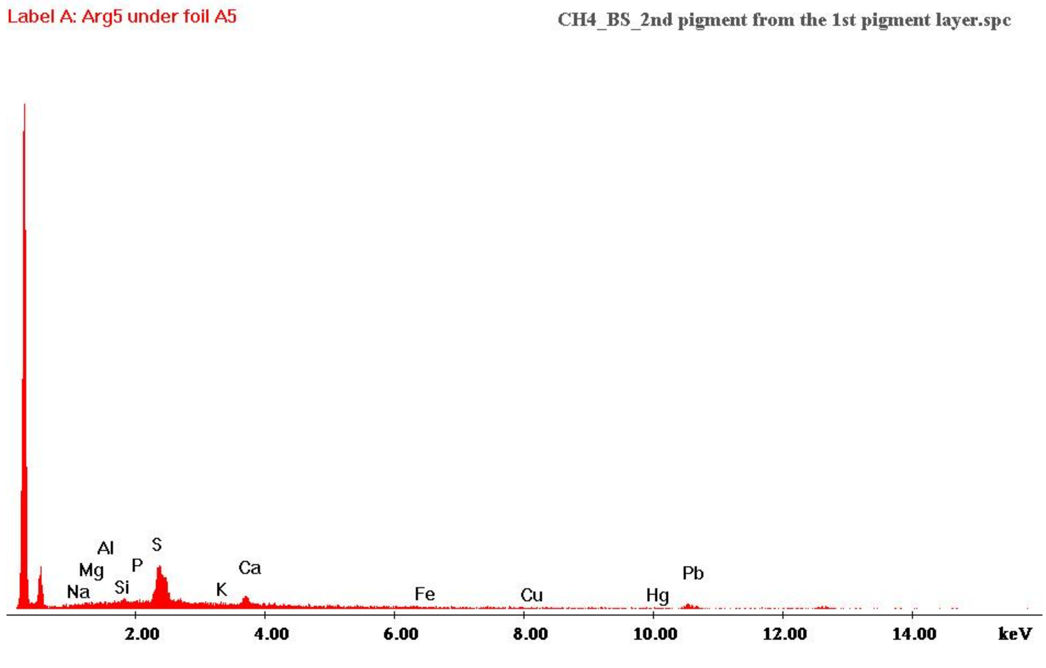


Fig.138 EDX spectrum from 2nd pigment from the 1st pigment layer (sample#4)
(personal archive Th. Mafredas)

EDX on the second painting layer revealed trace elements of Hg, S and some quantity of Pb, which could be explained under the hypothesis that Dionysius used cinnabar in mixture with red lead (**Fig.139-140)**. Finally, the upper organic layers seem to consist, besides the varnish, from pollutant particles and sediments (**Fig.141**), as shown by EDX elemental analysis.

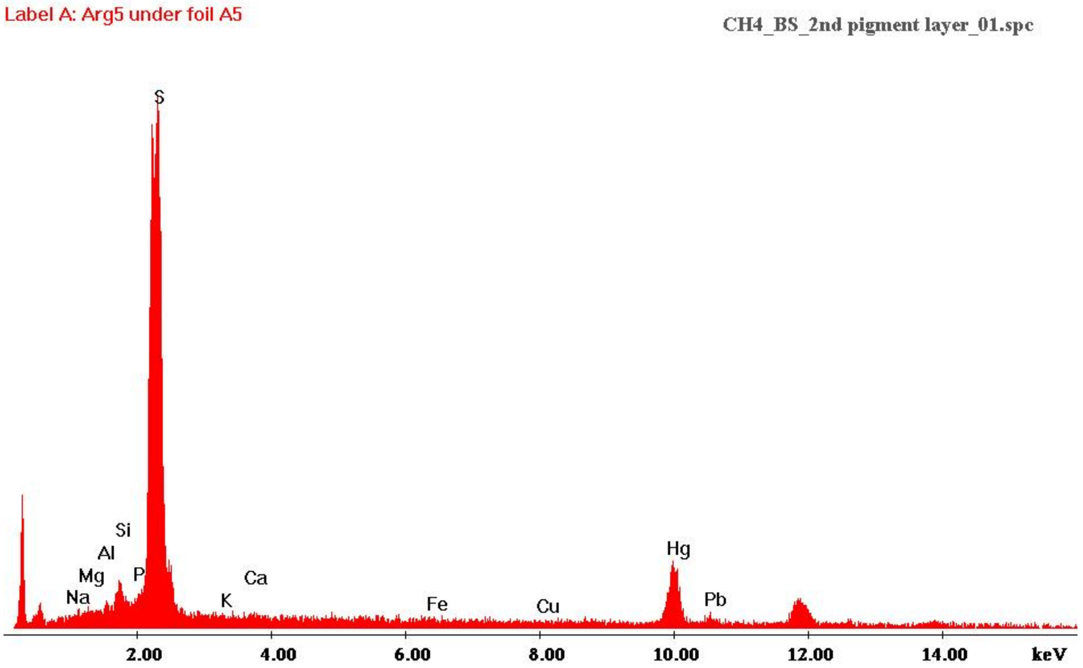


Fig.139 EDX spectrum (#1) from 2nd pigment layer (sample #4) (*personal archive Th. Mafredas)*

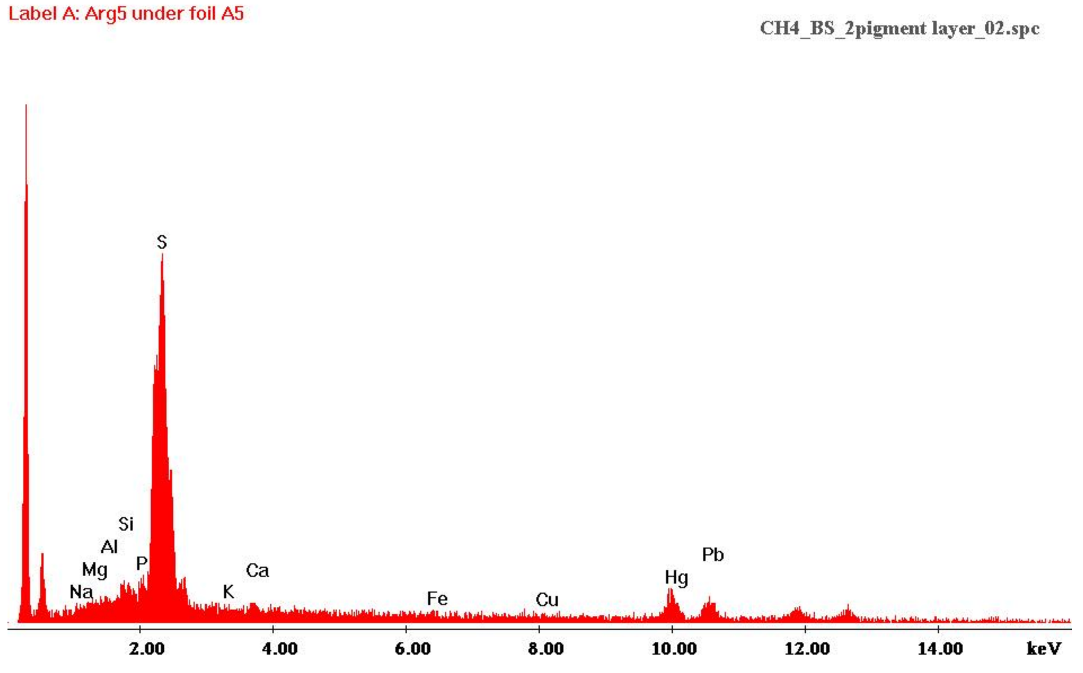


Fig.140 EDX spectrum (#2) from 2nd pigment layer (sample #4) *(personal archive Th. Mafredas)*

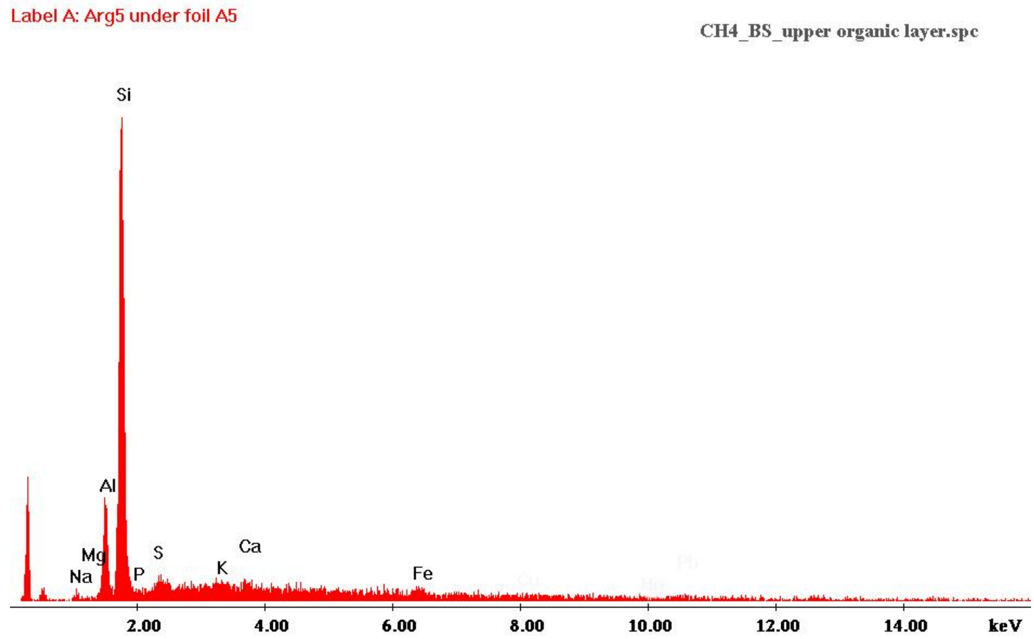


Fig.141 EDX spectrum from upper organic layer (sample #4) *(personal archive Th. Mafredas)*

Concerning the sample 6a, EDX analyses detected that the gesso preparation consisted of $CaSO_4$ (**Fig.142**), while a thin layer of bole preparation was detected over it. According to elemental analysis, the presence of Al, Si, Fe and S suggested the presence of bole clay (Chatzidaki et al. 1988, p. 235). The detection of Al and Si, as alumino-silicates in particular, is indicative of the presence of clay, while the presence of Ca is from gesso (**Fig.143**). Furthermore, if these results were examined in comparison to XRF results from respective areas (***Appendix 4***), then it could be assumed that Dionysius used one of the bole recipes that he had already mentioned in his treatise (Dionysius 1909, pp. 17-18). Over the gold layer, the presence of Au was identified for gilding (**Fig.144**) and finally, over that, three different layers–two organic layers separated by a layer of pollutant particles and different sediments (**Fig.145**).

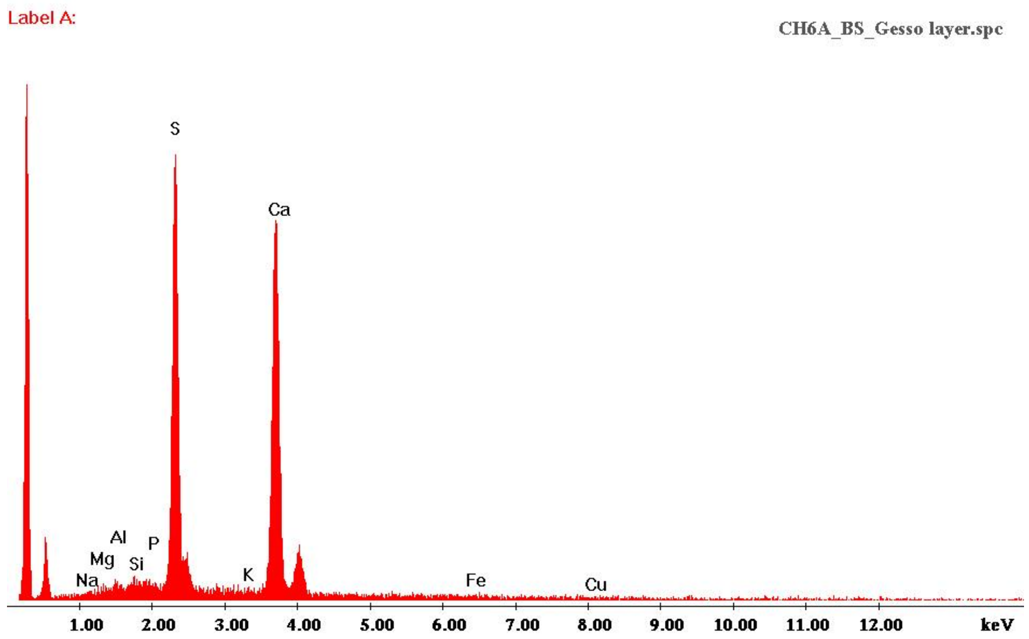


Fig.142 EDX spectrum from gesso layer (sample #6a) *(personal archive Th. Mafredas)*

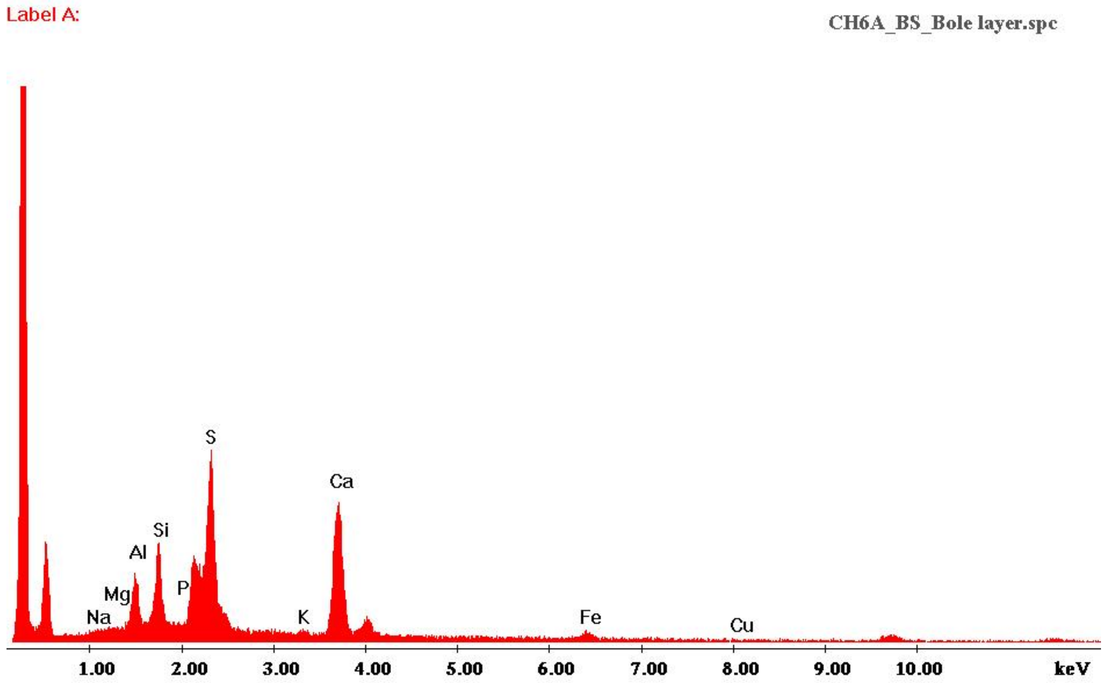


Fig.143 EDX spectrum from bole layer (sample #6a) *(personal archive Th. Mafredas)*

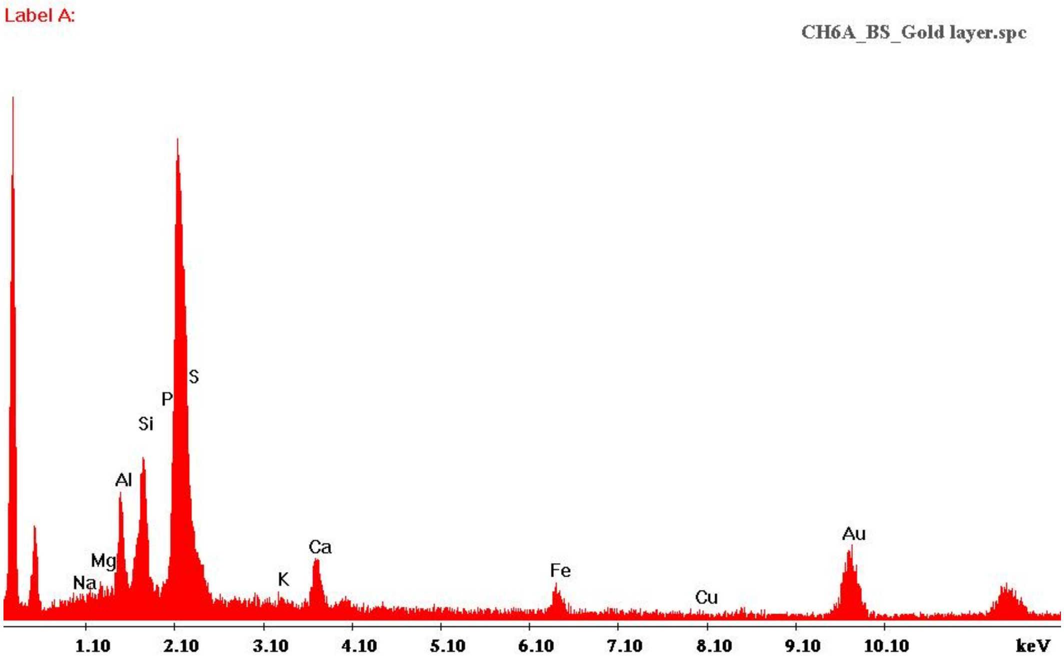


FIg.144 EDX spectrum from gold layer (sample #6a) *(personal archive Th. Mafredas)*

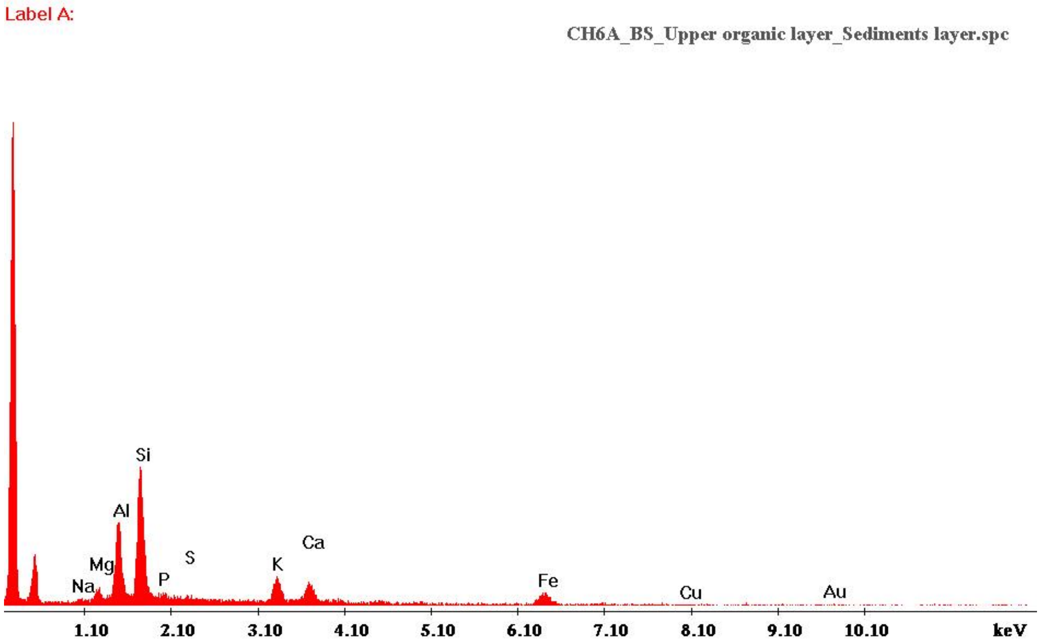


Fig.145 EDX spectrum from upper organic layer and sediments layer (sample #6a) *(personal archive Th. Mafredas)*

The use of EDX helped to identify the inorganic pigments in different layers and make a quantification of trace elements (**Table 8**). In this framework, it was possible to identify the mixtures in the painting layers and make a hypothesis about the recipe that Dionysius used for the bole preparation.

Furthermore, upon examining the results from EDX in comparison to XRF results, it was possible to make some hypotheses about the kind of pigments or recipes that Dionysius used for constructing the panel painting.

Table 8. *Panel #1 - Elemental Analysis - EDX*

# Sample	Spot	OM	Layer	Trace Elements
#3	Gesso preparation		1st	S, Ca
	Over gesso		Thin-non continuous	Pb, Ca
	Pigment layer	Orange with some white grains	2nd	Pb, S
	Pigment layer	Red with red grains	3rd	S, Hg
#4	Gesso preparation	Unspecified composition and texture layer	1st	S, Ca
	Painting layer	Orange and white grains	2nd	Pb
	Painting layer	Red and white grains	3rd	S, Hg, Pb
	Organic layer	Organic layer	4th	Si, Al, S, Ca, Fe
#6a	Gesso preparation	Opaque, unspecified composition layer	1st	S, Ca
	Bole	A few pigment grains (Red and Ochre)	2nd	S, Ca, Si, Al
	Gold	Gold leaf	3rd	Si, Al, Au, Fe, Ca
	Organic layer	Organic layer	4th	Si, Al, K, Ca, Fe

1.4.2. Molecular Techniques

Through molecular techniques it is possible to characterize and identify the materials by identifying the molecules that consists the sample material which is analyzed.

1.4.2.1. Fourier Transformer Infrared Spectroscopy

The final technique which was applied was FTIR from two different samples in order to characterize the gesso preparation and the kind of varnish which Dionysius used during the construction of his panel painting (***Appendix 2***). The sample from gesso (#1a) was taken from the left bottom part of the panel, in the horizontal frame, while the sample from the varnish (#2) was taken from the right vertical frame of the panel. Both of them were in powder form, prepared in a KBr disc, as discussed in a previous chapter (**Chapter 2.31.1.1** and **Chapter 3.8**).

From the obtained spectrum for sample 1a and from the respective bands, gesso was identified as hydrate (3551, 3402 cm^{-1}) gypsum (1139, 1115, 669, 602 cm^{-1}) and, more specifically, calcium sulfate dihydrate ($CaSO_4•2H_2O$) (**Fig.146**). The use of $CaSO_4$, as evidenced from the FTIR spectrum, was also confirmed by the obtained data from previous techniques, both during XRF and EDX application.

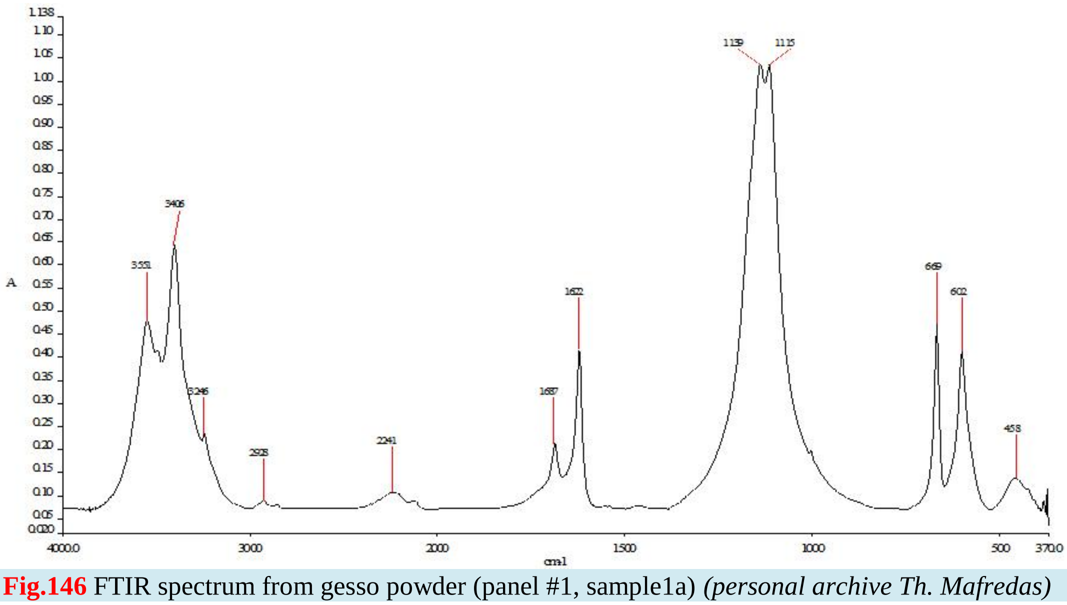


Fig.146 FTIR spectrum from gesso powder (panel #1, sample1a) *(personal archive Th. Mafredas)*

According to the obtained spectrum data and the respective bands, the varnish was identified as Sandarac (3425, 3080, 2935, 2874, (1696), 1648, 1462, 1410, 1378, 1175, 1033, 892 cm^{-1}). From the other bands of the spectrum (1709, 1643, 1451, 1391, 1245 cm^{-1}), it could be assumed also the presence of Mastic (**Fig.147**).

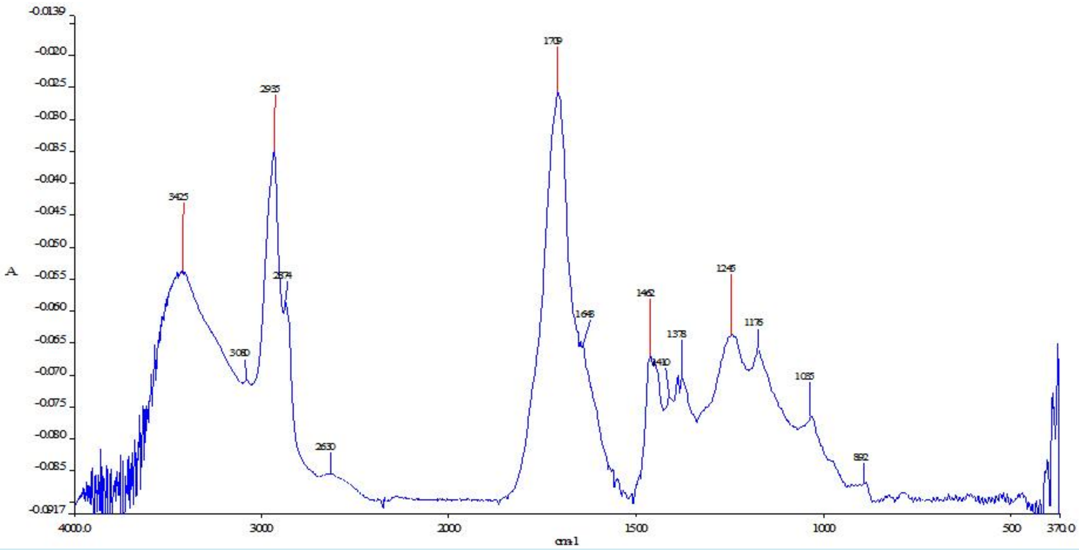


Fig.147 FTIR spectrum from varnish powder (panel #1, sample2) *(personal archive Th. Mafredas)*

Considering the obtained data from previous techniques, the mixture of Sandarac and Mastic could be justified, as it was a common occurrence both during observation in OM and during SEM application.

The use of infrared spectroscopy, as discussed above, justified the obtained data about inorganic elements during previous techniques, and verified the discrepant application of varnish layer, as was also found during the microscopic observations. With regards to varnish identification, it could be argued that Dionysius used some kind of resin for varnish, as he had already mentioned in his treatise, which is going to be further discussed below.

1.5. Discussion

The iconography of Christ as King of Kings and Great High Priest generally follows the relevant instructions on this subject found in Dionysius's earlier treatise. Reference to Christ as King of Kings and Great High Priest is made in three distinct contexts. First, in the section of the Hermeneia referring to the way churches are painted with scenes: "*The beginning of the second zone. In the two cupolas of the sanctuary paint in that on the prosthesis side Christ in high priest's robes, sitting on a cloud and blessing and holding a Gospel book open at the words 'I am the good shepherd' (John 10:11) with the inscription above him 'Jesus Christ the Great High Priest*'" (Dionysius 1909, p. 216; Hetherington 1974, p. 84). Second in the section describing the names and epithets which are written on Christ' panel paintings: "*When you show him as a high priest: 'The King of Kings and Great High Priest*'" (Dionysius 1909, p. 227; Hetherington 1974, p. 88), and finally third in the section proposing the texts to be written in the Gospel of Christ: "*When you show him as a High Priest: 'I am the good shepherd; the good shepherd gives his life for the sheep*'" (Dionysius 1909, p. 228; Hetherington 1974, p. 88) (**Fig.148**).

Fig.148 Christ as Great High Priest, Detail. The gospel epigram *(personal archive Th. Mafredas)*

It is noteworthy that this epigram, composed by Dionysius around 1737 to accompany his despotic panel painting of Christ, was not included in the text of his treatise in spite of the fact that Dionysius suggested many other epigrams to accompany certain panel paintings. According to Kakavas, this can be explained by taking into account that the epigram for this particular panel painting was composed specifically for this theme and after the completion of his treatise (Kakavas 2008, p. 205). Another difference between the Hermeneia's text and the presentation of the panel painting is the shape of Christ's throne. In the text, Christ is described as seated on a throne of clouds, while in Fourna's panel, Christ is enthroned on a wooden throne. The difference between the two representations can be explained, according to Kakavas, by the fact that, in the Hermeneias' text, Christ's image is included as a central figure of the Divine

Liturgy’s representation while, in Fourna’s panel, Christ's image functions as a portrait (Kakavas 2008, p. 204).

As discussed above, imaging techniques, such as IR photography, helped study detailed features of painting concerning Dionysius drawing line and observed same details which were not detectable or visible in the Vis.

The application of digital microscopy provided excellent and detailed data concerning the construction technique and the decoration of the painting surface giving the first conclusions about Dionysius’ painting technique. Applying DM helped to study and understood Dionysius’ technique for micro-decoration and dotted decoration as well as some details about the drawing for micro-decoration. Furthermore it was observed that he used to apply the pigments over the gold layer, in order to achieve the decoration of the throne or for the omophorion or even for the mitre. Concerning the construction techniques it was found that the layers of the painting surface were very thin, except some areas, such as Christ’s eyes or in the lower part of Christ’s garment, where it was found a thick layer of varnish. Thin layers were found also in gold areas of the panel, where it was difficult to distinguish the layer of bole, even in high magnification 200X. The thickness of the sample was verified also during OM and SEM, as it was possible to measure the thickness of the hall sample and the thickness of different layers of the sample.

The optical microscopy observation of the samples from this panel painting initially provided detailed information about the stratigraphy of the painting surface and for the gilding technique. It was able to observe a variation in the number of the varnish layers, an observation that helped to understand the preservation history of the panel. Furthermore, in the sample 6a it was found some spots that could be from bole layers, something that was not easily observed during DM. The same spot was observed during SEM and through EDX analysis it was able to identify the constituents of this layer, which was finally a bole layer. Additionally, in samples 3 and 4 were observed two different layers of pigments, something that again, it was not easily detectable in DM. Furthermore, during OM it was observed that the samples presented a disturbed stratigraphic structure and provided information about painting and gilding technique in order to evaluate Dionysius construction and painting technique.

As discussed above, imaging techniques, such as IR photography, helped study detailed features of painting concerning Dionysius drawing line, and observed some details which were not detectable or visible in the Vis.

The application of digital microscopy provided excellent and detailed data concerning the construction technique and decoration of the painting surface, giving some preliminary conclusions about Dionysius's painting technique. Applying DM helped to study and understand Dionysius's technique for micro-decoration and dotted decoration, as well as some details about the drawing of micro-decoration. Furthermore, it was observed that he used to apply the pigments over the gold layer in order to achieve the decoration of the throne or the omophorion, or even of the mitre. Concerning the construction techniques, it was found that the layers of the painting surface were very thin, with the exception of some areas, such as Christ's eyes or the lower part of Christ's garment which was found to be covered by a thick layer of varnish. Thin layers were also found in gold areas of the panel, where it was difficult to distinguish the layer of bole even in high magnifications of 200X. The thickness of the sample was also verified during OM and SEM, as it was possible to measure the thickness of the whole hall sample and the thickness of different layers of the sample.

The optical microscopy observation of the samples from this panel painting initially provided detailed information about the stratigraphy of the painting surface and the gilding technique. It was able to observe a variation in the number of the varnish layers–an observation that helped to understand the preservation history of the panel. Furthermore, in sample 6a, some spots were found that could correspond to bole layers, something that was not easily observed during DM. The same spot was observed during SEM and, through EDX analysis, the constituents of this layer, which was eventually a bole layer, could be identified. Additionally, in samples 3 and 4 two different layers of pigments were observed, a detail that, again, was not easily detectable in DM. Furthermore, during OM, it was observed that the samples presented a disturbed stratigraphic structure. Information was also provided about the painting and gilding technique in order to evaluate Dionysius's construction and painting technique.

During microchemical tests in sample #4, it was observed, through the staining of the layers, that there was a small concentration of proteinaceous materials in combination with the use of another binding medium. It is difficult to be certain about the other organic binding medium and, even more so, to determine whether this organic medium is a feature of Dionysius's painting technique or has been applied at a different time.

In addition, OM was aided by the SEM/EDX technique which was more sophisticated and targeted concerning, among others, the distinguishing of the pigment layers observed in OM, the quantification of the pigment in each painting layer, and the distinguishing of layers such as gesso preparation, which were not detectable in OM.

The application of SEM analysis provided detailed data about the different layers of the cross section of the samples, and helped to study Dionysius's construction technique. According to SEM, it was observed that he had not worked and applied the gesso layer with diligence (samples #4 and #6a), while the first painting layer seemed to contain large grains of pigment. In sample #4, some grains which look like small wax balls were observed, which supports the hypothesis that there was a possibility that Dionysius used quantities of wax in combination with the pigment.

Through the elemental analysis with XRF and EDX, a first perception about Dionysius's color palette was attained. So, according to the obtained spectra, it could be assumed that he used red lead (Pb_3O_4),red ochre (Fe_2O_3), and cinnabar (HgS) for red pigments, and white lead ($2PbCO_3 \cdot Pb(OH)_2$) for white pigments. It also seems that he used azurite ($2CuCO_3 \cdot Cu(OH)_2$) for blue pigments, verdigris $Cu(CH_3COO)_2 \cdot 2Cu(OH)_2$) for green pigments, and orpiment (As_2S_3) for yellow pigments. Furthermore, through the obtained data from the elemental analysis in comparison with OM and DM, it was possible to understand that, in some cases, he used a mixture of different pigments in order to achieve an exact color. A good example of this, can be seen in hit point 13 in XRF, which is located at the low background of the painting surface. It was necessary to understand the color that he had used because of the degradation of the varnish, which presented severe discoloration in this particular area. From the XRF analysis, trace elements of As were found in the same intensity as Pb, Fe, Ca and Cu. The hit point was located in the background, which represents earth and so, in this respect, the representation of earth should be green. According to this theory, it could be assumed that Dionysius used a yellow pigment, in this case, orpiment, in mixture with red lead. The mixture resulted in green, while he also added a quantity of other pigments, such as reddish ochre and azurite ($2CuCO_3 \cdot Cu(OH)_2$) in order to achieve the right tone of green. This kind of mixture which includes orpiment and azurite in order to produce green can be found in relevant literature (West FitzHugh 1997, p. 53).

Furthermore, EDX analysis verified that he used pigments, either separately or in a mixture of different quantities, according to the color result he wanted to achieve. A characteristic example comes from the second pigment layer of sample #4, which consisted of red and white opaque pigment grains and, according to EDX analysis, was the result of a combination of HgS and Pb.

It seems that all the pigments he used for this panel painting are mentioned in his treatise (Dionysius 1909, pp. 20-23, 34, 41).

The final analytic technique that was applied was FTIR and, through that, the kind of gypsum he used for gesso preparation was identified as$CaSO_4$, which verifies the XRF and EDX results about the presence of Ca and S, while the varnish he used seems to be Sandarac or Mastic. Because of the limitations of this technique, it was not possible to quantify the presence of each of the resins or to assume whether there was a previous restoration attempt. In any case, both of these resins are mentioned in Hermeneia’s manuscript as ingredients for varnish layer (Dionysius 1909, pp. 25-27). At this point it should be noted that these two resins are mentioned as constituents of different kinds of varnishes. So, according to the obtained spectrum, it is obvious that, for panel #1, the varnish layer consisted of two different resins, Sandarac and Mastic, which are the main ingredients for the varnish. But, according to Hermeneia’s text, there is no reference including both resins in the same recipe. So, a hypothesis could be made that the panel had been revarnished without cleaning the surface or removing the previous varnish layer. This hypothesis could also explain the presence of an intermediate layer of pollutants and sediments among the organic varnish layers, as it was identified through OM and SEM examinations for samples #4 and 6a.

2. The Zoodochos Pigi –The Phaneromeni

2.1. Description

The iconography of the Zoodochos Pigi (**Fig.149**), painted around 1737 by Dionysius', generally follows all the relevant instructions on this subject found in his Hermeneia. Dionysius represents Theotokos from the waist up, with arms outstretched above a circular basin, while Christ is represented as a child and is set before her from the waist up, bearing an open codex which is inscribed with a passage from John's Gospel: "But whoever drinks of the water that I shall give him will never thirst" (John 4:14) (**Fig.150**). In the gold background, over Theotokos' shoulders, an inscription identifies the Mother of God as the "Zoodochos Pigi" and the "Phaneromeni" -she who revealed Christ to the world. Theotokos is portrayed bearing a crown placed on her had by two winged angels carrying scrolls, one of which reads: "Hail, spotless and divine fountain" and the other one: "Hail, pure and life-giving fountain". The circular basin is supported on a pedestal rising from a spring of water in which fish are depicted. In the lower half of the composition, a multitude of figures surround the fountain, identified by their clothing as clerics and monarchs, as well as the sick and the infirm.

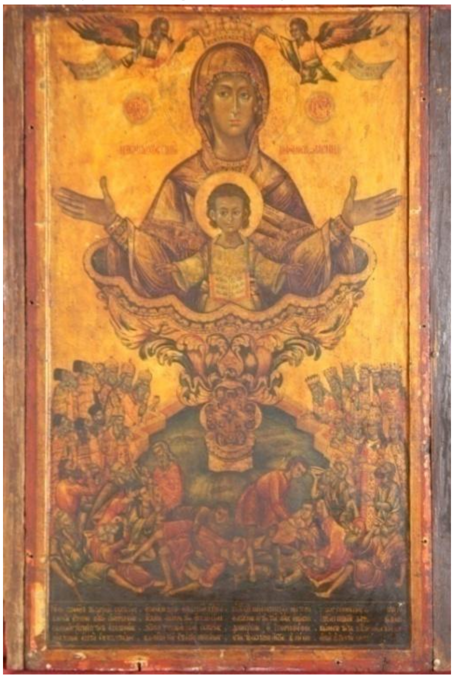


Fig.149 Zoodochos Pigi, 1737, Dionysius, Church of Transfiguration, Fournas *(personal archive Th. Mafredas)*

The figures in the lower foreground are depicted as emaciated and angular and are represented in attitudes of distress (Kakavas 2008, p. 190; Kakavas, Mafredas & Giannoulopoulos 2013, p. 317).

Fig. 150 Zoodochos Pigi-Detail. The epigram from the open Gospel held by young Christ in front of his chest *(personal archive Th. Mafredas)*

The dedicatory epigram is developed in four verses (**Fig.151**): "All of those who desire double salvation come forward with sincere intent, to venerate the Mother of God and drink the water that purifies the stomach. Just happened with my own illness, for which reason I have erected this church beautifying it with holy icons expending much sweat and money and offering everything even the Akolouthia, a soul-felt gift for my own salvation. Dionysius, the historiographer who hails from this town and from the family of Chalkeon. One-thousand and seven-hundred and thirty and seven units, in the current and new year of our salvation and more specifically, on the twenty-fifth of November"[32] (Kakavas 2008, p. 187; Dionysios 1938, p. 32).

Fig.151 Zoodochos Pigi. Detail. The dedicatory inscription
(personal archive Th. Mafredas)

The back side of the panel also bears a Cross with letters forming the name of Christ and the word of victory (in Greek): IC//XC//NI/KA (**Fig.152**).

Fig.152 The back side of panel #2
(personal archive Th. Mafredas)

[32] «Όσοι ποθείτε την διπλήν σωτηρίαν, ενθάδε δεύτε ειλικρινεί καρδία, την του Θεού μεν λιτανεύειν Μητέρα, ύδωρ πίνειν μεν δε το αγνίζον γαστέρα. Καθώς έτυχον καγω εν αρρωστία, ου χάριν ανήγειρα την εκκλησίαν, φαιδρύνας αυτήν ταις αγίαισ εικόσιν, ίδρωσιν πολλοίς δαψιλεί τε τη δόσει. Προσθείς τα πάντα της τε ακολουθίας, δώρον ψυχικόν ιδίας σωτηρίας, Διονύσιος ο ιστοριογράφος, κώμης τε ταύτης και του Χαλκέως κλάδος. Μία χιλιάς, επτά εκατοντάδες και δεκάδες τρεις, έτι επτά μονάδες, έτος το σωτήριον όντως και νέον, είκας και πεντάς νοεμβρίου ου πλέον» (=25 Νοεμβρίου 1737) (Dionysios 1938, p. 32)

2.2. Imaging Techniques

2.2.1. IR photography

The application of IR photography (**Fig.153**) provided numerous features concerning Dionysius's drawing. It was able to identify the intense drawing line in Christ's and Theotokos' garments, and the decoration in Christ's garment (**Fig.154**) (Kakavas, Mafredas & Giannoulopoulos 2013, p. 322).

Fig.153 Panel #2 IR Photography *(personal archive Th. Mafredas)*

Fig.154 Detail. Intense drawing of Christ' and Theotokos garments *(personal archive Th. Mafredas)*

Fig.155 Detail from Theotokos left maniple *(personal archive Th. Mafredas)*

Fig.156 Detail from Christ's garment *(personal archive Th. Mafredas)*

The intense drawing line identified in garments contrasts with the drawing line that Dionysius applied for the figures' faces, which is a gentle and discrete line. A characteristic example can be found in **Fig.155-156** where the intense drawing line in Christ's garment can be easily distinguished from the soft line used for Christ's neck. Another characteristic point can be seen in Theotokos' maniples, at which an intense perimetric drawing of the maniples can be observed.

The features of IR radiation allowed the identification of some details that were not easily recognizable because of the deterioration of varnish, such as the details of the dedicatory epigram and details from the figures over the epigram (**Fig.157-158**).

Fig.157 The dedicatory epigram in IR *(personal archive Th. Mafredas)*

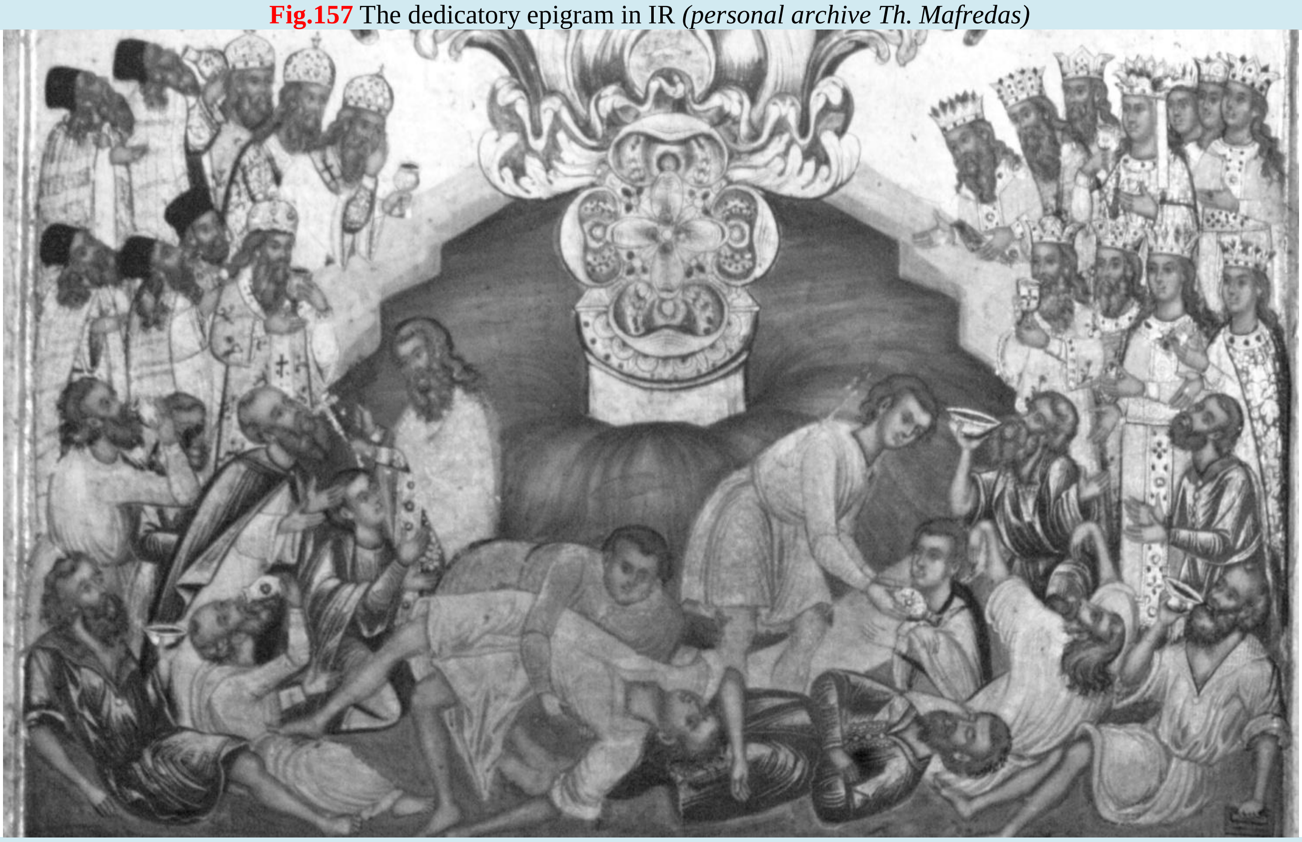


Fig.158 The figures in the lower part of the theme *(personal archive Th. Mafredas)*

Furthermore, it was able to identify details from the garments of the Angels which were not distinguishable because of the varnish deterioration, and to read the epigrams in the Angels' scrolls, which were not easily read in Vis (**Fig.159-160**).

Fig.159 Left Angel. Detail
(personal archive Th. Mafredas)

Fig.160 Right Angel. Detail
(personal archive Th. Mafredas)

Finally, through IR radiation, it was possible to study the drawing details in some areas, such as the Theotokos' mouth and eyebrows (**Fig.161**). For the mouth, some traces from the drawing line were identified, while the different directions for each eyebrow were also observed (**Fig.162**).

Fig.161 Detail from Theotokos
(personal archive Th. Mafredas)

Fig.162 Detail for mouth and eyebrasses
(personal archive Th. Mafredas)

Furthermore, details concerning the drawing of Christ's hair (**Fig.163**) and traces from the drawing line of both Christ's and Theotokos' hands (**Fig.164-166**) were identified.

Fig.163 Detail from Christ's face *(personal archive Th. Mafredas)*

Fig.164 Detail form Christ's right hand. Traces from the drawing line *(personal archive Th. Mafredas)*

Fig.165 Detail form Theotokos left hand. Traces from the drawing line *(personal archive Th. Mafredas)*

Fig.166 Detail form Theotokos right hand. Traces from the drawing line *(personal archive Th. Mafredas)*

2.3. Microscopic Techniques

2.3.1. Digital Microscopy (DM)

DM was applied at two different intervals, in order to uncover details about the painting and gilding technique. It was applied in 14 different point of the painting surface (**Fig.167**), (continuing the numbering from the previous panel) in different magnifications and the results helped to understand Dionysius' painting technology.

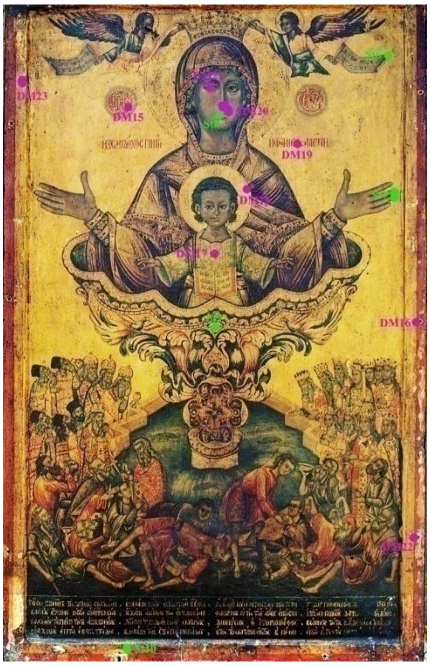


Fig.167 Panel #2 Digital Microscopy spots *(personal archive Th. Mafredas)*

The DM 15 point was in the upper left area, in the gold background (**Fig.168**) where the fonts of the epithet of the Theotokos as the mother of God were (in Greek: MHP). It seems that Dionysius used a red pigment over the gold layer in order to make the decoration and the two main letters of Theotokos' name appear metallic (**Fig.169-171**), a feature that had already been observed in panel #1.

Fig.168 The decoration metal with the letters of Mother of God *(personal archive Th. Mafredas)*

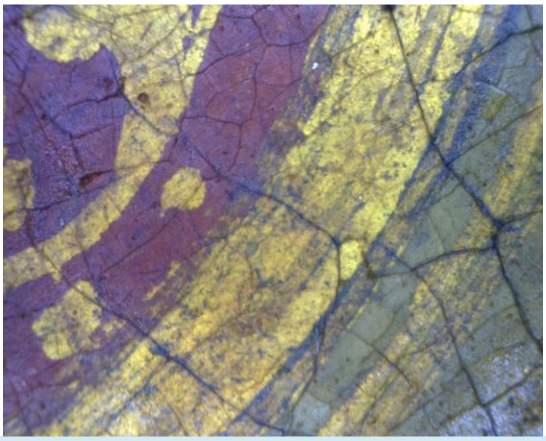


Fig.169 Detail from the gold perimetric line of the metal and the red pigment inside the metal (magnification 60X) *(personal archive Th. Mafredas)*

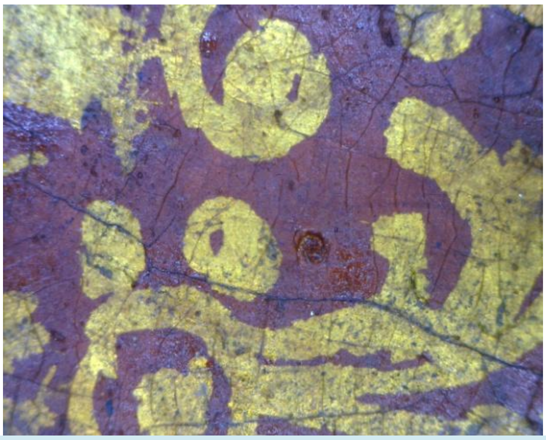


Fig.170 Detail of the decoration of the metal with red pigment over the gold layer (magnification 60x) *(personal archive Th. Mafredas)*

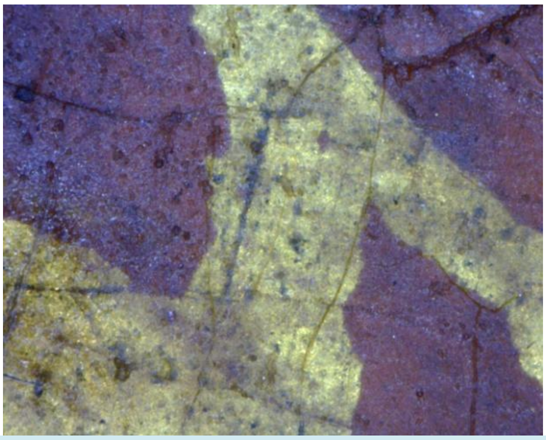


Fig.171 Detail of the decoration. The red pigment applied over the gold layer. (Magnification 160x) *(personal archive Th. Mafredas)*

The same specific feature of using pigment over the gold layer in order to achieve a specific decoration was also found in St9 (**Fig.172**), which was located in the upper part of the blessing vessel, where Dionysius used a dark pigment in order to decorated the vessel with a face (**Fig.173-175**) (Kakavas, Mafredas & Giannoulopoulos 2013, p. 320). Upon studying this point, there was an impression of similarity with the decoration in panel #1; more specifically, in the decoration of Christ's mitre with the painting of the face of the Father.

Fig.172 The upper place of the blessing vessel. Detail from the decoration *(personal archive Th. Mafredas)*

Fig.173 Detail from the decoration of the face in the upper place of the blessing vessel (Magnification 60X) *(personal archive Th. Mafredas)*

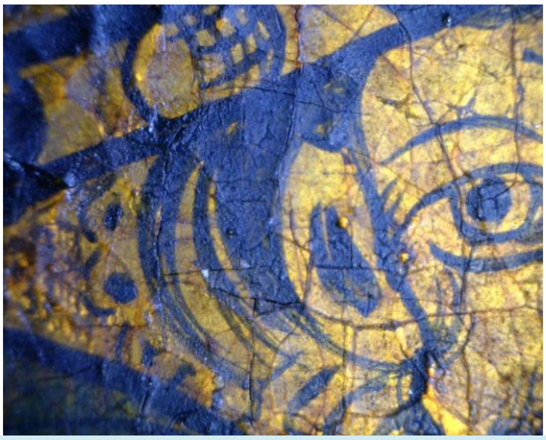


Fig.174 Detail from the decoration of the face in the upper place of the blessing vessel (Magnification 60X) *(personal archive Th. Mafredas)*

Fig.175 Detail from the decoration of the face in the upper place of the blessing vessel (Magnification 60X) *(personal archive Th. Mafredas)*

Furthermore, it was found that Dionysius repeats the same technique, using pigment over the gold layer, in order to achieve the decoration of the letters. For example, DM19 (**Fig.176** in the epigram of the panel shows that Dionysius applied red pigment over the gold layer for the letters of the epigram (**Fig.177**).

Fig.176 The epigram of the Panel 'The Phaneromeni' *(personal archive Th. Mafredas)*

Fig.177 Detail of the letter from the epigram. Red pigment over the gold layer. Magnification 60X *(personal archive Th. Mafredas)*

Studying the decoration in DM17 (**Fig.178-179**), which was located in the middle of Christ's garment; helped to make the hypothesis that Dionysius used gold pigment over the green garment in order to achieve the garment decoration (**Fig.180-183**).

Fig.178 The decoration on Christ's garment (Vis) *(personal archive Th. Mafredas)*

Fig.179 The previous image in IR. It is able to distinguish details from the decoration. *(personal archive Th. Mafredas)*

Fig.180 The decoration with gold pigment over the green garment. (Magnification 60X) *(personal archive Th. Mafredas)*

Fig.181 The decoration with gold pigment over the green garment. (Magnification 60x) *(personal archive Th. Mafredas)*

Fig.182 Detail. The decoration with gold pigment over the green garment. (Magnification 210X) *(personal archive Th. Mafredas)*

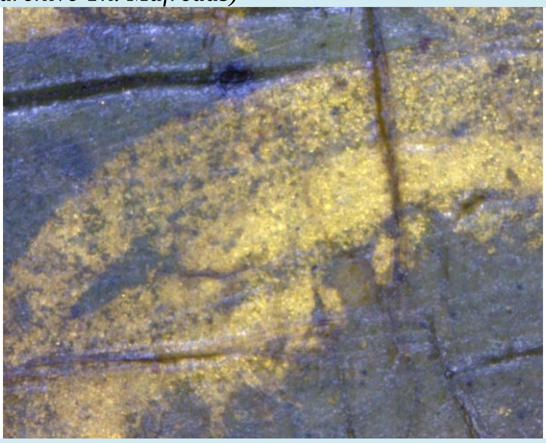


Fig.183 Detail. The decoration with gold pigment over the green garment. (Magnification 210X) *(personal archive Th. Mafredas)*

From the DM18 point, which was located at the right edge of Christ's halo near the letter N (**Fig.184**), it was possible to identify some traces from the drawing of the details of the halo, such as the horizontal line above the letter N and the connection of that horizontal line with the circle of the halo (**Fig.185-187**).

Fig.184 Detail. The right edge of Christ's halo *(personal archive Th. Mafredas)*

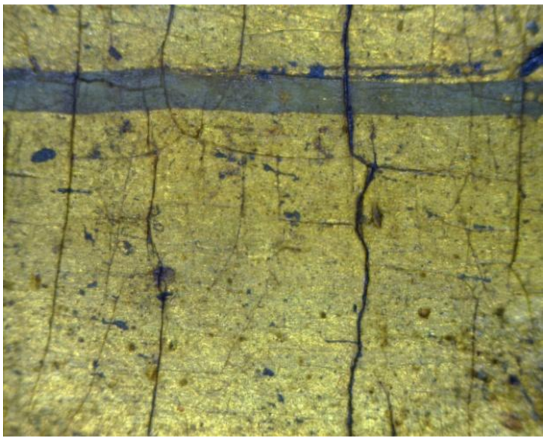


Fig.185 The horizontal line over the letter N in Christ's halo. Traces from the drawing line. (Magnification 60X) *(personal archive Th. Mafredas)*

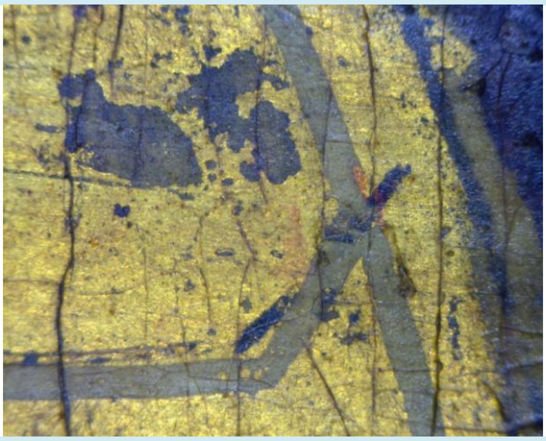


Fig.186 The connection point of the horizontal line with the cycle from Christ's halo. Traces from the drawing line. (Magnification 60X) *(personal archive Th. Mafredas)*

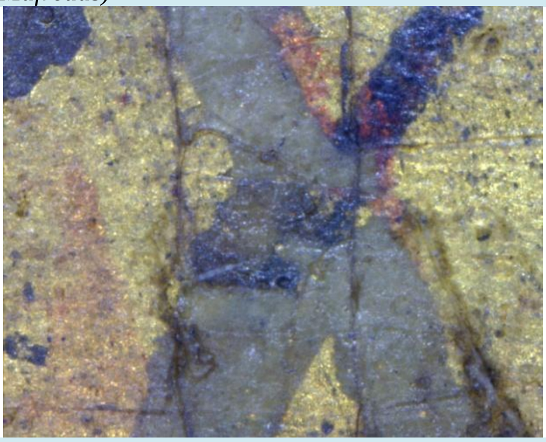


Fig.187 The connection point. Traces from the drawing line and from red pigment (Magnification 210X) *(personal archive Th. Mafredas)*

Besides the drawing traces, it should be noted that traces of red pigment were also found in the connection point of the horizontal line with the circle of Christ's halo (**Fig.187**). The same traces of drawing line were found in DM20 and St8, which were located on the Theotokos' mouth (**Fig.189**), both above and below the red pigment of the lips, as well as at the lower part of the nose (**Fig.190-191**).


Fig.188 Detail. Theotokos' face *(personal archive Th. Mafredas)*

Fig.189 Detail. Theotokos' mouth (Magnification 60X) *(personal archive Th. Mafredas)*


Fig.190 Detail. Theotokos' mouth. The lower lip (Magnification 210X) *(personal archive Th. Mafredas)*

Fig.191 Detail. Theotokos' lower part of nose (Magnification 60X) *(personal archive Th. Mafredas)*

Furthermore, the examination of the painting technique under digital microscopy helped to understand Dionysius's excellent technique as it was revealed during the study of DM 21, which was located in the Theotokos' eye. Even though the discoloration and the deterioration of the varnish layer diminished the clarity of the painting details, we can discern how clean and sophisticated the details of the eye are (**Fig.192**).

Fig.192 Detail from Theotokos' eye (Magnification 60X) *(personal archive Th. Mafredas)*

Traces from the initial drawing made by a brush were also found in St6 spot, located in the upper part of the painting surface and, more specifically, at the edge of the scroll of the right angel (**Fig.193**). These traces define the drawing, as it can be seen in the following figures (**Fig.194-196**).

Fig.193 Detail from the upper part of the painting surface. *(personal archive Th. Mafredas)*

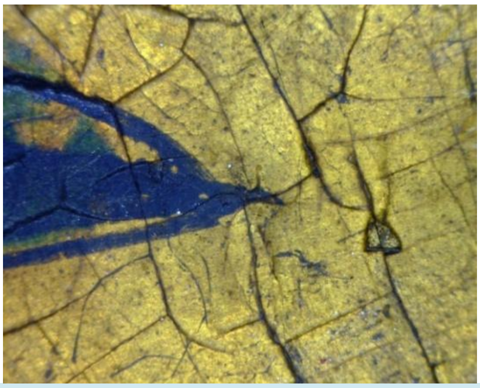


Fig.194 The edge of right Angel scroll. Traces from the initial drawing. Magnification 30X *(personal archive Th. Mafredas)*

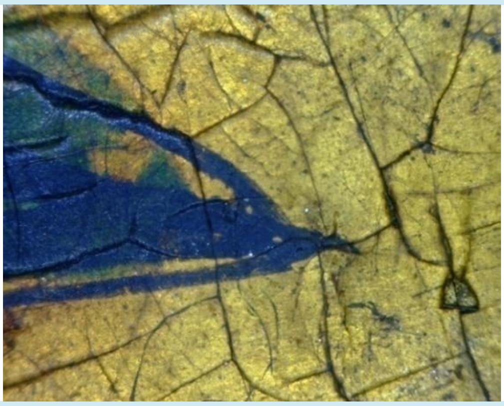


Fig.195 The edge of right Angel scroll. Traces from the initial drawing. Magnification 55X *(personal archive Th. Mafredas)*

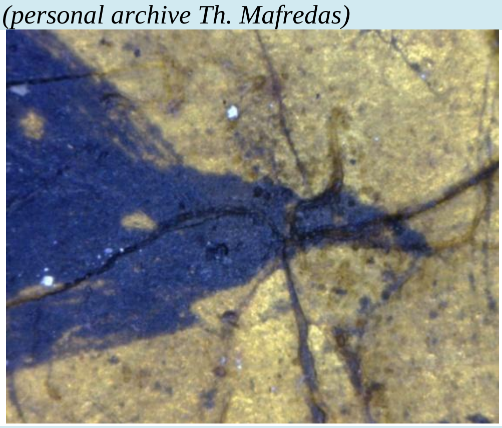


Fig.196 The edge of right Angel scroll. Traces from the initial drawing. Magnification 195X *(personal archive Th. Mafredas)*

Concerning the construction technique, through studying the painting surface in DM16 and DM22, two points in the vertical frame of the panel (the first in the middle and the second in the lower part), it was found that, in DM16, there was a thick layer of gesso preparation containing some black grains (**Fig.197**), and a thin red pigment layer (**Fig.198**). In DM22 beside the thickness of the layer which was very thin (**Fig.199-200**), the same traces of black grains (**Fig.201)** in and over the

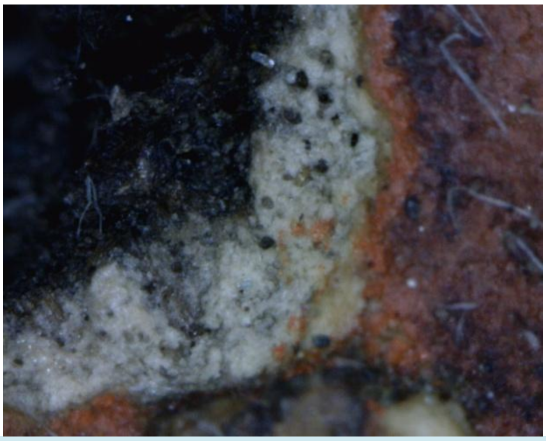


Fig.197 DM16 hit point. Thick layer of gesso preparation with same black grains and thin layer of red pigment (Magnification 60X) *(personal archive Th. Mafredas)*

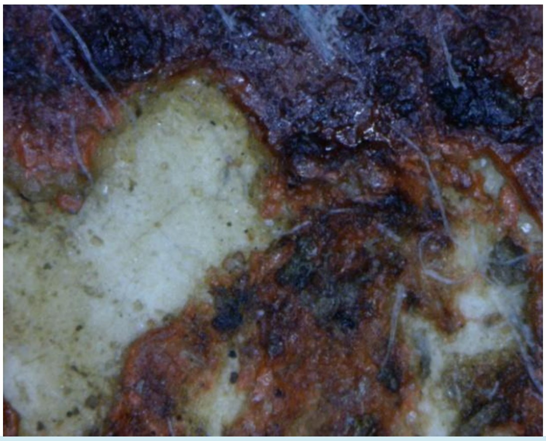


Fig.198 DM16 hit point. Thin layer of red pigment (Magnification 190X) *(personal archive Th. Mafredas)*

gesso preparation were found, making it difficult to distinguish whether these were remains from a bole layer.

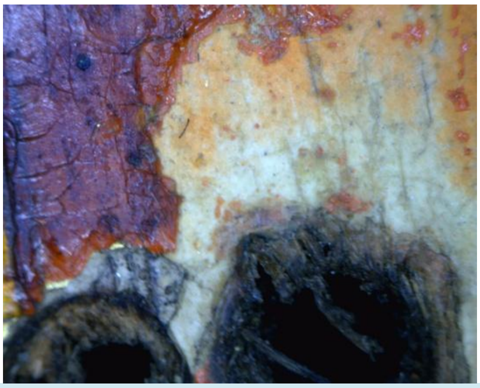


Fig.199 DM22 hit Thin layers of red pigment and gesso (Magnification 60X) ***(****personal archive Th. Mafredas)*

Fig.200 Thin layers of red pigment and gesso (Magnification 210X) *(personal archive Th. Mafredas)*

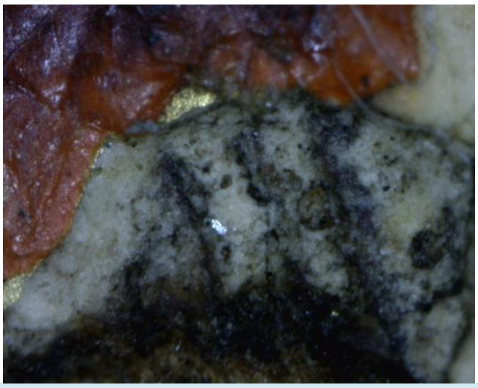


Fig.201 Black grains in the gesso preparation and traces from a gold leaf. (Magnification 210X) *(personal archive Th. Mafredas)*

Additionally, studying the panel on DM23 point (**Fig, 202-203**) which was located in the upper left part of the vertical side of the panel, in order to examine and study the gilding technique, a very thin layer of gold over the gesso preparation was found. Furthermore, it was difficult to understand whether there were any traces from bole preparation, even though there were some identical traces on the previous panel (panel #1) that could help to make the hypothesis that a layer of bole might be present.

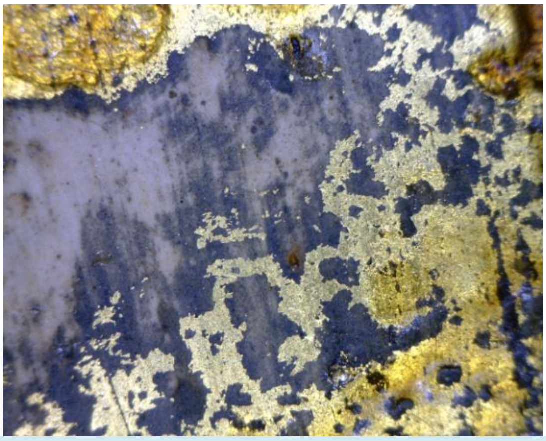


Fig.202 DM23 Very thin layer of gold. Traces from the presence of bole layer; (Magnification 60x) *(personal archive Th. Mafredas)*

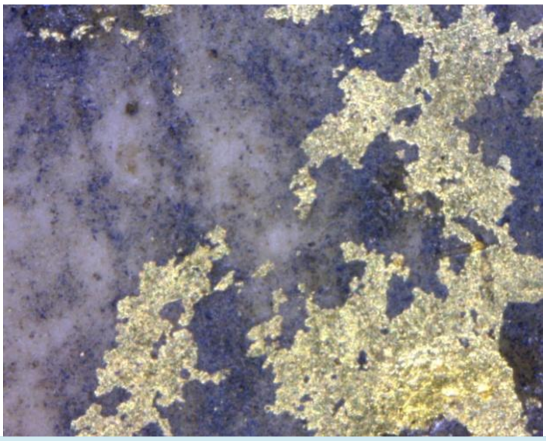


Fig.203 DM23 Very thin layer of gold. Traces from the presence of bole layer; (Magnification 210X) *(personal archive Th. Mafredas)*

Finally, thin painting and gold layers also were found in St10, which was located at the bottom left part of the horizontal frame of the panel (**Fig.204**).

Fig.204 St10. Thin painting and gold layers (Magnification 60X) *(personal archive Th. Mafredas)*

2.3.2. Optical and Fluorescence Microscopy

For applying OM, three (3) different samples in cross section were detached from the panel (***Appendix 2***); two of them (samples #9 and #9a) for studying the painting layer and one (sample #10) for studying the gilding technique. During the sampling process, it was found that all the layers were very thin, something that was also confirmed during DM. Thus, out of the three samples, only two (#9 and #10) were prepared properly for OM examination. All samples were examined both in Vis and in UV.

The first sample (#9) that was examined with OM was taken from the lower part of the panel and, more specifically, from the horizontal frame of the painting in order to examine the painting layer (**Fig.205-206**). Studying the sample from above, in Vis and under UV radiation, it was found that the pigment layers probably consisted of two distinct pigment layers (**Fig.207-208**).

Fig.205 The lower part of the horizontal frame of the icon for sample #9. In the cycle the area for sample (*personal archive Th. Mafredas*).

Fig.206 Sampling position for cross section sample #9 *(personal archive Th. Mafredas)*

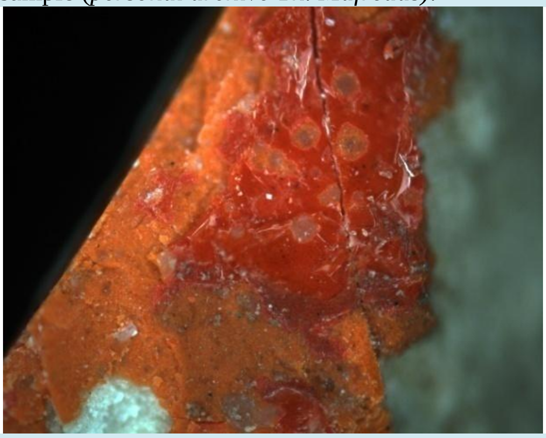


Fig.207 The upper part of the sample #9. Two layers of a red pigment *(personal archive Th. Mafredas)*

Fig.208 The upper part of the sample #9. Two layers of a red pigment under UV radiation *(personal archive Th. Mafredas)*

The microscopic examination of the sample #9 revealed the stratigraphy of the sample (**Fig.209**), which consisted of 4 different layers (**Fig.210**). The first was the gesso preparation layer and, over it, there were two different pigment layers: the first contained red-yellow pigment grains, and the second had red pigment grains. The fourth and final layer was of organic composition. From the microscopic examination, it was possible to distinguish the two different red pigment layers, as well as that the fact that the organic layer was very thin (**Fig.211-212**).

Fig.209 The cross section of sample #9 *(personal archive Th. Mafredas)*

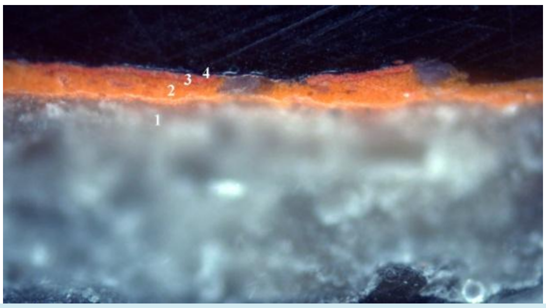
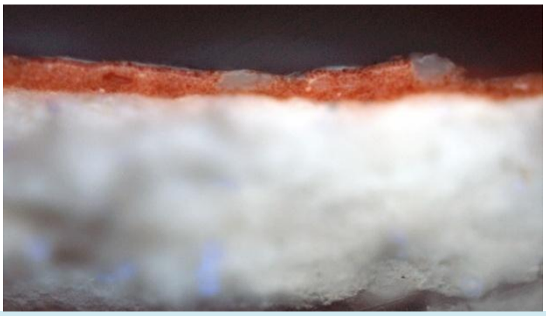


Fig.210 The stratigraphy of the sample #9. Four different layers *(personal archive Th. Mafredas)*



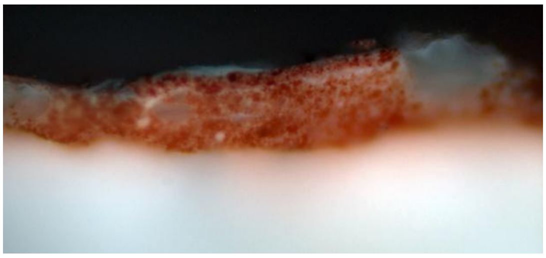


Fig.211 The sample #9 under UV radiation *(personal archive Th. Mafredas).*

Fig.212 The sample under UV radiation. Detail. It is able to distinguish the two different red pigment layers. Magnification 50x *(personal archive Th. Mafredas)*

The second sample (#10), was taken from the area in the upper part of the horizontal frame of the panel over Theotokos' crown, in an already damaged area (**Fig.213-214**)

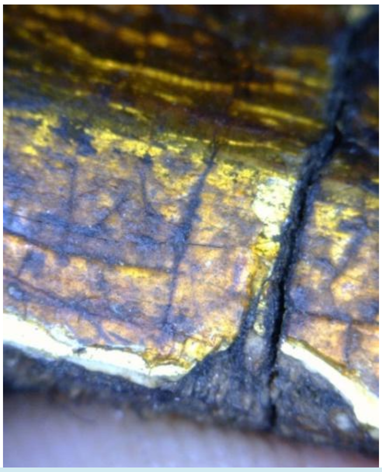


Fig.213 The sampling are for sample #10 *(personal archive Th. Mafredas)*

Fig.214 The sampling area for sample #10. In situ magnification 60X before the detachment of the sample. *(personal archive Th. Mafredas)*

From the microscopic examination, it was found that the gold layer is very thin, while traces of the presence bole were not identified. Traces of the varnish layer were not found either. So, according to the microscopic observation, the stratigraphy of the sample consisted of two layers: the gesso preparation and the gold leaf (**Fig.215-216**).

Fig.215 Stratigraphy of sample #10 *(personal archive Th. Mafredas)*

Fig.216 Stratigraphy of sample #10, under UV radiation *(personal archive Th. Mafredas)*

2.3.3. Microchemical Tests

A staining test for the identification of proteinaceous materials was performed on sample #10 using NA2as a reagent. From the staining test, it can be observed that the entire sample, including the gesso layer, has produced a blue stain (**Fig.217-218**).

Fig.215 Staining test. Sample #10, before NA2 *(personal archive Th. Mafredas)*

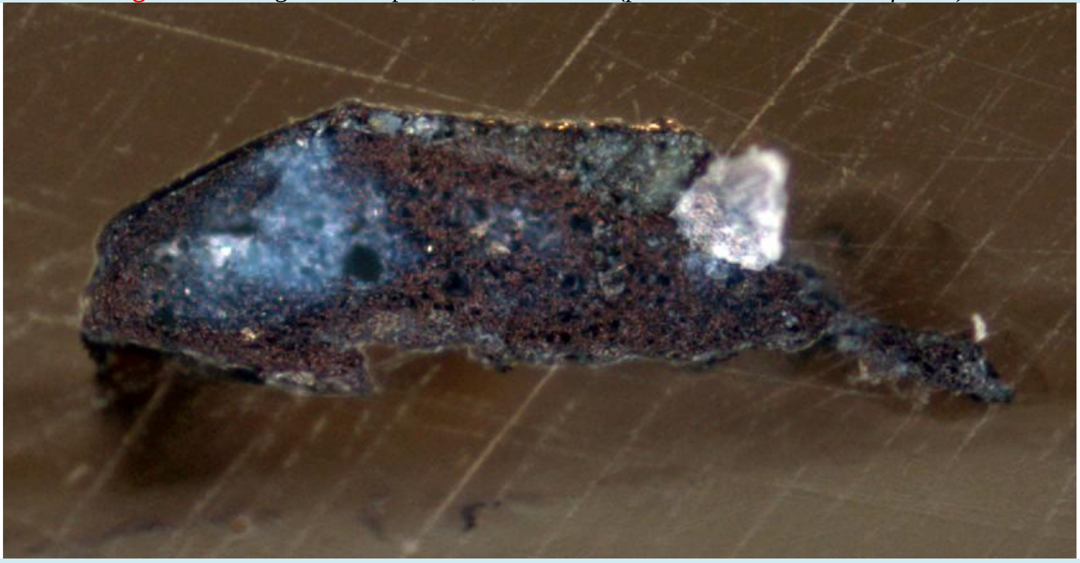


Fig.218 Staining test. Sample #10, after NA2 *(personal archive Th. Mafredas)*

From the staining test, a large concentration of proteinaceous materials can be observed underneath the gold leaf (**Fig.219-220**). A differentiation in the color distribution of the gesso layer can also be noted, which could be explained as a differentiation in the concentration of organic and inorganic materials. It could also be that the gesso layer, as a porous material, has the capability of absorbing more of the reagent.

In general, the reaction with the NA2 reagent appears to be more successful than sample #4 (panel #1), which can be indicative of a greater concentration of proteinaceous materials in the binding medium.

Fig.219 Staining test. Sample #10 before NA2, detail *(personal archive Th. Mafredas)*

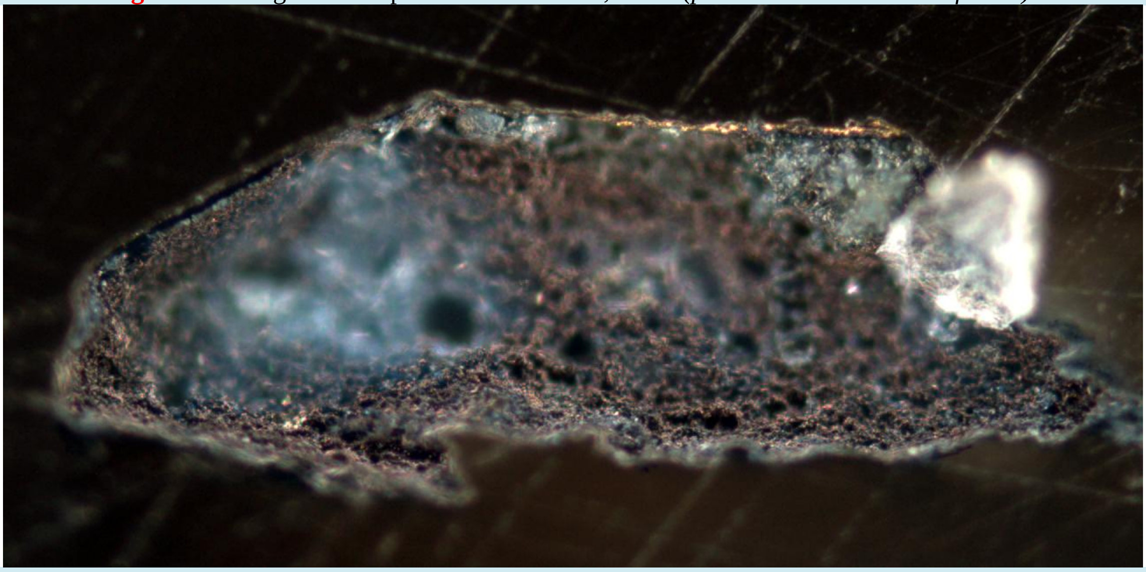
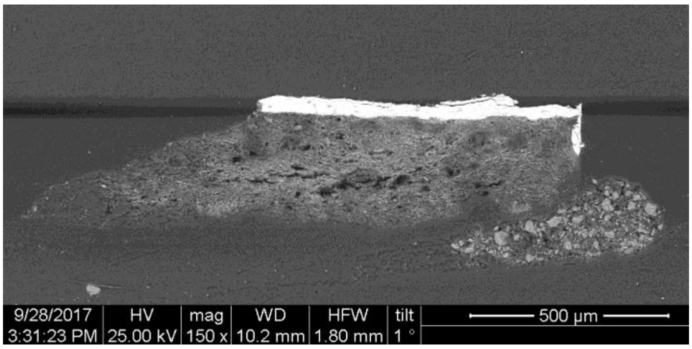


Fig.220 Staining test. Sample #10 after NA2, detail *(personal archive Th. Mafredas)*

2.3.4. Scanning Electron Microscopy

Upon examining sample #9 with SEM (**Fig.221**) through the BSE images it was possible to measure the thickness of each layer (**Fig.222**) and observe the pigment grain size, to distinguish the pigment layers, and identify a tiny layer over the preparation.



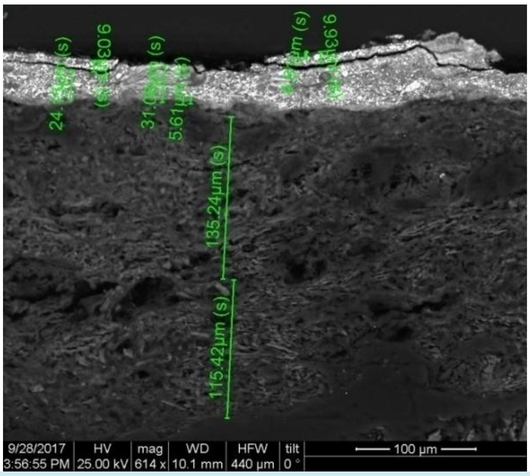
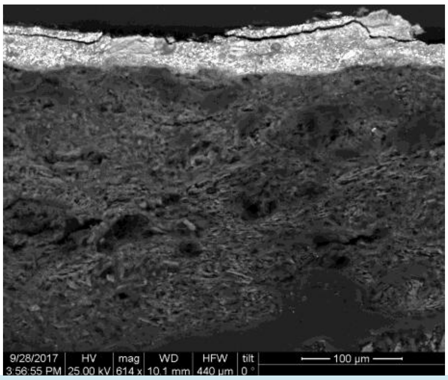


Fig.221 Sample #9. SEM *(personal archive Th. Mafredas)*

Fig.222 Sample #9. SEM. Measurements of layers' thickness *(personal archive Th. Mafredas)*

Besides those, some points of the second painting layer appear to be detached from the first paint layer directly below it. Concerning the preparation layer, it was found that it consisted of two layers which had not been worked with diligence; a common feature with the samples examined for panel #1. It was possible to recognize slightly different directions in preparation, as well as some points and areas with great holes and big grains (**Fig.223-224**).

The gesso preparation consisted of two different layers, each with a different thickness; the first is 115.42μm and the second is 135.24μm. From the direction of the flakes, the quality of work for each layer separately and for the total gesso preparation layer (which had not been worked with diligence) could be evaluated.



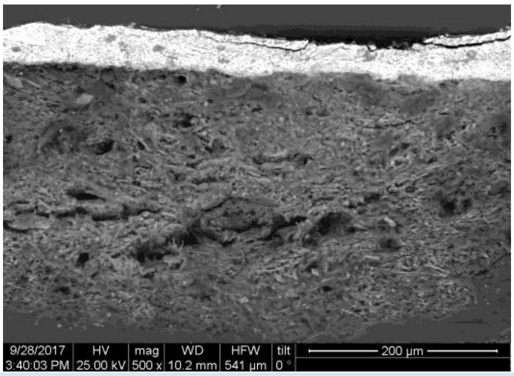


Fig.223 The gesso preparation at sample #9

Fig.224 The gesso preparation at sample #9 (personal archive Th. Mafredas) (personal archive Th. Mafredas)

Over the gesso layer, a very thin layer which was 5.61μm high was detected, and seemed to consist of organic material. Above this thin layer, the presence of two different pigment layers was found, which, however, exhibit some level of detachment from one another (**Fig.225-226**). The first pigment layer has a thickness ranging from 24.13μm to 31.08μm; the second pigment layer has a thickness of 9.03μm to 9.93μm.

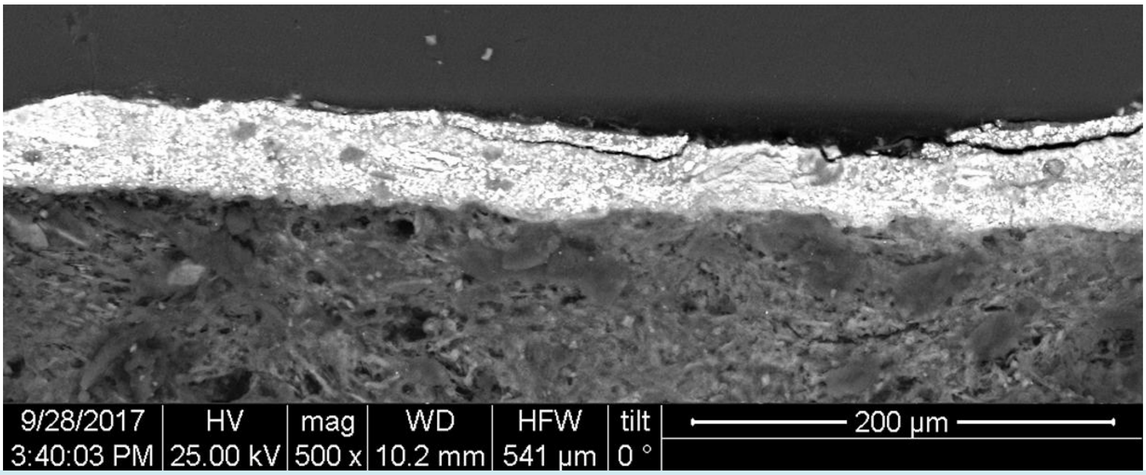


Fig.225 Detail of sample #9. Gesso layer, thin layer above it, two pigment layers, detachment of the 2nd pigment layer *(personal archive Th. Mafredas)*

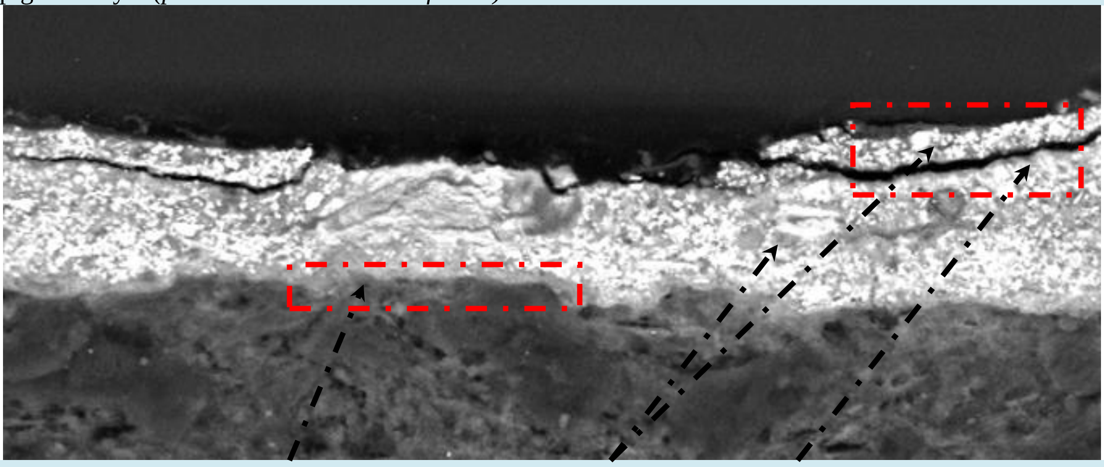


Fig.226 Detail. Thin layer above gesso, the two pigment layers, detachment of the 2nd pigment layer *(personal archive Th. Mafredas)*

Over the second pigment layer, a thin, non-continuous organic layer was found–probably the varnish layer–whose thickness was 4.81μm.

Studying sample #10 under SEM allowed us to see its stratigraphy. A thin, continuous gold layer over a very thin bole layer was detected. Above the gold leaf, a thin organic layer was also found, probably accounting for the varnish layer Below the bole layer, a thick gesso layer was identified, whose thickness was up to 185μm (**Fig.227**).

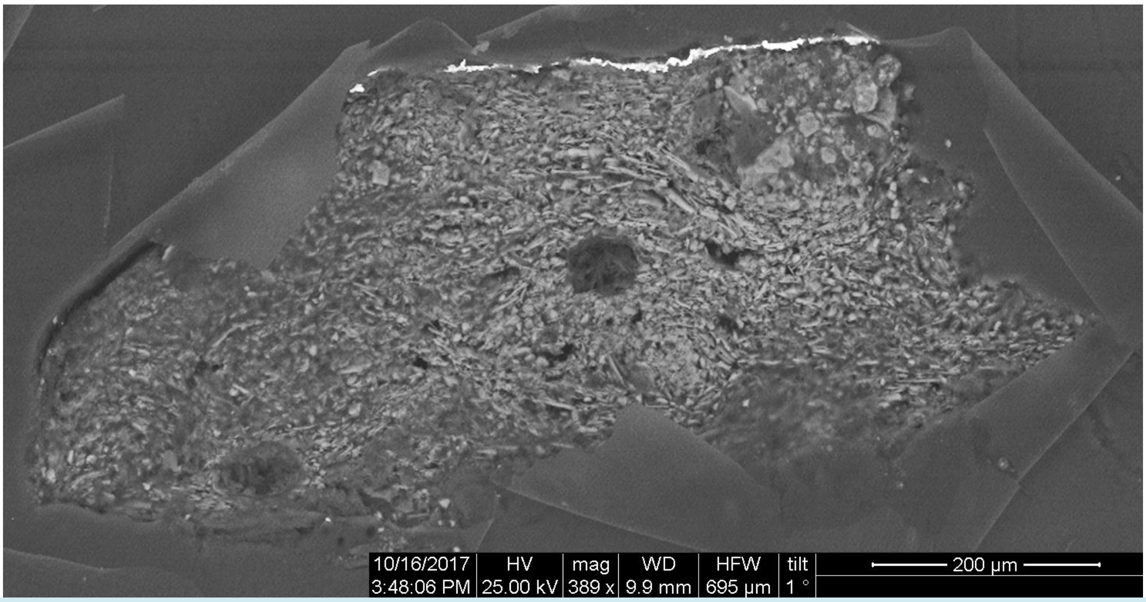


Fig.227 Sample #10 *(personal archive Th. Mafredas)*

Furthermore, the structure of the gesso layer was studied. From the direction of the flakes, it was found that the gesso layer consisted of two (and occasionally, three) different layers while, in the upper right part of the sample, there was an area containing big grains from the gesso layer. The differentiation in gesso directions was identified, along with multiple areas and points that contained great holes and big grains. As was found in previous samples either from panel #1 or from the same panel, it was common practice for Dionysius to apply two or three different layers of gesso, even though he had mentioned the implementation of six or, possibly, more layers in his book. Another characteristic feature is that, in both panels, these particular layers were worked without due diligence.

2.4. Analytical Techniques

2.4.1. Elemental Techniques

2.4.1.1. X-Ray Fluorescence

XRF was applied on the painting surface of the panel painting in 12 different points (**Fig.228**) (continuing the numbering from the previous panel),in order to obtain data from a variety of areas. The goal was to determine Dionysius's color pallet and identify pigments in areas where the varnish layer had lost its transparency and had become opaque, compromising the painting's purity. Furthermore, the use of XRF in gold areas provided data that helped to conclude about the use of a bole layer, the kind of it, and the type of metal used.

Fig.228 Zoodochos Pigi. XRF spots
(personal archive Th. Mafredas)

From hit points 18-20, the XRF data provided an elemental analysis of the ingredients of the bole layer (**Table 9**). According to the spectra (***Appendix 4***), Cu, Fe, Pb and Ca were identified in addition to the Au. In spot 18, among other trace elements, S and Hg were also identified, elements which are indicative of the presence of cinnabar. Having in mind that, in sample #9, two different red pigment layers were identified, and that the sampling area was in the same perimetric frame of the panel as hit spot 18, we could hypothesize that two kinds of red pigment, red lead (Pb_3O_4) and cinnabar (HgS), were used in the perimetric frame of the panel. The other two spots, 19 and 20, are located at the gold background of the panel, so the absence of Hg and S could be explained (***Appendix 4***).

The XRF analysis of the Theotokos' flesh in hit point 21 (**Table 9**) detected the presence of Pb, Fe, and Cu (***Appendix 4*)**, possibly coming from a mixture of lead white (2PbCO3•$Pb(OH)_2$) and a yellow/red ochre with a small quantity of green, pigments corresponding to Dionysius's recipe about proplasmos (Dionysius 1909, p. 20). The presence of Hg could be explained under Dionysius's instructions about using red pigment. More specifically, Dionysius clearly mentioned, among others, that on the Theotokos' face a small quantity of red should always be used, which could be a mixture of cinnabar with the pigments that constituted the flesh(Dionysius 1909, p. 22) –in this case, the same as the pigments for proplasmos.

The same elements of Pb, Hg, Fe and Cu (***Appendix 4***), were also traced in hit point 22 (**Table 9**), but there is an important difference from spot 21: spot 22 is located in a red area. So, according to the area and the obtained spectra, it could be assumed that Pb possibly comes from red lead instead of lead white, which was used in spot 21.

The XRF analysis of the whitish color in hit spot 23, Christ' open gospel, and in spot 24, the open scroll of the left angel, provided the same trace elements: Pb, Cu, and Fe (**Table 9**). The presence of Pb possibly results from the use of lead white ($2PbCO_3$•$Pb(OH)_2$), the presence of Fe comes from a yellow/red ochre, and the presence of Cu possibly comes from a small quantity of green. The combination of these three trace elements corresponds to the pigments that are used in Dionysius's recipe for proplasmos (Dionysius 1909, p. 20). Furthermore, the trace elements identified in these two spots are exactly the same with those found in hit spot #8 from panel #1 (***Appendix 4***).

The XRF analysis of spot 25 (***Appendix 4***) provided the same trace elements as spots 23 and 24: Pb, Cu, and Fe (**Table 9**). This spot was located in the water inside the blessing vessel, which in Vis appeared as green. From the ageing and the degradation of the varnish layer, it could be assumed with some degree of certainty that this color is probably false. It is known from the theme that the water is blue. As a result, it could be assumed that Cu is from Azurite ($2CuCO_3$•$Cu(OH)_2$) and Pb possibly comes from white lead in mixture with Azurite and a quantity of red/yellow ochre, in order to achieve the right tone of the color representing water.

Concerning a dark pigment which appeared as black in Vis, the XRF hit point #26 was located in the hat of the priest on the left side of the painting surface. According to the obtained spectra (***Appendix 4***), the trace elements were Au, Pb, Fe, Ca, Cu (**Table 9**). The presence of Au could be explained from a neighboring area that contains gold, while Pb possibly comes from red lead in mixture with a red/yellow ochre (Fe) and some quantity of Cu. The presence of Ca is explained by the penetration depth of the XRF analysis as coming from the gesso layer. The presence of Cu could provide two hypotheses. The first one supports that the Cu comes from the mixture with the Au leaf. The second one supports that Cu comes from Azurite, a pigment that Dionysius used in mixture with white lead and ochre in order to yield the color of the water.

Hit point 27, which was located in the ground of the theme, provided a number of trace elements (**Table 9**) in different intensities, as it could be seen from the obtained spectrum (***Appendix 4***). According to the spectrum, the trace elements detected are Pb, Cu, Fe, Mn, and Ca. Once again, the presence of Ca is explained by the penetration depth of the XRF analysis as coming from the gesso layer. For first time, though, Mn appears as a trace element on the painting, which in combination with Fe could suggest the presence of umber (Fe_2O_3+MnO_2), while the presence of Cu may be the result of the presence of a green pigment, while the Pb could imply the presence of red lead. The research spot comes from an area which represents the ground in painting, which theoretically should be attributed by a dark pigment. Under this hypothesis, the presence of red lead in mixture with green and some quantities of umber could be explained in order to achieve the right tone of color representing the ground.

The two last XRF hit spots are located on the perimetric frame of the panel: #28 is on the left vertical frame and #29 is on the bottom horizontal frame. The trace elements from these two spots are almost identical (**Table 9**), with a differentiation in the intensities of the elements for each spectrum (***Appendix 4***). Thus, for spot 28, the order of the trace elements is Ca, Au, Fe, Ar, Pb, S, Cu, and Ti and, for spot 29 the order is Au, Pb, Ca, Fe, Cu, and S. In both cases, the intensity band of Cu is almost the same, which helped to assume that it resulted from the mixture of the gold leaf and the presence of Ca coming probably from the gesso layer. The low intensity of S in both cases could be assumed to come from the gesso layer as an ingredient. An EDX examination in a gesso layer would provide more accurate data on the precise identification of the ingredients of preparation, such as $CaSO_4$. The presence of Pb may come from the bole layer as an ingredient of it. In general, the trace elements are almost the same as the trace elements from respective areas of panel #1; for example, Au, Pb, Fe, Ca, and Cu. This data could help to assume that Dionysius may have used his 2nd recipe for bole (Dionysius 1909, p. 18).

Table 9. *Panel #2- Elemental Analysis – XRF*

Spot	# of Spectrum	Color	Trace elements
18	1842	Gold	Au, Pb, Ca, Fe, Hg, S, Cu, Ti
19	1843	Gold	Au, Ca, Fe, Pb, Cu, Ti
20	1844	Gold	Au, Ca, Fe, Pb, Cu,
21	1845	Flesh	Pb, Hg, Fe, Cu
22	1846	Red	Pb, Hg, Fe, Cu
23	1847	Whitish	Pb, Cu, Fe
24	1848	Whitish	Pb, Cu, Fe
25	1849	Blue (appears as green)	Pb, Cu, Fe
26	1850	Black/ Dark pigment	Au, Pb, Fe, Ca, Cu
27	1851	Brown	Pb, Cu, Fe, Mn, Ca
28	1852	Ground	Ca, Au, Fe, Ar, Pb, S, Cu, Ti
29	1853	Ground	Au, Pb, Ca, Fe, Cu, S

XRF analysis was applied in 12 different spots on the painting surface and the respective spectra were obtained (***Appendix 4***). The interpretation of the data assisted to draw a first conclusion about Dionysius’s color palette (**Table 9**). According the data as presented above, it could be assumed that he used a variety of pigments, all of which are mentioned in his treatise. But, due to the limitations of this technique, quantification analysis couldn’t be provided; only qualification. Furthermore, elements below Al could not be traced because the XRF device used does not allow the detection of elements with an atomic number less than 13, which excluded the detection of C (Mastrotheodoros 2016, p. 163). Finally, trace elements, such as Ar and Ti, are detected, which appear to be impurities of the raw materials without their presence interfering with the presence of raw materials as they are recorded by the intensity bands of the spectra.

Thus, this panel painting, as well as the other three (3), was examined preliminarily with XRF, and then a portion of the pigments were identified by further study of the samples with SEM/EDX, as it will be discussed below.

2.4.1.2. Energy Dispersive X-ray Analysis

The Energy Dispersive X-ray (EDX) spectroscopy provided elemental information about the identity of inorganic materials present in the two samples of pigments and gesso preparation materials.

Upon examining sample #9 (**Fig.229**) with EDX, it was found that the thick layer (bearing no connection to the upper layer) in the right part of the sample was gesso preparation consisting of Ca (Calcium) and S (Sulfur) (**Fig.230**). The same constituents for gesso preparation were also detected in the main layer of gesso from the sample. It should be noted that low intensity bands from Pb probably come from some presence of Pb from rubbing (**Fig.231**).

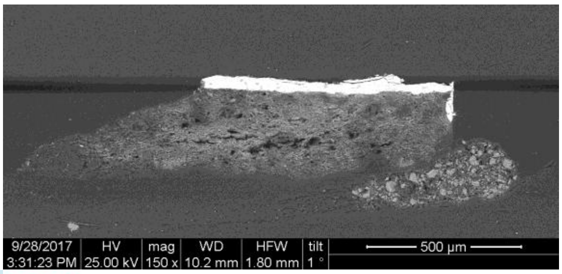


Fig.229 Sample #9 SEM *(personal archive Th. Mafredas)*

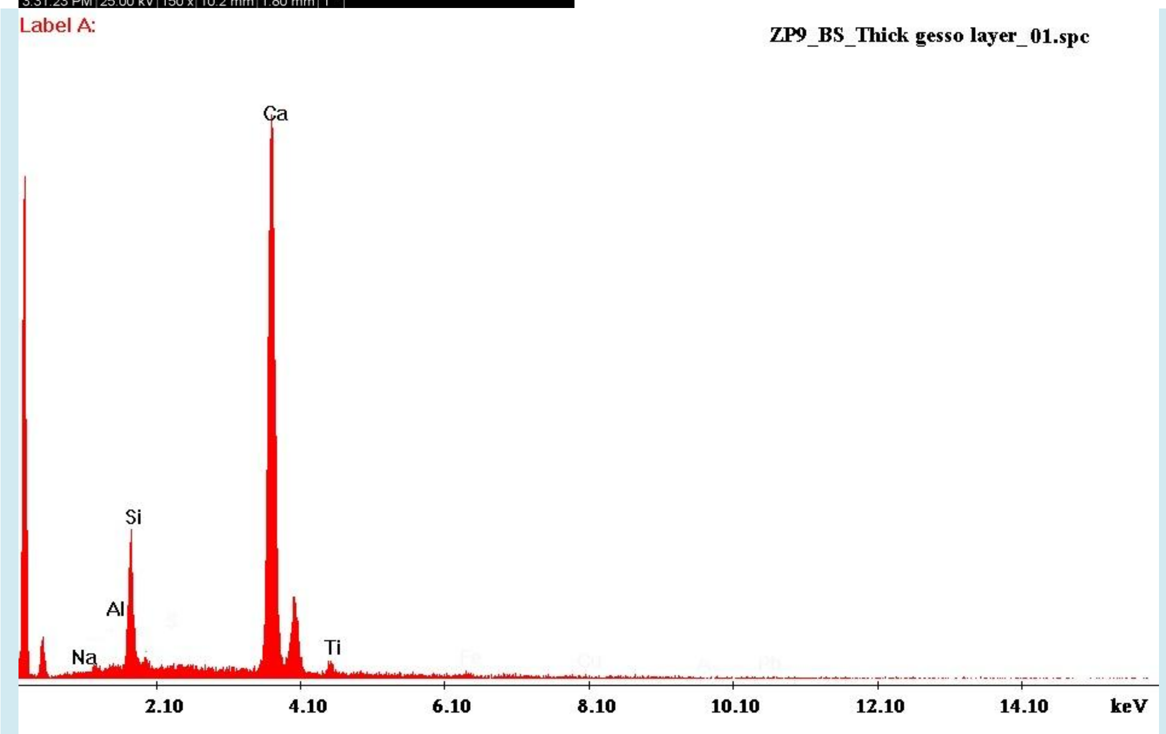


Fig.230 EDX spectrum from thick gesso layer (sample #9) *(personal archive Th. Mafredas)*

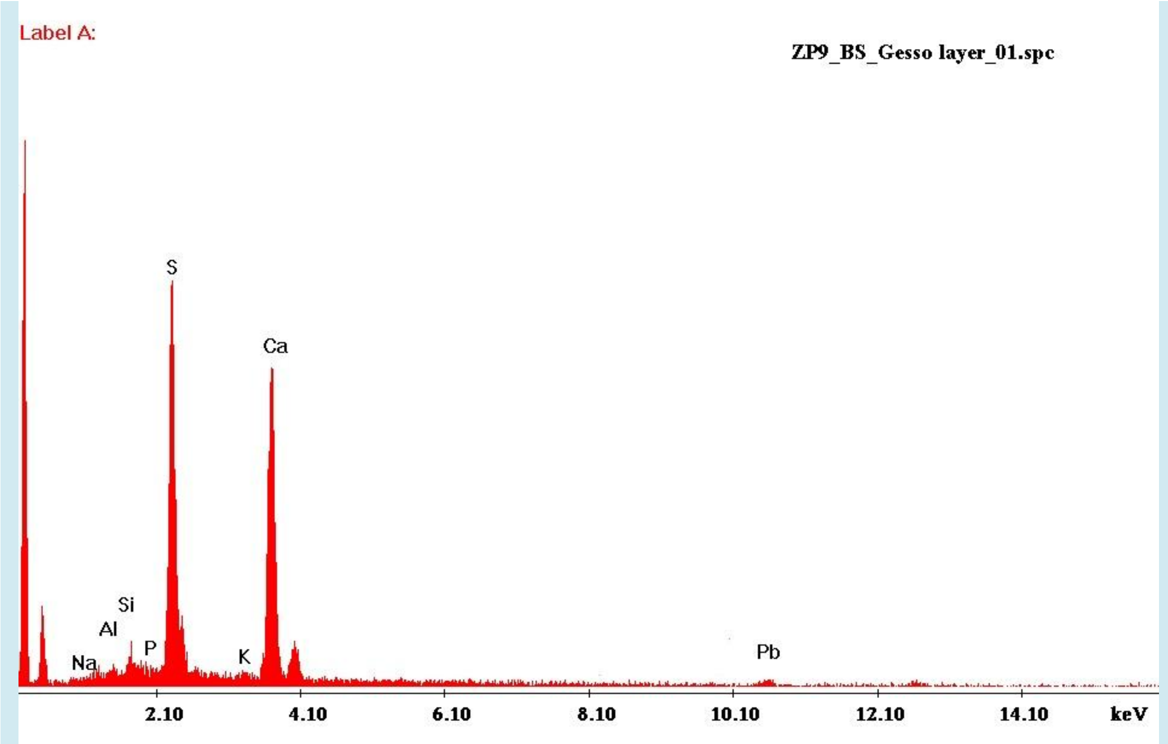


Fig.231 EDX spectrum from gesso layer (sample #9) *(personal archive Th. Mafredas)*

As a result, it could be assumed that the preparation layer was Calcium Sulfate ($CaSO_4$).

The obtained spectrum from the 1st pigment layer confirmed the presence of Pb (**Fig.232**). Knowing from OM that this layer was a red pigment; it was obvious that the Pb corresponded to red lead (Pb_3O_4). The 2nd pigment layer consisted of a combination of red lead and cinnabar (HgS), as it could be seen from the obtained spectrum (**Fig.233**).

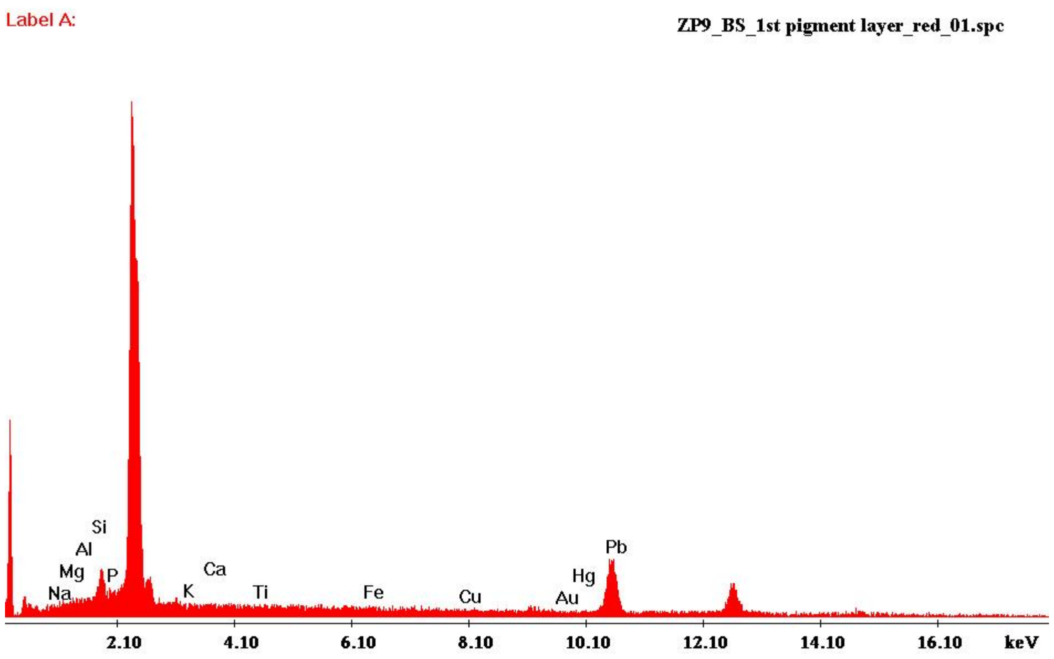


Fig.232 EDX Spectrum from 1st red pigment layer (sample #9) *(personal archive Th. Mafredas)*

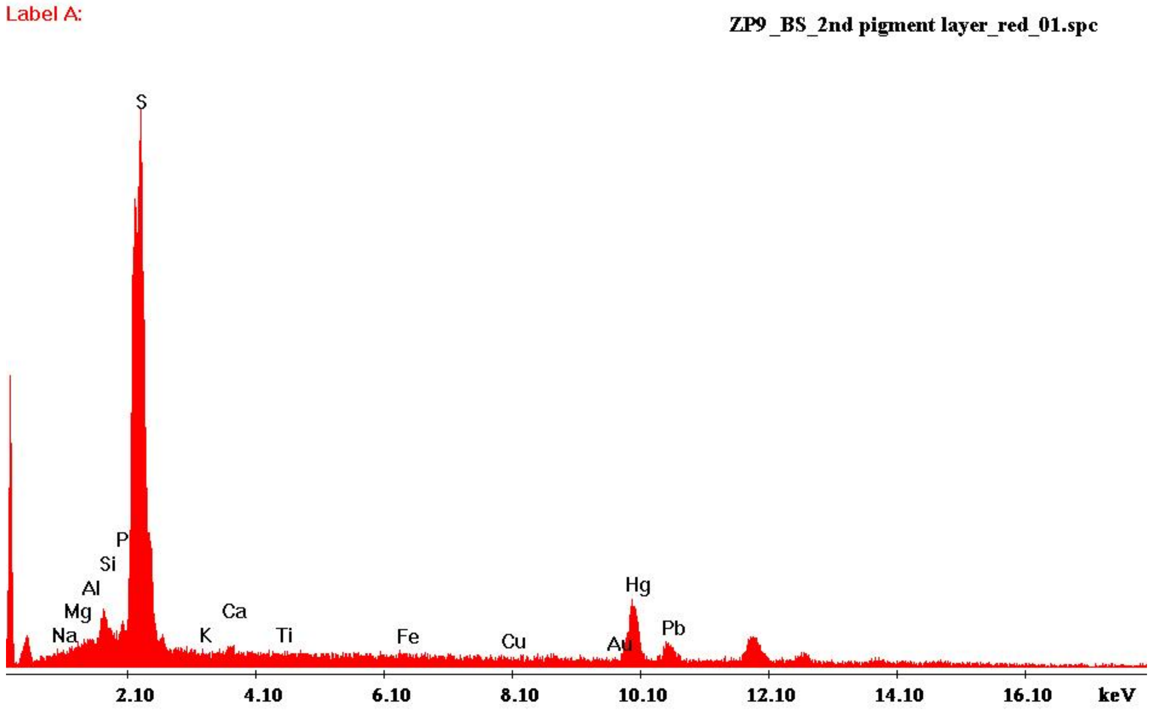


Fig.233 EDX Spectrum from 2nd red pigment layer (sample #9) *(personal archive Th. Mafredas)*

During the study of sample #10 (**Fig.234**) through EDX analysis, it was found that the preparation layer it was $CaSO_4$ (**Fig.235**). A bole layer was also found, consisting of Ca and S probably coming from the gesso layers, of Al and Si from the bole clay, and of Fe probably coming from ochre and Au from the gold leaf. Finally, it was difficult to distinguish an organic layer –varnish– over the gold leaf (**Fig.236**).

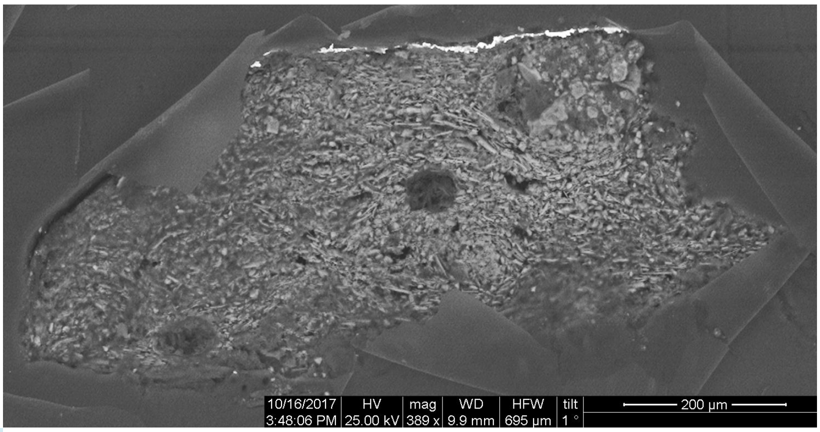


Fig.234 Sample #10. SEM *(personal archive Th. Mafredas)*

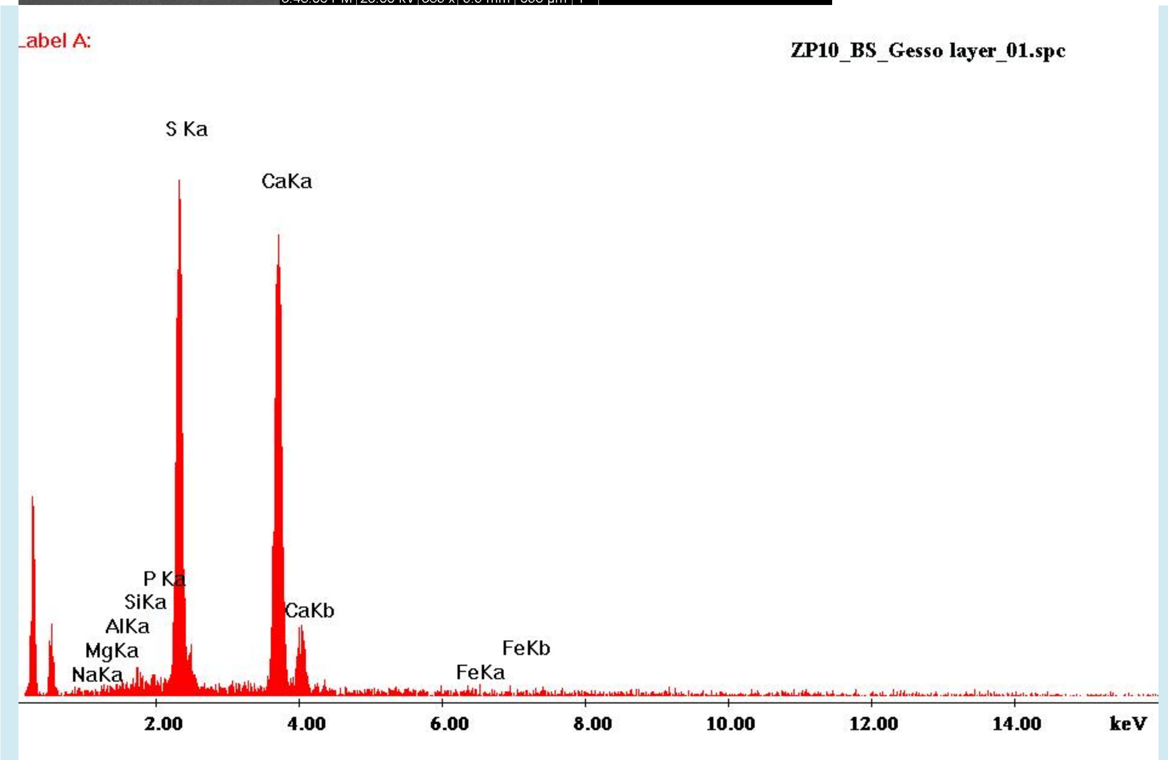


Fig.235 EDX Spectrum from gesso layer (sample #10) *(personal archive Th. Mafredas)*

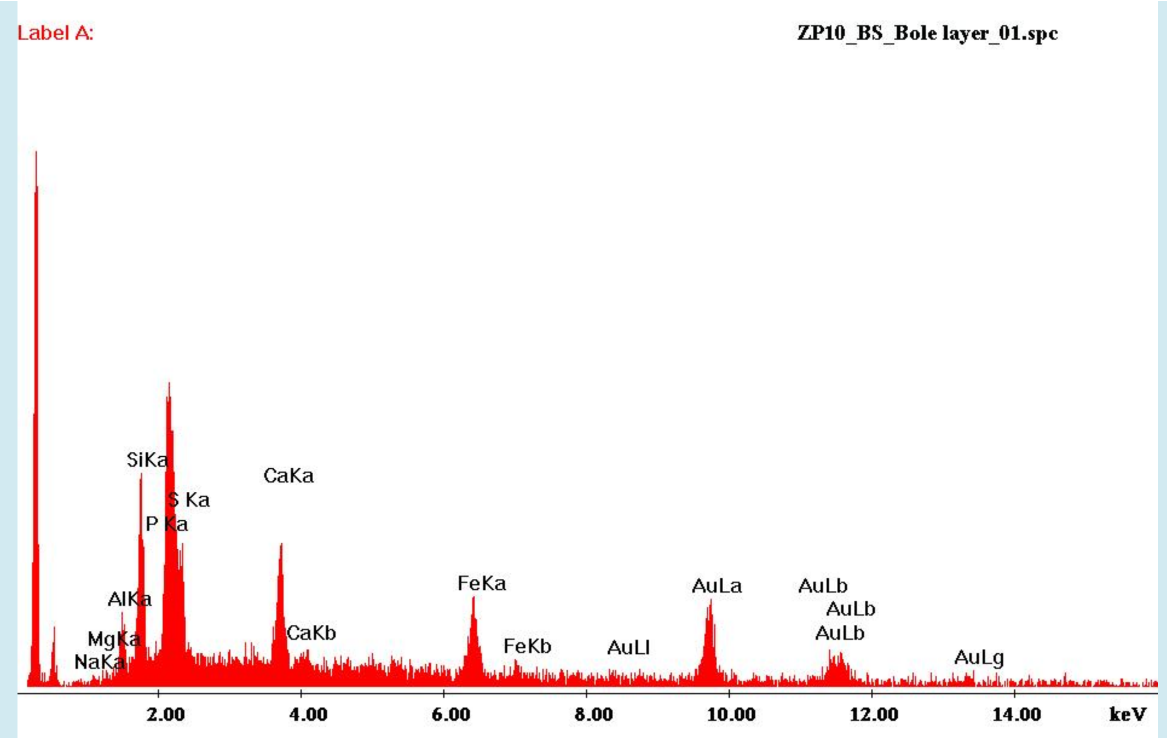


Fig.236 EDX Spectrum from bole layer (sample #10) *(personal archive Th. Mafredas)*

The use of EDX helped to identify the inorganic pigments in different layers and make a quantification of the trace elements (**Table 10**). In this framework, it was possible to identify different pigments in different layers, as well as the inorganic constituents for the bole layer, which pointed towards a hypothesis about Dionysius' recipe used for the bole preparation.

Table 10. *Panel #2 - Elemental Analysis - EDX*

# Sample	Spot	OM	Layer	Trace Elements
#9	Gesso preparation	Thick layer (right side of the sample with big grains)		S, Ca
	Gesso preparation	Thick layer of the sample	1st	S, Ca, Pb
	Organic	Thin organic layer	2nd	
	Pigment layer	Orange	3nd	Pb
	Pigment layer	Red	4th	S, Hg, Pb
	Organic	Very thin layer	5th	
#10	Gesso preparation	Thick layer	1st	Ca, S
	Bole layer		2nd	Ca, S, Al, Si, Fe
	Gold layer	Thin layer	3rd	Au
	Organic	Very thin layer	4th	

2.4.2. Molecular Techniques

2.4.2.1. Fourier Transformer Infrared Spectroscopy

The final technique applied on four different samples was FTIR (***Appendix 2***) in order to characterize the gesso preparation and the kind of varnish, and provide a first impression about the kind of binding medium used. The sample for gesso, (#7a) was taken from the bottom left part of the panel, in the horizontal frame. The second sample (#8) was pigment powder from a painting layer in the left bottom of the panel, near the end of the vertical frame. Concerning the study of varnish, two different samples were taken from two different areas. The first sample (#10a) of varnish was in the form of powder from the upper horizontal frame, in the middle of the panel, and the second (#8*) was in the form of cotton swab taken from the same area as sample #8. The samples in the form of powder were prepared in KBr discs, as was discussed in a previous chapter, while sample #8* from cotton swab was diluted in the ultrasonic bath, with acetone as a solvent.

From the obtained spectrum for sample #7a (**Fig.237**) and the respective bands, it was identified that the gesso was hydrate (3410 cm^{-1}) gypsum (1139, 1115, 670, 601 cm^{-1}) and more specifically calcium sulfate hydrate ($CaSO_4 \cdot xH_2O$). The use of $CaSO_4$, as evidenced from the relevant FTIR spectrum, could be justified from the obtained data from previous spectroscopic techniques, both XRF and EDX. The presence of band at 1384 cm^{-1}, corresponds to the presence of nitrates (NO_3^-), possibly as the result of microbial action in wet environments, while the bands at 2925, 2859, 1542, 1458 cm^{-1} are indicative for the presence of organic salts.

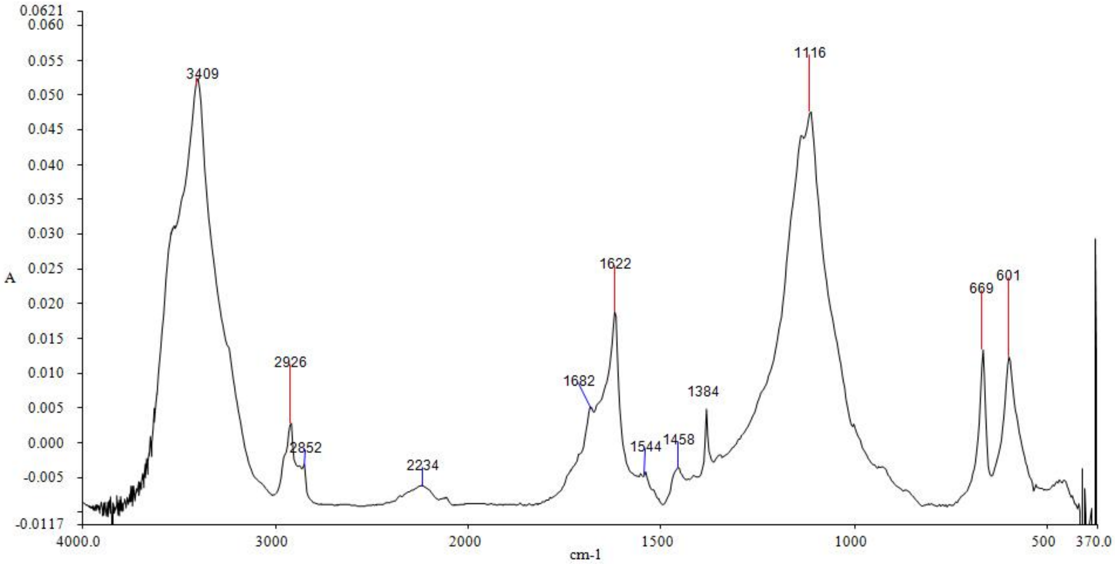


Fig.237 FTIR spectrum from gesso powder (panel #2, sample #7a) *(personal archive Th. Mafredas)*

From the obtained spectrum for sample #8 (**Fig.238**) and from the respective bands, the presence of proteinaceous material (1644, 1532 cm^{-1}) and of lipids (2921, 2852, 1712, 721cm^{-1}) was identified. The combination of the above possibly leads to the conclusion that the sample contains egg as a medium. The bands at 1408 cm^{-1} and 720 cm^{-1} are indicative of the presence of white lead (Pb), used as diluted white pigment.

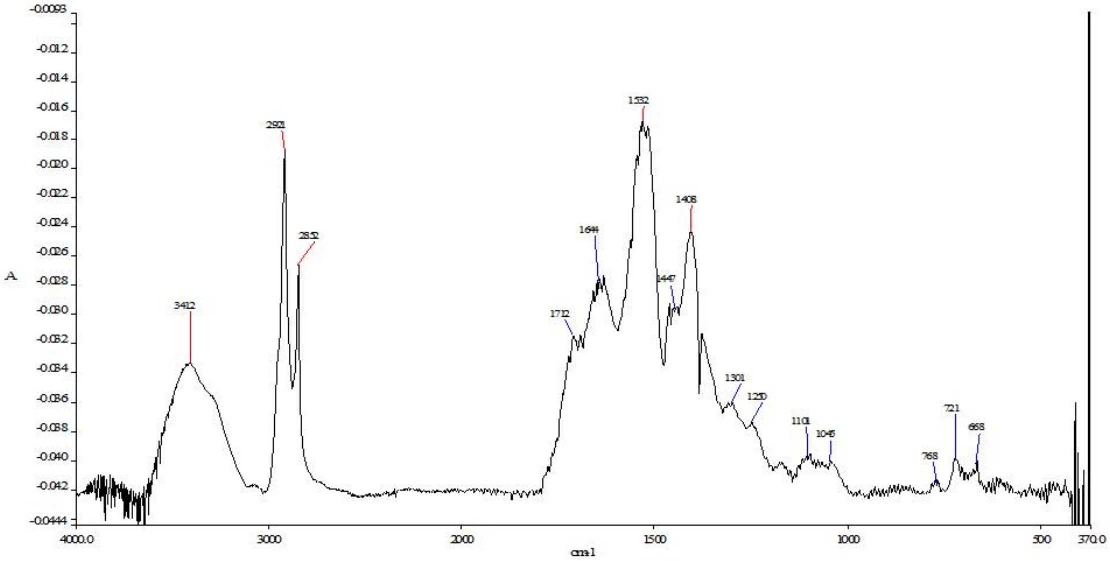


Fig.238 FTIR spectrum from painting powder (panel#2, sample#8) *(personal archive Th. Mafredas)*

In addition, the intensive band at 1532 cm^{-1} (**Fig.239**) indicates the possible contribution from the carboxylate salts. This could be a proof for the saponification of lipids in the presence of lead white

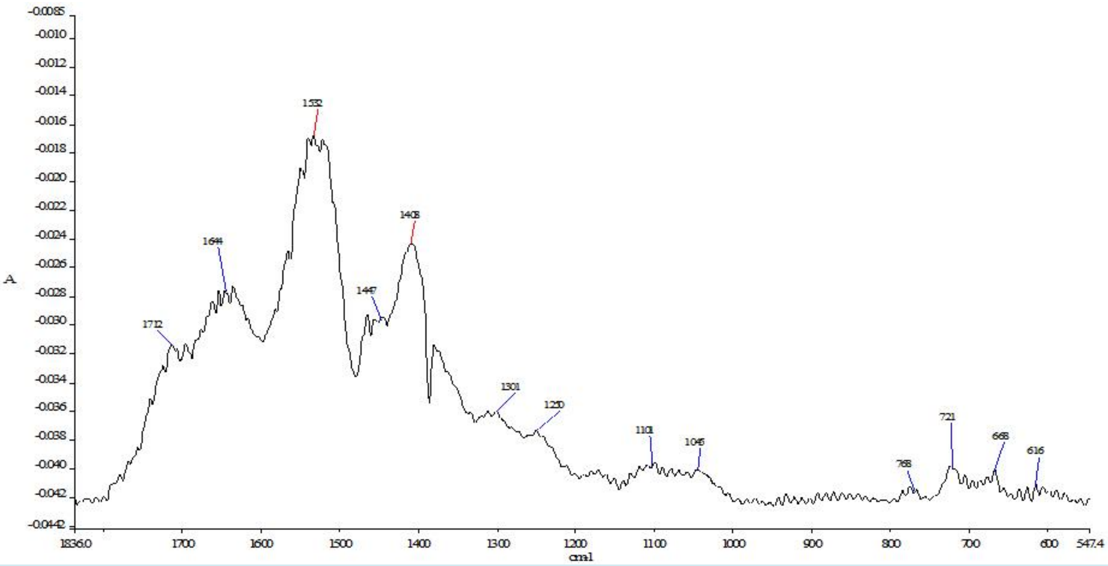


Fig.237 Detailed FTIR spectrum from painting powder (panel#2, sample#8)
(personal archive Th. Mafredas)

From the obtained spectra from sample #8* and #10a, concerning the type of varnish used, the presence of Sandarac and Mastic was identified

The obtained spectrum from sample #8* (**Fig.240**) also indicated, besides the presence of Mastic (1714cm^{-1}) and Sandarac (1699, 1457, 1415 cm^{-1}), the presence of oil (2926, 2855, 1733, 1463, 1377, 1250, 1181, 721 cm^{-1}). Furthermore, the band at 1373 cm^{-1} is indicative of the presence of natural resins; namely, Mastic and Sandarac.

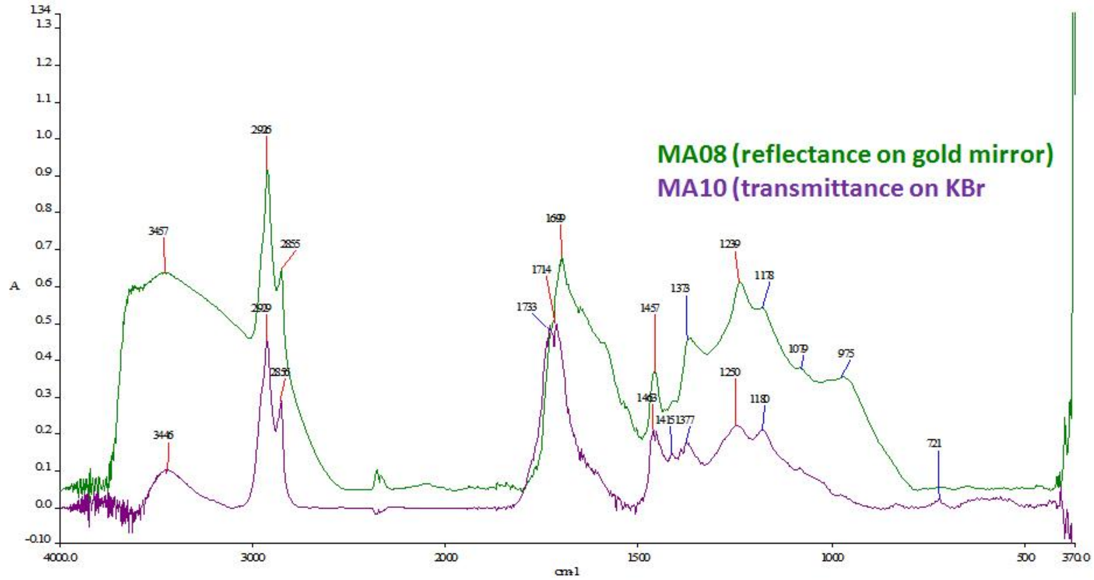


Fig.240 FTIR spectrum from varnish layer (from cotton) (panel#2, sample #8*)
(personal archive Th. Mafredas)

Additionally the obtained spectrum from sample #10a (**Fig.241**) verified the possibility of the presence of two different varnishes, Mastic (1714cm^{-1}) and Sandarac

(1966, 1462, 1415, 1388, 1178, 1138, 1032 cm^{-1}), either in the form of a mixture, or in consecutive layers.

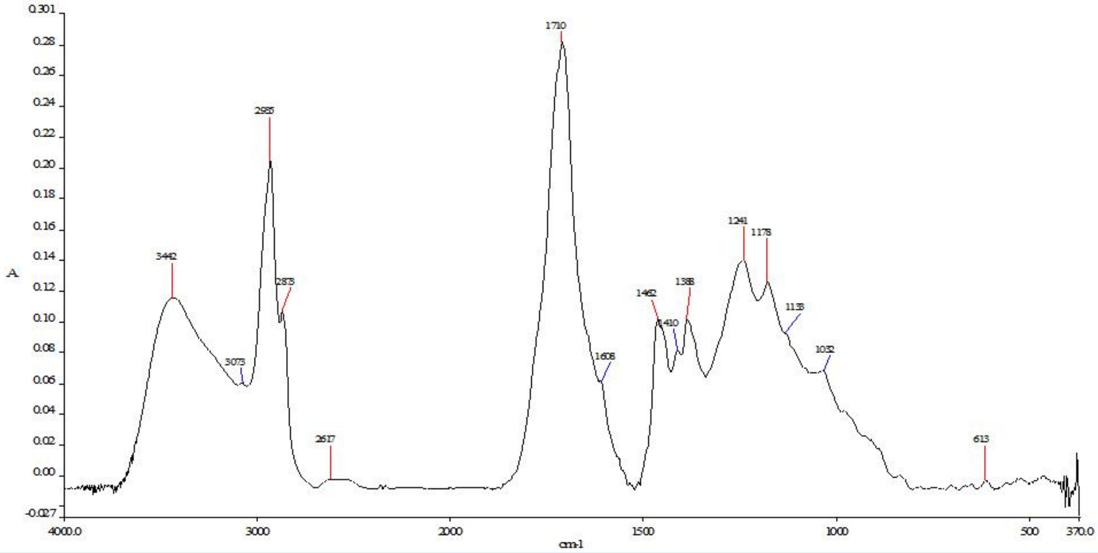


Fig.241 FTIR spectrum from varnish powder (panel #2, sample #10a)
(personal archive Th. Mafredas)

2.5. Discussion

The iconography of the Zoodochos Pigi generally follows all the relevant instructions on this subject found in his earlier Hermeneia. Reference to the Zoodochos Pigi is made in four contexts, with the first being found in the section of Hermeneia addressing iconographical types concerning how the feasts of the Mother of God are represented: *"A golden font, with the Mother of God in the midst, her hands are upraised and Christ is before her, blessing to right and left. On his breast he has the Gospel which says: 'I am the living water'. Two angels hold a crown over her head, each with one hand, while with the other they hold scrolls, one of which says: 'Hail, pure and life giving fountain', while the other says: 'Hail, spotless and divine fountain'. Below the fountain is a basin of water in which are three fish, to either side of it are patriarchs, bishops, priests, deacons and kings and queens, princes and princesses, washing and drinking from the cups and vases. Many other people, sick and with paralyzed hands and feet, do likewise; a priest with a cross sanctifies them. Before them is a man possessed by a devil, and the captain of a ship pours water on to the resurrected Thessalian"* (Dionysius 1909, p. 145; Hetherington 1974, p. 50). The second reference can be found in the section referring to the decoration of a phiale (Dionysius 1909, pp. 221-222; Hetherington 1974, p. 86), while the third section deals with the names and epithets written on the Theotokos' panel paintings (Dionysius 1909, p. 228; Hetherington 1974, p. 88). The fourth and final reference about Zoodochos Pigi can be found in the section in which Dionysius proposes the verses to accompany the Zoodochos Pigi: "*O pure mother of the Word that is both God and man, Spring of the divine and immortal water, Fill thy servant with thy holy waters, and as I have the power I shall depict thee worthily and exalt thy ineffable grace, since thou dost exist through the span of the heavens, and higher than the angels, and I in my humility call thee mother, seeking ultimate shelter and protection and wise divine guidance*" (Dionysius 1909, p. 230; Hetherington 1974, p. 89).

As discussed above, the panel painting of the Theotokos the Zoodochos Pigi is one of the four despotic panel paintings from the iconostasis of the homonymous church attached to its foundation. In Fourna's panel painting, it three main differences could be found in comparison to Dionysius's text about Zoodochos Pigi (Kakavas 2008, pp. 186-187). The first concerns the text written on the open Gospel held by the young Christ in front of his chest. In the Hermeneias' description, the suggested epigram is: "I am the water bringing life" while the one written in this panel painting is derived from a corresponding passage in John's Gospel: "...but whoever drinks of the water that I shall give him will never thirst" (John 4:14).

The second difference concerns the title given to the panel painting "Zoodochos Pigi" with the epithet of the "Phaneromeni" which is not mentioned in any part of Dionysius's text. Finally, the third difference is related to the dedicatory inscription written in the bottom part of the panel painting, which is totally different from what he had suggested about the same theme, and was not included in any part of his treatise. The dedicatory epigram is developed in four verses: "All of those who desire double salvation come forward with sincere intent, to venerate the Mother of God and drink the water that purifies the stomach. As happened with my own illness, for which reason I have erected this church, beautifying it with holy icons, expending much sweat and money and offering everything even the Akolouthia, a soul-felt gift for my own salvation. Dionysius, the historiographer who hails from this town and from the family of Chalkeon. One-thousand and seven-hundred and thirty and seven units, in the current and new year of our salvation and more specifically, on the twenty-fifth of November"[33] (Kakavas 2008, p. 187; Dionysios 1938, p. 32).

The explanation, however, for these three discrepancies, according to Kakavas, is straightforward if someone takes into account that Dionysius was both the iconographer and donor and, thus, includes his personal details and features in this panel painting (Kakavas 2008, pp. 187-193).

As discussed above, imaging techniques, such as IR photography, helped study detailed features of the painting concerning Dionysius's drawing line and observed some details which were not detectable or visible in the Vis.

The application of digital microscopy provided excellent and detailed data concerning the construction technique and the decoration of the painting surface, providing a first impression about Dionysius's painting technique. During DM, it was observed that he used to apply the pigments over the gold layer in order to achieve the

[33] «Όσοι ποθείτε την διπλήν σωτηρίαν, ενθάδε δεύτε ειλικρινεί καρδία, την του Θεού μεν λιτανεύειν Μητέρα, ύδωρ πίνειν μεν δε το αγνίζον γαστέρα. Καθώς έτυχον καγω εν αρρωστία, ου χάριν ανήγειρα την εκκλησίαν, φαιδρύνας αυτήν ταις αγίαισ εικόσιν, ίδρωσιν πολλοίς δαψιλεί τε τη δόσει. Προσθείς τα πάντα της τε ακολουθίας, δώρον ψυχικόν ιδίας σωτηρίας, Διονύσιος ο ιστοριογράφος, κώμης τε ταύτης και του Χαλκέως κλάδος. Μία χιλιάς, επτά εκατοντάδες και δεκάδες τρεις, έτι επτά μονάδες, έτος το σωτήριον όντως και νέον, είκας και πεντάς νοεμβρίου ου πλέον» (=25 Νοεμβρίου 1737) (Dionysios 1938, p. 32)

decoration, for example the decorating metal at Theotokos' name, or the decoration of the phiale. Concerning the construction techniques utilized, it was found that the layers of the painting surface were very thin, something that was also observed during OM. Thin layers were found in gold areas of the panel, and it was difficult to distinguish the bole layer even in high magnifications of 200x.One characteristic example is sample #10, in which the bole layer was identified during SEM in high magnification, at 390x. The thickness of the samples were verified also during OM and SEM, as it was possible to measure the thickness of the whole sample and the thickness of different layers comprising the sample.

The OM observation of the samples from this panel initially provided detailed information about the stratigraphy of the painting surface and the gilding technique. From the samples, it was not possible to observe the presence of varnish layer. Furthermore, in sample #9, the use of two different red pigments layers was found, and through EDX analysis, it was found that the first was red lead (Pb_3O_4) and the second was cinnabar (HgS).

In addition, OM was aided by the SEM/EDX technique which was more sophisticated and targeted concerning, among others, the distinguishing of the pigment layers observed in OM, the quantification of the pigment in each painting layer, and the distinguishing of layers such as gesso preparation (e.g. in sample #10), which were not detectable in OM.

The application of SEM analysis provided detailed data about the different layers of the cross section of the samples and helped to study Dionysius's construction technique. So, according to SEM it was observed that he had not worked and applied the gesso layer with diligence (samples #9 and #10), while he seemed to use two different kinds of red pigments.

Through the elemental analysis with XRF and EDX it was possible to have a first perception about Dionysius's color palette. So, according to the obtained spectra, it could be assumed that he used red lead (Pb_3O_4), red ochre (Fe_2O_3), and cinnabar (HgS) for red pigments, and white lead ($2PbCO_3 \cdot Pb(OH)_2$) for white pigments. Also, it seems that he used azurite ($2CuCO_3 \cdot Cu(OH)_2$) for blue pigments, and verdigris $Cu(CH_3COO)_2 \cdot 2Cu(OH)_2$) for green pigments, while in addition to panel #1, there was no indication of the use orpiment (As_2S_3). It seems that all the pigments, he used for this panel painting are mentioned in his treatise (Dionysius 1909, pp. 20-23, 34, 41).

The final analytic technique that was applied was FTIR and, through it, the kind of gypsum he used for gesso preparation was characterized as CaSO4, which verifies the XRF and EDX results about Ca and S. The varnish he used seems to be Sandarac or Mastic in the form of two different varnishes, either in a mixture or in consecutive layers. Once more, both of these resins are mentioned in Hermeneia's manuscript as ingredients for varnish layer (Dionysius 1909, pp. 25-27), and are the same resins that were identified in panel #1. Furthermore, through FTIR analysis, it was identified that the binding medium he used consisted of proteinaceous materials and lipids, which lead to the conclusion that the sample probably contains egg as medium. Through staining test in sample #10, the staining of the different layers of the sample was observed, which provide a first perception about the presence of proteinaceous binding media, something that was confirmed by FTIR.

Additionally, the same sample, #8, provided two bands in the spectrum at 1408 cm-1 and 720 cm-1, which are characteristics for the presence of white lead. But, according to the sampling area, it was known that the sample powder had been taken from red pigment. Besides, studying sample #9, from neighboring area to sample #8 by OM and SEM/EDX, the presence of red lead was confirmed. Furthermore, on the same spectrum the intensity band at 1532 cm^{-1} provides the possible contribution of carboxylate salts. Thus, a hypothesis could be made that this is a case of contamination of red Pb and transformation to white Pb because of the presence of CO_2. In bibliography, various authors (West FitzHugh 1997, p. 119; Parry & Coste 1902, pp. 100-102; Brown & Nees 1912; Feller 1986, pp. 109-139) have pointed out that red lead exposure to sunlight, rain and atmospheric CO_2 can cause the formation of basic lead carbonate, -lead white ($2PbCO_3 \cdot Pb(OH)_2$)- (Feller 1986, pp. 67-82). So, according to these, it could be assumed that this is a case of contamination of red Pb to white Pb through the presence of CO_2

3. Saint John the Baptist-The Forerunner

3.1. Description

The third panel painting which is found in the Church of Transfiguration at Fourna made by Dionysius is Saint John the Baptist, the Forerunner. He depicts the saint (**Fig.242**), as winged, tall and frontal with an impressive bearing, while he is clad in a himation and goatskin. He is raising his right hand in blessing and holding an open scroll in his left (**Fig.243**) along with a long staff with a cross on the top. His severed haloed head is depicted in a gold basin in the foreground (**Fig.244**), as an allusion to its miraculous Third Discovery, while on the opposite side there is an axe lying on the tree trunk, as an allusion to his preaching **(Fig.245)** (Kakavas 2008, p. 209; Kakavas, Mafredas & Giannoulopoulos 2013, p. 317; Keiko 1995, pp. 159-161).

Fig.242 Saint John the Baptist. The Forerunner 1737, Dionysius, Church of Tranfiguration, Fournas.
(personal archive Th. Mafredas)

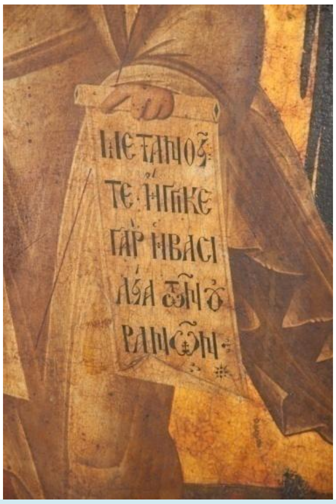


Fig.243 Detail, The scroll's text
(personal archive Th. Mafredas)

Fig.244 Detail. Haloed head in a gold basin
(personal archive Th. Mafredas)

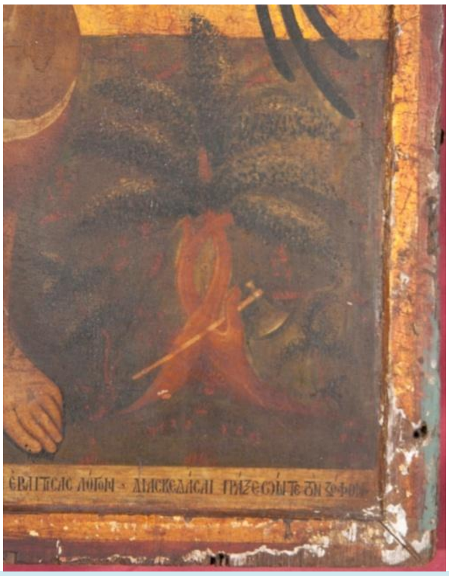


Fig.245 Detail, The axe among the roots of a tree *(personal archive Th. Mafredas)*

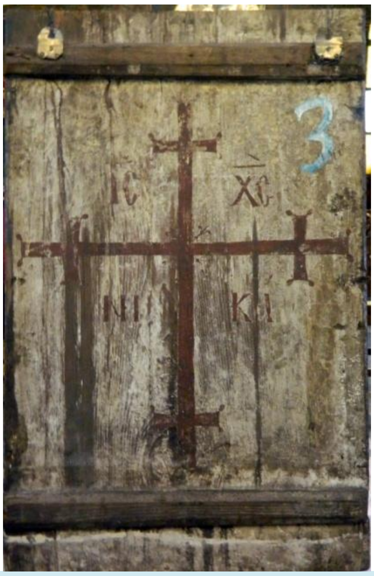


Fig.246 The back side of panel #3 *(personal archive Th. Mafredas)*

A dedicatory epigram (**Fig.247**) is painted in the lower part of the panel, a practice found in the previous two panel paintings, which mentions: "Baptist of Christ, John the Forerunner, bestow your grace on Dionysius with all your power, beseech to the logos whom you baptized and dispel the darkness of sinful deeds"[34] (Kakavas 2008, p. 209; Dionysios 1938, p. 31)

Fig.247 Saint John the Baptist, The dedicatory epigram-Vis *(personal archive Th. Mafredas)*

The back space of the panel also bears a Cross with letters forming the name of Christ and the word of victory (in Greek): IC//XC//NI/KA (**Fig.246**), another common feature with the other two panel paintings.

[34] «Βαπτιστά Χριστού, Πρόδρομε Ιωάννη, χάριν παρασχείν Διονυσίω πάνω. Καθικέτευε ον εβάπτισας Λόγον, διασκεδάσει πράξεων τε τον ζόφον» (Dionysios 1938, p. 31)

3.2. Imaging Techniques

3.2.1. IR photography

The application of IR photography (**Fig.248**) provided a lot of features concerning Dionysius's drawing. Through IR photography, it was possible to observe some points in which the initial drawing of the painter was distinguishable, such as in the two heads of St. John, especially at the joint point of hairs with the skull (**Fig.249-250**), where an intense drawing line could be identified. Another characteristic spot was the spot in the eyes of the head of the Forerunner in the gold basin, in which the initial drawing of the painter was distinguishable (**Fig.251**).

Fig.248 Panel #3 IR photography *(personal archive Th. Mafredas)*

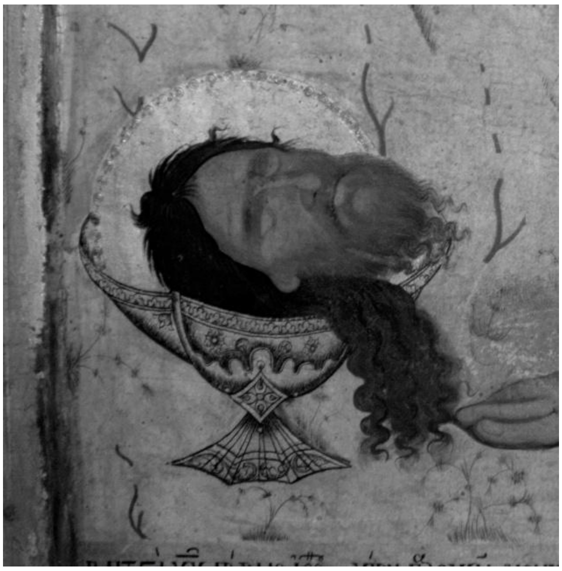


Fig.249 John the Forerunners' head in gold basin *(personal archive Th. Mafredas)*

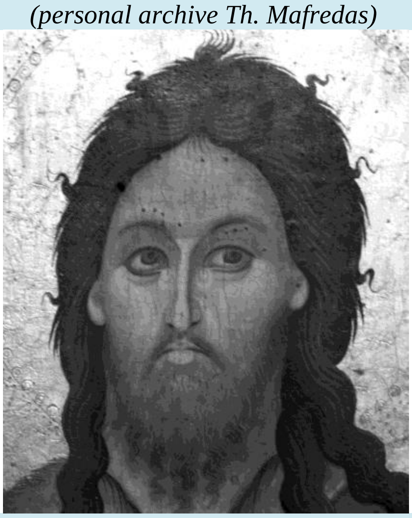


Fig.250 John the Forerunners' head *(personal archive Th. Mafredas)*

Fig.251 Details from the John the Forerunners' head in gold basin *(personal archive Th. Mafredas)*

In the same area, the drawing and Dionysius’ painting technique for hairs and the beard can easily be defined. Features of the initial drawing were also found in the fingers of the left foot of the saint (**Fig.252**).

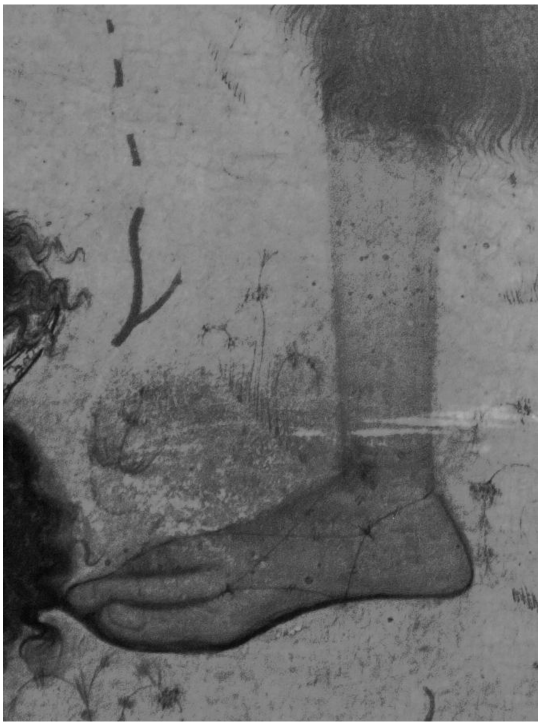


Fig.252 The John the Forerunners' left foot *(personal archive Th. Mafredas)*

The implementation of IR photography eliminated varnish deterioration, so it became possible to observe some characteristic features of Dionysius’ painting technique, such as the decoration of the wings of the Forerunner (**Fig.253-252**) the clean drawing line for John’s goatskin (**Fig.255-256**) and the drawing line in John’s right sandal, especially in the upper part where the sandal is tied up on the foot (**Fig.257**).

Fig.253 Decoration of John the Forerunners' wings-Right wing *(personal archive Th. Mafredas)*

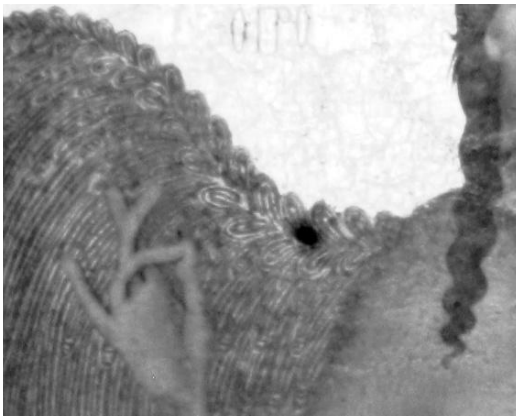


Fig.254 Decoration of John the Forerunners' wings-Left wing *(personal archive Th. Mafredas)*

Fig.255 John the Forerunners' goatskin. Upper part *(personal archive Th. Mafredas)*

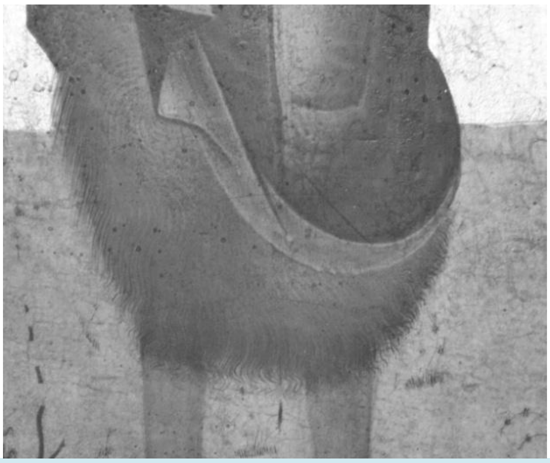


Fig.256 John the Forerunners' goatskin. Bottom part *(personal archive Th. Mafredas)*

Fig.257 The John the Forerunners' right foot *(personal archive Th. Mafredas)*

Because of the ageing of varnish, a discoloration through a yellow film appeared on the surface. With IR radiation, some details were able to be identified, especially in the ground decoration, which was more distinguishable in IR, while the leaves of the tree are not visible in IR (**Fig.258**), due to the absorption of IR radiation (Kakavas, Mafredas & Giannoulopoulos 2013, p. 322). Thus, the axe lying on the tree trunk and the perimetric decoration from leaves became clearly visible, even though they were not detectable in Vis (**Fig.259**).

Fig.258 The bottom part of the depicted theme *(personal archive Th. Mafredas)*

Fig.259 The right bottom part of the depicted theme. The tree root and the axe *(personal archive Th. Mafredas)*

Through IR radiation, the epigram at the bottom of the panel was easily readable (**Fig.260**), providing some characteristic details about the fonts. Finally, it could be argued that through IR photography it was easier to find, discern, observe and study details of the drawing which were not easily distinguishable in the visible, such as the eyes, the mouth, the hairs, the beards in both heads, as well as the ground at the background.

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Fig.260 The dedicatory epigram *(personal archive Th. Mafredas)*

3.3. Microscopic Techniques

3.3.1. Digital Microscopy (DM)

DM was applied in order to identify details about the painting and gilding technique. It was applied in 10 different points of the painting surface (**Fig.261**), (continuing the numbering from the previous panels) in different magnifications, and the results helped to understand Dionysius's painting technology.

Fig.261 Panel #3. Digital Microscopy spots *(personal archive Th. Mafredas)*

Studying the gilding technique from hit points DM24 (**Fig.262-263**), DM27 (**Fig.264-265**) and St16, it was found that there was a thin layer of gold, while some traces were also identified, possibly coming from the presence of the bole layer (*inside the red frame*). Especially from St16 (**Fig.266-267**) the thickness of the gold layer could be clearly understood because, in some spots, the gold has been damaged, exposing the gesso preparation layer. This estimation concerning the thickness of the gold layer was something that needed to be studied during OM and SEM, as it will be discussed below.

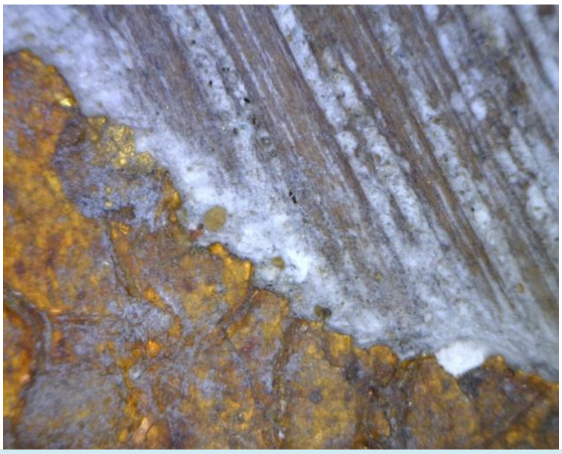


Fig.262 Gilding technique. Thin gold layer (DM24) (Magnification 60X) *(personal archive Th. Mafredas)*

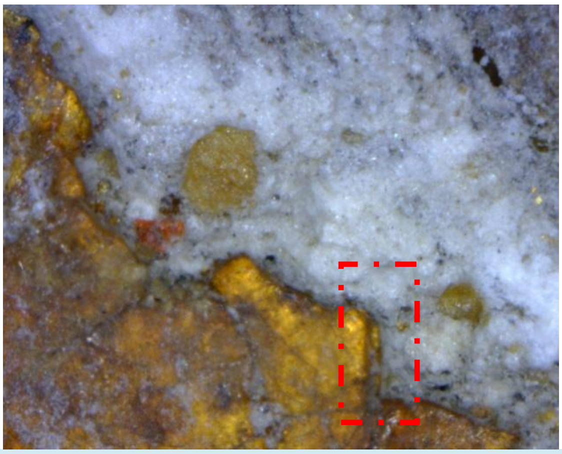


Fig.263 Thin gold layer (Magnification 210X) *(personal archive Th. Mafredas)*

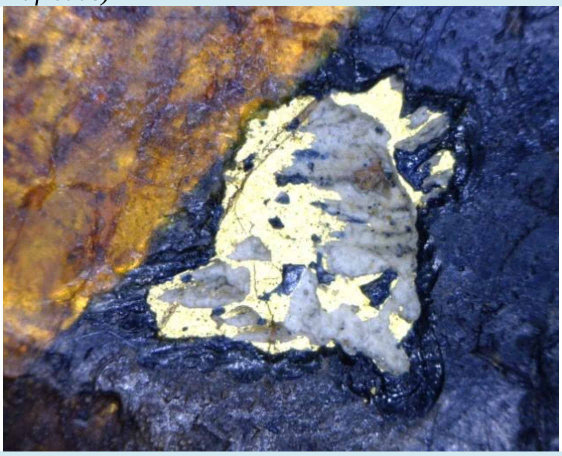


Fig.264 Gilding technique. Thin layer of gold (DM27) (Magnification 60X) *(personal archive Th. Mafredas)*

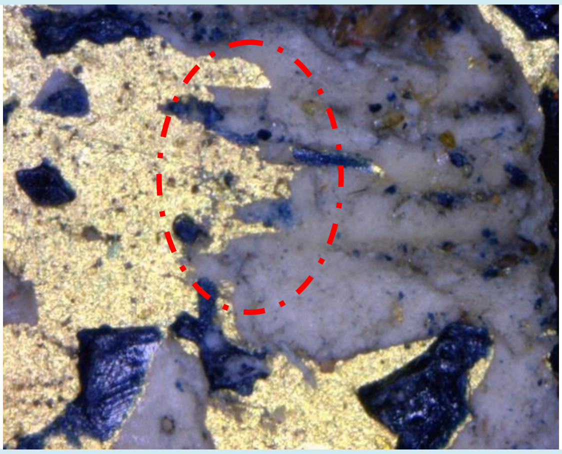


Fig.265 Construction Technique. Thin layer of gold-Traces of bole presence (Magnification 210X) *(personal archive Th. Mafredas)*

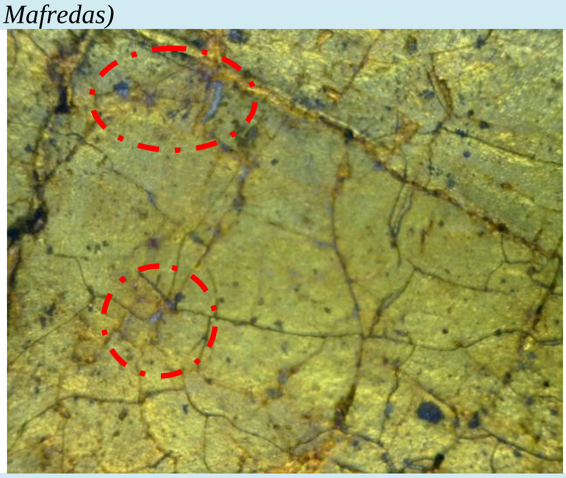


Fig.266 Gilding technique. Thin layer of gold (St16) (Magnification 60X) *(personal archive Th. Mafredas)*

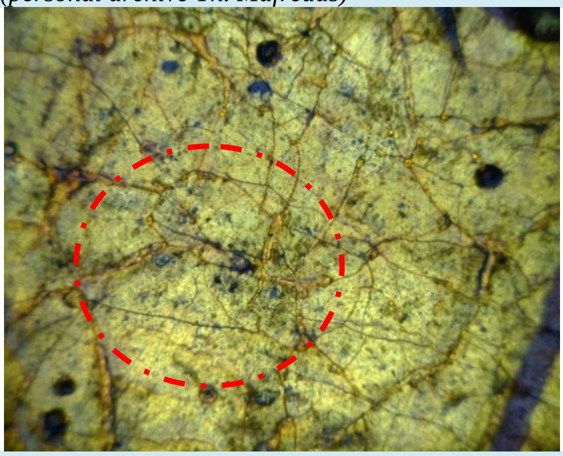


Fig.267 Gilding technique. Thin layer of gold (St16) (Magnification 60X) *(personal archive Th. Mafredas)*

Concerning the painting technique through the examination with DM, studying the spot DM25, located at the mouth of St. John, it was possible to understand the magnificent skills of Dionysius, as the shape and volume of the mouth are described by different color variations (**Fig.268-269**). The theme at the depicted areas is delineated by applying the pigments. It is obvious that there is no penetration of one pigment into the other, but clear boundaries. The same delimitation of pigments could be found in DM26, in the fonts of the open scroll (**Fig.270-271**).

Fig.268 Magnificent painting of the mouth. Delimitation of pigments (Magnification 60X) *(personal archive Th. Mafredas)*

Fig.269 Delimitation of pigments at St. Johns' mouth (Magnification 210X) *(personal archive Th. Mafredas)*

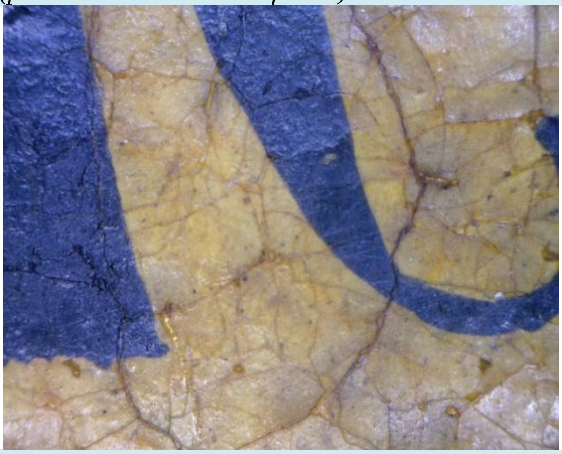


Fig.270 Delimitation of pigment used for the letters (Magnification 60X) *(personal archive Th. Mafredas)*

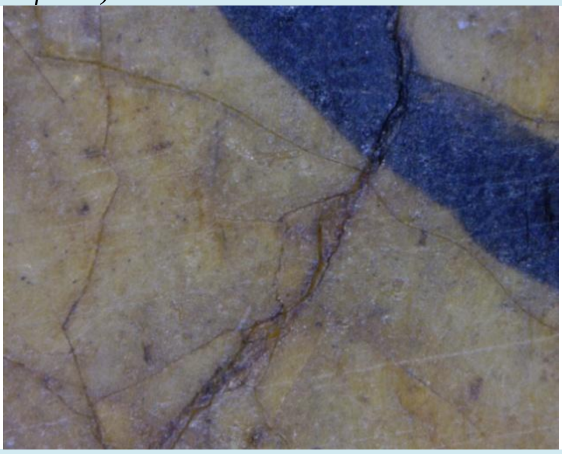


Fig.271 Delimitation of pigment used for the letters (Magnification 210X) *(personal archive Th. Mafredas)*

At the same time, studying different areas of the painting surface, trying to identify delimitation of pigments (**Fig.272**), it was observed that, besides that, traces from the initial drawing were found in some areas, such as St11, in the right arm of St. John (**Fig.273**), St12 in the bottom left of St. John's garment (**Fig.274**) and St13 in St. John's left arm. Especially in St13, distinct traces of the original drawing made by a brush are visible (**Fig.275**), at the point where the arm was joined with the wings (**Fig.276**). Also, traces from the initial drawing were found in St15, in the upper left part of St. John's wings (**Fig.277-278**).

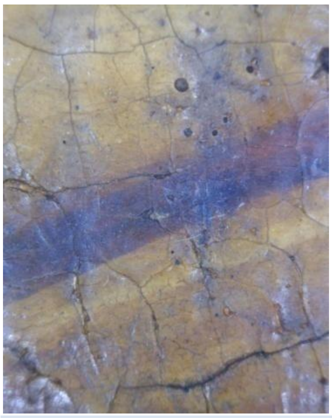
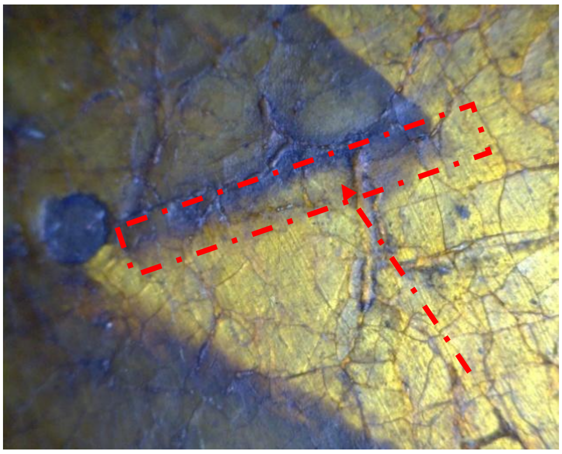


Fig.272 Delimitation of painting and traces from drawing (Magnification 210X) *(personal archive Th. Mafredas)*



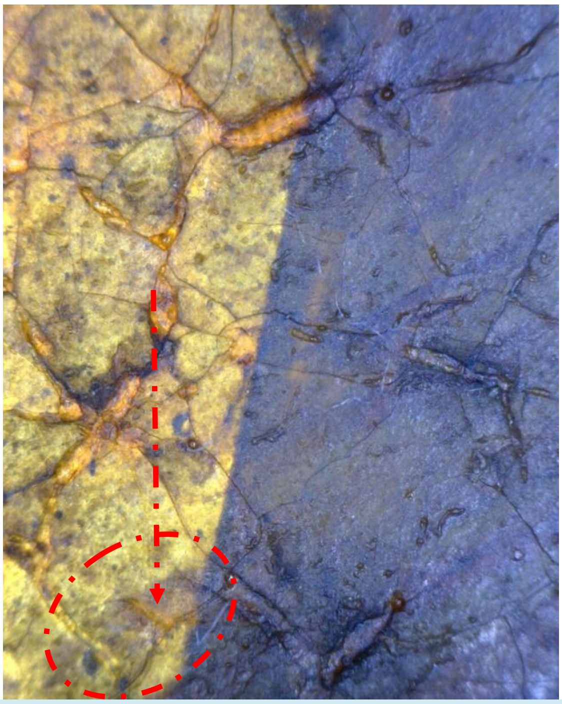
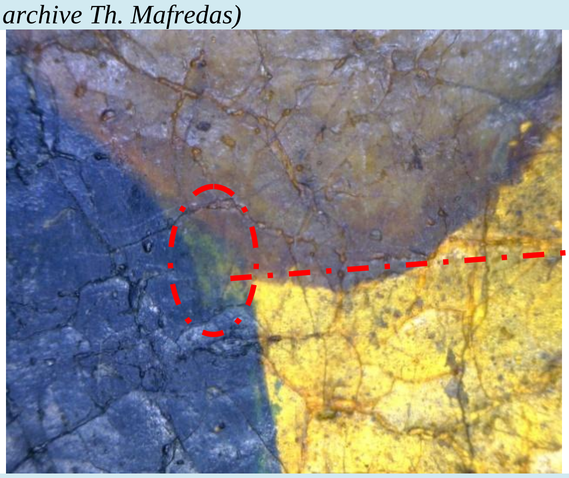


Fig.273 Right arm of St. John (St11). Traces from initial drawing (Magnification 60X) *(personal archive Th. Mafredas)*

Fig.274 St. John's garment-bottom left (St.12). Traces from initial drawing (Magnification 60X) *(personal archive Th. Mafredas)*



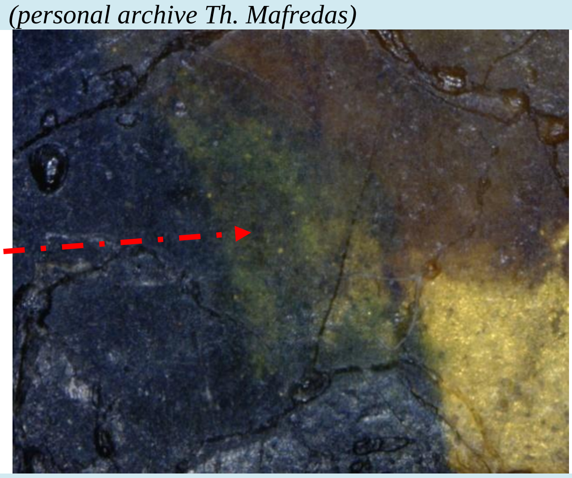
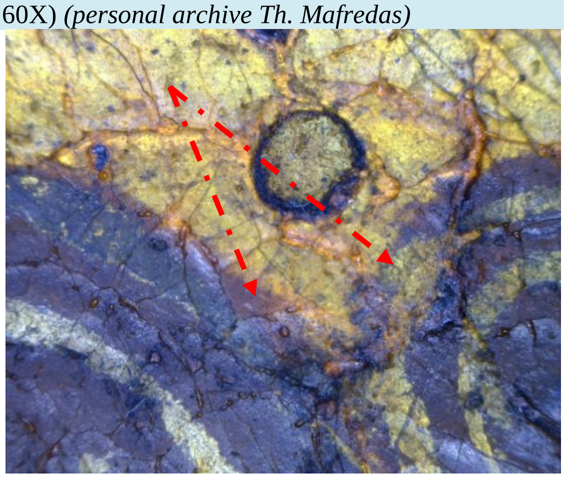


Fig.275 St. John's left arm (St.13) Traces of the original drawing made by a brush (Magnification 60X) *(personal archive Th. Mafredas)*

Fig.276 St. John's left arm (St.13) Traces of the original drawing made by a brush (Magnification 210X) *(personal archive Th. Mafredas)*



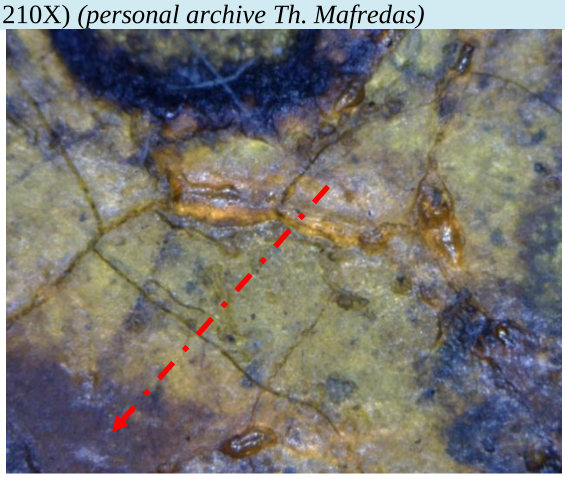


Fig.277 St. John's wings-upper left. Traces from initial drawing (Magnification 60X) *(personal archive Th. Mafredas)*

Fig.278 St. John's wings-upper left. Traces from initial drawing (Magnification 210X) *(personal archive Th. Mafredas)*

One final spot was at the middle of St. John's left wing, where the use of gold pigment over a red pigment was found in order to achieve the decoration of the wings. The use of gold as a pigment over an existing pigment layer is something in common to the three panel paintings which have been studied until now. Thus, in this case as well, it seems that Dionysius was using gold as a pigment in order to achieve the decoration of St. John's wings. The gold lines area symmetric and give the impression of having been applied over the existing pigment (**Fig.279-280**).

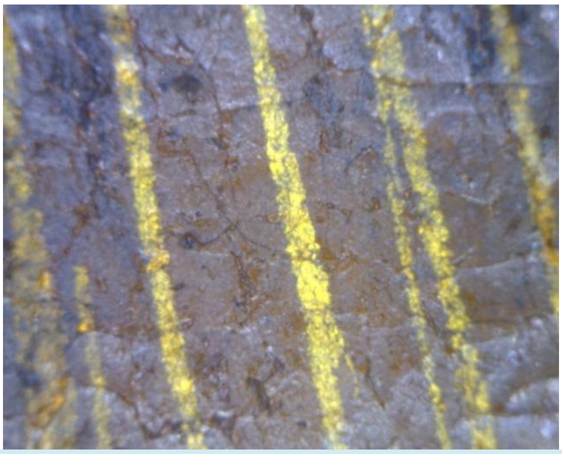


Fig.279 Gold painting over existing pigment in order to achieve wing's decoration (St14. Magnification 60X) *(personal archive Th. Mafredas)*

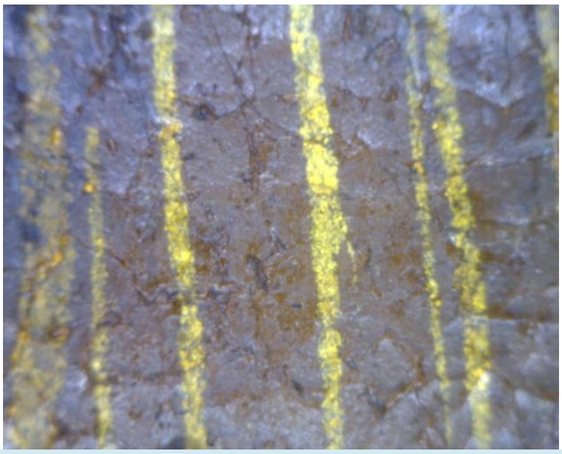


Fig.280 Gold painting over existing pigment in order to achieve wing's decoration (St14. Magnification 60X) *(personal archive Th. Mafredas)*

3.3.2. Optical and Fluorescence Microscopy

For applying OM, three (3) different samples in cross section were detached from the panel (***Appendix 2***); two of them (samples #11 and #11a) for studying the gilding technique and one (sample #13) for studying the painting layer. During the sampling process, it was found that all the layers were very thin, something that was also confirmed during DM; thus, out of the samples, only two (2) of them were examined in OM: sample #11a for gilding technique and #13 for painting layer. All samples were examined both in Vis and in UV.

The first sample (#11a) which was examined with OM was taken from the lower part of the panel and, more specifically, from the joint point of the vertical and the horizontal frame of the painting in order to examine the gilding technique e (**Fig.281-282**).

Fig.281 Sampling area for sample #11a and 13 *(personal archive Th. Mafredas)*

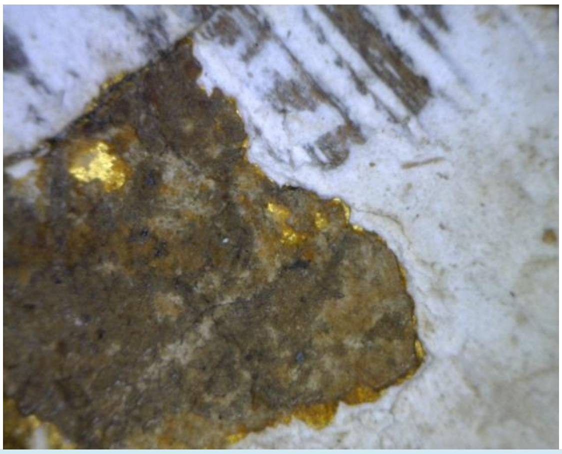


Fig.282 Sampling position for cross section sample #11a *(personal archive Th. Mafredas)*

Studying the sample from above in Vis, an identifiable layer composition was not found while studying the sample from above made the presence of gesso layer obvious (**Fig.283-284**).

Fig.283 Sample #11a from above

Fig.284 Sample#11a from below

(personal archive Th. Mafredas) *(personal archive Th. Mafredas)*

Observation by OM revealed the stratigraphy of the sample and identified the gold layer (**Fig.285**). Studying the sample under UV radiation it was possible to observe the fluorescence of the varnish layers and discern them (**Fig.286**)

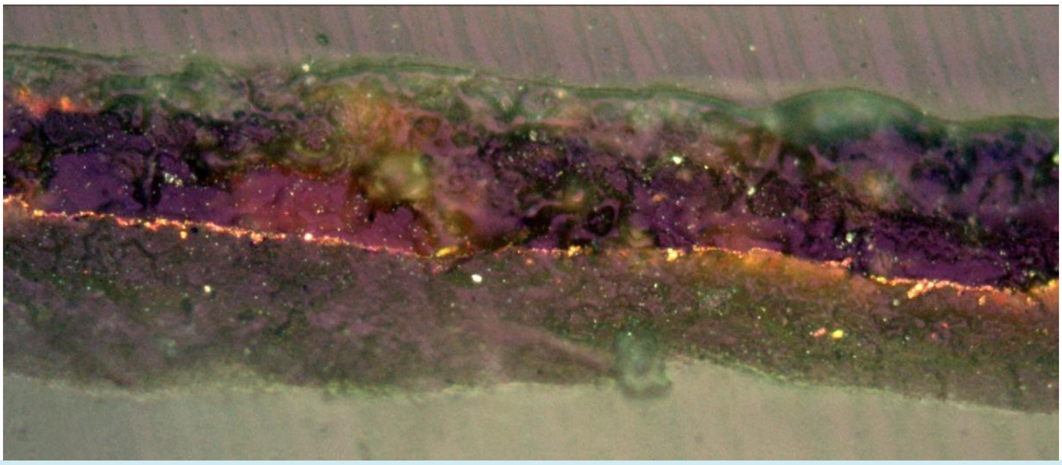


Fig.285 Sample #11a. Stratigraphic observation *(personal archive Th. Mafredas)*

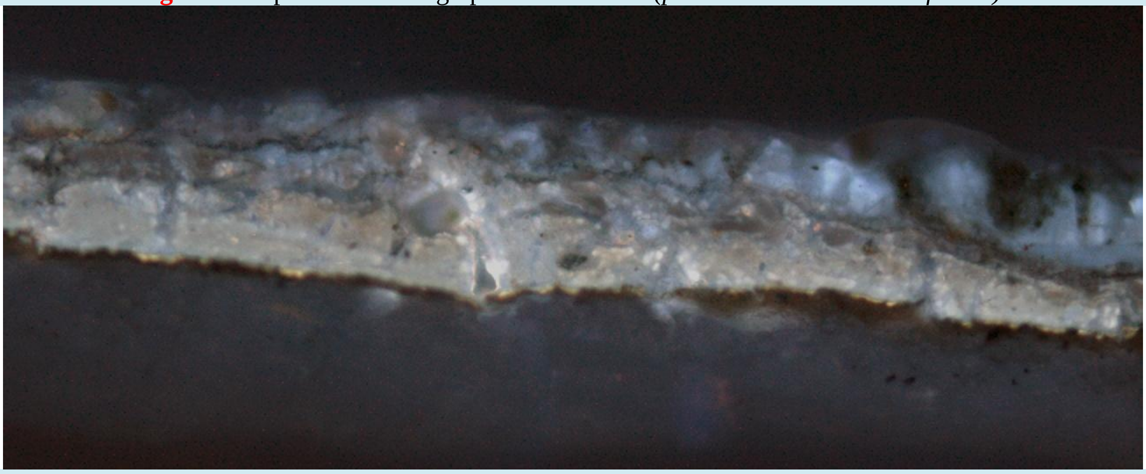


Fig.286 Sample #11a. Stratigraphic observation under UV radiation
(personal archive Th. Mafredas)

Below the gold layer, a tiny line was observed (**Fig.287** which, in high magnification, could be identified as a very thin layer which might be a kind of bole layer (**Fig.288**) while some grains could also be discerned, probably coming from bole ingredients. Over the gold layer, an organic layer was observed, which may be the initial organic coating. Over this, at least 2 coating layers were identified while, at some points 3 layers could be identified (**Fig.289-290**). Thus, from the stratigraphic observation, it was possible to observe and discern 5 different layers, with two more at some points, marked with the letter a (**Fig.291-292**)

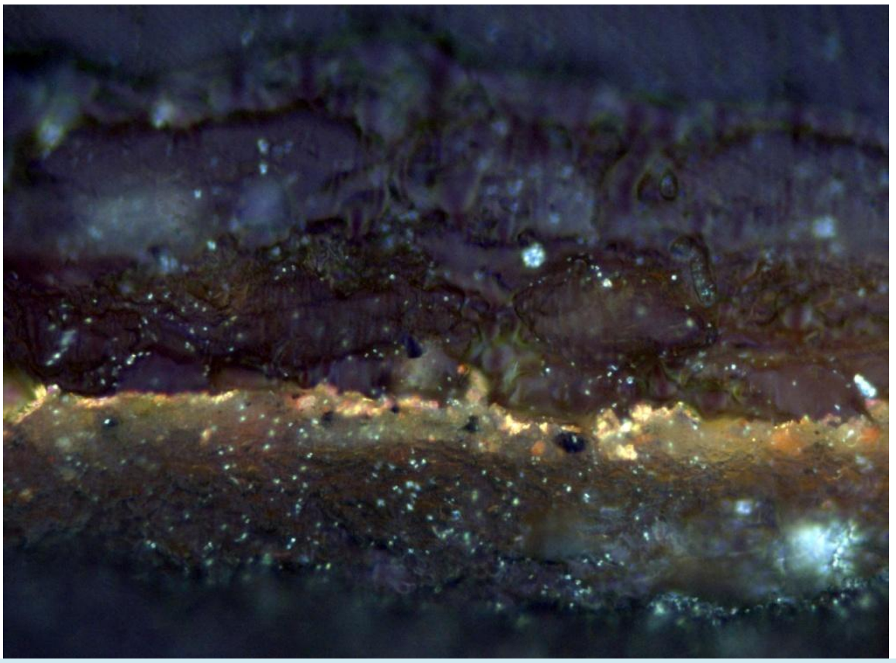


Fig.287 Sample #11a. A thin layer below the gold layer *(personal archive Th. Mafredas)*.

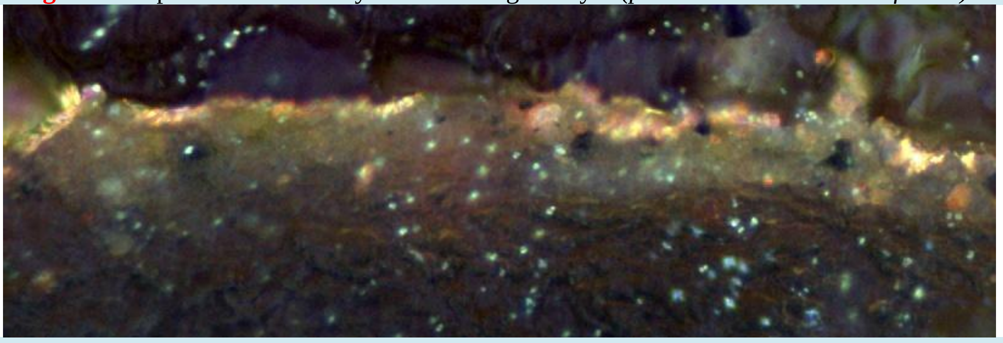


Fig.288 Detail. Thin layer below the gold layer *(personal archive Th. Mafredas)*

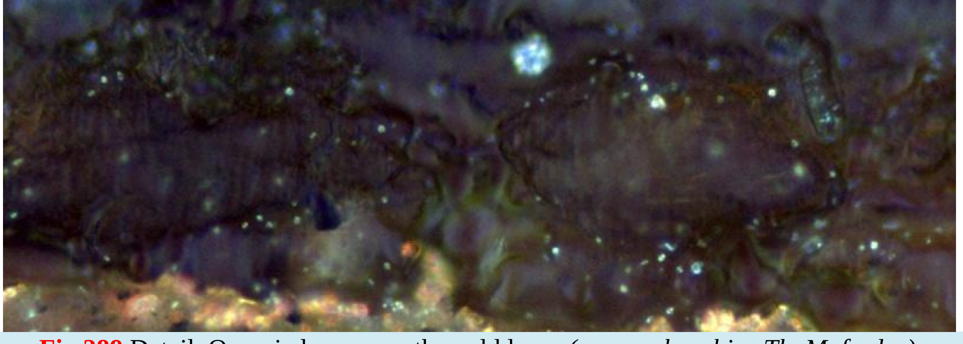


Fig.289 Detail. Organic layer over the gold layer *(personal archive Th. Mafredas)*

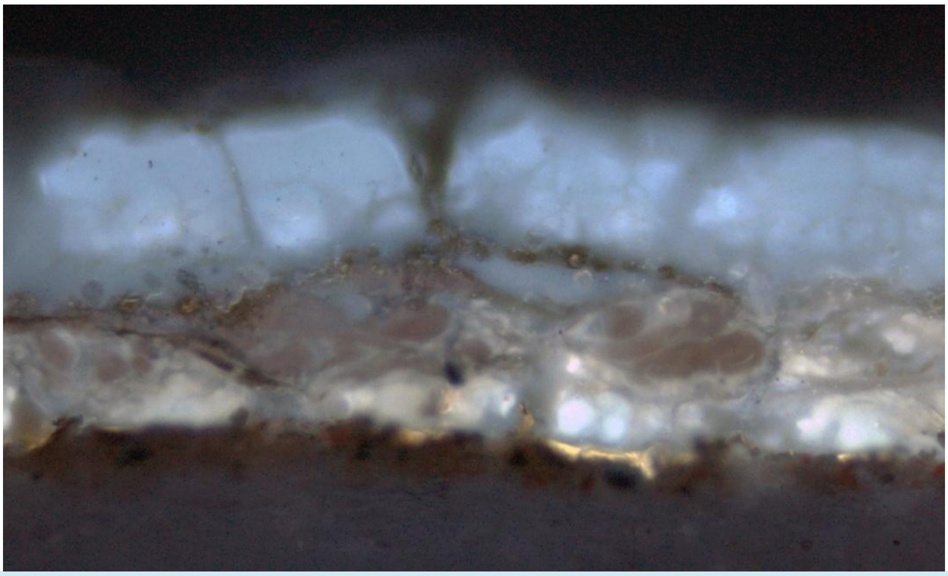


Fig.290 Sample #11a. High magnification under UV radiation
(personal archive Th. Mafredas)

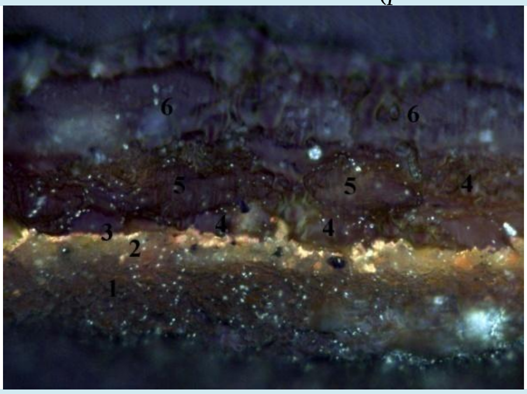


Fig.291 The discern of layers
(personal archive Th. Mafredas)

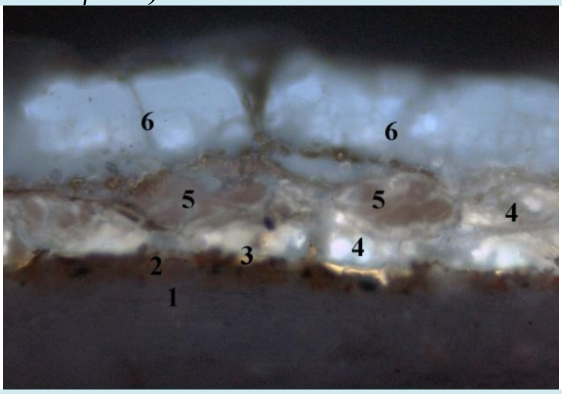


Fig.292 The discern of layers under UV
(personal archive Th. Mafredas)

The second sample (#13) was from the same area as sample #11a in order to study the painting layer (**Fig.293**).

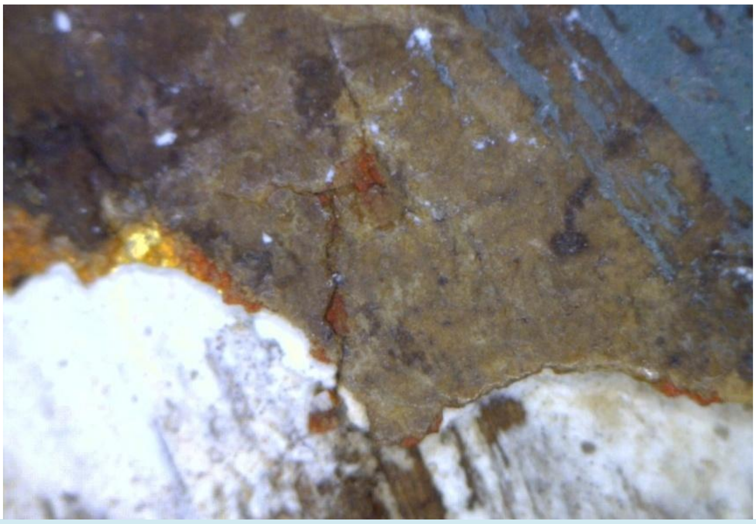


Fig.293 Sampling position for cross section sample #13 *(personal archive Th. Mafredas)*

From OM observation 6 different layers were identified. The first is a transparent layer of non-identifiable composition, the second one looks like a tiny gold layer, and the third one gives the impression of a non-continuous painting layer. The upper surface of this layer seems to contain more red grains in concentration compared to the rest of the layer. The fourth seems to be an organic layer –probably the initial coating and, finally the other two layers, the fifth and the sixth could also be organic coating layers (**Fig.294-298**).

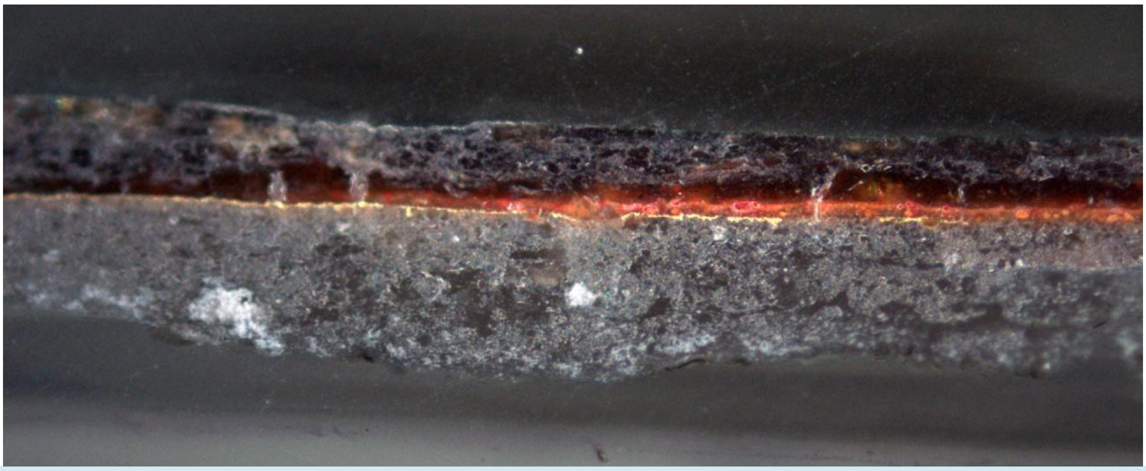


Fig.294 Stratigraphy of sample #13 *(personal archive Th. Mafredas)*

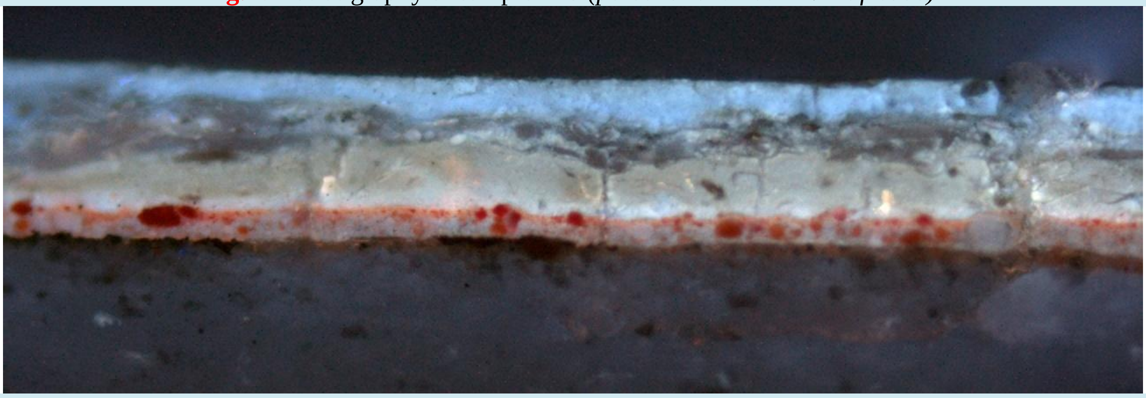


Fig.295 Stratigraphy of the sample under UV radiation *(personal archive Th. Mafredas)*

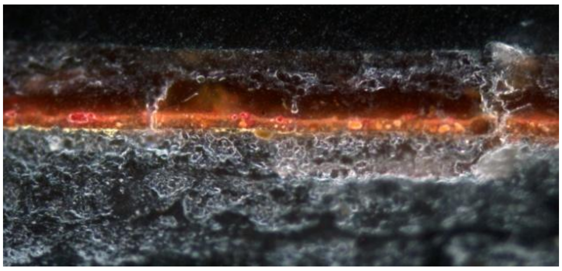


Fig.296 Stratigraphy of sample #13. Discern th gold and the red pigment layer *(personal archive Th. Mafredas)*

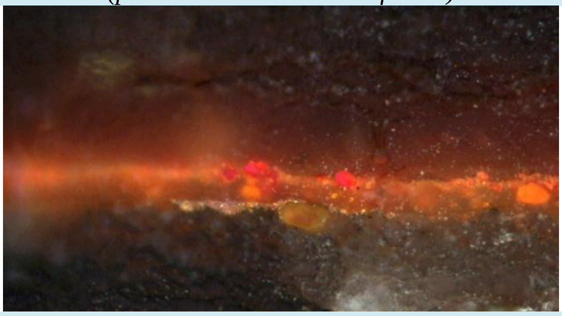


Fig.297 Detail. The pigment layer. It could be discerned the pigment grains (Magnification 50X) *(personal archive Th. Mafredas)*

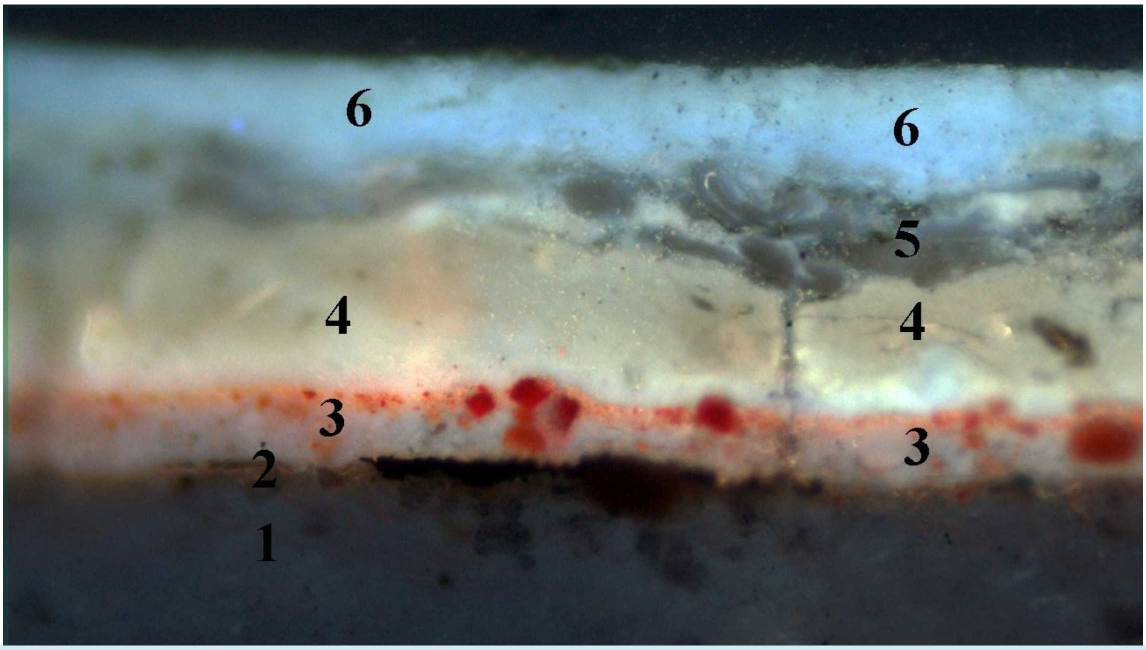


Fig.298 Detail. The discern of sample's layers, under UV radiation (Magnification 50X)
(personal archive Th. Mafredas)

It should be noted that these three upper organic layers seems to have a good adhesion to each other.

3.3.3. Microchemical Tests

A staining test for the identification of proteinaceous materials was applied in sample #13, using NA2 as a reagent in order to identify the presence of proteinaceous materials to the binding medium.

From the staining test, a very small staining can be observed, which might indicate the presence of proteinaceous materials in low concentration (**Fig.299-300**). The preparation layer has also been colored but, compared to the previous samples, the coloration is less significant. Finally, a light staining can be observe on the layers above and below the gold leaf, which may indicate the low concentration of proteinaceous material at the specific points (**Fig.301-302**).

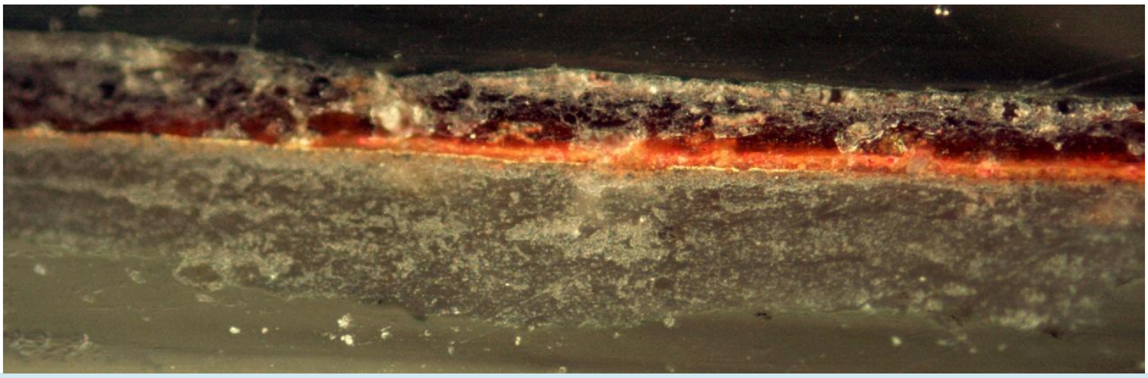


Fig.299 Sample #13 before staining test with NA2 *(personal archive Th. Mafredas)*

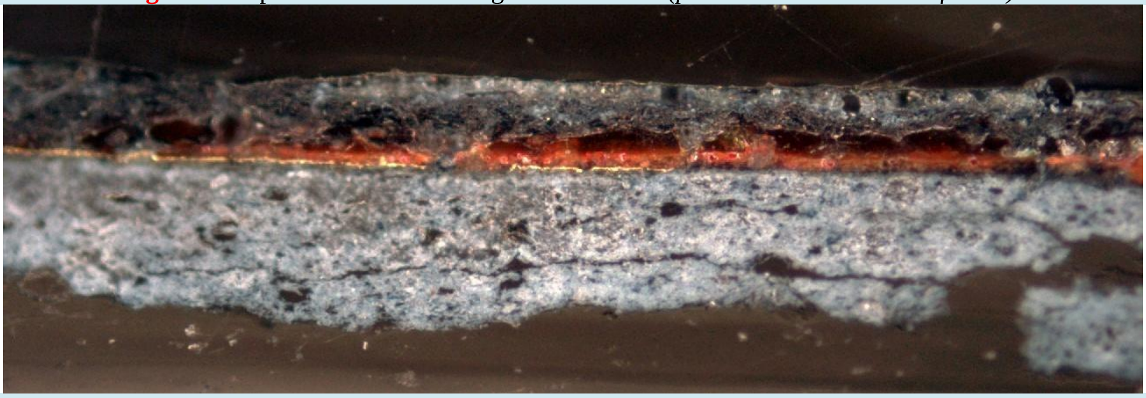


Fig.300 Sample #13 after staining test with NA2 *(personal archive Th. Mafredas)*

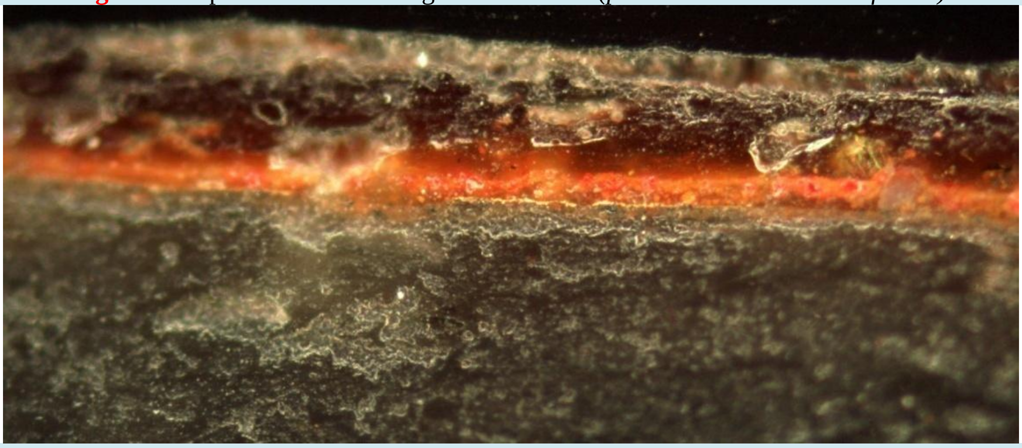


Fig.301 Detail from sample #13 before staining test with NA2 *(personal archive Th. Mafredas)*

Fig.302 Detail from sample #13 after staining test with NA2 *(personal archive Th. Mafredas)*

3.3.4. Scanning Electron Microscopy

Upon examining sample #11a with SEM (**Fig.303**), through the BSE images, it was possible to discern the layers comprising the sample, measure the thickness of each layer, and observe layers which were not easily distinguishable during OM, such as the bole and the gold layers.

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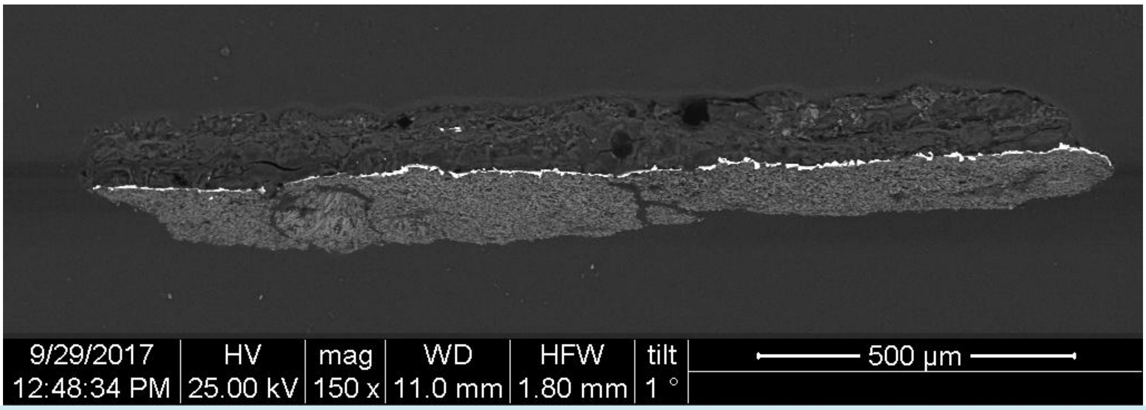


Fig.303 Sample #11a *(personal archive Th. Mafredas)*

During SEM observation, the thickness of the layers was identified and measured (**Fig.304**), first, of the gesso layer which was 85,35µm[35]; second, a thin bole layer at 4,49µm and, third, the gold layer at 2,29µm. Over the gold layer, a fourth layer was observed which was organic in nature, probably from the varnish coating. This layer seemed to consist of two different layers; the first with a non-uniform thickness of 80.47µm and 83.47µm, and the second with a thickness of 37.25µm.

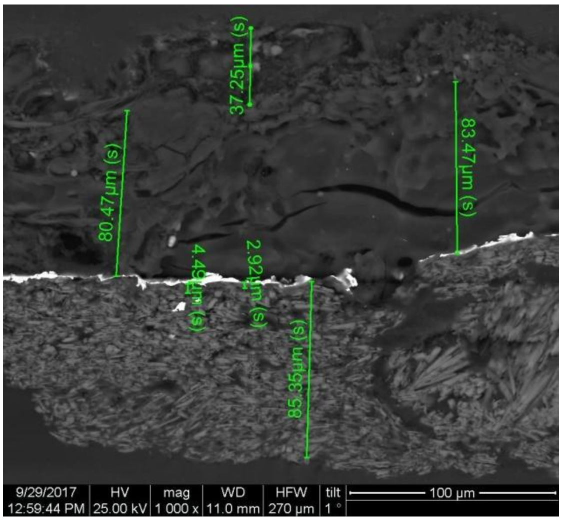


Fig.304 Thickness of sample's layers *(personal archive Th. Mafredas)*

Studying the gesso layer, it could be seen that the preparation layer consisted of 2 different layers which could be identified through the direction, thickness and size of

[35] The thickness of the gesso preparation layer depends on the thickness of the sample.

the flakes (**Fig.305-307**). It seems like Dionysius was negligent in applying the gesso layer, a feature also found in the other two panel paintings, especially for the gesso layer. Concerning the bole and the gold layer, the small thickness of both layers was observed, (**Fig.308**) especially for the bole layer which was difficult to identify during OM observation. Finally, concerning the upper organic layer, it was easy to discern the different layers of organic coating and observe that these varnish layers presented a disturbed stratigraphic structure (**Fig.309-310**).

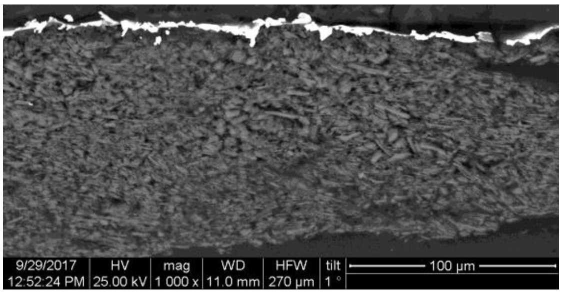


Fig.305 The gesso layer (sample #11a)
(personal archive Th. Mafredas))

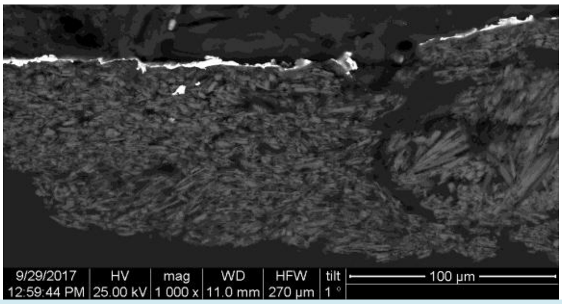


Fig.306 The gesso layer (sample #11a)
(personal archive Th. Mafredas)

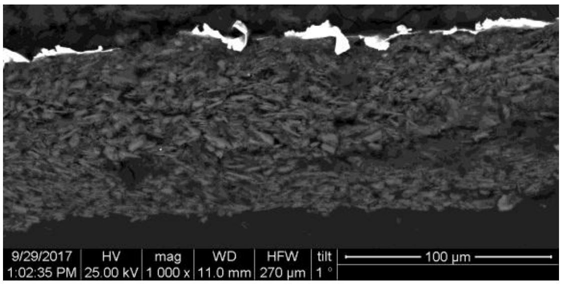


Fig.307 The gesso layer (sample #11a)
(personal archive Th. Mafredas)

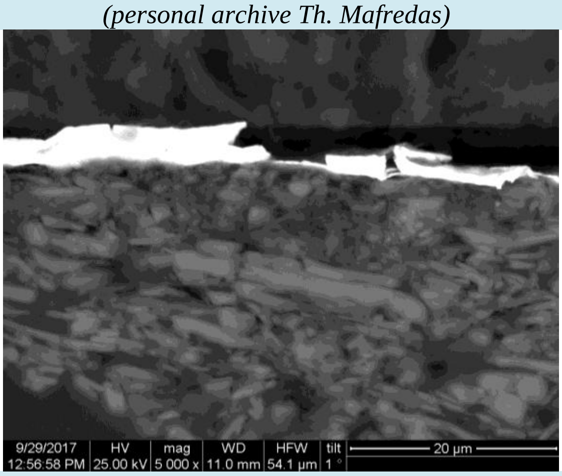


Fig.308 Detail The bole and the gold layer (sample #11a) *(personal archive Th. Mafredas)*

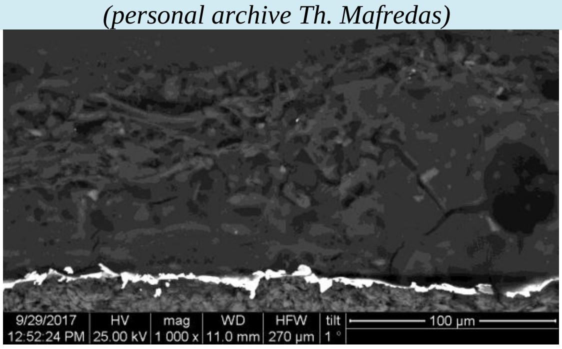


Fig.309 The varnish layer (sample #11a)
(personal archive Th. Mafredas)

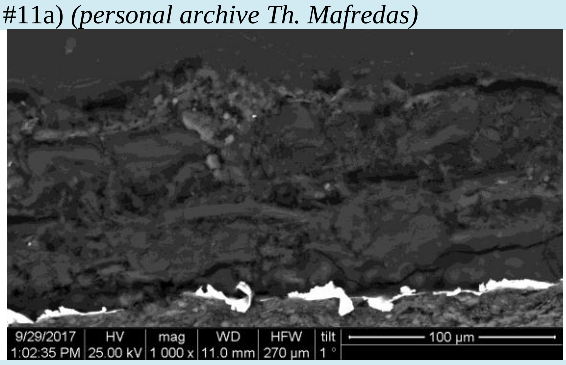


Fig.310 The varnish layer (sample #11a)
(personal archive Th. Mafredas)

Studying sample #13 by SEM (**Fig.311**) it was possible to discern the layers comprising the sample which were not so easily detectable during OM. Besides that, it was possible to measure the thickness of the layers (**Fig.312**).

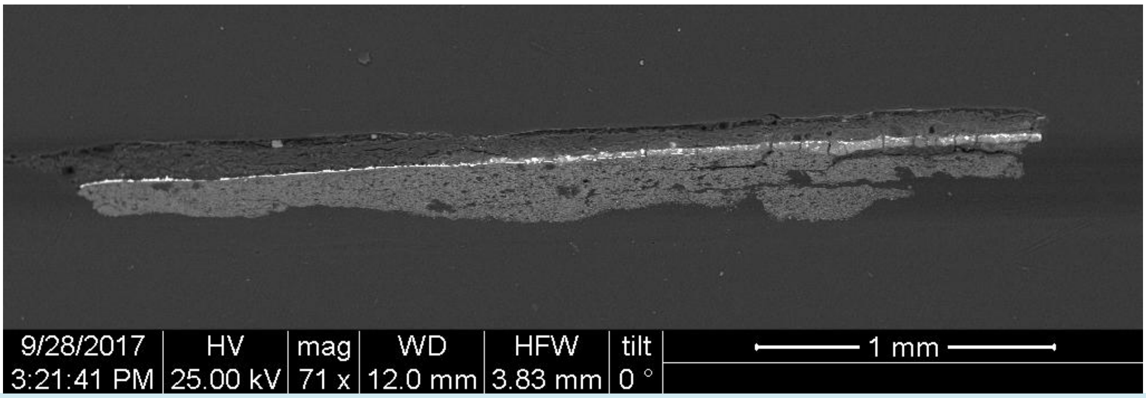


Fig.311 The sample #13 *(personal archive Th. Mafredas)*

Among others, three different layers of gesso preparation were observed, each with a different thickness: the first at 47,87μm, the second at 66,72μm and the third at 43,25μm. Also, a thin bole layer was detected at 2,64μm, over the gesso layer, while a gold layer was observed (2,33μm). Over the gold layer, the pigment layer was observed (18,20 μm),and over that, an organic layer distinguishable in two different thin layers (44,24μm and 27,40μm).

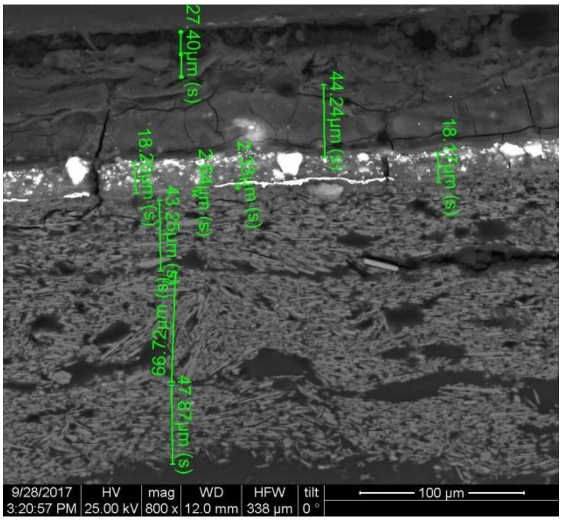


Fig.312 Thickness of sample's layers *(personal archive Th. Mafredas)*

Studying the gesso layer, it could be seen that the preparation layer consisted of 3 different layers which could be identified through the direction, thickness and size of the flakes (**Fig.313-314**). Once more, it seems that Dionysius was negligent in applying the gesso layer, something in common both with the previous sample (#11a), and with the previous two panel paintings. Concerning the bole and the gold layer, the thin thickness of both layers was observed (**Fig.315**), as well as, the discontinuity of the gold layer (**Fig.314**). In the pigment layer, the presence of big dispersed pigment grains (**Fig.317-319**) was observed and, finally, the organic layer looked like a first layer of well-homogenized varnish (**Fig.320**). Over that, a second layer of unmelted varnishes could be observed. (**Fig.321**), while the external layers could be characterized as dirt and dust layers (**Fig.322**).

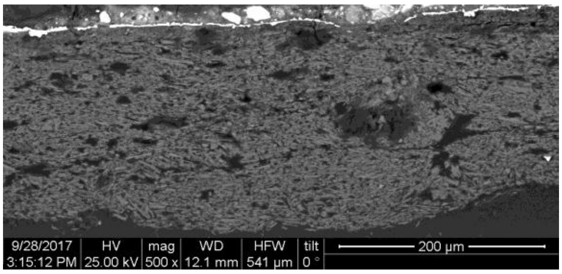


Fig.313 The gesso layer (sample #13) *(personal archive Th. Mafredas)*

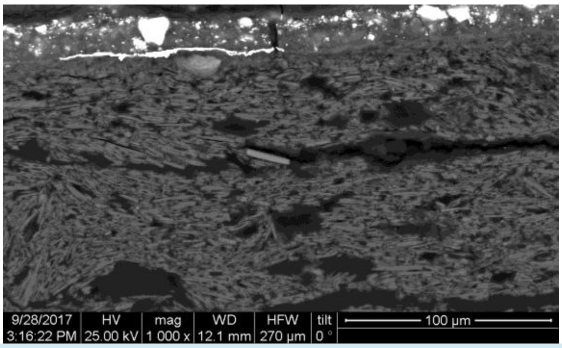


Fig.314 The gesso layer (sample #13) *(personal archive Th. Mafredas)*

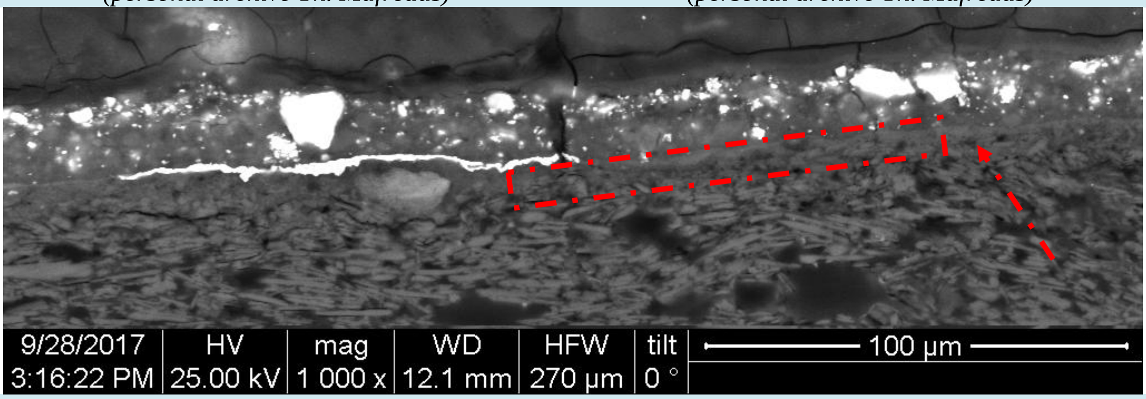


Fig.315 The bole layer (Sample #13) *(personal archive Th. Mafredas)*

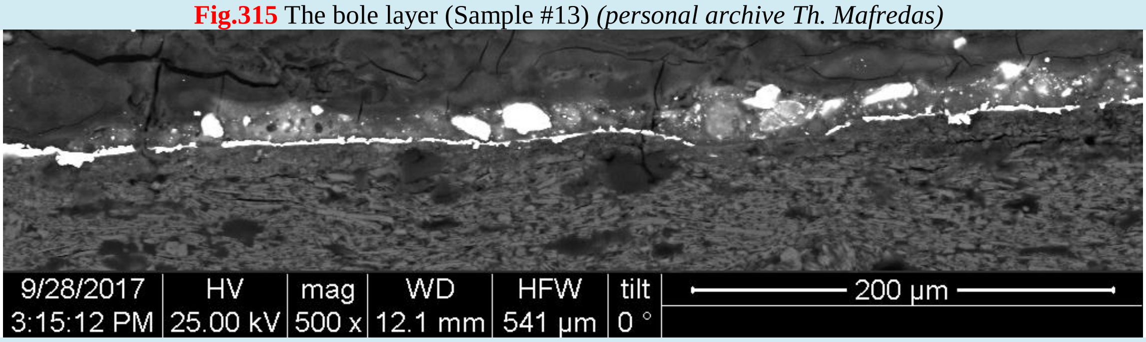


Fig.316 The discontinuity of the gold layer (Sample #13) *(personal archive Th. Mafredas)*

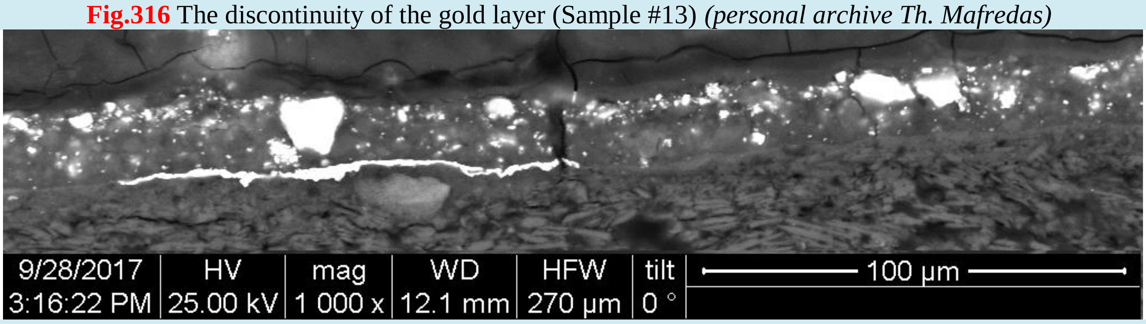


Fig.317 Big pigment grains in the pigment layer (Sample #13) *(personal archive Th. Mafredas)*

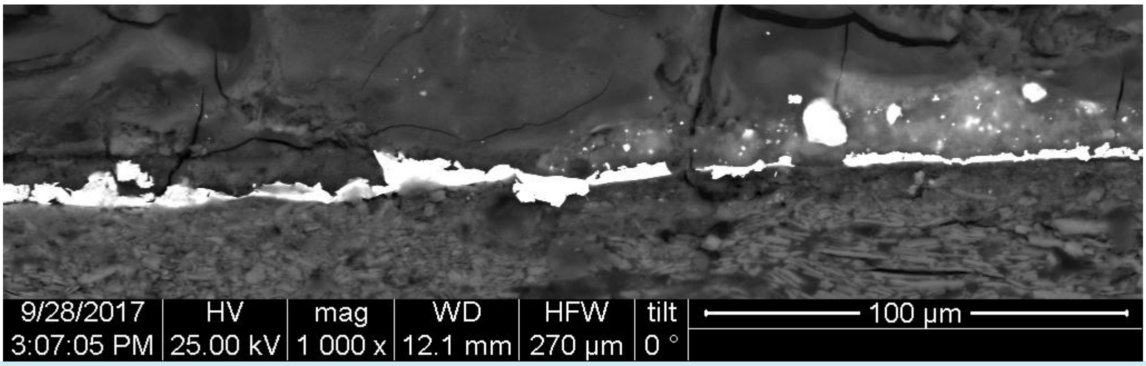


Fig.318 Big pigment grains in the pigment layer (Sample #13) *(personal archive Th. Mafredas)*

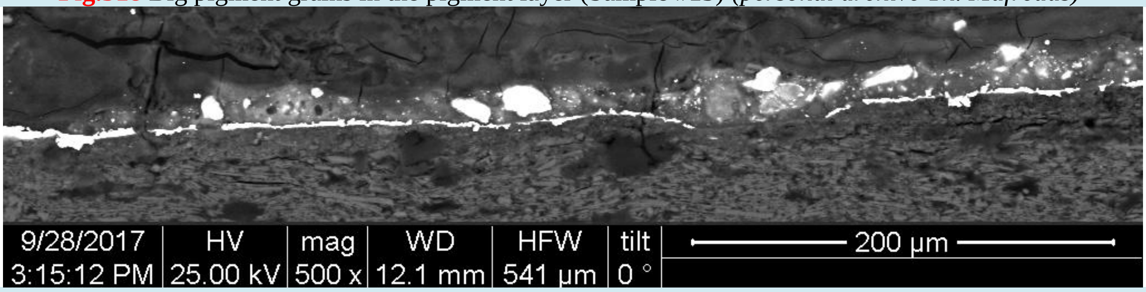


Fig.319 Big pigment grains in the pigment layer (Sample #13) *(personal archive Th. Mafredas)*

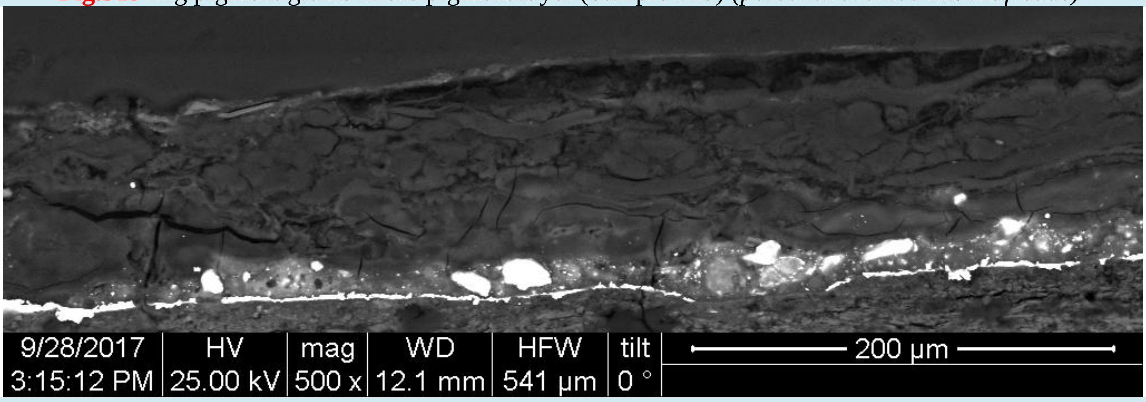
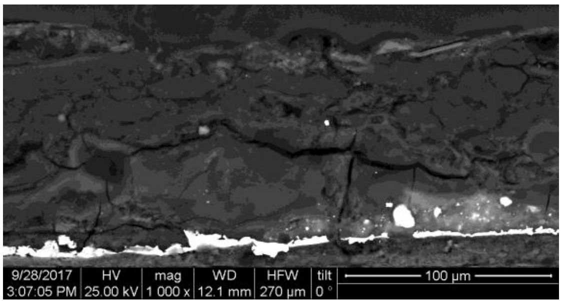


Fig.320 The varnish layer (sample #13) *(personal archive Th. Mafredas)*



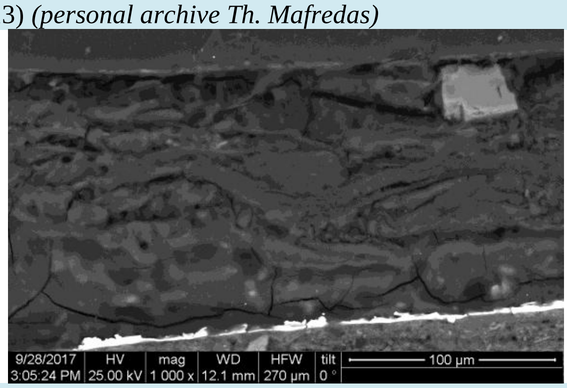


Fig.321 The varnish layer (sample #13) *(personal archive Th. Mafredas)*

Fig.322 The varnish layer (sample #13) *(personal archive Th. Mafredas)*

3.4. Analytical Techniques

3.4.1. Elemental Techniques

3.4.1.1. X-Ray Fluorescence

XRF was applied on the painting surface of the panel painting in 14 different points (**Fig.323**) (continuing the numbering from the previous panels) in order to obtain data from a variety of areas concerning Dionysius' color pallet, and identify pigments in areas where the varnish layer had lost its transparency and become opaque, compromising the painting's purity. Furthermore, the use of XRF in gold areas provided data that helped to conclude about the use of a bole layer, the kind of it, and the type of metal used.

Fig.323 Saint John the Baptist. The Forerunner. XRF spots *(personal archive Th. Mafredas)*

From hit points 30-32, the XRF data provided an elemental analysis of the ingredients of the bole layer (**Table 11**). According to the spectra (***Appendix 4***), Fe, Ca, Pb, S and Cu were identified in addition to the Au. Studying the obtained data from panel #3 in comparison to the data from the same areas from panels #1 and #2 (hit spots 1, 2, 3, 20) it was found that they were almost identical, except for some differentiations at the intensity bands. Thus, it could be assumed that Au comes from the gold leaf, Fe probably indicates the presence of red/yellow ochre, and Pb probably comes from red Pb, as constituents of bole.

The XRF analysis at St. John's hands (#33-#34) and face (#35) detected the presence of Pb, Hg and Fe (***Appendix 4***) (**Table 11**), possibly coming from a mixture of lead white (2PbCO3•Pb(OH)2)with cinnabar and a small quantity of yellow ochre, pigments corresponding to Dionysius's recipe for flesh (Dionysius 1909, p. 20).

The XRF hit point #36 was taken from a red area at the left vertical frame of the panel. According to the spectrum, the trace elements found were Pb, Hg, S, Ca, and Fe and Cu with low intensity bands–almost undetectable. From the trace elements with the high intensity bands, the presence of Hg and S are indicative for the use of cinnabar, and it could be assumed that Ca probably comes from the gesso layer. Concerning the presence of Pb, it could be assumed that it suggests the use of red lead (Pb_3O_4), as it had been proven in the previous panels from EDX on samples taken from similar areas (vertical and horizontal frame of panels).

The XRF analysis of the whitish areas of the panel, such as #37 at the scroll's background, #38 at the middle of St. John's himation, and #39 at St. John's left elbow (**Table 11**), indicated the presence of Pb. From the obtained spectra, (***Appendix 4***) the only trace element is Pb. Studying the panel in Vis shows that these areas are whitish. It would be too risky to make any assumptions about the use of other inorganic or organic pigments which he may have used in these areas and are not detectable due to XRF limitations. A further examination of these points through a more sophisticated research protocol could provide more specific answers about the use of more pigments.

Studying the background of the painting theme at hit points #40 and #43, the trace elements from the obtained spectra (***Appendix 4***) remain the same (**Table 11**); Pb and As with the same intensity bands, Ca, Fe, and Cu with a small differentiation at Ca intensity band. According to the trace elements, it could be assumed that As probably comes from orpiment, (As_2S_3) which is yellow (Katsaros 2015, p. 536), Fe probably comes from a red/yellow ochre, and Cu from Azurite ($2CuCO_3$•$Cu(OH)_2$ because, in bibliography, it was found that orpiment was often mixed with Azurite to produce green (West FitzHugh 1997, p. 53).In this mixture, if a quantity of red and a small quantity of red/yellow ochre is added, then the color of the mixture will be a quite clean green. These two hit points are almost identical with hit point #13 at panel #1.

The two last XRF hit spots, #41 and #42, are located on the right vertical frame of the panel. The trace elements from these two spots are almost the same (**Table 11**) with a differentiation in the intensities of the elements for each spectrum (***Appendix 4***). Thus, for spot #41, the order of the trace elements is Au, Ca, Fe, Pb, Cu, and for spot #42 the order is Ca, Pb, Au, S, Fe, Cu, Zn, and Ar. For spot #41, the presence of Fe and Pb at the same intensity bands could be attributed to the presence of a bole layer, and the trace of Ca could come from the gesso layer. For spot #42 the intensity band of Ca in addition with the presence of S could be attributed to the gesso layer. The intensity band of Pb is bigger than Au, which indicates a higher concentration of Pb. Taking into account the data from the OM and from the SEM concerning sample #13, which is taken from the same area as hit point #42, then it could be assumed that the presence of Pb probably comes from red lead (Pb_3O_4), and the lower intensity band of Au could be explained under the view that the gold layer is below the red lead layer, something already seen during microscopic examination. The presence of Fe could probably indicate the presence of red/yellow ochre as one of the constituents for the bole layer. Finally, trace elements, such as Zn and Ar, are detected, which appear to be impurities of the raw materials without their presence interfering with the presence of raw materials as they are recorded by the intensity bands of the spectra. This is a feature that has already been noticed during the study of the XRF spectra for previous panels, such as spots #11-13 and #16 for panel #1 (**Table 7**), and spots #18 and #28 for panel #2 (**Table 9**). In panel #3 the same data was found at spot #30 (**Table 11**).

Table 11. *Panel #3- Elemental Analysis – XRF*

Spot	# of Spectrum	Color	Trace elements
30	1854	Gold	Au, Ca, Fe, Pb, Ar, S, Cu, Ti
31	1855	Gold	Au, Ca, Fe, Pb, S, Cu
32	1856	Gold	Au, Ca, Fe, Pb, Cu
33	1857	Hand	Pb, Hg, Fe
34	1858	Hand	Pb, Hg, Fe
35	1859	Flesh	Pb, Hg, Fe
36	1860	Red	Pb, Hg, S, Ca, Fe, Cu
37	1861	Whitish	Pb
38	1862	Whitish	Pb
39	1863	Whitish	Pb
40	1864	Greenish (ground of the theme)	Pb, As, Ca, Fe, Cu
41	1865	Ground	Au, Ca, Fe, Pb, Cu
42	1866	Ground	Ca, Pb, Au, S, Fe, Cu, Zn, Ar
43	1867	Dark pigment (ground of the theme)	Pb, As, Ca, Fe, Cu

XRF analysis was applied in 14 different spots on the painting surface and the respective spectra were obtained (***Appendix** 4*). The interpretation of the data assisted to draw a first conclusion about Dionysius's color palette (**Table 11**). According the data as presented above, it could be assumed that he used a variety of pigments, all of which are mentioned in his treatise. But, due to the limitations of this technique, quantification analysis could not be provided; only qualification. Furthermore, elements below Al could not be traced because the XRF device used does not allow the detection of elements with an atomic number less than 13, which excluded the detection of C (Mastrotheodoros 2016, p. 163). Thus, this panel painting, as well as the other three (3), was examined preliminarily with XRF, and then a portion of the pigments were identified by further study of the samples with SEM/EDX, as it will be discussed below.

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3.4.1.2.Energy Dispersive X-ray Analysis

The Energy Dispersive X-ray (EDX) spectroscopy provided elemental information about the identity of inorganic materials present in the two samples about pigments and gesso preparation materials.

Upon examining sample #11a **(Fig.324)** with EDX, it was found that the first thick layer was gesso preparation consisting of Ca (Calcium) and S (Sulfur) (**Fig.325**), so it could be characterized as $CaSO_4$. Over the gesso layer and below the gold leaf, the thin existing layer was identified as a bole layer through its constituents. Besides the presence of Ca and S from the gesso, Al and Si from the bole clay were also found, as well as Fe, probably due to the presence of red/yellow ochre (Katsaros 2015, p. 536) (**Fig.326**).

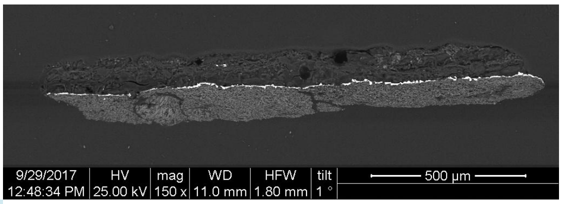


Fig.324 Sample #11a.SEM *(personal archive Th. Mafredas)*

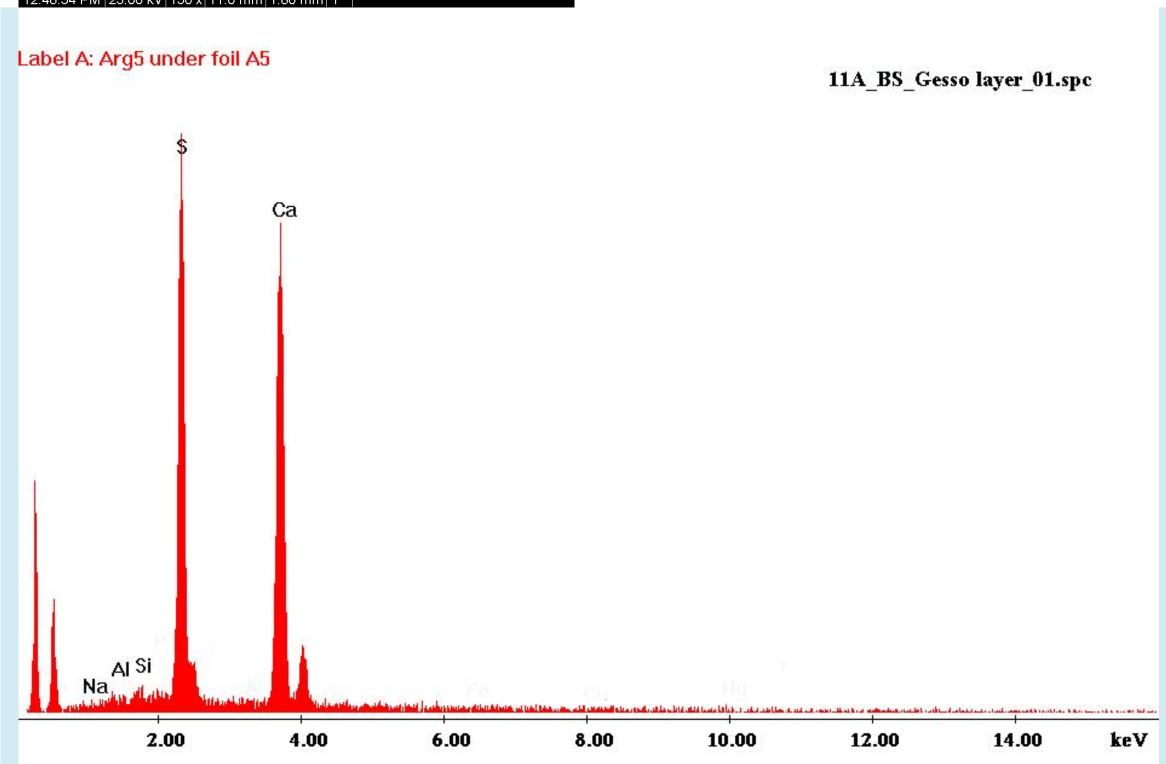


Fig.325 EDX Spectrum from gesso layer (sample #11a) *(personal archive Th. Mafredas)*.

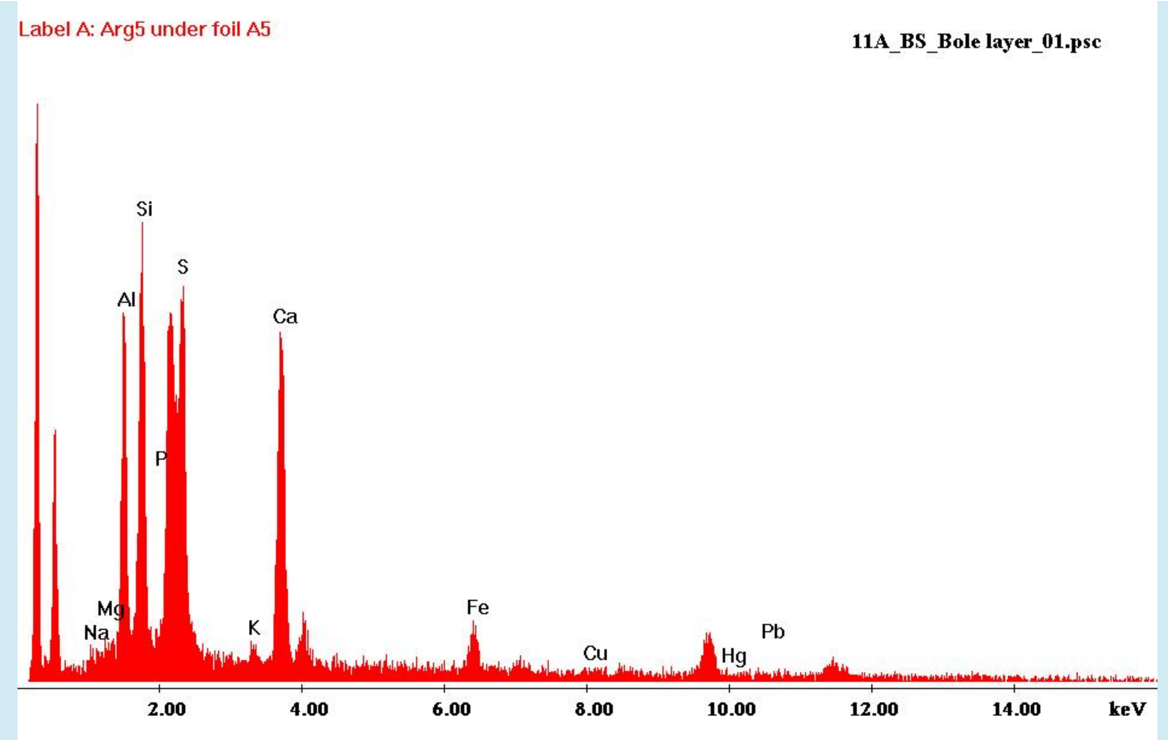


Fig.326 EDX Spectrum from bole layer (sample #11a) *(personal archive Th. Mafredas)*

During the study of sample #13 (**Fig.327**) through EDX analysis, it was found that the preparation layer was $CaSO_4$ (**Fig.328**). A bole layer was also found, consisting, of Ca and S probably coming from the gesso layers, of Al and Si from the bole clay, and of Fe probably coming from ochre, and of a low intensity band of Au from the gold leaf (**Fig.329**).

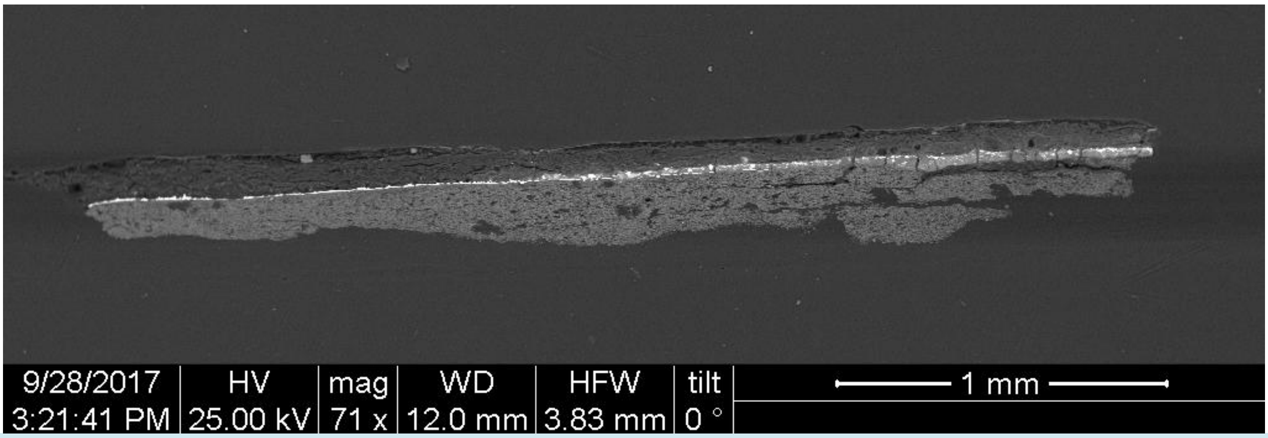


Fig.327 The sample #13. SEM *(personal archive Th. Mafredas)*

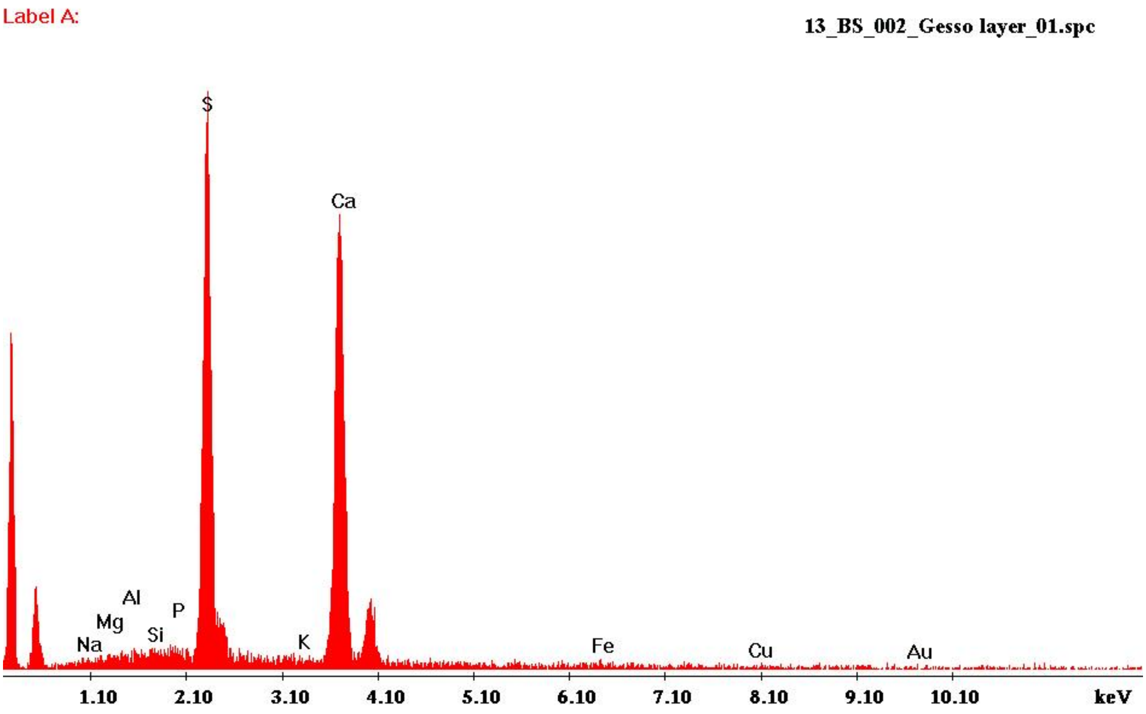


Fig.328 EDX Spectrum from gesso layer (sample #13) *(personal archive Th. Mafredas)*

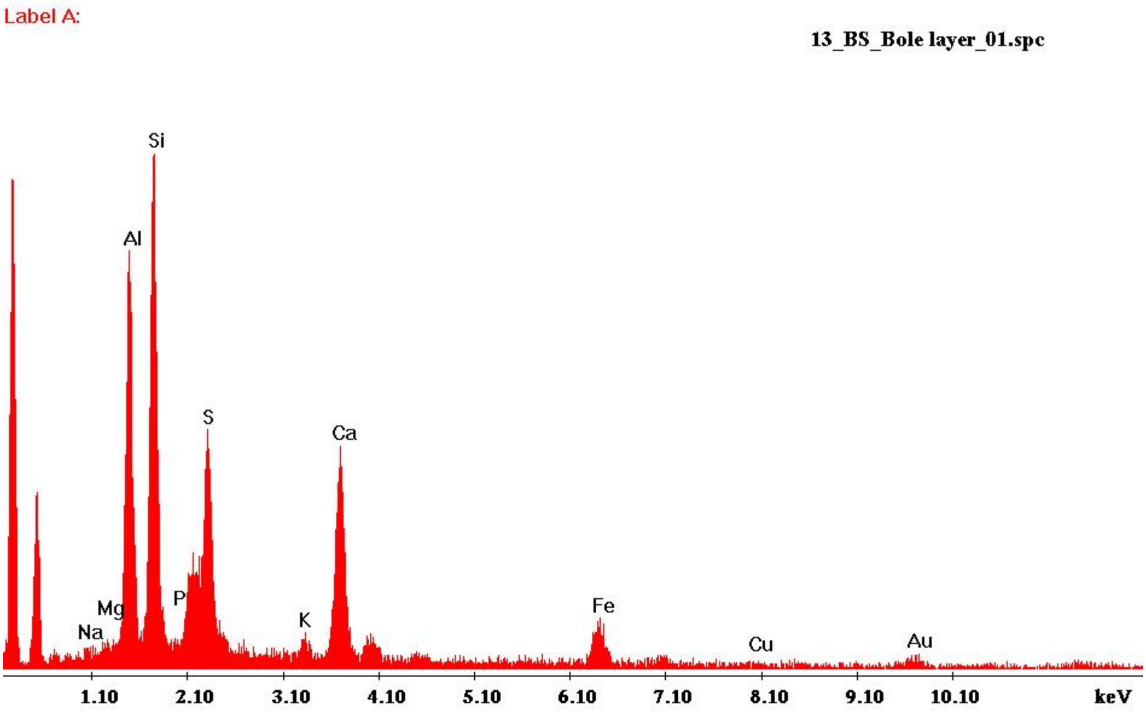


Fig.329 EDX Spectrum from bole layer (sample #13) *(personal archive Th. Mafredas)*

Over the bole layer, the EDX analysis provided the data about the presence of the gold leaf (**Fig.330**). Over the gold layer, during OM and SEM microscopic examination a thin pigment layer was found. Through EDX analysis it was identified as pigments grains from Hg, S and Pb (**Fig.331**). By OM it was know that the pigment grains are red and yellow –red, so it could be assumed that the thin pigment layer consisted of a mixture of cinnabar and red lead.

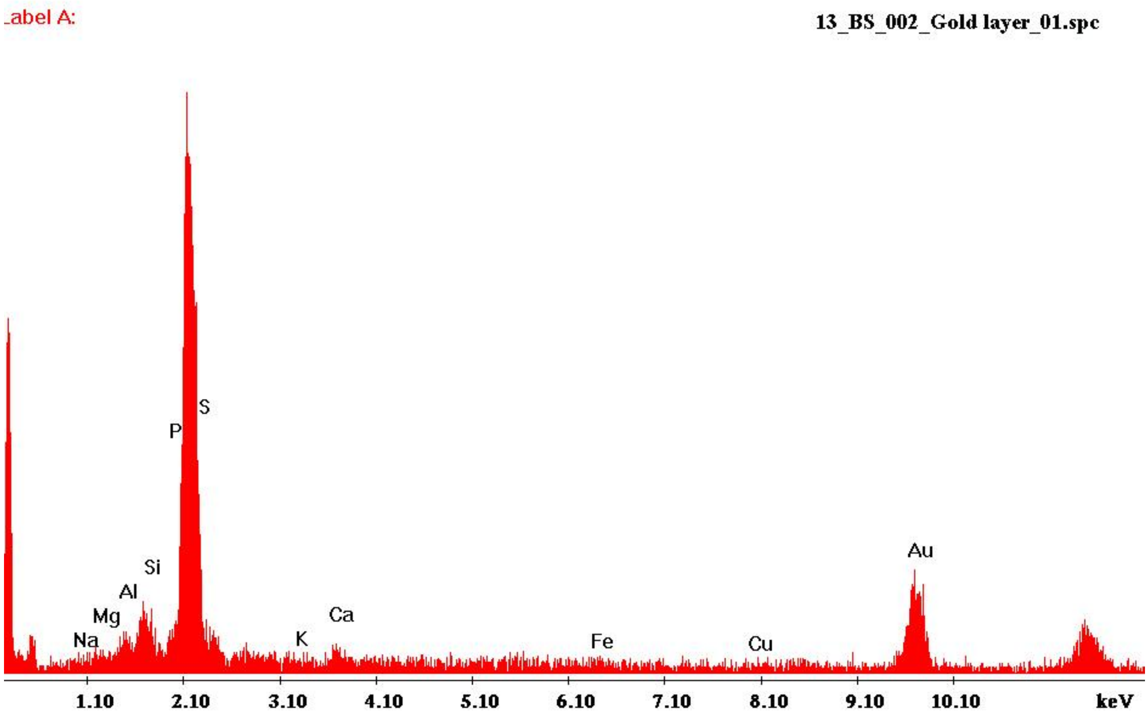


Fig.330 EDX Spectrum from gold layer (Sample #13) *(personal archive Th. Mafredas)*

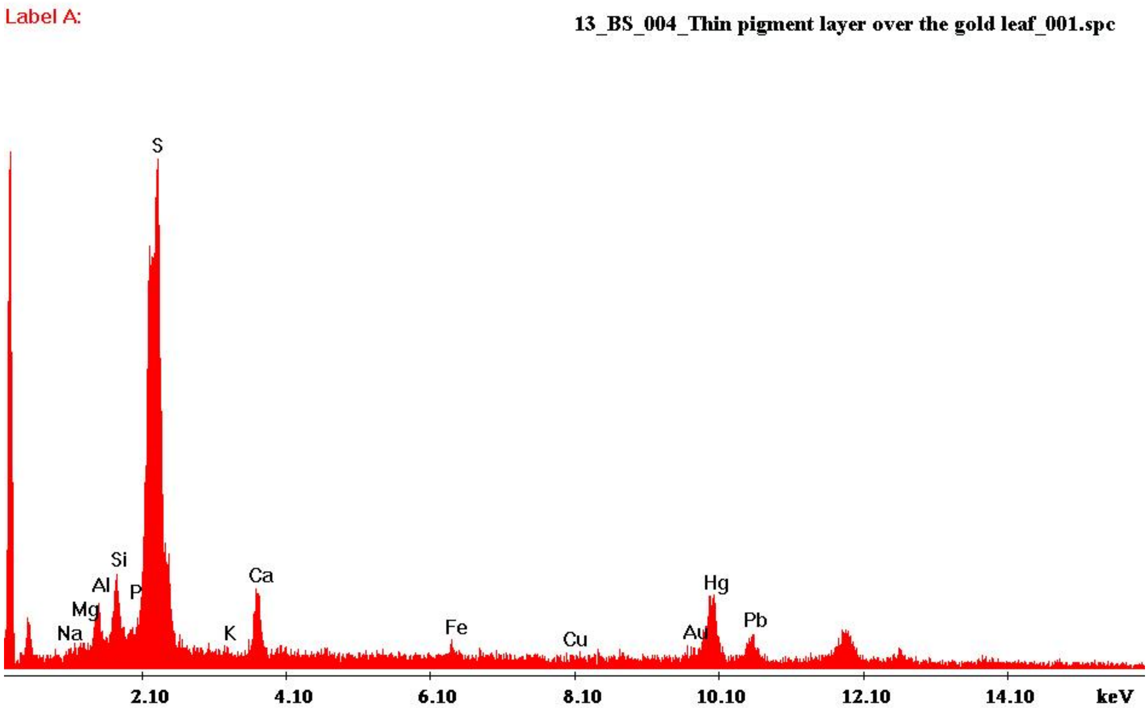


Fig.331 EDX Spectrum from the thin pigment layer over the gold leaf (Sample #13) *(personal archive Th. Mafredas)*

The use of EDX helped to identify the inorganic pigments in different layers and make a quantification of the trace elements (**Table 12**). In this framework it was possible to identify different pigments, especially in sample #13 which was over the gold leaf and, at the same time it helped a lot to characterize the thin layers below the gold leaves as bole layer. Characterizing the constituents of the bole layer in both samples was combined with a parallel study of the obtained data from the previous two panels, which helped to make a first hypothesis about the bole recipe that Dionysius used during the construction of these three panels, in comparison to the instructions that he provided in his treatise. For one more time, it was observed that he usually used a mixture of red lead with cinnabar for the red layer.

Table 12. *Panel #3 - Elemental Analysis - EDX*

# Sample	Spot	OM	Layer	Trace Elements
#11a	Gesso preparation	Thick layer (right side of the sample with big grains)	1st	S, Ca
	Bole layer	Thin layer. It is visible only in high magnification	2nd	Ca,, S, Al, Si, Fe
	Gold layer		3rd	
	Organic	Thick layer (3 different layers)	4th-6th	
#10	Gesso preparation	Thick layer	1st	Ca, S
	Bole layer	Thin layer	2nd	Ca,, S, Al, Si, Fe
	Gold layer	Thin layer	3rd	Au
	Pigment layer	Thin layer over the gold leaf	4th	S, Hg, Pb
	Organic	Thick layer	5th -6th	Ca, S, Al, Si, Mg, K
	External pollutant layer	Thin layer	7th	Si, Al, S, Ca, K, Fe, P, Mg, Na

3.4.2. Molecular Techniques

3.4.2.1. Fourier Transformer Infrared Spectroscopy

The final technique applied on two different samples was FTIR (***Appendix 2***) in order to characterize the gesso preparation and the kind of varnish which Dionysius used during the construction of his panel painting. The sample for gesso (#12) was taken from the bottom right part of the panel in the joint point of the horizontal and vertical frame, while the sample of varnish (#14) was taken from an already damaged area in the middle of the painting surface, at the left end of the open scroll. Both of them were in powder sample, prepared in KBr disc, as was discussed in a previous chapter.

From the obtained spectrum for sample #12 and the respective bands, it was identified that the gesso was hydrate (3551, 3496, 3407, 1687, 1622 cm^{-1}) gypsum (1140, 1116, 669, 602 cm^{-1}) and, more specifically, calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) (**Fig.332**). The use of $CaSO_4$, as evidenced from the relevant FTIR spectrum, could be justified from the obtained data from previous spectroscopic techniques, both XRF and EDX.

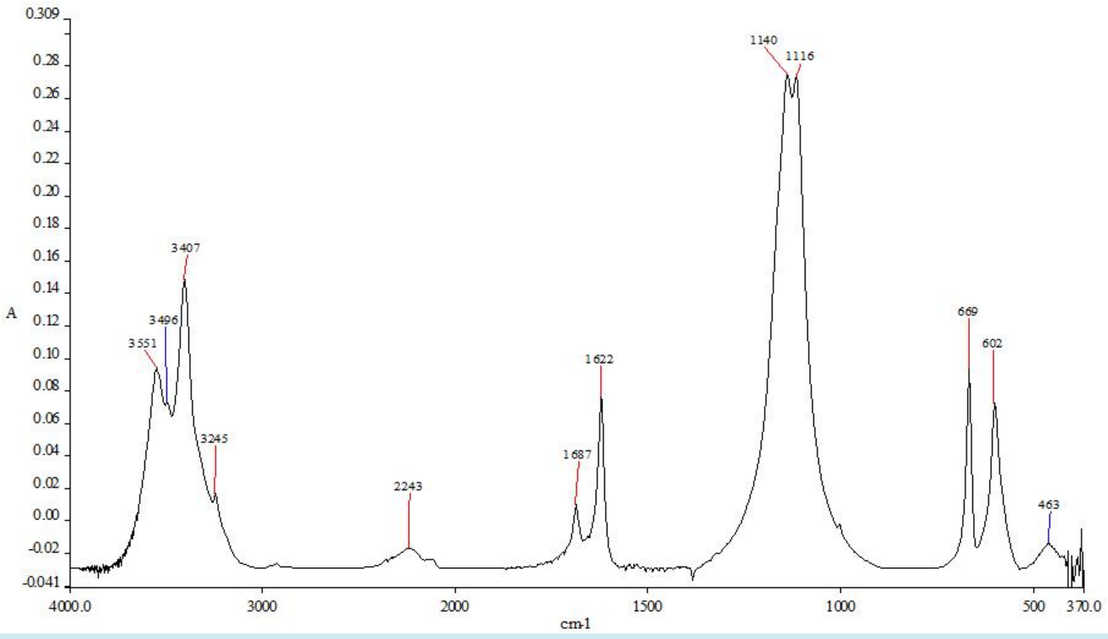


Fig.332 FTIR spectrum from gesso powder (panel #3, sample #12) *(personal archive Th. Mafredas)*

The obtained spectrum from sample #14 (**Fig.333**) indicated the presence of oil (1724, 1246, 1180, 1069, 721 cm^{-1}) besides the presence of Mastic (1714cm^{-1}) and Sandarac (1699, 1462, 1415, 1388, 1178, 1138, 1032 cm^{-1}). Furthermore, the band at 1388 cm^{-1} is indicative of the presence of natural resins, which could be explained as the possibility of the presence of two different varnishes, either in the form of a mixture, or in consecutive layers, with the presence of some quantity of oil.

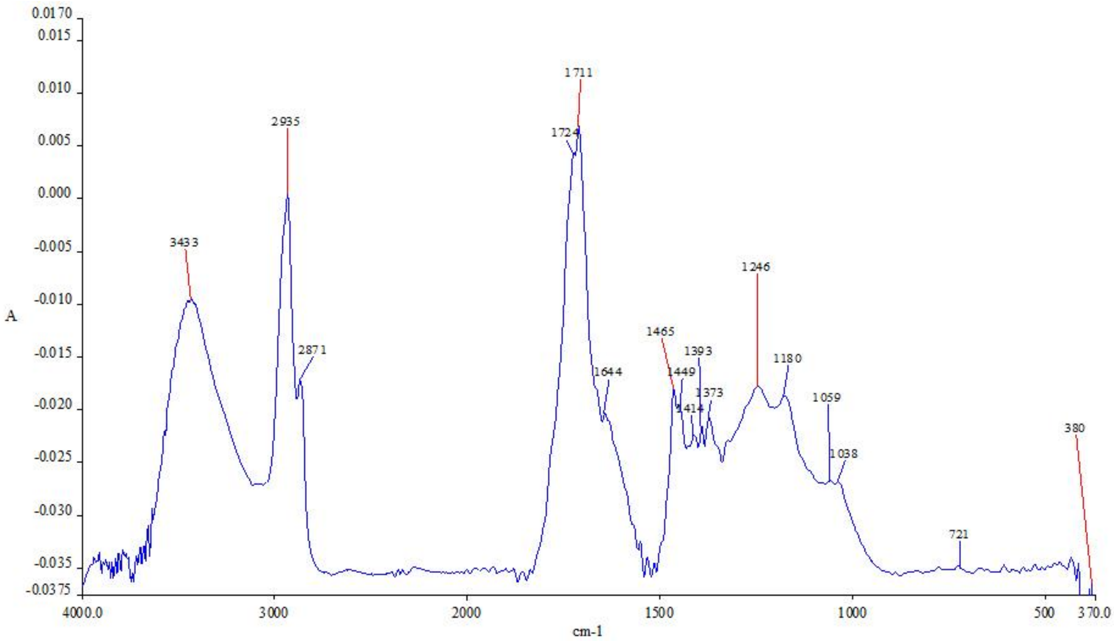


Fig.333 FTIR spectrum from varnish powder (panel #3, sample #14) *(personal archive Th. Mafredas)*

The use of infrared spectroscopy, as discussed above, justified the obtained data about inorganic elements during previous techniques and verified the different application of varnish layers, as was also found during microscopic observations. From the varnish identification, it could be argued that Dionysius used some kind of resin for varnish, which he had already mentioned in his treatise, as it will be further discussed below.

3.5. Discussion

The iconography of St. John the Forerunner (**Fig.334**) follows all the relevant instructions on this subject found in his earlier Hermeneia. References to Saint John the Forerunner are found in many sections of Dionysius's treatise (Dionysius 1909, pp. 88, 89, 110, 128, 141, 147, 166, 175-178, 208, 215, 217, 221, 223, 224, 229), but none of them contains a description of his physical appearance, his features are not provided, and it is not mentioned whether he should be depicted with wings or not. It seems that Dionysius follows the prototype of the Palaeologian period, also adopted by 15th century Cretan painters (Keiko 1995, pp. 152-154). St. John's scroll's text (**Fig.335**) is the same that Dionysius suggests in his treatise (Dionysius 1909, p. 229), and the detail of the axe (**Fig.336**) is also mentioned in his description of: "The Forerunner teaching the Jews and the Pharisees" (Dionysius 1909, p. 176), and derives from the Gospels of Matthew (Matthew 3:10) and Luke (Luke 3:9) (Kakavas 2008, pp. 208,209).

Fig.334 Panel #3 St. John the Baptist, the Forerunner. 1737
(personal archive Th. Mafredas)

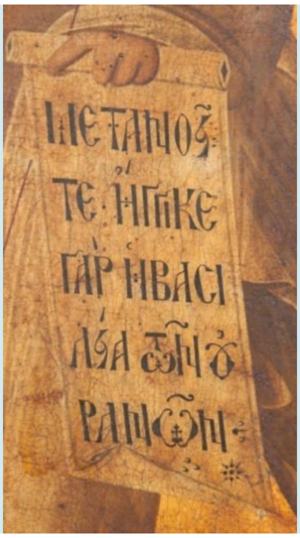


Fig.335 Detail, the scroll's text *(personal archive Th. Mafredas)*

Fig.336 Detail, the axe among the roots of a tree *(personal archive Th. Mafredas)*

Fig.337 Detail, the dedicatory epigram *(personal archive Th. Mafredas)*

Finally, the dedicatory epigram (**Fig.337**) is also painted at the bottom part of this panel painting, a practice found in the previous two panel paintings. It mentions: "Baptist of Christ, John the Forerunner, bestow your grace on Dionysius with all your power, beseech to the logos, whom you baptized and dispel the darkness of sinful deeds"[36] (Kakavas 2008, p. 209; Dionysios 1938, p. 31). It should be mentioned that nowhere in the text of the Hermeneia was an epigram included to accompany the Forerunner's panel painting. This can be explained by the fact that Dionysius was, at the same time, both the painter and donor of this panel painting.

As discussed above, imaging techniques, such as IR photography, helped study detailed features of painting concerning Dionysius' drawing line and observed same details which were not detectable or visible in the Vis.

The application of digital microscopy provided excellent and detailed data concerning the construction technique and the decoration of the painting surface, providing a first impression about Dionysius's painting technique. Through the examination with DM, Dionysius's magnificent painting skills became apparent, as he uses the pigments to achieve the desired volume and shape of his depicted themes. For

[36]«Βαπτιστά Χριστού, Πρόδρομε Ιωάννη, χάριν παρασχείν Διονυσίω πάνω. Καθικέτευε ον εβάπτισας Λόγον, διασκεδάσει πράξεων τε τον ζόφον» (Dionysios 1938, p. 31)

one more time, the use of gold as pigment over existing pigment layer (Greek: χρυσοκονδυλιά) was identified. Studying this panel in combination with the previous two, it was found that this feature is something that all three panels have in common. Common features with the previous two panels were also found while studying the technical construction where, among others, the presence of very thin layers was observed.

Studying the samples under OM and SEM confirmed the feature of very thin layers. A noteworthy example of this technique is sample 11a, where the bole layer was measured at 4.49 μm. The OM observation of the samples from this panel initially provided detailed information about the stratigraphy of the painting surface and the gilding technique. Also it was possible to observe a variation in the number of the varnish layers; in some cases, up to 3 different varnish layers were identified.

The microchemical test performed with NA2 in order to identify the presence of proteinaceous materials in the binding medium did not provide clear answers. If the binding medium was purely proteinic, then the staining should be stronger. Therefore, it can be assumed that the binder contains a low concentration of proteinaceous material, which has probably been mixed with another organic material. Applying the microchemical test, we got a first perception of the composition of the binder as to the existence of proteins. However, a more sophisticated physicochemical analysis, as GC/MS is necessary in order to receive exact answers about the composition of the binder.

During SEM observation it was possible to discern and measure the thickness of the samples' layers. Furthermore, SEM provided detailed data about the different layers of the cross section of the samples and helped to study Dionysius's construction technique. So, according to SEM it was observed that he had not worked and applied the gesso layer with diligence. A characteristic example is the gesso layer from both samples (#11a and #13). It seems like Dionysius was negligent during the application of the gesso layer. This feature could well lead to the assumption that he was not preoccupied with the panel's construction technology, as much as in the excellence of the depicted themes.

Through the elemental analysis with XRF and EDX it was possible to have a first perception about Dionysius' color palette. So, according to the obtained spectra, it could be assumed that he used red lead (Pb_3O_4), red ochre (Fe_2O_3), and cinnabar (HgS) for red pigments, and white lead ($2PbCO_3•Pb(OH)_2$) for white pigments. Also, it seems that he used azurite ($2CuCO_3•Cu(OH)_2$) for blue pigments, and orpiment (As_2S_3) for yellow pigments. For once more, it seems that all the pigments he used for this panel painting are mentioned in his treatise (Dionysius 1909, pp. 20-23, 34, 41).

The final analytic technique that was applied was FTIR and, through it, the kind of gypsum he used for gesso preparation was characterized as $CaSO_4$, which verifies the XRF and EDX results about Ca and S. The varnish he used seems to be Sandarac or Mastic in the form of two different varnishes, either in a mixture or in consecutive layers. As was observed in the previous panels, the presence of the same resins was identified, Mastic and Sandarac, both mentioned in the Hermeneia manuscript as ingredients for varnish layer (Dionysius 1909, pp. 25-27).

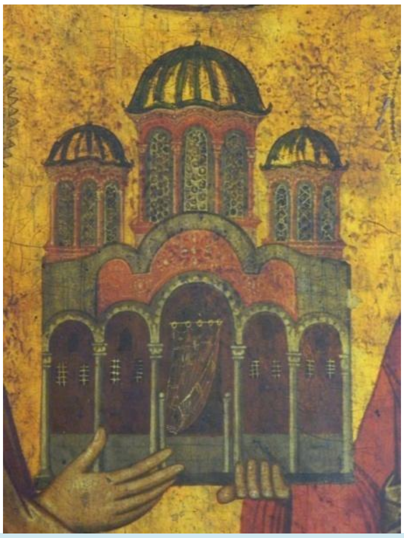
4. The Apostles Peter and Paul

4.1.Description

The last panel painting, from this set of four portable panels painted and donated by Dionysius is the painting of the apostles Peter and Paul. The two Apostles, Peter and Paul, (**Fig.338**), are portrayed facing each other and holding a model of an imaginary church while, in the middle of the upper part of the composition, Christ appears in bust, surrounded by a semicircle of sky with beams of light, blessing the two apostles with both of his hands. In front of his chest, there is an open Gospel with the inscription: “Go therefore and teach all nations, baptizing them” (Matthew 28:19).

Fig.338 Apostles, Peter and Paul 1737, Dionysius, Church of Transfiguration, Fournas
(personal archive Th. Mafredas)

The Apostles are represented with their traditional characteristics, just as they are described in the additional part of the Hermeneia (Dionysius 1909, p. 175; Hetherington 1974, p. 52). Peter, on the left, is turned to the right with his right hand holding one side of the church’s model, and with his left hand the scroll of his epistles and keys. Paul, on the right, is turned to the left, holding with his right hand the other side of the church and, with his left, the gold-bound codex of his epistles. The model of the church (**Fig.339**) is painted in remarkable detail, covered with three vaults, from which the middle one stands highest, and with an open portico on the façade. The five arches supported by columns in front of the portico, as well as the windows of the façade allow the inner part of the church to be seen (**Fig.340**) (Kakavas 2008, p. 195; Kakavas, Mafredas & Giannoulopoulos 2013, p. 317).



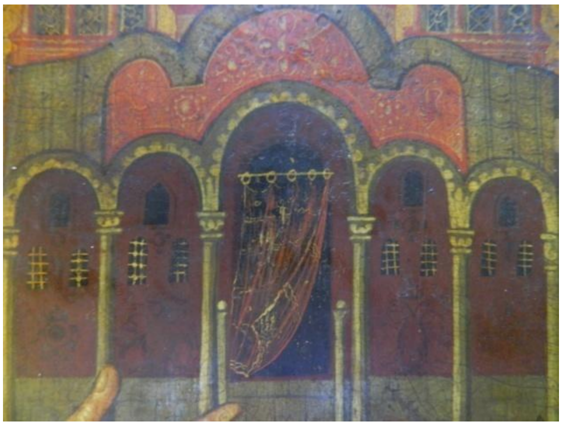


Fig.339 Apostles, Peter and Paul, Detail, The church's' model *(personal archive Th. Mafredas)*

Fig.340 Apostles, Peter and Paul, Detail, The inner part of church's' model *(personal archive Th. Mafredas)*

A dedicatory epigram (**Fig.341**), as the case was with the previous three despotic panel paintings, can be found in the bottom part of this panel: "O Peter and Paul, the gate keepers of the upper world, who immediately open the gates to all those who repent, that moment when historiotechnites knocks, open the gates to the priest Dionysius"[37] (Kakavas 2008, p. 194; Dionysios 1938, p. 31).

Fig.341 Apostles, Peter and Paul Detail, dedicatory epigram-Vis *(personal archive Th. Mafredas)*

The back side of the panel also bears a Cross with letters forming the name of Christ and the word of victory (in Greek): IC//XC//NI/KA (**Fig.342**), a common feature with the other three panels.

Fig.342 The back side of panel #4 *(personal archive Th. Mafredas)*

[37] «Ω Πέτρε, Παύλε, οι θυρωροί των άνω, μετανοούσιν ως ανοίγοντες αφνω, κρούοντι άρτι Ιστοριοτεχνίτη, άρατε πύλας Διονυσίω θύτη» (Dionysios 1938, p. 31)

4.2. Imaging Techniques

4.2.1. IR photography

The application of IR photography (**Fig.343**) provided a lot of features concerning Dionysius's drawing. Through IR photography, it was possible to observe

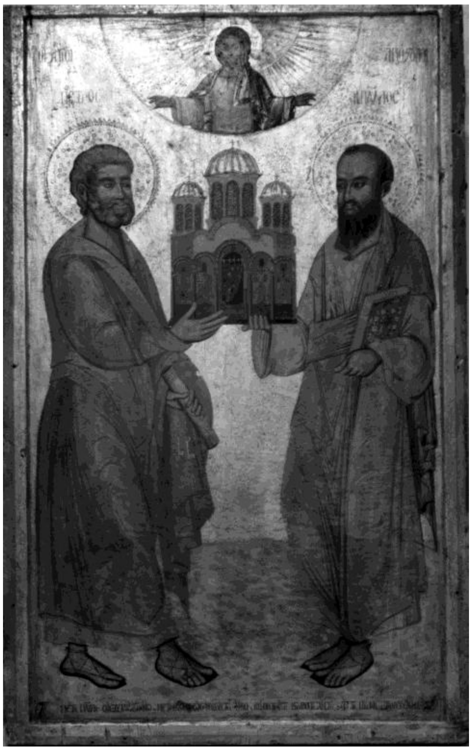


Fig.341 Panel #4 IR photography

some points in which the initial drawing of the painter was distinguishable, such as in St. Paul's foot (**Fig.344**), and a differentiation in the bottom of the garment in St. Peter's left foot (**Fig.345**). Through IR radiation the epigram at the bottom of the panel was more easily readable (**Fig.346**). Also, it was identified that the dedicatory epigram has the form of an open scroll, as became distinct from the edges of the epigram where the details of an open scroll were drawn (**Fig.347-348**). In the same area, traces from a line over and below of the fonts were detected; Dionysius probably used these as a guide for writing the epigram (**Fig.349**). Furthermore, in the epigram, the letter Ω on the left side of the epigram was not detectable during IR photography, even though it was distinguishable by Vis photography. Studying this area in Vis, it was found that the letter Ω was created with some kind of red pigment which was absorbed below IR radiation (**Fig.350**).

Fig.344 St. Paul's foot. Traces from initial drawing *(personal archive Th. Mafredas)*

Fig.345 Differentiation in the bottom of St. Peter's garment *(personal archive Th. Mafredas)*

Fig.346 Detail, dedicatory epigram-IR *(personal archive Th. Mafredas)*

Fig.347 Details from the right edge of the dedicatory epigram (Forms an open scroll) *(personal archive Th. Mafredas)*

Fig.348 Details from the left edge of the dedicatory epigram (Forms an open scroll) *(personal archive Th. Mafredas)*

Fig.349 Traces from a line over and below the letters, used as guide line *(personal archive Th. Mafredas)*

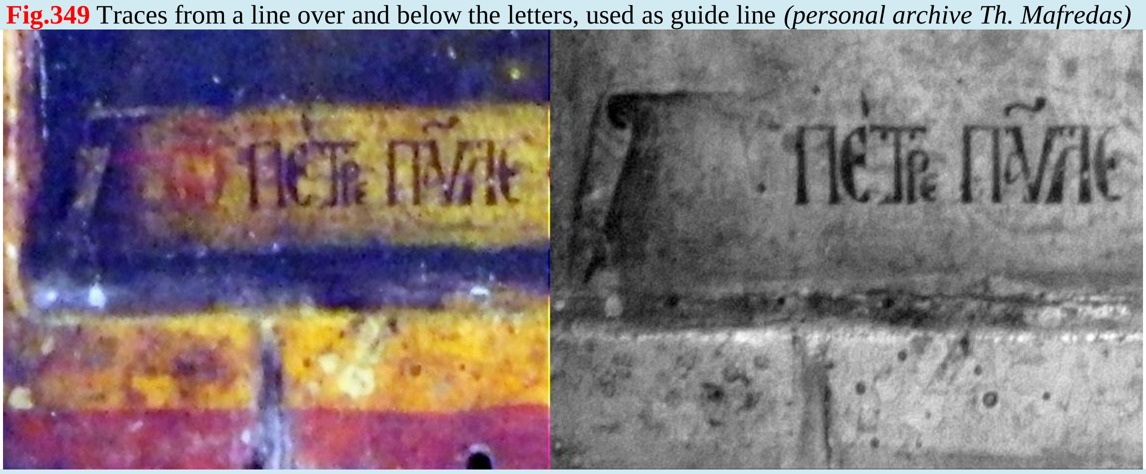


Fig.350 The left side of the epigram. Detail of letter Ω (left in Vis and right in IR) *(personal archive Th. Mafredas)*

The implementation of IR photography eliminated varnish deterioration, so it became possible to observe some details which were not easily detectable through Vis photography (**Fig.351**). A characteristic example was the decoration of the façade (**Fig.352**), while, at the same time, it was possible to understand Dionysius's magnificent painting skills, as revealed in the drawing of the curtain at the center of the façade (**Fig.353**). In the upper part of the three vaults, the IR photography helped to ascertain that the pigments were applied over the gold layer (**Fig.354**).

Fig.351 Panel #4 IR Photography. Details from the center of the painting theme
(personal archive Th. Mafredas)

Fig.352 The decoration of the façade
(personal archive Th. Mafredas)

Fig.353 The drawn of the curtain at the center of the façade (left in Vis and right in IR) *(personal archive Th. Mafredas)*

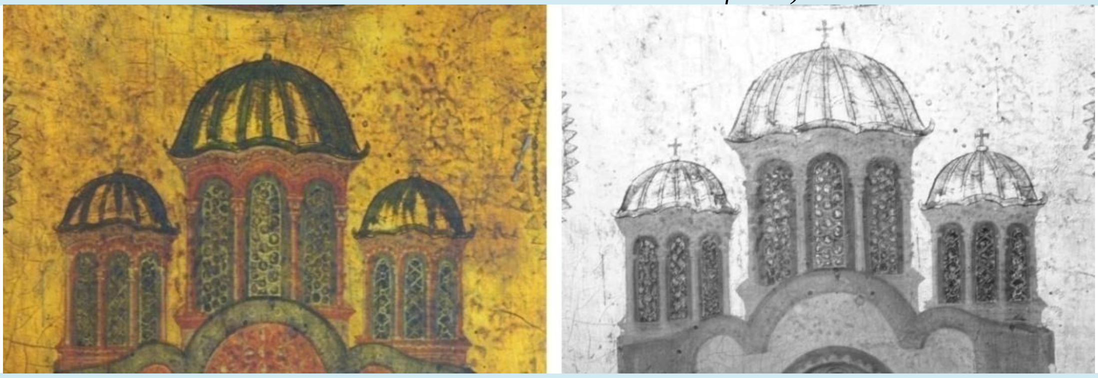


Fig.354 The three vaults of the Church. Pigments have been applied over the gold layer
(left in Vis and Right in IR) *(personal archive Th. Mafredas)*

Another characteristic feature achieved through IR photography was the identification of the decoration from St. Paul's book, which was not clear and easily detectable in Vis (**Fig.355**), while, at the same time, it became clear that Dionysius once more used gold as a pigment (in Greek: χρυσοκονδυλιά) to set some distinctive details (**Fig.356**).

Fig.355 The decoration from St. Paul's book (left in Vis and right in IR) *(personal archive Th. Mafredas)*

Fig.356 Details from book's decoration. Use of gold as pigment (in Greek: χρυσοκονδυλιά) *(personal archive Th. Mafredas)*

Finally, it could be argued that, through IR photography, it was easier to find, discern, observe and study details of the drawing which were not easily distinguishable in visible, such as details from the faces of the two Apostles (**Fig.357-358**), as well as from the background (**Fig.359**).

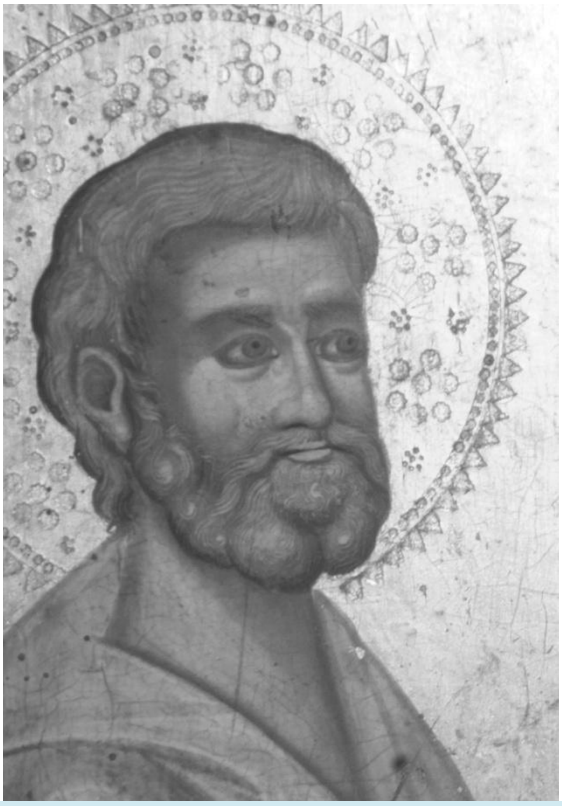


Fig.357 St. Peter's face *(personal archive Th. Mafredas)*

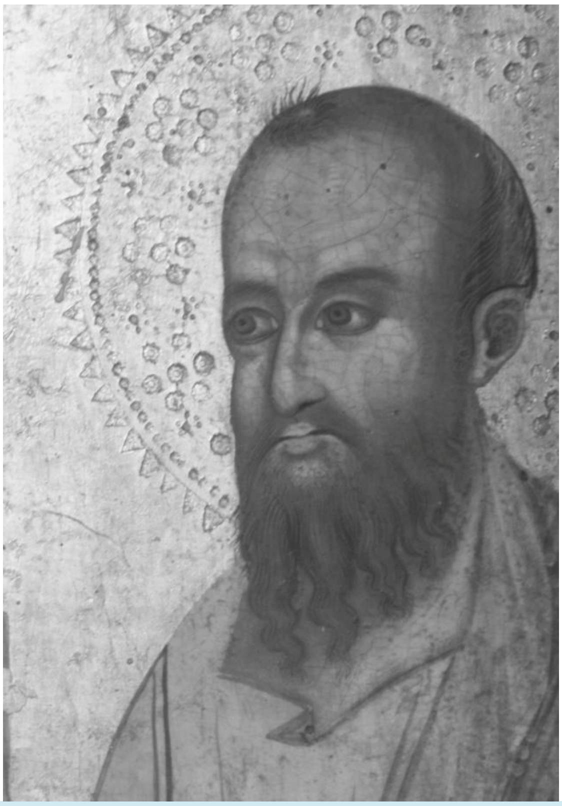


Fig.358 St. Paul's face *(personal archive Th. Mafredas)*

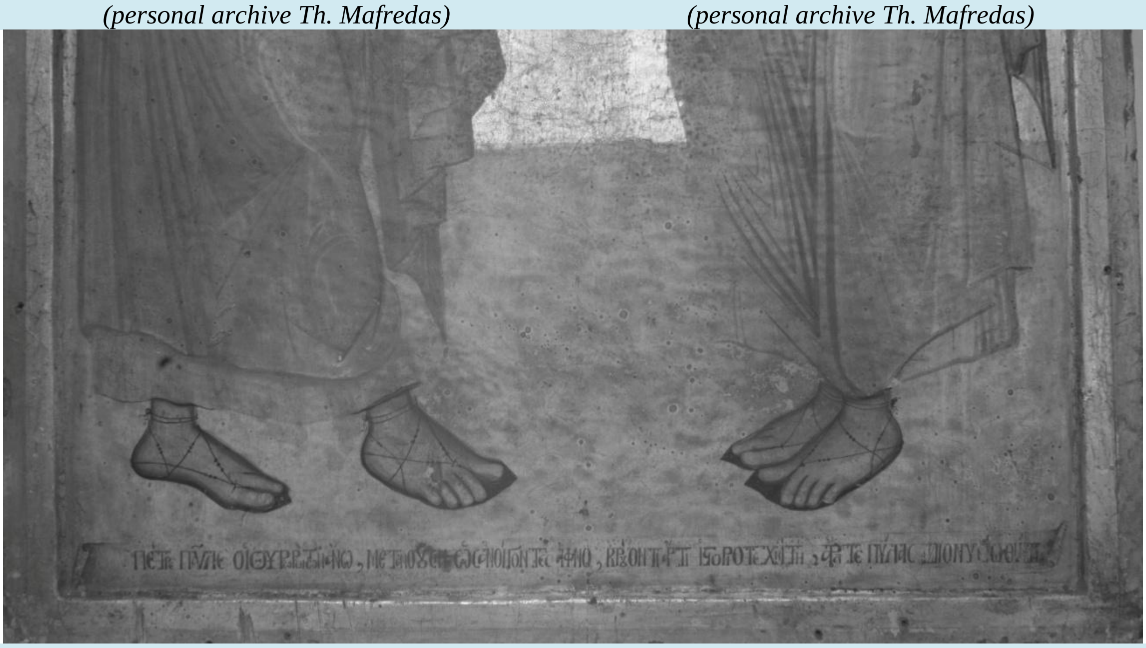


Fig.359 The below part from panel #4 *(personal archive Th. Mafredas)*

4.3. Microscopic Techniques

4.3.1. Digital Microscopy (DM)

The DM application contributed to identifying details about the painting and gilding technique used. It was applied in 14 different points of the painting surface (**Fig.360**) (continuing the numbering from the previous panels) in different magnifications, and the results helped to understand Dionysius's painting technology.

Fig.360 Panel #4 Digital Microscopy spots *(personal archive Th. Mafredas)*

Studying Dionysius' construction technique from hit points DM29 (**Fig.361-362**), DM30 (**Fig.363**) and St21 (**Fig.364**), it was found that there was a thin layer of gold even though the spots were taken from different areas, while some traces were identified, possibly resulting from the presence of the bole layer (*inside the red frame*).The same traces from a rather brownish layer below the gold leaf together with traces of some grains (**Fig.365**), have already been found and marked during DM in the previous three panels. Especially from DM30, the thickness of the gold layer could be clearly understood because, in some spots, the gold has been damaged, exposing the gesso preparation layer.

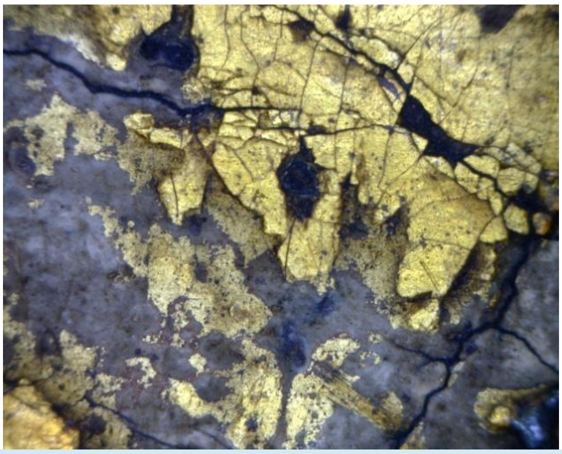


Fig.361 Thin gold layer DM29. Traces probably from bole layer (Magnification at 60X) *(personal archive Th. Mafredas)*

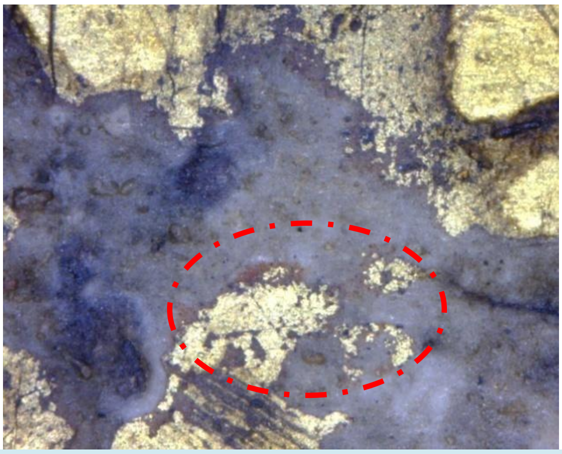


Fig.362 Thin gold layer DM29. Traces probably from bole layer (Magnification at 210X) *(personal archive Th. Mafredas)*

Fig.363 Thin gold layer DM30 (Magnification at 60X) *(personal archive Th. Mafredas)*

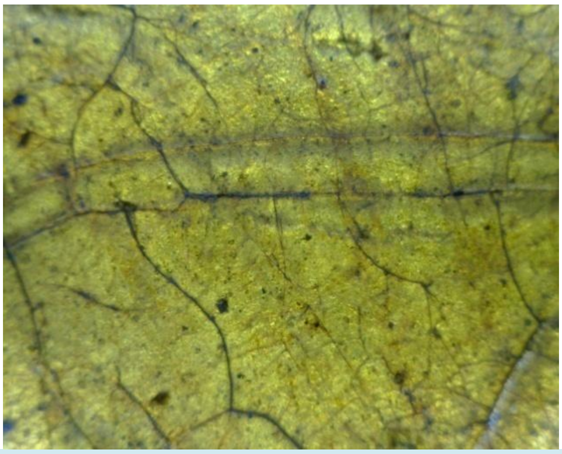


Fig.364 Thin gold layer St21 (Magnification at 60X) *(personal archive Th. Mafredas)*

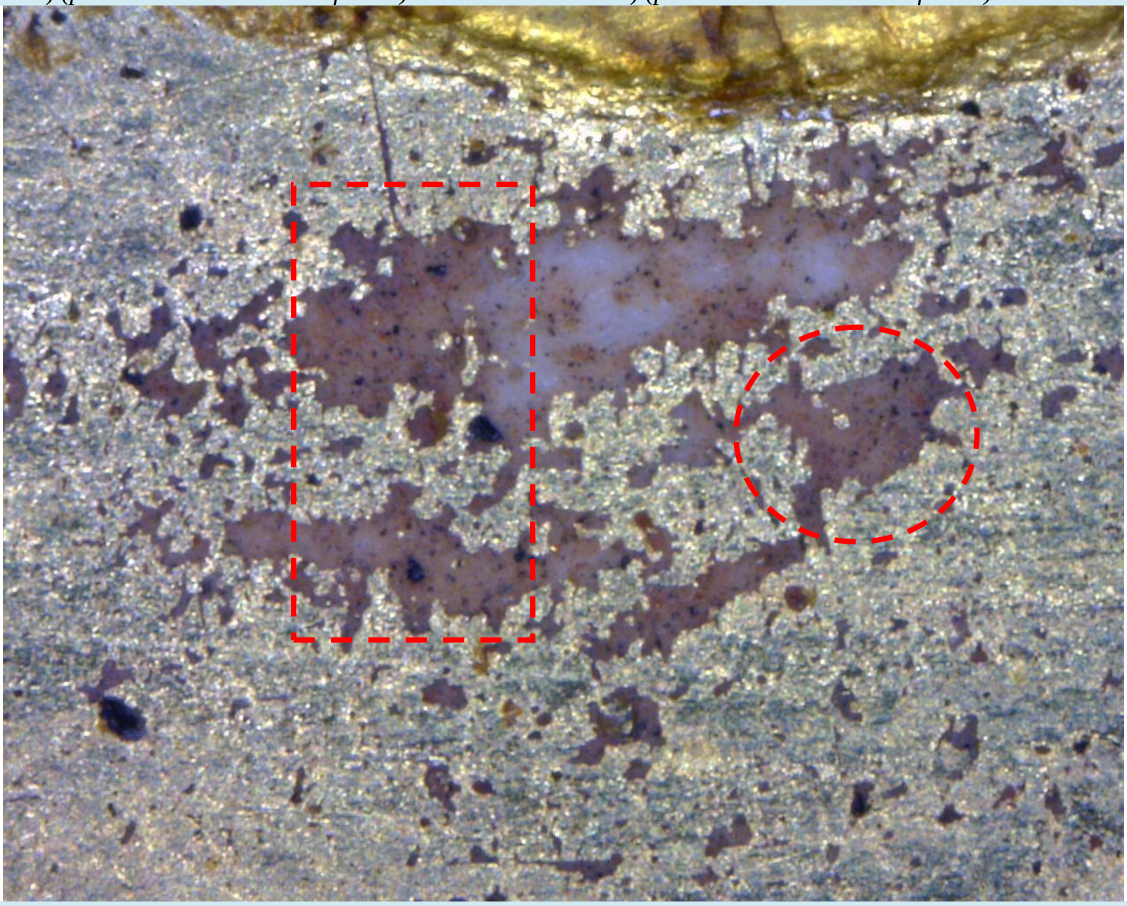


Fig.365 Thin gold layer (DM30) with a kind of brownish layer, below the gold leaf together with traces of some grains-probability of bole layer (Magnification 210X) *(personal archive Th. Mafredas)*

Concerning the painting technique through the examination with DM, studying the spots DM28 (**Fig.366-367**) St19 (**Fig.368-369**) and St20 (**Fig.370**), the use of gold pigment over a red pigment was detected in order to achieve the decoration of the curtain at the center of the façade. The use of gold as a pigment over an existing pigment layer is something in common with the previous three panel paintings which have been studied. Thus, in this case, it seems that Dionysius used gold as pigment in order to achieve the decoration of the curtain. The gold lines are not symmetric (**Fig.371**) and give the impression that they have been applied over the existing pigment (**Fig.372-373**). This is more apparent in St20, where the gold has been applied over the existing red pigment (**Fig.372**). The same feature of using gold as pigment has already been found during IR photography for the decoration in St. Paul's book.

Fig.366 Painting technique (DM28). Use of gold as pigment (in Greek: χρυσοκονδυλιά) (Magnification 60X) *(personal archive Th. Mafredas)*

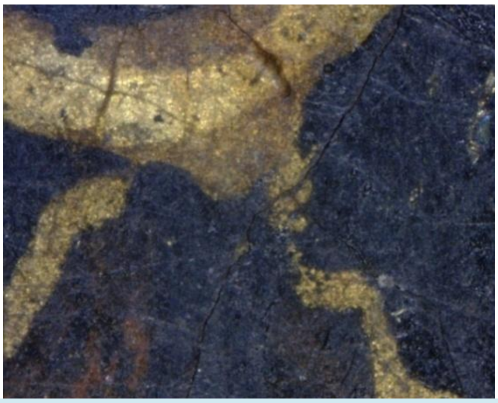


Fig.367 Painting technique (DM28). Use of gold as pigment (in Greek: χρυσοκονδυλιά) (Magnification 210X) *(personal archive Th. Mafredas)*

Fig.368 Painting technique (St19). Use of gold as pigment (in Greek: χρυσοκονδυλιά) (Magnification 60X) *(personal archive Th. Mafredas)*

Fig.369 Painting technique (St19). Use of gold as pigment (in Greek: χρυσοκονδυλιά) (Magnification 60X) *(personal archive Th. Mafredas)*

Fig.370 Painting technique (St20). Use of gold as pigment (in Greek: χρυσοκονδυλιά) (Magnification 60X) *(personal archive Th. Mafredas)*

Fig.371 Painting technique (St20). Use of gold as pigment (in Greek: χρυσοκονδυλιά) (Magnification 60X) *(personal archive Th. Mafredas)*

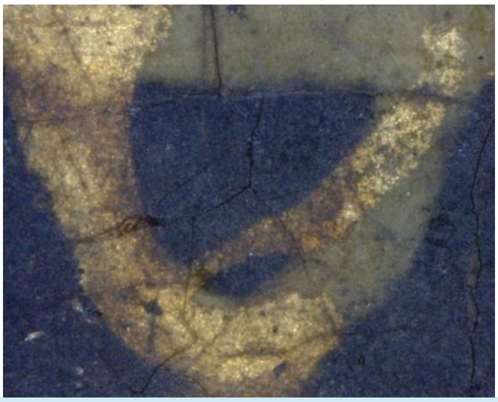


Fig.372 Painting technique (St19). Use of gold as pigment (in Greek: χρυσοκονδυλιά) (Magnification 210X) *(personal archive Th. Mafredas)*

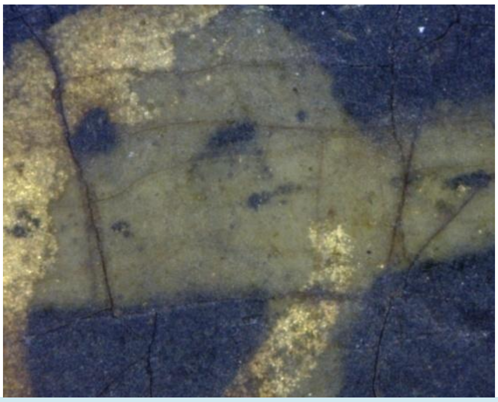


Fig.373 Painting technique (St19). Use of gold as pigment (in Greek: χρυσοκονδυλιά) (Magnification 210X) *(personal archive Th. Mafredas)*

Fig.374 Painting technique (St20). Use of gold as pigment (in Greek: χρυσοκονδυλιά) (Magnification 210X) *(personal archive Th. Mafredas)*

Concerning the painting technique, through the examination with DM, studying spot St22 at St. Paul's mouth, it was possible to evaluate the magnificent skills of Dionysius, as the shape and volume of the mouth are described by different color variations. Some traces of drawing line were also identified, especially in the upper part of the mouth, over the red and white pigment of the lips (**Fig.375**). It is obvious that there is no penetration of one pigment into the other, but clear boundaries. The same delimitation of pigments was also found during DM in the previous three panels.

Fig.375 Magnificent painting of the mouth. Delimitation of pigments (Magnification 60X) *(personal archive Th. Mafredas)*

At the same time, studying different areas of the painting surface, trying to identify delimitation of pigments, it was observed that, besides that, traces from the initial drawing were found in some areas, such as the St17 (**Fig.376**) and St18 (**Fig.377**), at the fingers Of Christ's left hand. St18 in particular gives the impression that Dionysius might have used some kind of pencil, especially in high magnification (**Fig.378**).

One of the most characteristic areas where traces from the initial drawing were found was in the dedicatory epigram and, more specifically, over and below the letters, in spots St24-St27 (**Fig.379-382**), where the presence of a guideline for applying the fonts was identified. The same guideline was traced through IR photography.

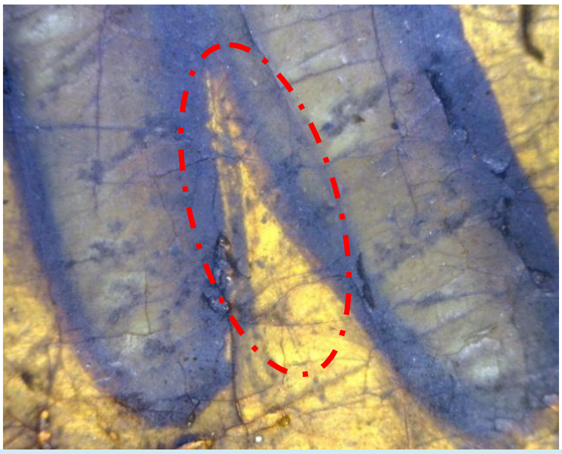


Fig.376 Traces from the initial drawing (St17). (Magnification 60X) *(personal archive Th. Mafredas)*

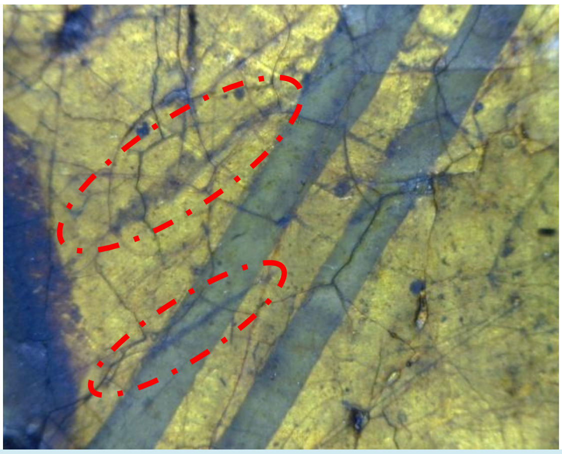


Fig.377 Traces from the initial drawing (St18). (Magnification 60X) *(personal archive Th. Mafredas)*

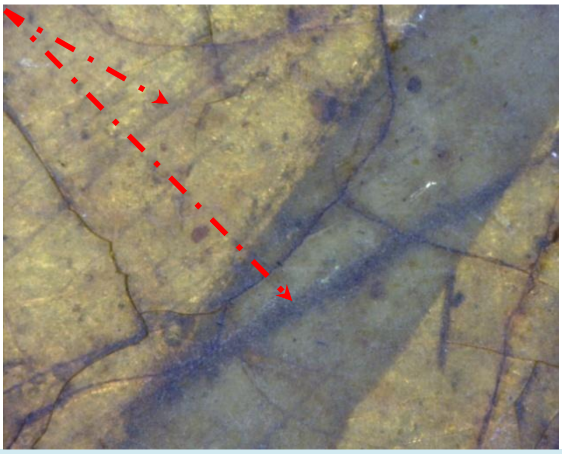


Fig.378 Traces from the initial drawing (St18). (Magnification 210X) *(personal archive Th. Mafredas)*

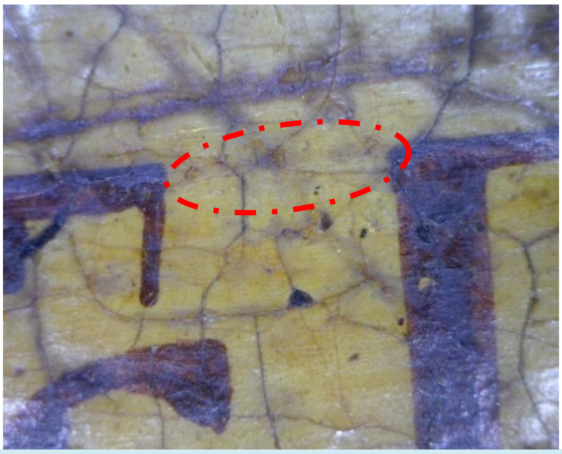


Fig.379 Traces from guide line over the epigram's fonts (St24) (Magnification 60X) *(personal archive Th. Mafredas)*

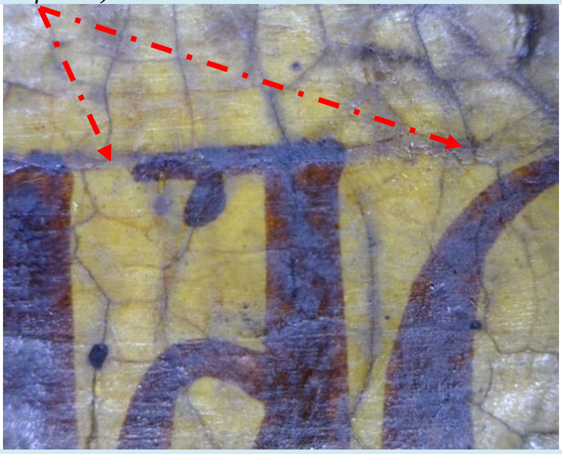


Fig.380 Traces from guide line over the epigram's fonts (St25) (Magnification 60X) *(personal archive Th. Mafredas)*

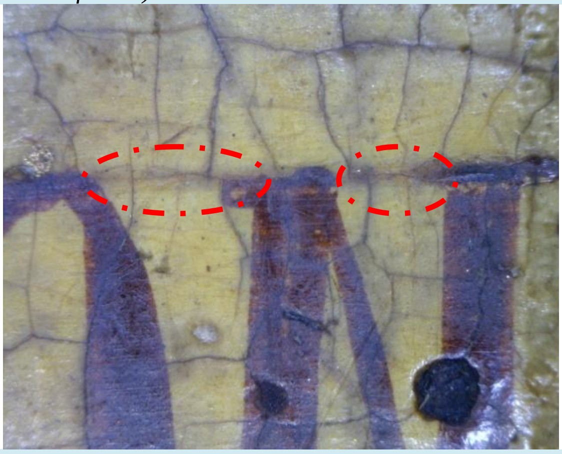


Fig.381 Traces from guide line over the epigram's fonts (St26) (Magnification 60X) *(personal archive Th. Mafredas)*

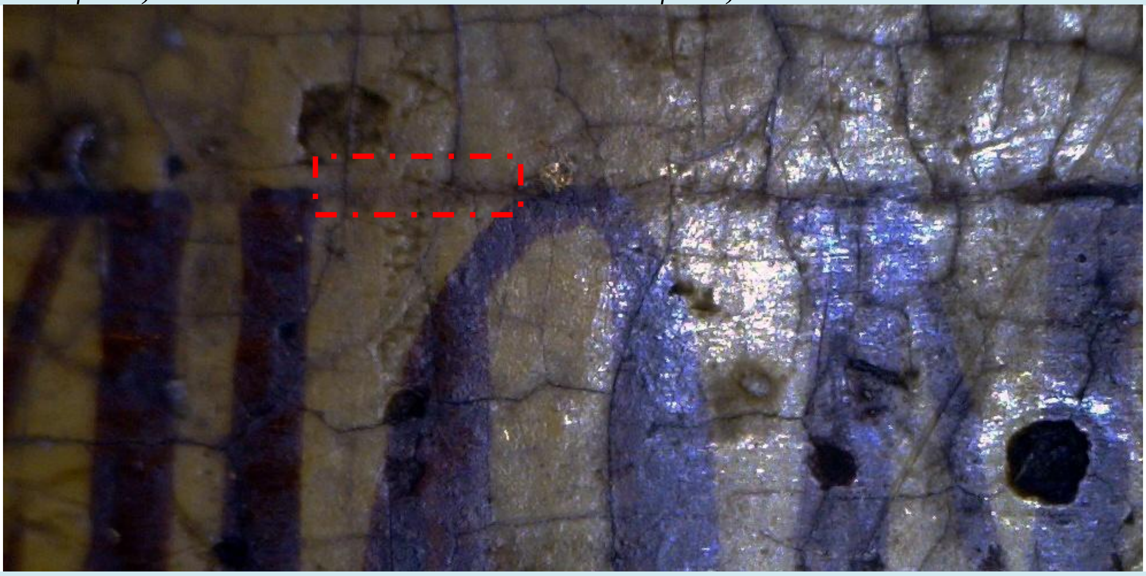


Fig.382 Traces from guide line over the epigram's fonts (St27) (Magnification 60X) *(personal archive Th. Mafredas)*

4.3.2. Optical and Fluorescence Microscopy

For applying OM, four (4) different samples in cross section were detached from the panel (***Appendix 2***); all of them (samples #19, #19a, #19b, #20) for studying the painting layer. During the sampling process, it was found that all the layers were very thin, something that was also confirmed during DM; thus, out of all the samples, only two (2) of them were examined with OM: sample #19a and #19b. All samples were examined both in Vis and in UV.

The first sample (#19a) which was examined by OM was taken from the lower part of the painting surface, in an already damaged area on St. Peter's the right foot (**Fig.383-384**).

Fig.383 Sampling area panel #4 for sample #19a *(personal archive Th. Mafredas)*

Fig.384 Sampling position for cross section sample #19a *(personal archive Th. Mafredas)*

The microscopic examination of the sample #19a revealed the stratigraphy of the sample (**Fig.385**), which consisted of four (4) layers. The first layer, at 400μm, was the gesso layer. The second layer was the first pigment layer, at 40μm. Approximately in the middle of the layer, a thin yellow, non-continuous line was observed. Furthermore, apart from the basic pigment which attributed the color, some grains from black and red pigment could be observed (**Fig.386-387**). The third identified layer was the second pigment layer of the sample, at 30μm. The hue of this layer was a bright pink-orange color, and some small grains from red pigment and vertical cracks could be observed (**Fig.388**). The fourth and final layer was probably organic, from the varnish coating which had entered the cracks (**Fig.389**), while, in one of them, it seems to have reached the gesso layer. Studying the sample under UV radiation (**Fig.390**) another layer of organic coating could be identified (**Fig.391**), while it seems that a big part of the organic layer was abruptly interrupted, especially at the left part of the sample (**Fig.392**).

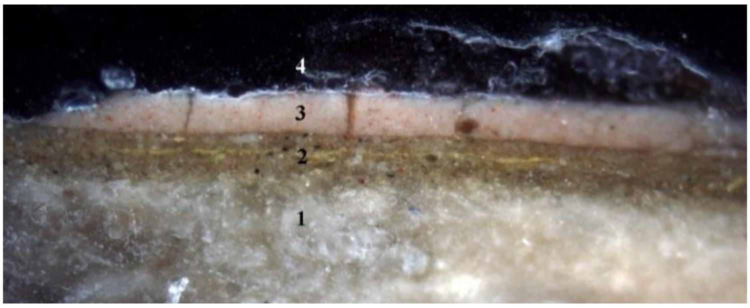


Fig.385 Stratigraphy of sample #19a *(personal archive Th. Mafredas)*

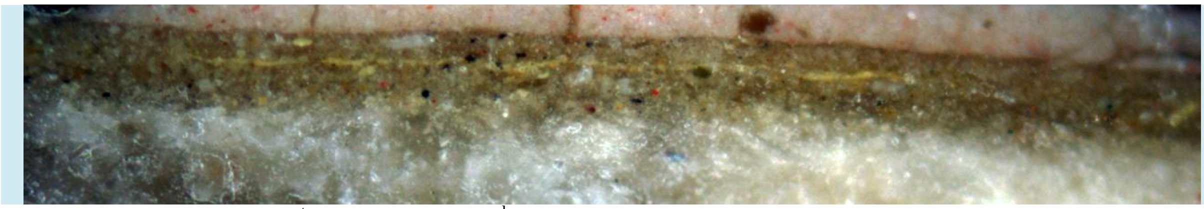


Fig.386 The 1st pigment layer (2nd stratigraphic layer) *(personal archive Th. Mafredas)*

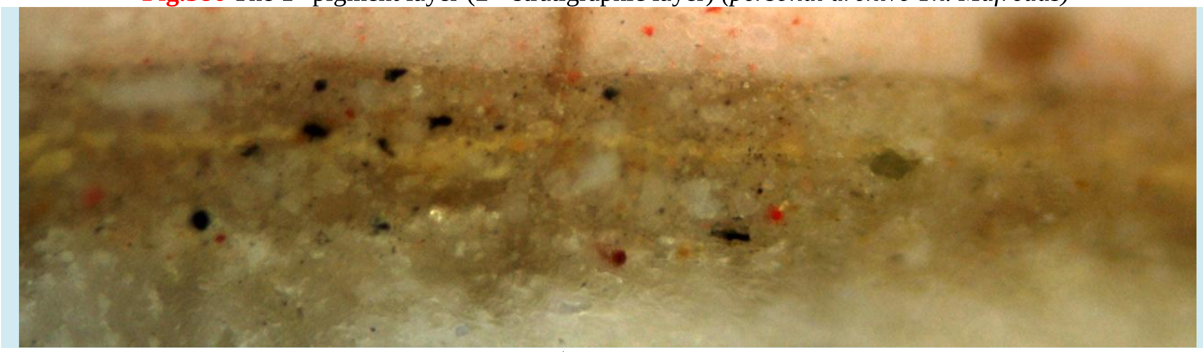


Fig.387 The 1st pigment layer. Detail.
It is distinguishable the thin, non-continuous yellow line in the middle of the pigment layer *(personal archive Th. Mafredas)*

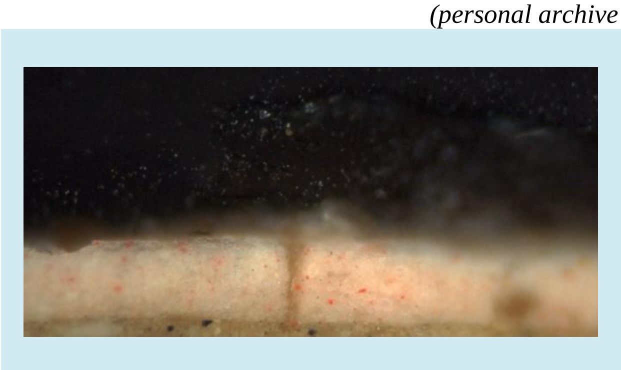


Fig.388 The second pigment layer (3rd stratigraphic layer) and the organic layer (4th stratigraphic layer) *(personal archive Th. Mafredas)*

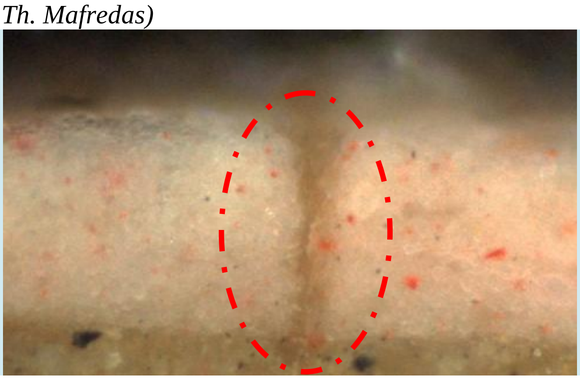


Fig.389 Detail from the 2nd pigment layer. It could be observed the vertical crack in which the organic layer has entered *(personal archive Th. Mafredas)*

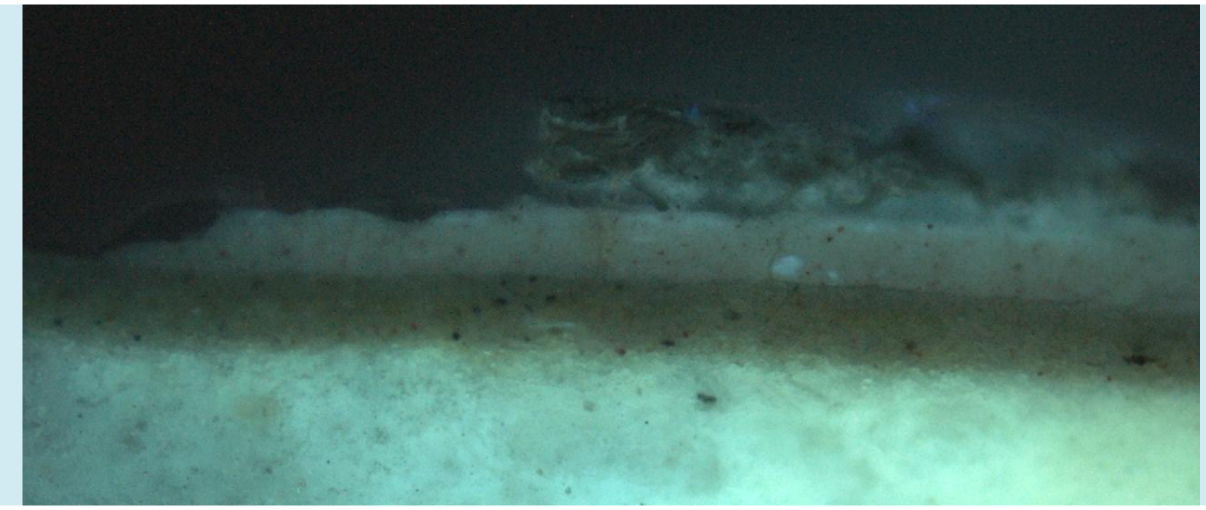


Fig.390 The sample #19a under UV radiation *(personal archive Th. Mafredas)*

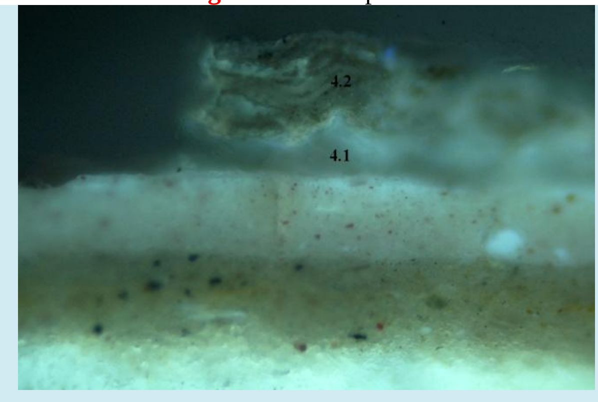


Fig.391 Detail. The sample #19a under UV radiation. It could be observed the distinguish of the organic layer in two different layers *(personal archive Th. Mafredas)*

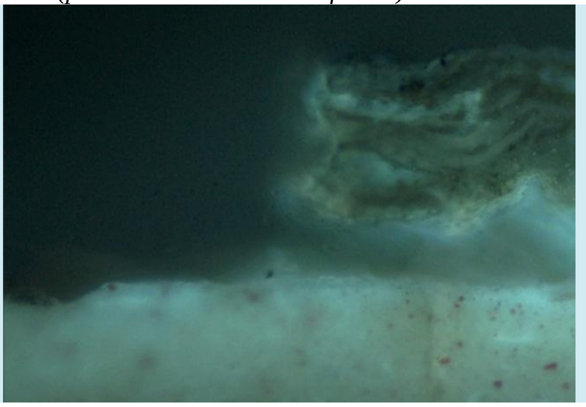


Fig.392 Detail. Abrupt cessation of a part of the organic layer *(personal archive Th. Mafredas)*

During OM observation, except for the vertical cracks and the thin yellow, non-continuous line, it was observed that the two pigment layers were thicker than the pigment layers from previous samples, and that they seemed to have a good adhesion to each other. The good quality of adhesion could be explained by the fact that the painting of each layer was applied after the underlying layer had dried quite well.

The second sample (#19b) was taken from St. Peter's garment (**Fig.393-394**) in order to study the painting layer.

Fig.393 Sampling area panel #4 for sample #19b *(personal archive Th. Mafredas)*

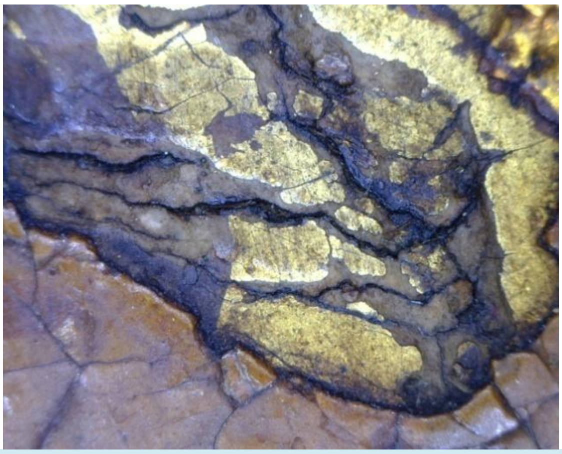


Fig.394 Sampling position for cross section sample #19b *(personal archive Th. Mafredas)*

The sample failed for unknown reasons. Although the painting layer had been previously recorded (**Fig.395**), the color layer does not appear in the stratigraphic section while observing the surface of the sample by the microscope. The only layer that could be observed was that of gesso preparation (**Fig.396**). The result was the same when observing the sample under UV radiation (**Fig.397**).

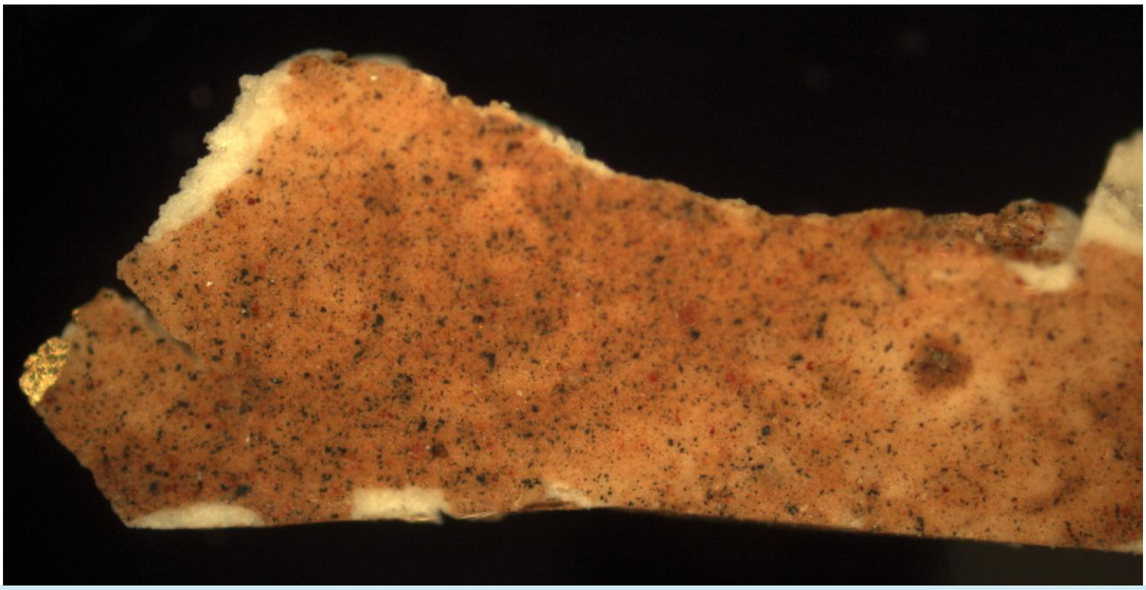


Fig.395 The painting surface of sample #19b *(personal archive Th. Mafredas)*

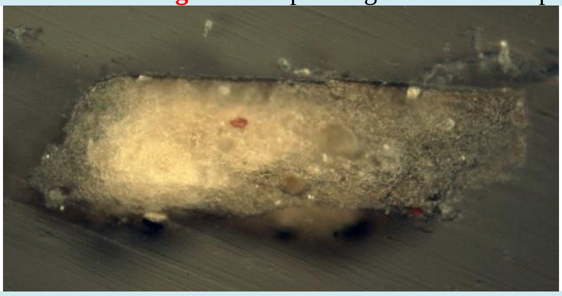


Fig.396 The sample #19b *(personal archive Th. Mafredas)*

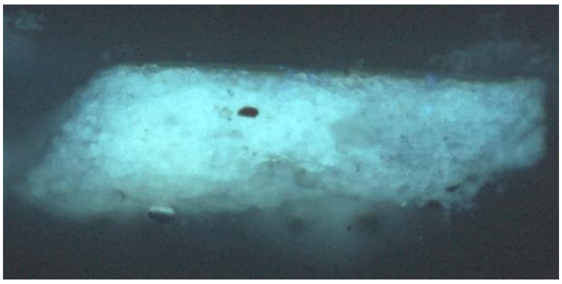


Fig.397 The sample #19b under UV radiation *(personal archive Th. Mafredas)*

4.3.3. Microchemical Tests

A staining test for the identification of proteinaceous materials was applied in sample #19A,using NA2 as a reagent in order to identify the presence of proteinaceous materials to the binding medium (**Fig.398-399**).

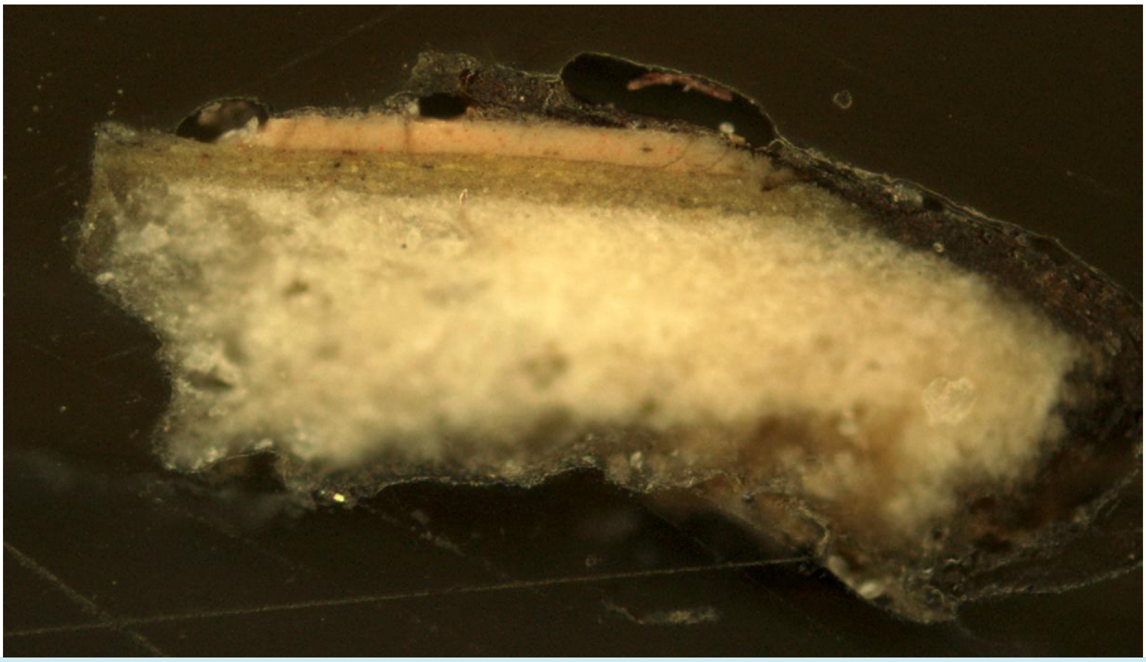


Fig.398 Staining test for sample #19A before NA2 *(personal archive Th. Mafredas)*

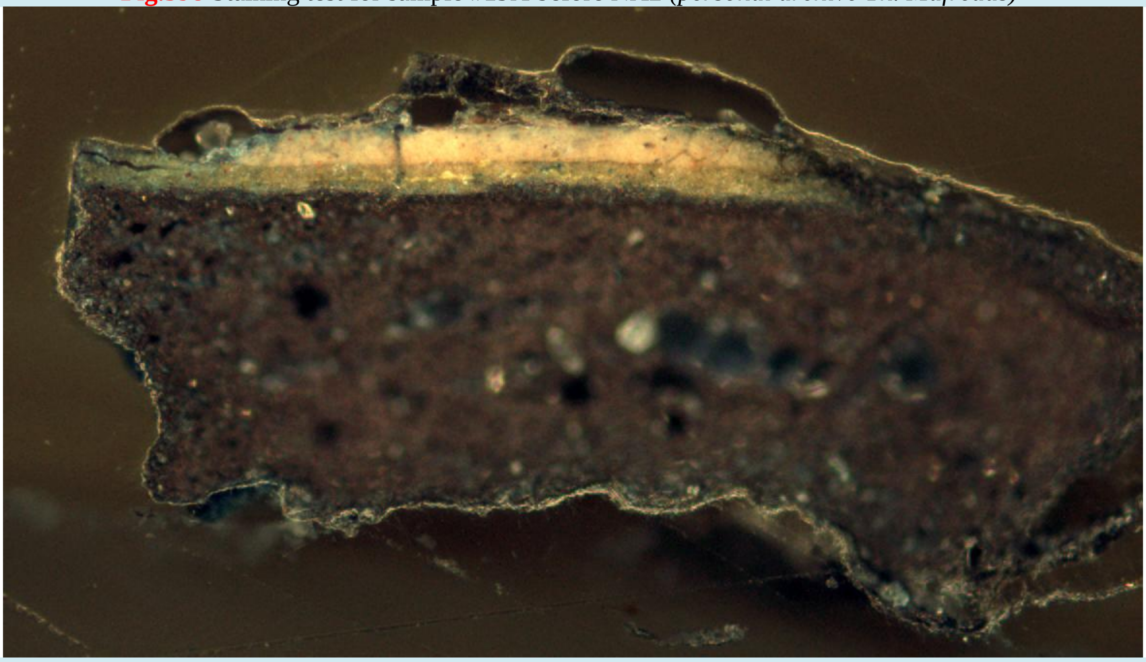


Fig.399 Staining test for sample #19A after NA2 *(personal archive Th. Mafredas)*

From the staining test, a very small staining can be observed, which might indicate the presence of proteinaceous materials in low concentration, especially in the paint layers (**Fig.398-399**). At the same time, it can be observed that the staining in the gesso layer is more intense than in the other layers due to the fact that the preparation is a porous material and, therefore, absorbs larger quantities of reagent. Furthermore, it is an indicator of the presence of proteinaceous materials in the gesso layer's binding medium.

Studying the paint layer before and after the application of NA2 it is obvious that the staining is much less significant than in the previous layer (**Fig.400-401**)

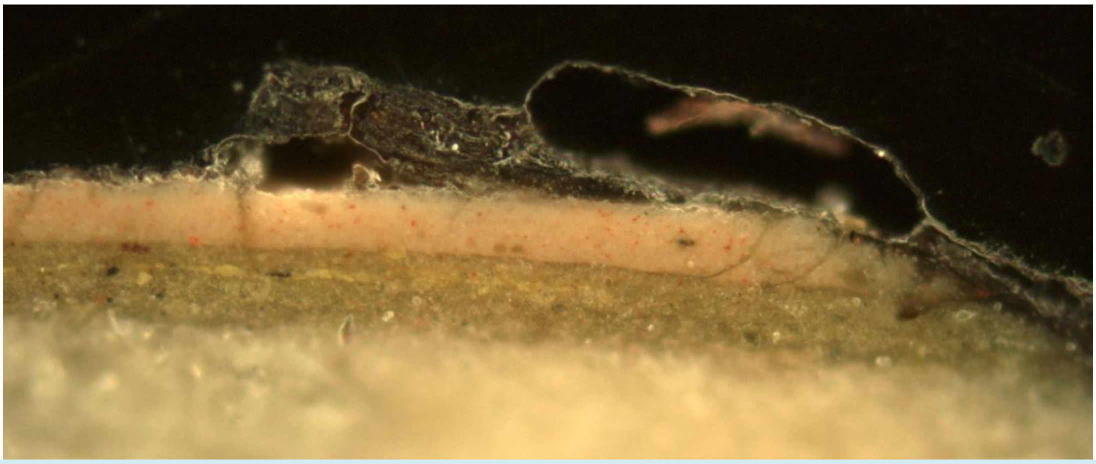


Fig.400 Detail from the paint layer of sample #19A. Before staining test with NA2 *(personal archive Th. Mafredas)*

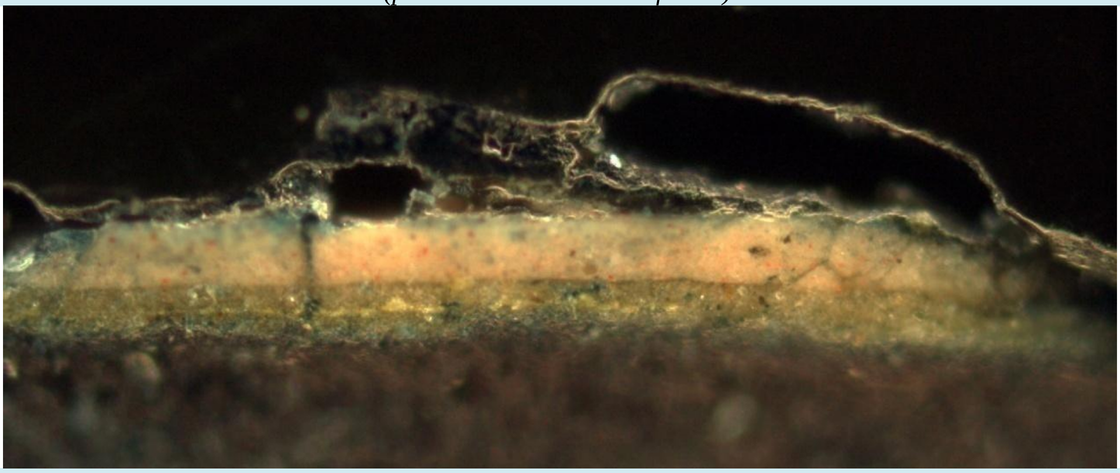


Fig.401 Detail from the paint layer of sample #19A. After staining test with NA2 *(personal archive Th. Mafredas)*

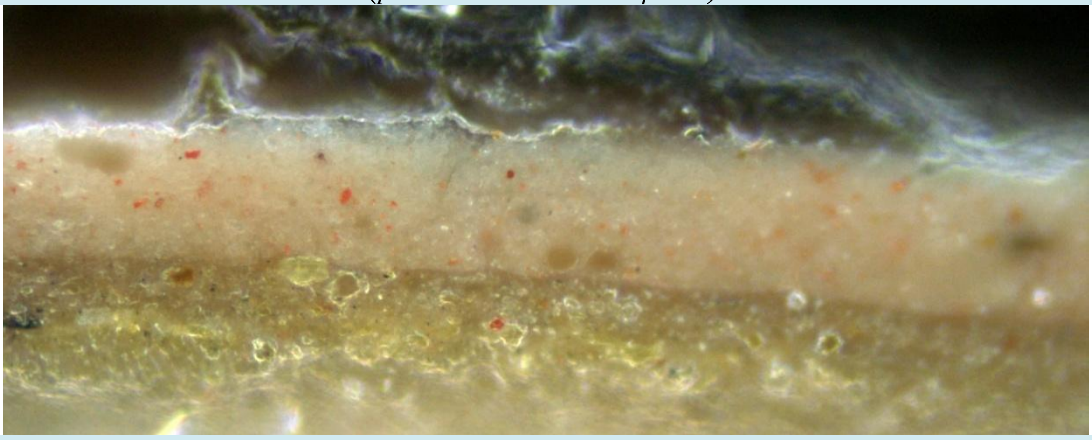


Fig.402 Detail from the paint layer of sample #19A. Before staining test with NA2 *(personal archive Th. Mafredas)*

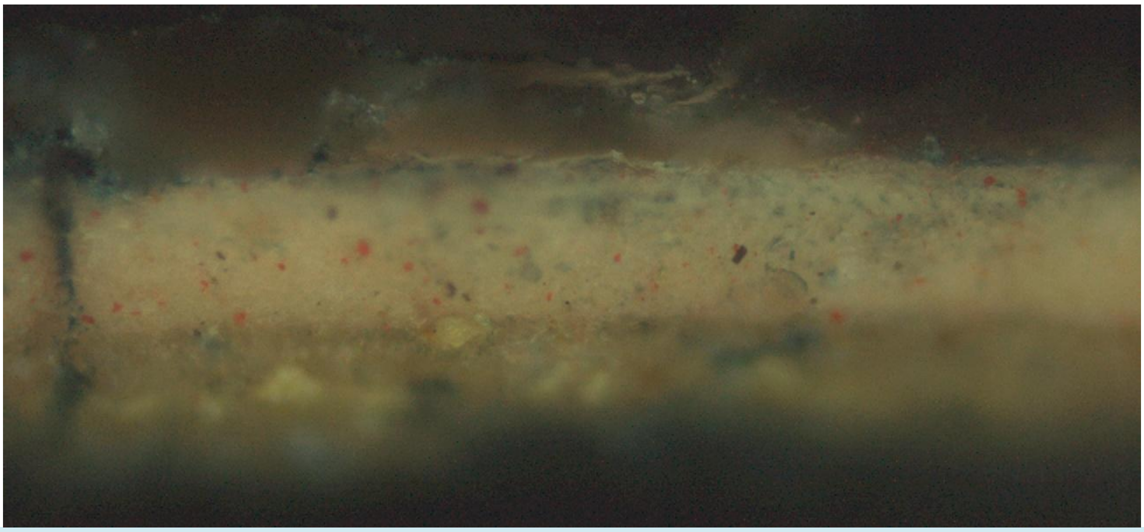


Fig.403 Detail from the paint layer of sample #19A. After staining test with NA2 *(personal archive Th. Mafredas)*

The preparation layer has been colored but compared, to the previous samples the coloration is less intense, especially in the paint layers (**Fig.402-403**).

Form the staining test, it could be assumed that the binding medium consisted of a small concentration of proteinaceous materials in combination with the use of another organic medium as binder.

4.3.4. Scanning Electron Microscopy

Upon examining sample #19a with SEM (**Fig.404**) through the BSE images, it was possible to discern the layers comprising the sample, measure the thickness of each layer, and observe details of the layers which were not easily distinguishable during OM.

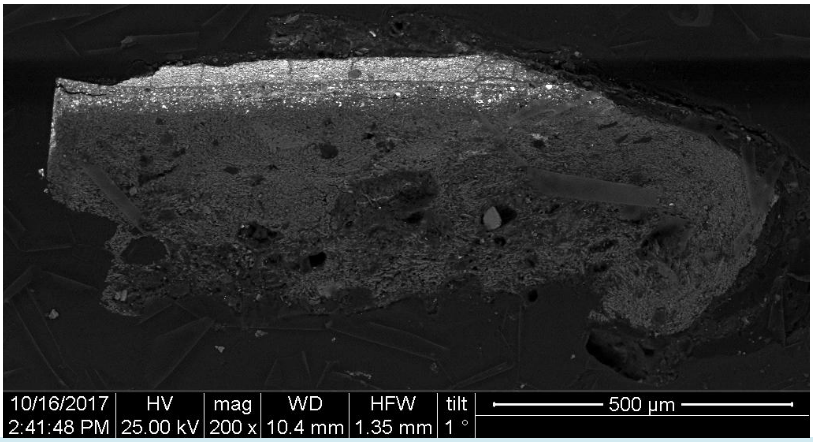


Fig.404 Sample #19a *(personal archive Th. Mafredas)*

During SEM observation, the thickness of the layers was identified and measured (**Fig.405**), first, of the gesso layer which was 344,97μm; second, of the first pigment layer at 41,39μm and, third, the second pigment layer at 34,66μm. The thickness of the thin, non-continuous yellow line on the second layer was measured at 8,60μm. Over the gold layer, a fourth layer was observed which was organic in nature, probably from the varnish coating. This layer seemed to consist of two different layers; the first at 80.47μm and 18.88μm, and the second with a thickness of 47,17μm.

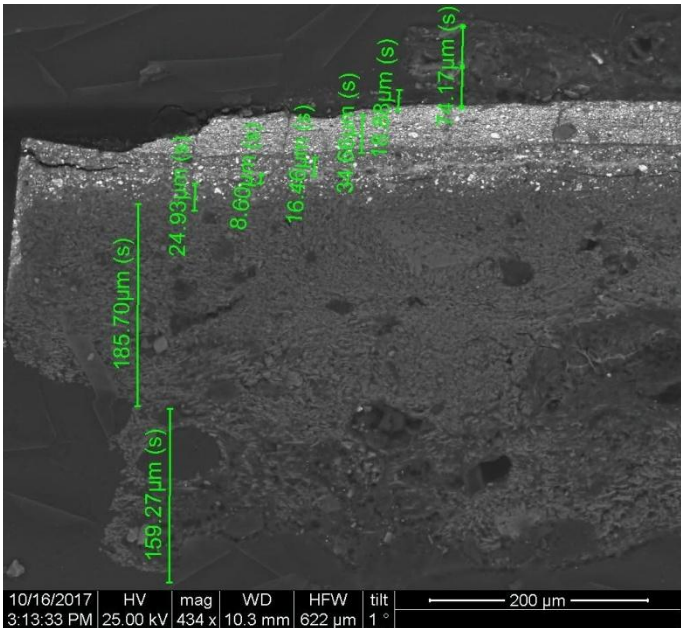


Fig.405 Thickness of sample's layers *(personal archive Th. Mafredas)*

Measurements of the layers' thickness are almost identical to the measurements by OM, except for some small discrepancies which are not usable. This differentiation could be explained through the ability of SEM to facilitate high quality magnification, thus providing accurate information.

Studying the sample under SEM, the same stratigraphy as in OM was observed. Starting from the gesso layer, two different layers could be identified: in the first, which was measured at 159.27μm, there are large, detectable grains, while the second one, at 185.70μm, seems to be more diligent than the previous one (**Fig.406**).

In the first pigment layer, it is easier to detect and observe the different pigment grains (**Fig.407**) and the thin, non-continuous yellow line in the middle of this layer (**Fig.408**). Furthermore, a crack to the right side of the sample of the pigment layer is detectable (**Fig.409**), which could be explained as an indication of detachment from the gesso layer.

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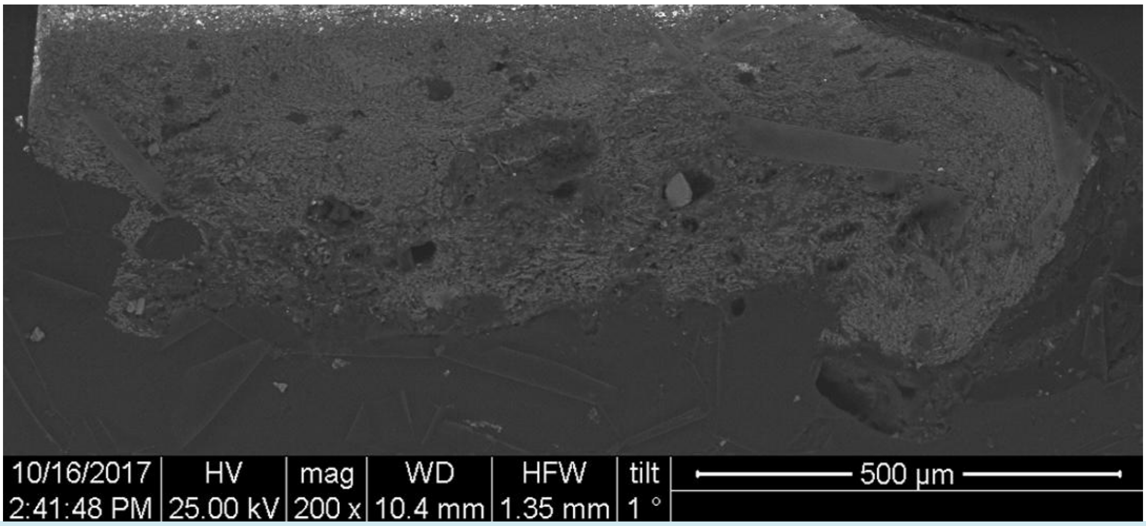

Fig.406 The gesso layer (sample #19a) *(personal archive Th. Mafredas)*

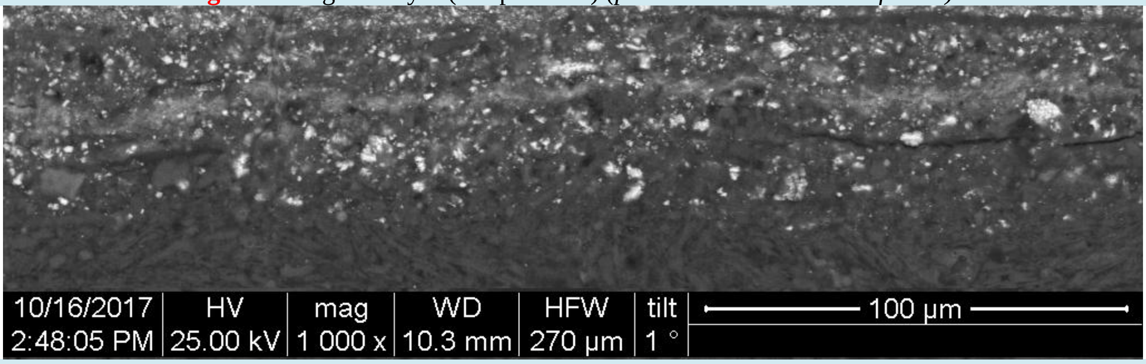

Fig.407 The first pigment layer *(personal archive Th. Mafredas)*

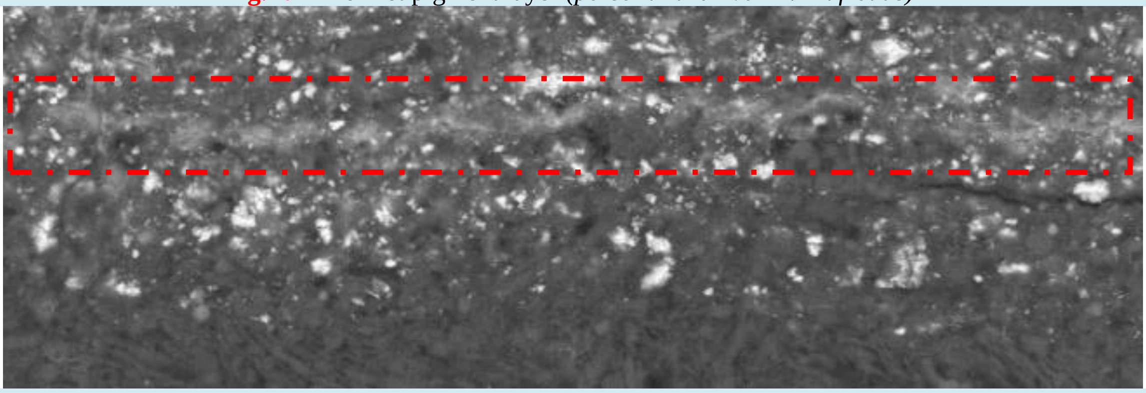

Fig.408 The thin yellow line in the first pigment layer *(personal archive Th. Mafredas)*

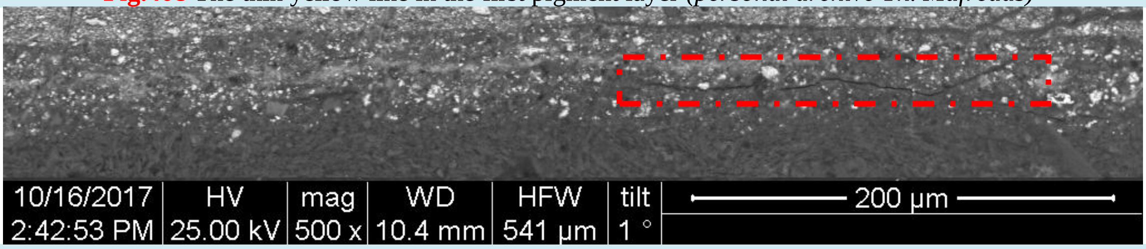

Fig.409 The crack of the first pigment layer *(personal archive Th. Mafredas)*

The second pigment layer is clearly distinguishable from the first layer and the presence of various grains from different pigments was observed (**Fig.410-411**).

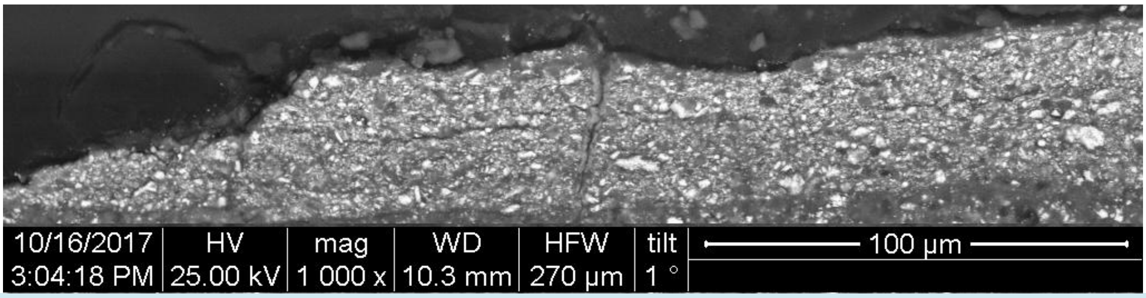

Fig.410 The second pigment layer *(personal archive Th. Mafredas)*

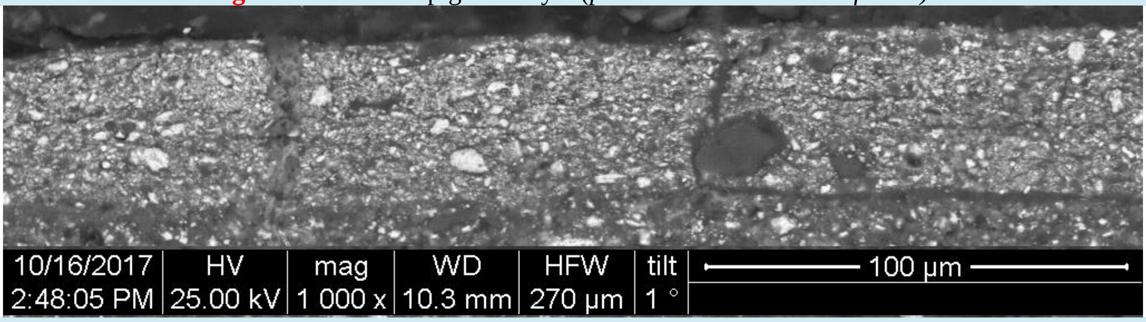

Fig.411 Detail the second pigment layer. *(personal archive Th. Mafredas)*

A remarkable feature of this pigment layer is the presence of cracks in different directions (**Fig.412**), both vertical and horizontal. Furthermore, it could be observed that these cracks are not as clear as the crack found at the first pigment layer. The fact that the cracks at the second layer are more opaque than the one in the first layer could probably be explained by the probability that these cracks have been filled from the upper organic layer.

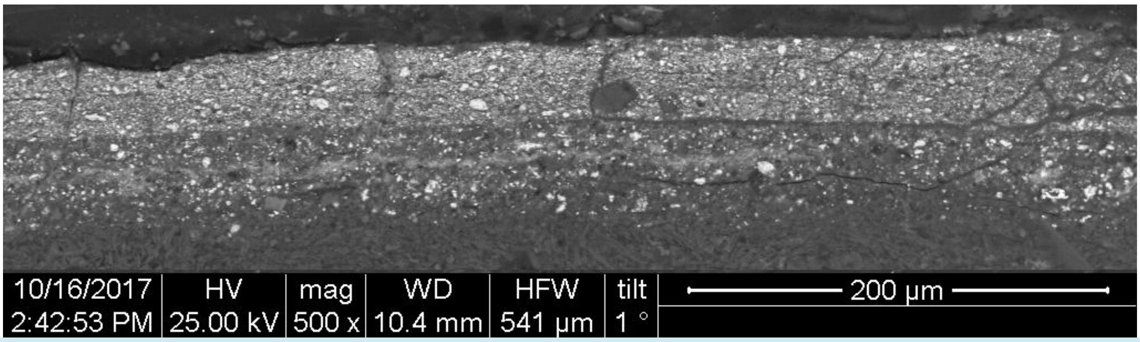

Fig.412 The cracks at the two pigments layers *(personal archive Th. Mafredas)*

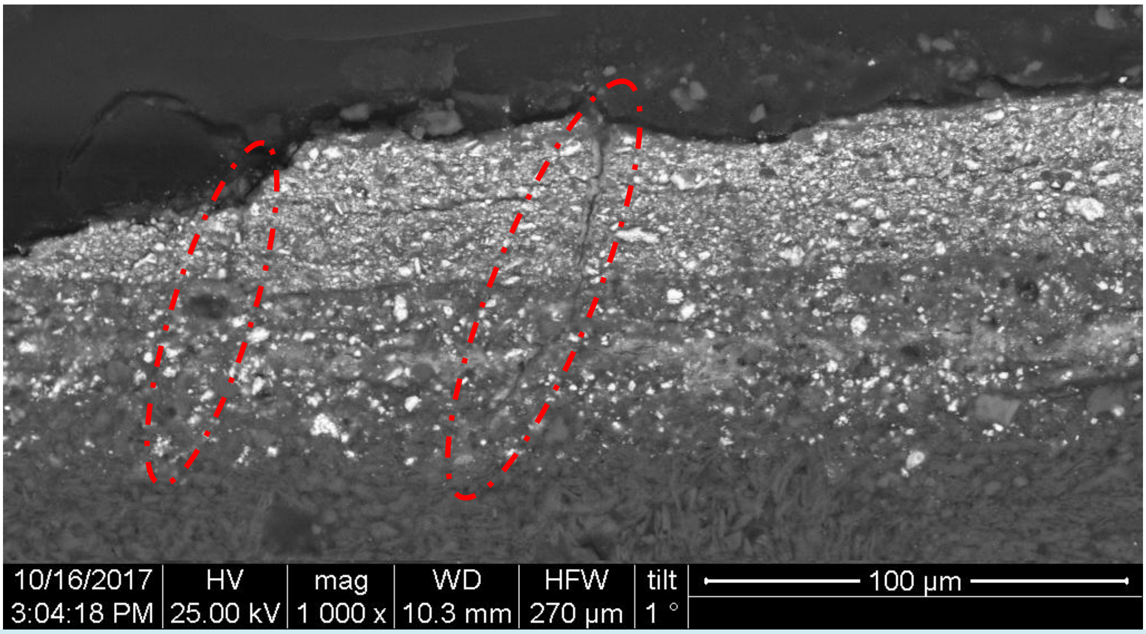

Fig.413 The cracks with direction from the organic layer to the gesso layer
(personal archive Th. Mafredas)

At this point, it should be noted that the vertical crack which was observed by OM set the hypothesis that it could probably reach down to the gesso layer. Studying the sample by SEM made it obvious that the crack started from the organic layer and reached all the way down to the gesso layer. Apart from that, another crack at the left of side of the sample follows the same direction from the organic layer to the gesso layer (**Fig.413-414**).

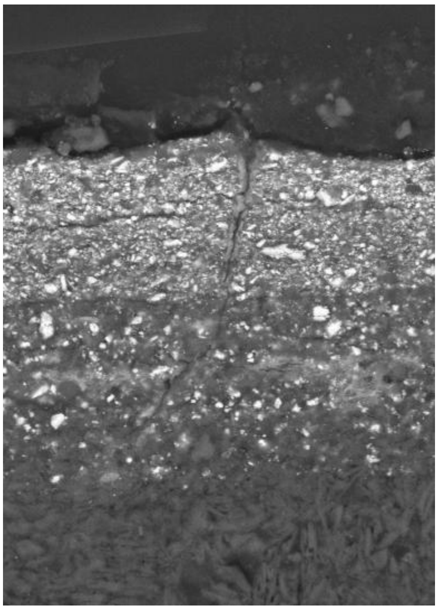

Fig.414 Detail of the crack starting from the upper layer and reaching to the gesso layer *(personal archive Th. Mafredas).*

4.4. Analytical Techniques

4.4.1. Elemental Techniques

4.4.1.1. X-Ray Fluorescence

XRF was applied in the painting surface of panel painting, in 13 different points (**Fig.415**), (continuing the numbering from the previous panels) in order to obtain data from a variety of areas concerning Dionysius's color pallet, and identify pigments in areas where the varnish layer had lost its transparency and become opaque, compromising the painting's purity. Furthermore, the use of XRF in gold areas provided data that helped to conclude about the use of a bole layer, the kind of it, and the type of metal used.

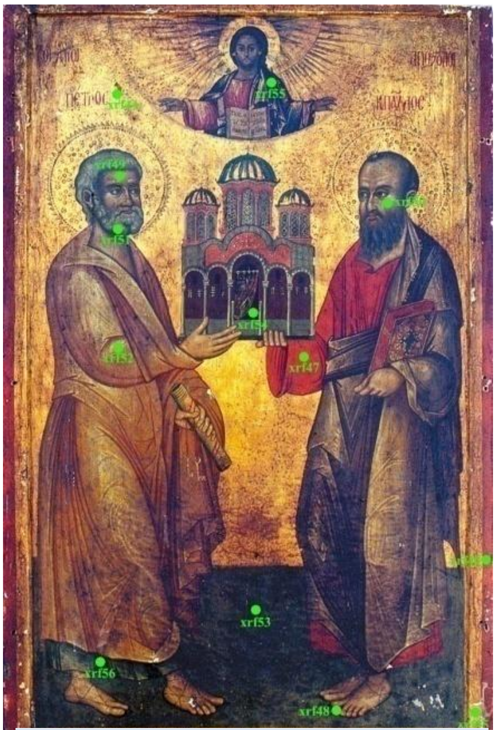

Fig.415 Apostles, Peter and Paul XRF spots *(Personal archive Th. Mafredas)*

From hit points 44-45, the XRF data provided an elemental analysis of the ingredients of the bole layer (**Table 13**). According to the spectra (***Appendix 4***), Fe, Ca, Pb, and Cu were identified in addition to the Au. In spot 44, the presence of Hg was also identified, probably from cinnabar. In spot 45, Hg was not detected. The presence of Au could be explained from the presence of the gold leaf, while the detection of Fe could probably come from the presence of red/yellow ochre, the Pb from red lead, and the Ca from the gesso layer. A quite remarkable feature is the differentiation about Hg detection which, in turn, differentiates the hypothesis that could be made about the bole recipe used by Dionysius (Dionysius 1909, p. 18).

The XRF analysis on the red pigment at the left vertical frame of the panel (#46) detected the presence of Pb, Hg, S, Cu and Fe (***Appendix 4***) (**Table 13**). The detection of Hg and S are indicative of cinnabar, while the detection of Pb could probably come from red lead. During EDX examination of samples from the red perimetric line of the other three panels, it was observed that Dionysius usually applies two layers of red pigment, the first consisting of cinnabar (HgS) and the second of red lead (Pb_3O_4). So, according to this information, it could be assumed that, in this case, the detection of Pb could probably indicate the presence of red lead.

Another quite remarkable feature came from spot #47, which was on the right sleeve of St' Paul's red garment (***Appendix 4***). From the obtained spectrum of this area, Au was the only element detected, even though it was obvious that this area was red. A logical explanation that can be provided is due to the limitations of the XRF in the detection of organic elements. So, according to the obtained spectrum, it could be assumed that he used some kind of organic material for the red pigment, such as a red lacquer. At this point, further examination through a more sophisticated research protocol could provide more specific answers about the kind of the materials Dionysius used for this pigment. This sample spot provides another feature concerning Dionysius's painting technique: the detection of Au could set the hypothesis that he had painted over a gold leaf.

Studying the background of the painting theme at hit points #48 and #53,the trace elements from the obtained spectra (***Appendix 4***) remain the same (**Table 13**); Pb and As with the same intensity bands, and Ca, Fe, and Cu with low intensity bands. According to the trace elements, it could be assumed that As, probably comes from orpiment (As_2S_3) which is yellow (Katsaros 2015, p. 536), Pb probably from red lead, Fe from a red/yellow ochre, and Cu from Azurite ($2CuCO_3{\bullet}Cu(OH)_2$. References were found, supporting that the mixture of yellow as orpiment with blue as azurite and red lead would provide a green color (West FitzHugh 1997, p. 53; Phipps, Turner & Trentelman 2008, p. 139; Duffy & Elgar 1995, p. 80). This hit point is almost the same as hit point #13 from panel #1 and hit points #40 and #43 from panel #2.

The XRF analysis performed on St. Peter's and St. Paul's faces (hit points #49 and #50) in order to trace elements that could help to identify the pigments detected the presence of Pb, Fe, and Cu (***Appendix 4***), possibly coming from a mixture of lead white (2PbCO3•Pb(OH)2)and a yellow/red ochre with a small quantity of green, pigments corresponding to Dionysius's recipe for proplasmos and flesh (Dionysius 1909, pp. 20-21). Furthermore, it is almost identical to the trace elements found at hit point #21 from panel #2, with the exception of the presence of Hg which, according to Dionysius's recipes, should be used only on the Theotokos' and young saints' faces (Dionysius 1909, p. 20). The same trace elements of Pb, Fe and Cu were detected in hit point #51, which was taken from St. Peter's beard. If Dionysius's recipe is followed, then the detection of these elements is explained, as he mentions the use of white lead in conjunction with a black pigment as the main ingredients for painting hair and beards (Dionysius 1909, p. 22). The detection of Fe and Cu could probably come from yellow/red ochre and from green (Dionysius 1909, p. 20 & 22), as the main pigments, along with white lead, for proplasmos and flesh.

Studying spot #52, from the right hand of St. Peter's garment (***Appendix 4***), the trace elements were, again, Pb and Fe (**Table 13**). It could be assumed that Pb indicates the presence of white lead and Fe could come from ochre, the two main pigments for St. Peter's garment.

The XRF spectrum obtained from spot #54 (***Appendix 4***), which was taken from theopen portico on the Church's façade, confirmed the presence of Ca, Pb, Hg, Fe and Cu (**Table 13**). The Ca, with a high intensity band, could probably be considered as a white pigment, while the presence of Hg and Pb could probably come from cinnabar and red lead, Fe from a yellow/red ochre and Cu from green.

The two last spots, #55 and #56, were taken from different areas: the first from Christ's garment, and the second from the bottom part of St. Peter's garment. Their XRF analysis provided the same trace elements, but with differentiation to the intensity bands, (***Appendix 4***) which differentiates the order of the elements (**Table 13**). Concerning the identification of pigments used, both areas are counted as green in the Vis, always taking into account the degree of discoloration due to varnish degradation. Under this point of view, it could be assumed that Cu comes from green, Pb from white lead, Fe from yellow/red ochre and Ca from the gesso layer due to its low intensity bands in both spectra.

At this point it should be noted that, to obtain more specific information about the exact pigments that Dionysius used, a more sophisticated research protocol needs to be implemented not only for this panel, but also for the previous three panels that were examined. XRF analysis was applied in 14 different spots on the painting surface and the respective spectra were obtained (***Appendix 4***).The interpretation of the data assisted to draw a first conclusion about Dionysius's color palette (**Table 13**).

Table 13. *Panel #4- Elemental Analysis – XRF*

Spot	# of Spectrum	Color	Trace elements
44	1868	Gold	Au, Hg, Ca, Fe, Pb, Cu
45	1869	Gold	Au, Ca, Fe, Pb, Cu, Ti

46	1870	Red	Pb, Hg, S, Cu, Fe
47	1871	Red	Au
48	1872	Dark color	Pb, As, Fe, Ca, Cu
49	1873	Flesh	Pb, Cu, Fe
50	1874	Flesh	Pb, Cu, Fe
51	1875	Beard	Pb, Cu, Fe
52	1876	Yellow-white	Pb, Fe
53	1877	Dark green	Pb, As, Fe, Ca, Cu, Zn
54	1878	Dark color	Ca, Pb, Hg, Fe, Cu
55	1879	Green	Cu, Pb, Fe, Ca
56	1880	Green	Pb, Cu, Fe, Ca

Trace element, such as Zn, is detected, which appear to be impurity of the raw materials without their presence interfering with the presence of raw materials as they are recorded by the intensity bands of the spectra.

4.4.1.2. Energy Dispersive X-ray Analysis

The Energy Dispersive X-ray (EDX) spectroscopy provided elemental information about the identity of inorganic materials present in the sample about pigments and gesso preparation materials.

Upon examining sample #19a (**Fig.416)** with EDX, it was found that the first thick layer was gesso preparation consisting of Ca (Calcium) and S (Sulfur) (**Fig.417**), so it could be characterized as $CaSO_4$.

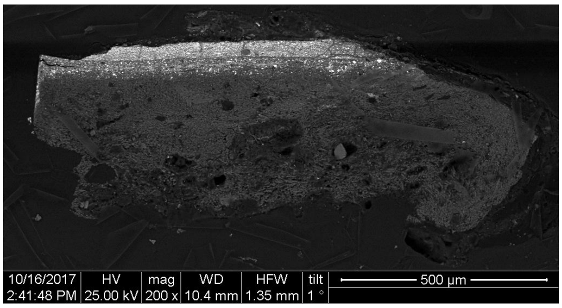

Fig.416 Sample #19a.SEM
(personal archive Th. Mafredas)

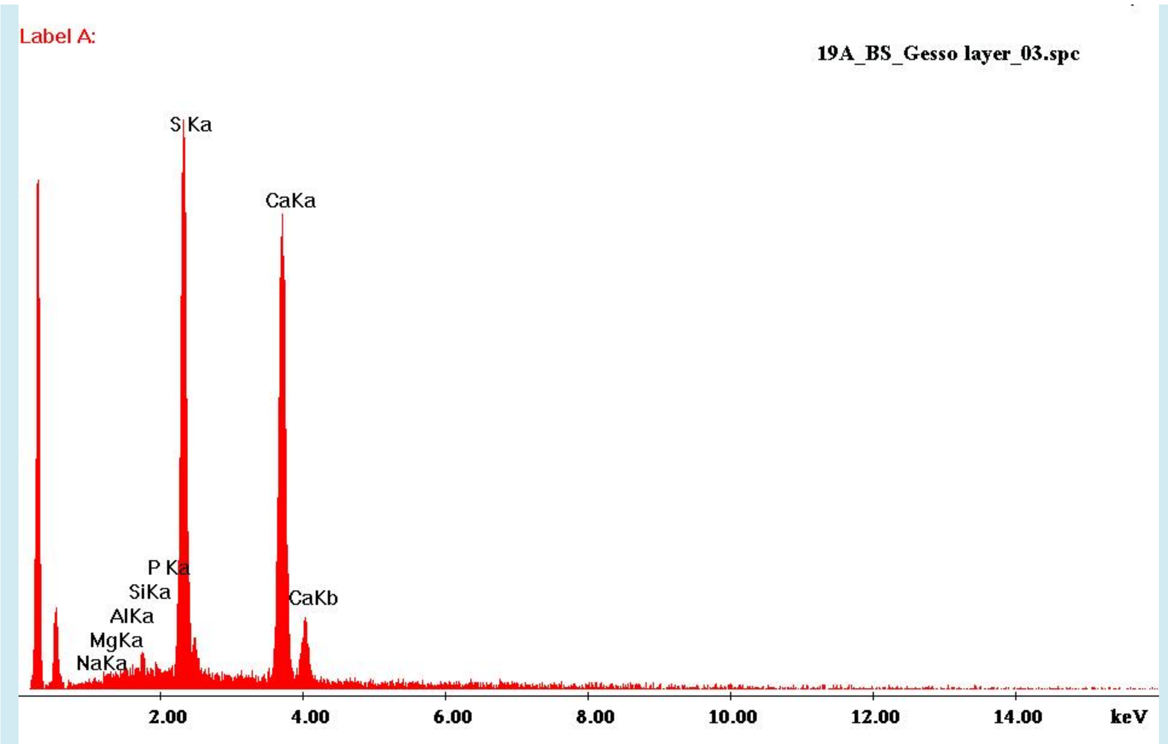

Fig.417 EDX Spectrum from gesso layer (sample #19a) *(personal archive Th. Mafredas)*

EDX analysis for the first pigment layer (**Fig.418**) detected the presence of Ca, Fe and Pb, Al, Si, Mg and K. According to bibliography (Chatzidaki et al. 1988, p. 235), the detection of Fe with the presence of Al, Si, Mg and K could probably stem from the presence of green earth pigment, also known as terra verde (Eastaugh et al. 2008, pp. 180-181; Grisom 1986, p. 147). Thus, the detection of these elements, among which Pb was also found, in addition to the known sampling area, could support the hypothesis that this layer was the first layer of proplasmos, according to Dionysius's recipe (Dionysius 1909, p. 20).

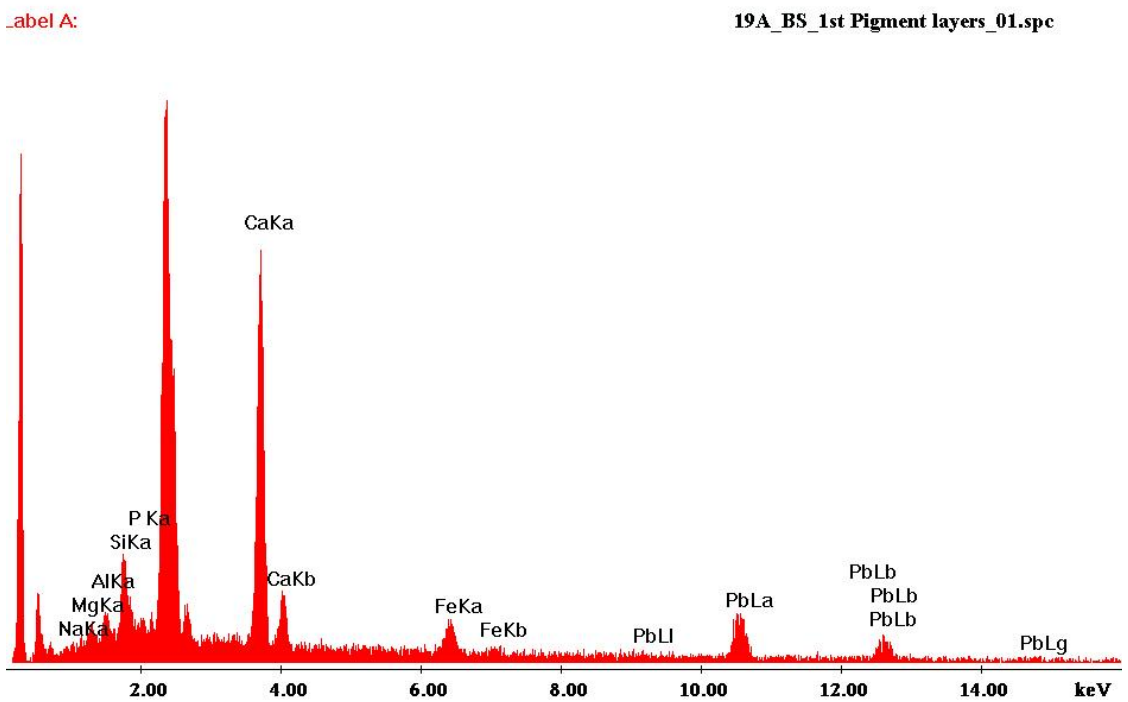

Fig.418 EDX Spectrum from 1st pigment layer (Sample #19a) *(personal archive Th. Mafredas)*

In the middle of the first pigment layer, the presence of a non-continuous, thin yellow line was observed during OM and SEM. Thus, through EDX analysis, this line was studied in order to trace basic elements. According to the obtained spectrum (**Fig.419**), the same elements that were found in the first layer were detected: Ca, Pb, Fe, Al, Si, Mg and K, which means that, elementally, it is the same as the first pigment layer. This could indicate some kind of chemical reaction from the elements contained in the pigment layer.

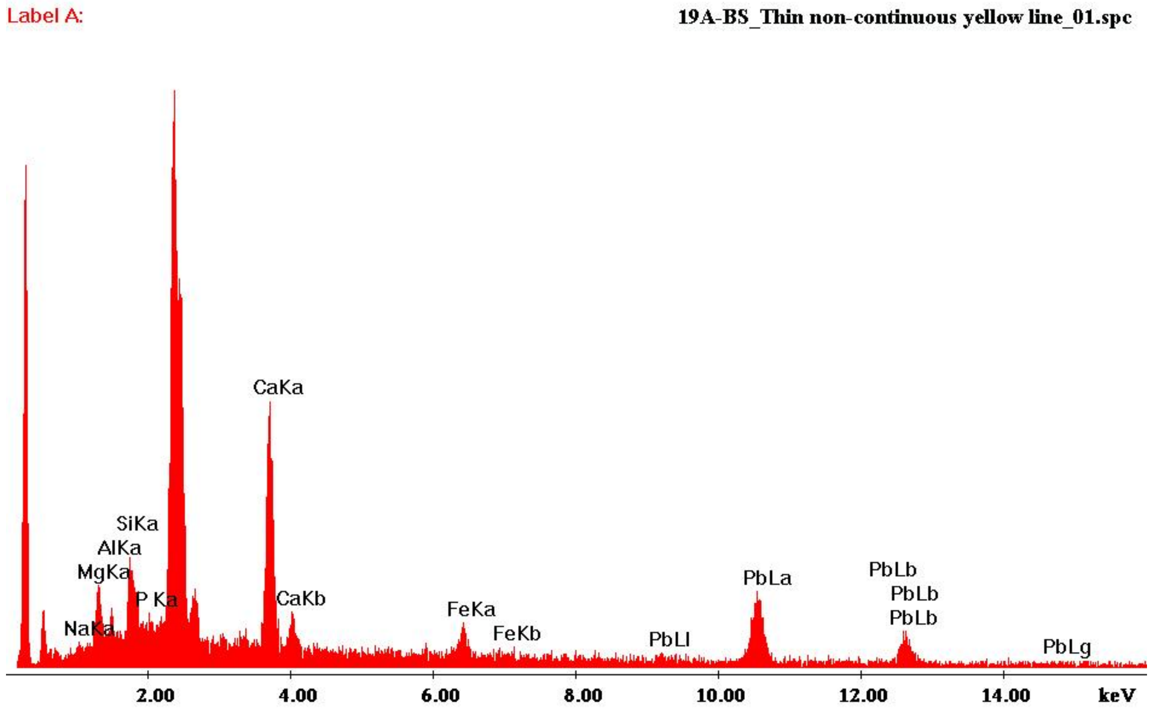

Fig.419 EDX Spectrum from thin, non-continuous yellow line (Sample #19a)
(personal archive Th. Mafredas)

EDX analysis over the yellow line (**Fig.420**) again provided the same elements to previous analyses with some differentiation to the intensity band of the Ca, which appears higher than the previous two. It seems to be the same layer with different ratios.

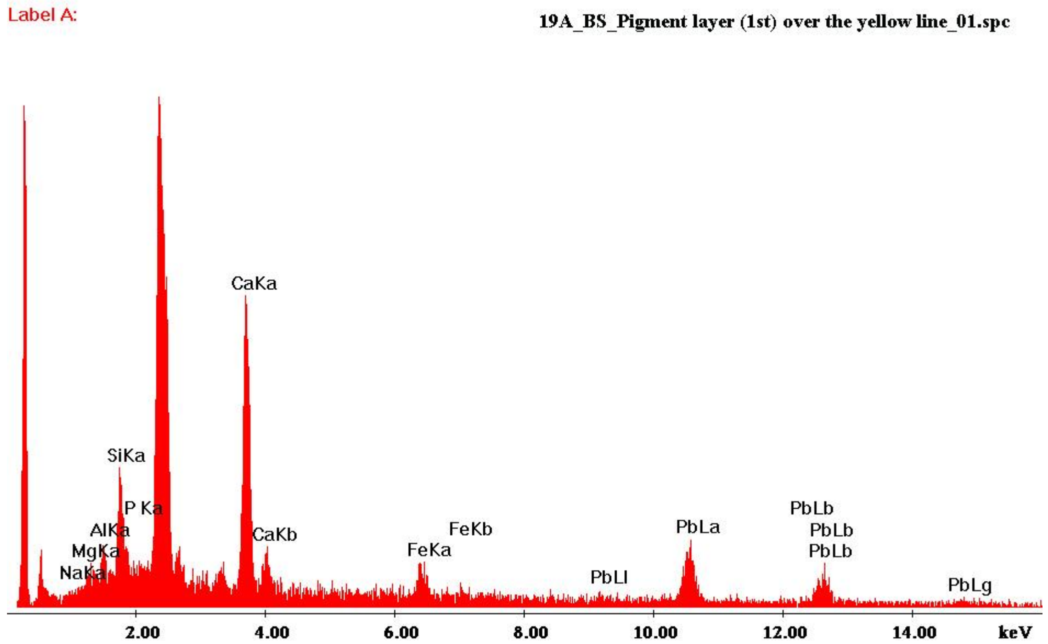

Fig.420 EDX Spectrum from pigment layer (1st) over the yellow line (Sample #19a)
(personal archive Th. Mafredas)

Finally, EDX an analysis of the second pigment layer detected Pb exclusively (**Fig.421**), while the presence of dust and deposits were identified on the upper layer (**Fig.422**).

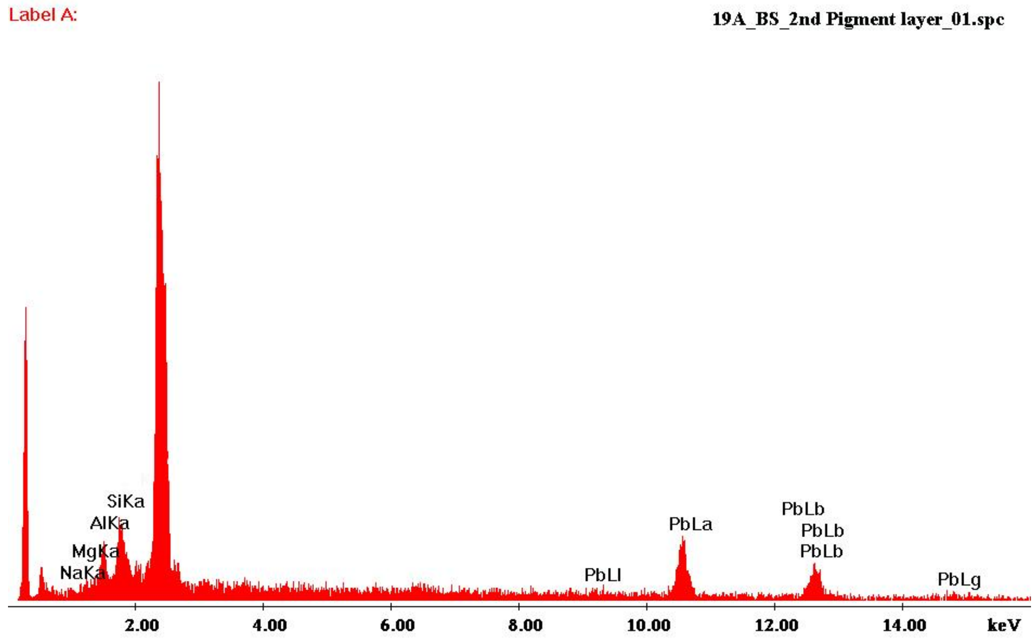

Fig.421 EDX Spectrum from 2nd pigment layer (Sample #19a) *(personal archive Th. Mafredas)*

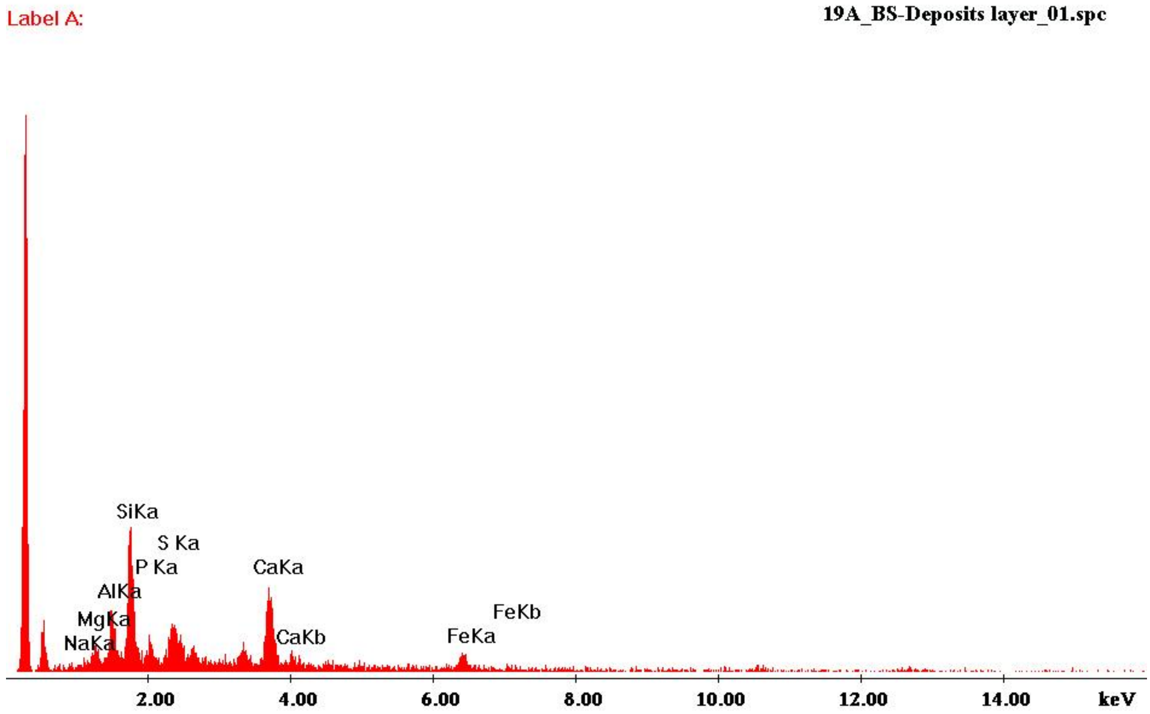

Fig.422 EDX Spectrum from deposits layer (Sample #19a) *(personal archive Th. Mafredas)*

Table 14. *Panel #4 - Elemental Analysis - EDX*				
# Sample	**Spot**	**OM**	**Layer**	**Trace Elements**
#19a	Gesso preparation	Thick layer (right side of the sample with big grains)	1st	S, Ca
	1st pigment layer (below the yellow line)	1st pigment layer	2nd	Ca, Fe Pb, Al, Si, Mg, K
	Thin yellow line	Thin yellow line	3rd	Ca, Fe Pb, Al, Si, Mg, K
	1st pigment layer (over the yellow line)	1st pigment layer	4th	Ca, Fe Pb, Al, Si, Mg, K
	2nd pigment layer	2nd pigment layer	5th	Pb
	External layer	Organic layer	6th	Si, Al, Ca, Mg, Na

4.4.2. Molecular Techniques

4.4.2.1. Fourier Transformer Infrared Spectroscopy

The final technique applied on two different samples was FTIR (***Appendix 2***) in order to characterize the gesso preparation and the kind of varnish which Dionysius used during the construction of his panel painting. The sample for gesso (#16a) was taken from the upper horizontal frame of the panel, while the sample of varnish (#17) was taken from the lower side of the vertical frame of the panel. Both of them were in powder form, prepared in KBr disc, as was discussed in a previous chapter.

From the obtained spectrum for sample #16a and the respective bands, it was identified that the gesso was dihydrate (3550, 3408, 1688, 1622 cm^{-1}) gypsum (1144, 1116, 670, 602 cm^{-1}) and, more specifically, calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) (**Fig.423**). The intensive bands at 2932, 2865, 1655, 1547, 1461 cm^{-1} indicated the possible contribution of carboxylate salts.

The use of $CaSO_4$, as evidenced from the relevant FTIR spectrum, could be justified from the obtained data from previous spectroscopic techniques, both XRF and EDX.

From the obtained spectra for sample #17 concerning the kind of varnish that was used, the presence of Sandarac and Mastic was identified.

The obtained spectrum from sample #17 (**Fig.424-425**) indicated the presence of Mastic (3451, 2934, 2873, 1706, 1655, 1458, 1377, 1239 cm^{-1}) and Sandarac (3074, 1416, 1177,890 cm^{-1}).

The use of infrared spectroscopy, as discussed above, justified the obtained data about inorganic elements during previous techniques and verified the different application of varnish layers, as was also found during microscopic observations. From the varnish identification, it could be argued that Dionysius used some kind of resin for varnish, which he had already mentioned in his treatise, as it will be further discussed below.

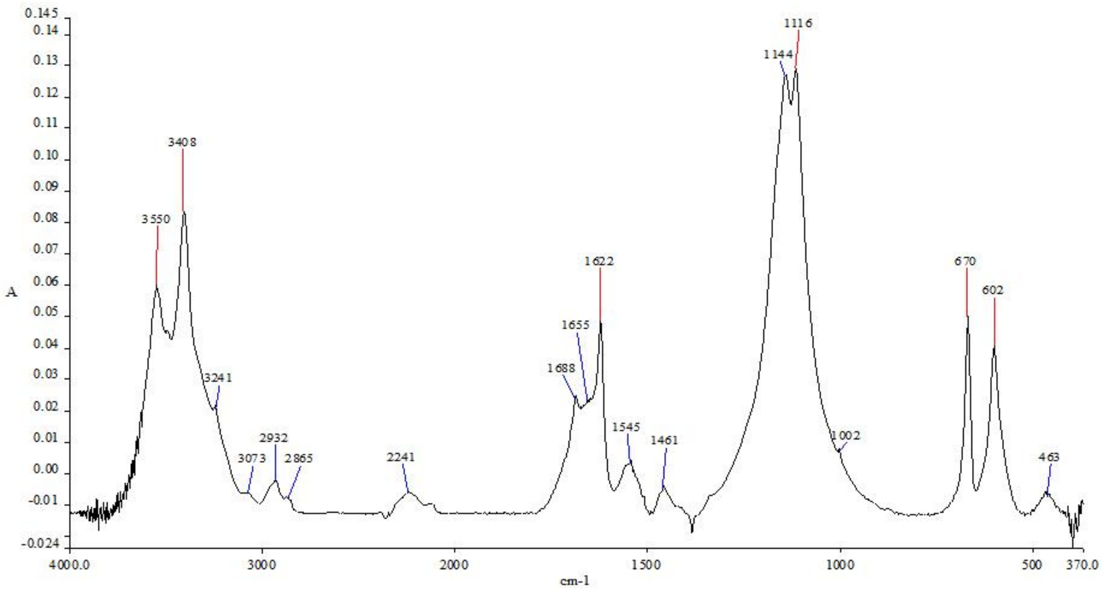

Fig.423 FTIR spectrum from gesso powder (panel#4, sample #16a) *(personal archive Th. Mafredas)*

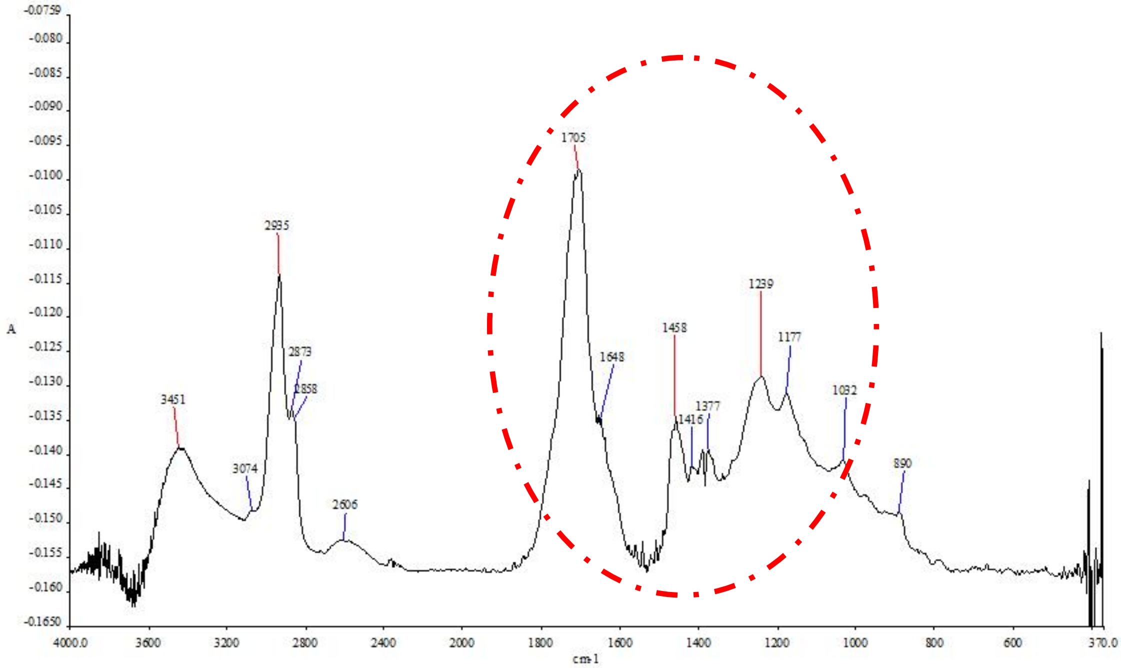

Fig.424 FTIR spectrum from varnish powder (panel #4, sample #17) *(personal archive Th. Mafredas)*

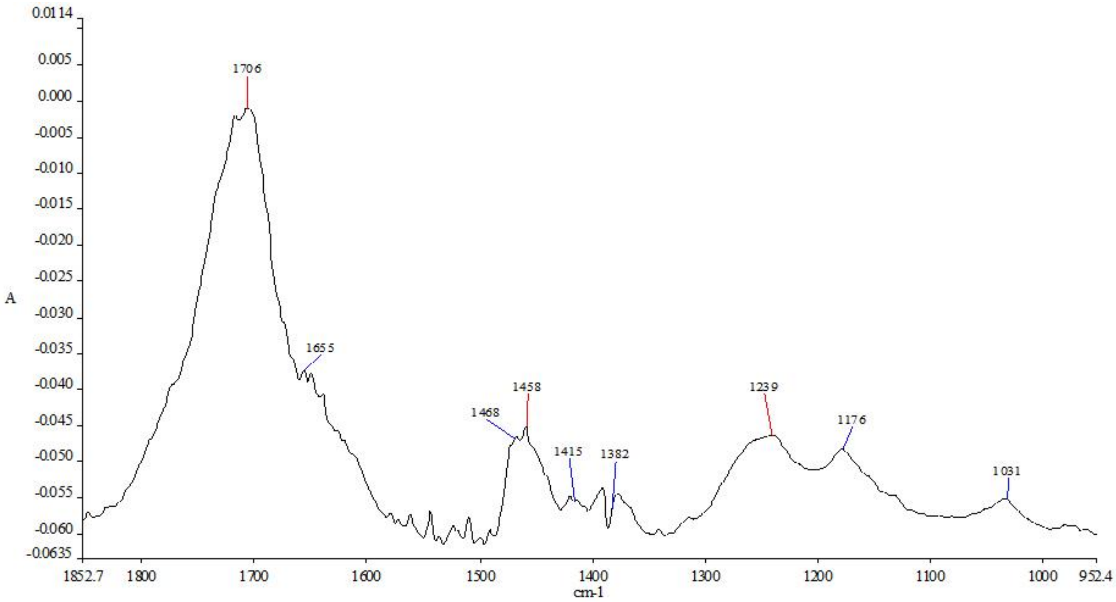

Fig.425 FTIR spectrum from varnish powder. Details (panel #4, sample #17)
(personal archive Th. Mafredas)

4.5. Discussion

The last panel painting from this set of four portable panels painted and donated by Dionysius, is the painting of the apostles Peter and Paul. The iconography of the Apostles Peter and Paul holding a model of a church, as painted on this despotic panel painting, is not included as a subject in the descriptions of his Hermeneia. Aside from that, references to the Apostles Peter and Paul can be found in several contexts; however, the most important mentions are found in the section describing the main characteristics of the twelve Apostles (Dionysius 1909, p. 150; Hetherington 1974, p. 52) and in the section proposing the verses to accompany the Apostle Peter and Paul paintings (Dionysius 1909, p. 232; Hetherington 1974, p. 90).

Fig.426 Apostles, Peter and Paul, Detail. The mistake on the depiction of Peter's right arm *(personal archive Th. Mafredas)*

The panel painting includes a noteworthy and substantial mistake, as Kakavas notes (Kakavas 2008, p. 195), concerning the depiction of Peter's right arm, which does not really support the model of the church (**Fig.426**).

A dedicatory epigram, as in the previous three despotic panel paintings, can be found at the bottom part of this panel, which is not mentioned anywhere in Dionysius's treatise.

As discussed above, imaging techniques, such as IR photography, helped study detailed features of painting concerning Dionysius's drawing line and observed same details which were not detectable or visible in the Vis. Furthermore, it was possible to observe some differentiation from the initial drawing, such as at the bottom part of St. Peter's garment.

The application of digital microscopy provided excellent and detailed data concerning the construction technique and the decoration of the painting surface, providing a first impression about Dionysius's painting technique on this panel. Through the examination with DM, it was possible to appreciate Dionysius's magnificent painting skills, using the pigments to achieve the volume and the shape of his depicted themes. Once more, the use of gold as pigment over existing pigment layer (Greek: χρυσοκονδυλιά) was identified. Studying this panel in combination with the previous three, it was found that this feature is something that all four panels have in common. Common features with the previous three panels were also found while studying the technical construction where, among others, the presence of very thin layers was observed.

The two cross section samples, as discussed above, were taken from different sampling areas in order to study Dionysius's painting technique. Unfortunately, one of the samples, 19b, failed, so it was really difficult to gather information. Thus, OM and SEM/EDX was performed in only one sample, without the chance for a comparative study of the results from both samples.

During OM observation of sample 19a, it was possible to discern the different layers of which the sample consisted. Furthermore, three remarkable features were observed: The first one was the good adhesion between the two pigment layers; the second was a, thin, yellow, non-continuous line in the middle of the first pigment layer, and the third one was the existence of some vertical cracks which seemed to have been filled from the upper organic layer. Concerning the thin yellow line, it was difficult to make a hypothesis before examining it through SEM/EDX. The good adhesion of the two pigment layers could be explained by the fact that the painting of each layer was applied after the underlying layer had dried quite well. The presence of vertical cracks filled with the organic material could be explained if two cases were taken into account: The first has to do with a technical failure. The upper pigment layer may have cracked after its application at the same time when the painting surface was varnished. This resulted in the filling of the gaps from the varnish as it appeared in the sample by optical microscopy. The second case has to do with a previous conservation attempt, during which, the initial varnish was removed by cleaning the painting surface, and a new varnish was applied on it. But, in this case, the presence of deep cracks that reach the gesso layer could not be explained.

The microchemical test performed with NA2 in order to identify the presence of proteinaceous materials in the binding medium did not provide clear answers, especially for the paint layers. Therefore, it can be assumed that the binder contains a low concentration of proteinaceous material and may have been mixed with another organic material. In any, case the microchemical test provided a first perception of the composition of the binder as to the existence of proteins.

Studying the sample by SEM, the observation provided detailed data about the different layers of the cross section of the sample and helped to study Dionysius's construction technique. For one more time, good adhesion was observed between the two pigment layers. Also, it was confirmed that the vertical cracks reached all the way to the gesso layer, and the presence of more than two cracks were observed which were filled by the organic layer. In the first pigment layer was a clean crack detected, which could be explained as an indication of detachment from the gesso layer.

Concerning the application of the gesso layer, two–and maybe, at some points, three– different layers of gesso were observed. From the direction of the flakes, it was possible to evaluate the quality of the work for each layer, as well as for the total gesso preparation layer, which had not been worked with diligence. This feature is common in all four panels, which makes it clear that Dionysius did not follow the instructions of his treatise in these four panel paintings.

Through the elemental analysis with XRF and EDX it was possible to have a first perception about Dionysius's color palette. So, according to the obtained spectra, it could be assumed that he used red lead (Pb_3O_4), red ochre (Fe_2O_3), and cinnabar (HgS)for red pigments, and white lead ($2PbCO_3 \cdot Pb(OH)_2$)for white pigments. Also, it seems that he used azurite ($2CuCO_3 \cdot Cu(OH)_2$) for blue pigments, and orpiment (As_2S_3) for yellow pigments. For green pigment, he probably used green earth, also known as Terra Verde (Fe2+/Fe3+ and Al, Si, Mg, and K) For once more, it seems that all the pigments he used for this panel painting are mentioned in his treatise (Dionysius 1909, pp. 20-23, 34, 41).A remarkable feature was the identification of Au by XRF in a spot which was red. This particular spot provided two different pieces of information concerning Dionysius's painting technique: The first was the probability of use of an organic pigment as red lacquer, and the second has to do with the detection of Au underneath the red. This could probably mean that he had applied the pigment over an existing gold leaf.

The final analytic technique that was applied was FTIR and, through it, the kind of gypsum he used for gesso preparation was characterized as $CaSO_4$, which verifies the XRF and EDX results about Ca and S. The varnish he used seems to be Sandarac, with a possibility of mixture with Mastic. Because of the limitations of this technique, it was not possible to quantify the presence of each of the resins, or to assume whether there was a previous restoration attempt. But, in any case, both of these resins are mentioned in Hermeneia’s manuscript as ingredients for varnish layer (Dionysius 1909, pp. 25-27), and are the same resins that were identified for panels #1 #2 and #3.

The implementation of the research protocol in these four despotic panel paintings by Dionysius allowed us to reach some results and conclusions concerning the construction technique and compare his works with the text of his treatise. For example, it was possible to have a perception about Dionysius’ color palette in comparison to his instructions in a particular part of the treatise (Dionysius 1909, pp. 20-23, 41). Furthermore, through analytical techniques, it was possible to identify the kind of varnishes and compare the results with the Hermeneia’s text (Dionysius 1909, pp. 24-27), while the microscopic observation helped to have a closer look at the internal structure of the panels, and to characterize Dionysius's painting and construction technique. A characteristic example was the application of the gesso layer (Dionysius 1909, pp. 14-15) and the bole layer for the gilding technique (Dionysius 1909, pp. 17-19). A basic principle for the implementation of all the examination was to find out whether Dionysius applies the recipes or the instructions which he had already mentioned in his book. At this point, it should be noted that these four panel paintings were constructed by him after he had finished writing the "Hermeneia of the Byzantine Painting Art"

CHAPTER E – CONCLUSIONS

As discussed in the previous chapters, Dionysius's created these four panel paintings to dedicate them to the Zoodochos Pigi monastery, which was founded by himself. According to one of the epigrams found in the Benaki Museum Codex, these four panel paintings were constructed to adorn the catholicon –the central church of the monastery- and, more specifically, the iconostasis of the church (Kakavas 2008, p. 108; Ferens 2015, p. 18). The same epigram states that, in 1733, Dionysius had begun to paint four despotic icons, which were later used for the iconostasis of the monastery of the Zoodochos Pigi at Fourna (Kakavas 2008, p. 108). As per the monastery's code (Dionysios 1938, p. 8) and related works (Kakavas 2008; Dimitrakopoulos 1979; Ferens 2015), Dionysius began building the monastery in 1734 and completed the construction in 1738. In 1740, his monastery was characterized as Stavropigion -which means that it was under Patriarchate protection. The Patriarchate letter concerning its recognition is being kept, until today, in the Transfiguration church of Fourna (Siaksabani 2013, p. 168). Finally, in 1743 the monastery was inaugurated (Siaksabani 2013, pp. 166-167). According to Kakavas it is possible that Dionysius had begun to work on these four icons while still in Karyes, in the knowledge that he would soon be moving to Fourna to build a monastery there, and wished to use them for the embellishment of its iconostasis (Kakavas 2008, p. 109). After the monastery of Zoodochos Pigi collapsed in 1906, the four icons were rescued and they have been kept in the church of Transfiguration at Fourna ever since. (Dimitrakopoulos 1979, p. 85; Dionysios 1938, p. 8; Siaksabani 2013, pp. 168-170).

The content of this Thesis was intended to characterize the materials used by Dionysius for these four (4) panel paintings, to recognize the construction technology of these artifacts, to study Dionysius's painting method, and evaluate whether he eventually applied everything described in the text of his Hermeneias, taking into consideration that the studied panel paintings were constructed in 1737, a few years after he completed the writing of his treatise (1729-1732).It was the first step to confirming and verifying the technical information regarding the construction of panel paintings as presented in Dionysius's treatise.

During the study of these four panel paintings, it was necessary to keep two main features in mind in order to evaluate Dionysius's construction technique in comparison to his treatise.

The first was that he hadn't written the technical instructions himself but, as he claimed in the introduction of his treatise, he had collected them with great effort, assisted by his pupil, Cyril (Dionysius 1909, p. 4). He may not have written the instructions, but as he points in another part of his preface, he corrected them, where he considered that it was necessary (Dionysius 1909, p. 4). Therefore, according to what he claimed, it may be assumed that any correction he did concerning the technical part, required excellent technical knowledge from him (Dionysius 1909, p. 7).

The second feature that should be kept in mind was the fact that, at the same time, he was both a painter and a donor. So, some discrepancies could be explained under this consideration because, in the case of these panel paintings, Dionysius as iconographer and donor could have included some more personal features, regardless of the Hermeneia's text instructions (Kakavas 2008, p. 187).

Through a research protocol of non-destructive techniques, applying imaging techniques (Vis and IR photography), microscopic techniques (OM, SEM and DM), elemental techniques (XRF and EDX) and molecular techniques (FTIR), these four panel paintings were studied in the context of a two-directional study: first, a systematic investigation of the materials used for the construction of his panel paintings during the various stages of his creation and, second, a study of the internal construction technology, identification of the methodology and the specific way that materials were selected and combined by Dionysius in order to construct these specific artifacts (Alexopoulou, Theodoropoulou & Tsairis 1997, p. 151).

The aim of this research was to determine the characteristics of the structural materials and Dionysius's painting technique. So, according to the obtained data from all the techniques implemented during the study of these panel paintings, compared with the basic queries set in a previous chapter, we were able to reach the following conclusions in relation to Hermeneia's text

Having studied the iconography of four panels, it was found that Dionysius had followed the given instructions in Hermeneia's text for two of them: Christ as King of the Kings and Great High Priest (Dionysius 1909, pp. 216, 227-228; Hetherington 1974, pp. 84, 88; Kakavas 2008, p. 205) and Theotokos Zoodochos Pigi (Dionysius 1909, pp. 145, 221-222, 228, 230; Hetherington 1974, pp. 50, 86, 88-89; Kakavas 2008, pp. 186-187, 190; Kakavas, Mafredas & Giannoulopoulos 2013, p. 317). Concerning the third panel, even though there are abundant references to Saint John the Forerunner that could be found in many sections of Dionysius' treatise (Dionysius 1909, pp. 88, 89, 110, 128, 141, 147, 166, 175-178, 208, 215, 217, 221, 223, 224, 229), none of them is a description about his physical appearance, his features are not provided and it is not mentioned whether he should be depicted with wings or not (Kakavas 2008, p. 209; Kakavas, Mafredas & Giannoulopoulos 2013, p. 317; Keiko 1995, pp. 159-161). It seems that Dionysius' follows the prototype of the Palaeologian period, also adopted by 15th century Cretan painters (Keiko 1995, pp. 152-154). The rest of the features of the specific depicted theme, such as the details of the axe and the haloed head in a gold basin in the foreground, could be found in Hermeneias' text (Dionysius 1909, pp. 175-178). The iconography of the last panel painting of Sts. Paul and Peter holding a church model is also remarkable, as it is not included as a subject in the descriptions of Dionysius's text (Kakavas 2008, pp. 194-195).

All the panel paintings have a dedicatory epigram. It is noteworthy that the epigrams, composed by Dionysius around 1737 to accompany his despotic panel paintings, were not included in the text of his treatise despite the fact that Dionysius suggested many other epigrams to accompany these kinds of depicted themes for panel paintings. According to Kakavas, this can be explained by taking into account that the epigrams for these particular panel paintings were composed specifically for these themes and after the completion of his treatise (Kakavas 2008, p. 205).

Finally, in the back side of the four panels, a Cross was also depicted with letters forming the name of Christ and the word "victory" (in Greek): IC//XC//NI/KA, even though there is no a relative reference in the text of the Hermeneia.

In terms of the constructing technology, the research focused on the identification of materials and study of the internal microstructure of the panels, which would provide answers concerning specific instructions from Hermeneia's text followed by Dionysius.

Starting from the wooden substrates, it was found that in Hermeneia's text, Dionysius never mentioned any details about the kind of the wood that should be chosen for substrates. For example, when he refers to the wooden substrate, he simply names it as a plank or a plain piece of wood, without giving further details or information about it (Dionysius 1909, pp. 43-44, §71).

Concerning the gesso preparation layer for panel paintings, Dionysius provided particular instructions about this procedure (Dionysius 1909, pp. 14-15). According to his instructions, the painter should use gypsum for the gesso layer with an organic substance, i.e. animal glue. Furthermore, he suggested the combination of animal glue with gypsum and linseed oil, along with a small quantity of soap. Besides them, Dionysius provided instructions about the quality of gypsum grains, insisting on using fine-grained gypsum, and not coarse. Fine-grained gypsum is appropriate for good adhesion and prevents the gesso layers from detaching from each other. This is the reason that he mentioned, among others, that the gesso layer should consist of up to seven different layers (Dionysius 1909, pp. 14-15 §6).

During SEM observation of the samples taken from the panels, it was found that, in all cases, Dionysius hadn't applied the gesso layer with diligence. Furthermore, it was observed that the gesso layer consisted of two different layers most of the times, with the exception of samples #13 (Panel #3) and #10 (Panel #2), where an indication of three gesso layers was observed. By SEM observation we were able to define a number of different layers for gesso preparation, but in no case were we able to discern and measure the exact number of gesso layers that he mentioned in his treatise. A common feature for all the samples, as was observed during SEM, is the thinness of the preparation layer which, along with the negligent application of the gesso layer, made it clear that Dionysius hadn't followed his own instructions.

Concerning the gilding technique, Dionysius provides three different recipes for the bole preparation in his text (**Table 15**).

Table 15. Dionysius' recipes for bole (Dionysius 1909, pp. 17-19)		
1st recipe for red bole	**2nd recipe for bole**	**3rd recipe for bole**
Bole (=clay), not so red	Bole (=clay), not so red	Bole (=clay), not so red
Ochre	Ochre	Ochre
Red Lead	Soap	Red lead
Wax	Egg white	Cinnabar
Burned paper		Egg White
Mercury		Gall
		Wax
		Mercury

The study of the panels by DM found the presence of a thin layer which could be indicative of the presence of bole, but it was difficult to be certain about it. Thus, the application of OM and SEM helped to identify the presence of the bole layer, and the EDX provided an elemental analysis of this layer. According the obtained data, besides the presence of bole clay, ochre, red lead and cinnabar were also found in some cases. Furthermore, it was difficult to characterize the organic ingredients of the bole from these samples due to limitations in the applied techniques. Collecting and studying the obtained data, we were able to make a hypothesis about the bole recipe that Dionysius used for these panels. It seems that he mainly used the 2nd recipe (Dionysius 1909, p. 18 §11), while the occasional presence of red lead and cinnabar could point towards the use of the 3rd recipe (Dionysius 1909, p. 18 §12). During a discussion of the results with Dr. Mastrotheodoros, it was argued that Dionysius probably just recorded the first bole recipe without ever having used it because the mercury in combination with gold destroys it, creating an amalgam.

Through the elemental analysis by XRF and EDX, a first perception about Dionysius's color palette was possible. According to the obtained data from both elemental analyses of selected pigments, it could be assumed that he used a variety of pigments, all of which are mentioned in his treatise (Dionysius 1909, pp. 20-23, 34, 41). Thus, he used red lead (Pb_3O_4), red ochre (Fe_2O_3) and cinnabar for red pigments (HgS), and white lead ($2PbCO_3{\bullet}Pb(OH)_2$) for white pigments. For blue pigments, azurite ($2CuCO_3{\bullet}Cu(OH)_2$) was most likely used, while verdigris $Cu(CH_3COO)_2{\bullet}2Cu(OH)_2$) and Terra Verde ($Fe^{2+}/Fe^{3+}$ and Al, Si, Mg, and K) were utilized for green pigments, and orpiment (As_2S_3) for yellow pigments. It seems that all the pigments he used for these four panel paintings are mentioned in his treatise (Dionysius 1909, pp. 20-23, 34, 41).

One remarkable feature was the identification of Au by XRF in a spot (panel #4, spot #47) which was red. This spot was on the right sleeve in St' Paul's red garment. From the obtained spectrum of this area, the sole presence of Au was detected, even though it is obvious that this area is red. A logical explanation that can be given is due to the limitations of the XRF in the detection of organic elements. This particular spot provided two different pieces of information concerning Dionysius's painting technique. The first was the probability of the use of an organic pigment as red lacquer, and the second has to do with the detection of Au below red, which could mean that he applied the pigment over an existing gold leaf. At this point, further examination through a more sophisticated research protocol could provide more specific answers about the kind of materials Dionysius used for this pigment.

Furthermore, as far as red pigments are concerned, OM and SEM found that he seems to use a combination of red lead and cinnabar in most of the cases. During the study of the samples by OM, it was found that he typically used a first red pigment layer of red lead, and then applied a thin red layer of cinnabar over it. Additionally, it seems that he used a combination of pigments in order to achieve the right color hue. Characteristic examples are the pigments that he used for the background for panels #1, #3 and #4, where a mixture of orpiment with red lead and blue appears to have been used.

Concerning the mixing pigments for flesh, as Dionysius' described them in his text (**Table 16**) the elemental analysis in different spots confirmed that he followed the Hermeneia's instructions. Thus, in panel #2, elemental analysis identified the presence of lead white, yellow/red ochre with a small quantity of green, pigments corresponding to Dionysius's recipe for proplasmos (Dionysius 1909, p. 20). Furthermore, the presence of Hg could be explained under Dionysius's instructions for using red pigment. More specifically, in his treatise, Dionysius clearly mentions-among others- that a small quantity of red should always be used on the Theotokos's face. The red tint which could be a mixture of cinnabar with the pigments used for the flesh (Dionysius 1909, p. 22) which, in this case, are the same as the pigments for the proplasmos. Another example is derived from panel #4, where trace elements corresponding to Pb, Fe, and Cu were detected on St. Peter's and St. Paul's faces, which could be the result of a mixture of lead white and a yellow/red ochre with a small quantity of green, pigments corresponding to Dionysius's recipes for proplasmos and flesh (Dionysius 1909, pp. 20-21).

At this point it should be noted, that, trace elements, such as Zn and Ar, detected in four panel painitngs, it seems to be impurities of the raw materials without their presence interfering with the presence of raw materials as they are recorded by the intensity bands of the spectra

Table 16*. The main pigments mentioned by Dionysius for panel painting (Dionysius 1909, pp. 20-23, 31-34, 41)*

Proplasmos	**Flesh (skin color)**	**Red skin tone**	**Rosiness of face**	**Optionally**
Lead white	Lead white	Lead white	Flesh color	Blue
Ochre	Yellow venetian Ochre	Reddish ochre	Cinnabar	Red lake
Green	Cinnabar	Reddish ochre	Boles (for shadows and lines)	Orpiment (yellow)
Black		c) yellow ochre		Green
		d) bolos		

Concerning the binding medium for the pigments, it was really difficult to discern a specific instruction about the exact use of a binding medium. For example, he mentions one kind of binding medium which is made by glue, potash solution and white wax (Dionysius 1909, pp. 28, §36; Partington 1934, p. 146), or from garlic juice (Dionysius 1909, p. 21 §27), for applying gold as a pigment (in Greek: χρυσοκονδυλιά). Furthermore, he mentions the use of egg medium for the pigments (Dionysius 1909, pp. 9 §1, 23 §25, 23 §26; Partington 1934, pp. 146-147; Markozanis 2017, pp. 56-57), and the use of egg white as a binding medium for the bole layer (Dionysius 1909, pp. 17-18, §10-12).

During microchemical tests in four cross-section samples -one sample from each panel painting- the presence of proteinaceous elements was observed, which could possibly come from the use of egg white. Especially for panel #2, the identification of proteinaceous elements through microchemical tests corresponds to the obtained data by FTIR analysis (for sample #8) where the presence of proteinaceous material and lipids was detected. The combination of the above possibly leads to the conclusion that the sample contains egg as medium.

For the other three cross sections samples from panels #1, #3 and #4, the microchemical tests provided a subtle staining about the presence of proteinaceous materials, which could set the hypothesis that Dionysius had used a proteinaceous binding medium in mixture with another organic binder, whose presence was not able to be identified by microchemical tests. Besides that, the use of microchemical tests could only provide indications of the use of binding media, and a first perception about the kind of binding media used.

Concerning the binding media for gesso layer, Dionysius's instructions mention the use of animal glue. During microchemical tests in cross section samples, the staining test for the identification of proteinaceous materials was intense. However, it should be taken seriously into account that the porous structure of the gesso preparation layer could be the cause of an intense staining of protein materials. There is a need for the application of a more sophisticated research protocol in order to achieve exact answers concerning the binding media of the gesso preparation layers.

Finally, regarding the organic protective coating, whatever assumption could be made, none of the cases would involve the authentic varnish layer used by Dionysius. Over time, the varnish ages and degrades, resulting in the discoloration of the painting surface, which loses its transparency, thus making pigments appear opaque. It was common practice to apply a new varnish on top of a previous one that had lost its gloss and transparency. This makes the stratigraphic and compositional study of old panel paintings varnishes very complex (Matteini & Mazzeo 2009, p. 19).

In general, there are two kinds of varnish: the first consists of a solution of a resin in a volatile solvent; the second is made of a resin dissolved in a drying oil. Spirit varnishes consist of a soft resin, such as mastic or sandarac, dissolved in turpentine or alcohol (Gettens & Stout 1966, p. 73; Kouloumpi, Moutsatsou & Terlixi 2012, p. 372). According to these and the study of Dionysius's text, five different recipes for varnish could be discerned (**Table 17**).

<table>
<tr><td colspan="4">Table 17. Dionysius' recipes for Varnishes (Dionysius 1909, pp. 24-27)</td></tr>
<tr><th>1) Varnish from Linseed oil</th><th colspan="2">2) Sandalwood Varnish</th><th>3) Naphtha Varnish</th></tr>
<tr><td>Linseed oil</td><td colspan="2">Sandalwood</td><td>Sandalwood</td></tr>
<tr><td>Fir resin (=turpentine)</td><td colspan="2">Linseed oil OR</td><td>Linseed oil</td></tr>
<tr><td>Naphtha</td><td colspan="2">Naphtha</td><td rowspan="3">Naphtha</td></tr>
<tr><td>Unboiled linseed oil</td><td colspan="2" rowspan="2">Boiled linseed oil</td></tr>
<tr><td>Mastic</td></tr>
<tr><th colspan="2">4) Yellow Varnish</th><th colspan="2">5) Alcohol Varnish</th></tr>
<tr><td colspan="2">Sandalwood</td><td colspan="2">Alcohol</td></tr>
<tr><td colspan="2">Aloe</td><td colspan="2">Sandalwood</td></tr>
</table>

Boiled linseed oil		Fir resin (=turpentine)
Naphtha, as a solvent		
Notes:	**Peziri =**	raw unboiled linseed oil
	Pegoula =	fir resin (=turpentine)

During spectroscopic analysis by FTIR, the presence of Mastic and Sandarac was detected in addition to drying oil. Furthermore, studying the cross section samples by OM and SEM, the presence of different layers of varnish was observed. Thus, it is too risky to assume the presence of a mixture of Sandarac and Mastic, even though bibliography points out that the varnish most widely used from the 9th century A.C. till the late 17th century A.C. was made by dissolving mastic, or both mastic and sandarac, in linseed oil (Gettens & Stout 1966, p. 34).

It is safer to assume that these are two different kinds of varnish applied on the panels in different times. But, in any case, both of these resins are mentioned in the "Hermeneia" manuscript as ingredients for varnish layer (Dionysius 1909, pp. 25-27). Besides that, the identification of the presence oil could suggest that Dionysius used one of the recipes mentioned above, but it is difficult to identify which exact recipe he used. Finally, the mixture of pigments with varnish was not detected, at least to the extent that it could be assumed from the examined cross section samples and powder varnish samples.

In the table below (**Table 18**) Dionysius's recipes and instructions as found in Hermeneia's text can be compared with the obtained data from the research techniques.

Table 18. Comparison of instructions and recipes from the Hermeneias' text with the obtained data from research techniques				
	Hermeneias' text		**Analytical data**	**Comments**
Wood	No details about the kind of the wood		——	No research technique was performed
Glue	Animal		——	No research technique was performed
Gesso layer	Gypsum		Calcium sulfate (**$CaSO_4$**)	Dehydrate (Panel #1, #3, #4)
				Hydrate (Panel #2)
Bole layer	**1st recipe**	Bole (=clay), not so red	——	Dionysius had probably just recorded the first bole recipe without having used it, because the mercury in combination with gold destroys it, creating an amalgam.
		Ochre		
		Red lead		
		Wax		
		Burned paper		
		Mercury		
	2nd recipe	Bole (=clay), not so red	**X**	By elemental techniques (XRF and EDX), the presence of inorganic elements that could result from the use of this recipe was found.
		Ochre		
		Soap		
		Egg white		
	3rd recipe	Bole (=clay), not so red	**X**	By elemental techniques (XRF and EDX) the presence of inorganic elements that could be coming from the presence of this recipe was found.
		Ochre		
		Red lead		
		Cinnabar		
		Egg White		
		Gall		
		Wax		
		Mercury		
Gold layer	Use of gold leaf		**Au** (with Cu impurities)	By elemental techniques (XRF and EDX) the presence of Au. By XRF was detected low intense bands of Cu which probably could coming from impurities was detected
Painting layers	**Proplasmos**	Lead white	**X**	Panel #1
		Ochre		Panel #2
		Green		Panel #4

		Black		
	Flesh (skin color recipe #1)	Lead white	**X**	Panel #2
		Yellow venetian Ochre		Panel #3
		Cinnabar		
	Flesh (skin color recipe #2)	Lead white	**X**	Panel #1
		Yellow venetian Ochre		Panel #4
	Red skin tone	Lead white	——	
		Reddish ochre		
		Yellow ochre		
		Bole		
	Rosiness of face	Flesh color	**X**	Panel #2
		Cinnabar		
		Boles (for shadows and lines)		
	Optionally	Blue	**X**	Panel #2
		Red lake	**X**	Panel #4
		Orpiment (yellow)	**X**	Panel #1
				Panel #3
				Panel #4
		Green	**X**	Panel #1
				Panel #3
				Panel #4
Pigments	**White**	White lead [$2PbCO_3 \cdot Pb(OH)_2$]	**X**	Panel #1
				Panel #2
				Panel #3
				Panel #4
	Yellow	Orpiment [As_2S_3]	**X**	Panel #1
				Panel #3
				Panel #4
		Venetian Ochre [$Fe_2O_3H_2O+SiO_2Al_2O_3+SiO$]	——	
	Red	Cinnabar [HgS]	**X**	Panel #1
				Panel #2
				Panel #3
				Panel #4
		Red lead [Pb_3O_4]	**X**	Panel #1
				Panel #2
				Panel #3
				Panel #4
		Hematite Ochre (Constantinopolitan Ochre) [[$Fe_2O_3+SiO_2Al_2O_3+SiO_2$]	**X**	Panel #1
				Panel #2
				Panel #4
	Red-Brown	Umber [$Fe_2O_3+Al_2O_3SiO_2+MnO_2$(8-16%]	**X**	Panel #2
		Hematite [Fe_2O_3]	**X**	Panel #1
				Panel #2

				Panel #4
		Lacquer	——	
	Green	Verdigris $[Cu(CH_3COO)_2•2Cu(OH)_2]$	X	Panel #1 Panel #2 Panel #3
		Terra Verde $[Fe^{2+}/Fe^{3+}$ and Al, Si, Mg, and K]	X	Panel #4
	Blue	Azurite $[CuCO_3•Cu(OH)_2]$	X	Panel #1 Panel #2 Panel #3 Panel #4
		Lazouli $[3Na_2O•3Al_2O_3•6SiO_22NaS_2]$	——	
	Black	Carbon [C]	——	
Binding Media	**Anthiboles** **Working on wood** **Working on fibers** **Russian painting technique**	Egg yolk	X (Proteinaceous materials and lipids)	Detection of proteinaceous material and presence of lipids (Panel #2)
	Bole layer	Egg white	X (Proteinaceous materials)	From three cross section samples (panels #1, #3 and #4) the microchemical tests provided a subtle staining for the presence of proteinaceous materials. **Probably** Dionysius' had used a proteinaceous binding medium in mixture with another organic binder, whose presence was not able to be identified by microchemical tests
	How to make glazed color	Animal glue	——	Indication of wax presence by SEM/EDX (panel #1)
		White wax	X	
		Potash solution	——	
	Western painting technique	Linseed oil	——	
		Walnut oil	——	
Varnish	**Varnish**	Linseed oil	——	The presence of Mastic

<table>
<tr><td rowspan="19">layer</td><td rowspan="4">from Linseed oil</td><td>Fir resin (=turpentine)</td><td>——</td><td rowspan="19">and Sandarac was detected (Panels #1, #2, #3 and #4).

The presence of oil was also detected (Panels #2 and #3).

Both of these resins are mentioned as ingredients for varnish layer (Panel #1, #2, #3 and #4).</td></tr>
<tr><td>Naphtha</td><td>——</td></tr>
<tr><td>Unboiled linseed oil</td><td>——</td></tr>
<tr><td>Mastic</td><td>X</td></tr>
<tr><td rowspan="4">Sandalwood Varnish</td><td>Sandalwood</td><td>X</td></tr>
<tr><td>Linseed oil</td><td>——</td></tr>
<tr><td>Naphtha</td><td>——</td></tr>
<tr><td>Boiled linseed oil</td><td>——</td></tr>
<tr><td rowspan="3">Naphtha Varnish</td><td>Sandalwood</td><td>X</td></tr>
<tr><td>Linseed oil</td><td>——</td></tr>
<tr><td>Naphtha</td><td>——</td></tr>
<tr><td rowspan="4">Yellow Varnish</td><td>Sandalwood</td><td>X</td></tr>
<tr><td>Aloe</td><td>——</td></tr>
<tr><td>Boiled linseed oil</td><td>——</td></tr>
<tr><td>Naphtha, as a solvent</td><td>——</td></tr>
<tr><td rowspan="3">Alcohol Varnish</td><td>Alcohol</td><td>——</td></tr>
<tr><td>Sandalwood</td><td>X</td></tr>
<tr><td>Fir resin (=turpentine)</td><td>——</td></tr>
</table>

Dionysius of Fourna has been known to Byzantine and post-Byzantine scholars since the discovery of a copy of his Hermeneia on Mt Athos in 1845. This painter's manual has been of continuing interest to those seeking to discover the traditions and practices of Byzantine and Orthodox iconography (Kakavas 2008, p. 217). This thesis has studied the first part of Hermeneia's text, the Technical part, in an effort to identify the materials used by Dionysius on four (4) panel paintings, to recognize the construction technology of these artifacts, to study Dionysius's painting method, and evaluate whether he eventually applied everything described in Hermeneia's text, taking into account that the studied panel paintings were constructed in 1737, a few years after he completed the writing of his treatise (1729-1732).

An effort to examine the significance of Dionysius as an artist and an author was made, and to study the connections between his painted and written works. Most of the data obtained from the research protocol has evidenced that Dionysius presented a more conservative point of view in his Hermeneia, as opposed to the execution of his artistic works. For example, it seems that he didn't follow the instructions concerning the application of the gesso layer to his panel paintings but, at the same time, it seems that he followed the instructions for making proplasmos, or the color for skin, and even adhered to specific instructions about the rosiness of the Theotokos' face.

It is really difficult to give a specific answer to the question: Did he follow the instructions of Hermeneia's text in his artistic work? The scientific examination from these four panel paintings may provide some answers concerning material identification and recognition of manufacturing technology, but in order to be able to give a specific answer to the above question, the research protocol should be extended, and other works of Dionysius need to be studied.

Ultimately, the above question could be the cause for further study of Dionysius's painting technique and, at the same time, the answer to the query of whether he deals with his painting as a form of art or as a religious depiction.

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APPENDIX 1

1. **Application for sampling permission to:**
   a) **Ephorate of Antiquities in Fthiotida and Evrytania**
   b) **Holy Diocese of Karpenisi**
   c) **Church of Transfiguration in Fourna**

2. **Permission for sampling from Directorate of Conservation of Ministry of Culture**

Αίτηση του

Θωμά Μαφρέδα

Συντηρητή Αρχαιοτήτων & Έργων Τέχνης, Μεταπτυχιακού φοιτητή στο ΜΠΣ Msc in Cultural Heritage, Materials and Technologies, του Πανεπιστημίου Πελοποννήσου

Τηλ. Επικ. 6936143226

E-mail: Mafredas@gmail.com

Διευθ.: Πλάτωνος 50, Καλλιθέα, Αθήνα, ΤΚ 17673

Προς

1. Εφορεία Αρχαιοτήτων ν. Φθιώτιδος & Ευρυτανίας,
Διευθ. Κάστρο Λαμίας ΤΚ 35100
***Τηλ.*:** 22310 29992, ***E-mail*:** efafeu@culture.gr

2. Ιερά Μητρόπολη Καρπενησίου
Αγίου Γεωργίου 1 Καρπενήσι, ΤΚ. 36100

Κοιν.

Ιερός Ναός Μεταμορφώσεως του Σωτήρος
Φουρνάς Ευρυτανίας ΤΚ 36080

Θέμα: Αίτηση για άδεια δειγματοληψίας από τέσσερεις φορητές μεταβυζαντινές εικόνες του ιερομονάχου Διονυσίου, από τον Ι.Ν. Μεταμορφώσεως του Σωτήρος, στο Φουρνά Ευρυτανίας

Στο πλαίσιο του Μεταπτυχιακού Προγράμματος Σπουδών: Msc in Culture Heritage. Materials and Technologies, που διοργανώνεται από το τμήμα Ιστορίας, Αρχαιολογίας και Διαχείρισης Πολιτισμικών Αγαθών, του Πανεπιστημίου Πελοποννήσου, έχω αναλάβει ως θέμα διπλωματικής εργασίας την αναγνώριση της τεχνολογίας κατασκευής τεσσάρων (4) φορητών εικόνων μεταβυζαντινής περιόδου και σύγκριση με τις τεχνικές κατασκευής που περιγράφονται στο βιβλίο: «Ερμηνεία της Ζωγραφικής Τέχνης».

Πιο συγκεκριμένα το θέμα της διπλωματικής εργασίας είναι: “Characterization of construction techniques and materials from four (4) icons of hieromonk Dionysius from Fourna, author of “Hermeneia of the art painting” and comparison with the techniques described in the book”, με επιβλέποντες καθηγητές την Δρ. Ελένη Κουλουμπή, συντηρήτρια αρχαιοτήτων & έργων τέχνης της Εθνικής Πινακοθήκης-Μουσείο Αλέξανδρου Σούτσου και τον Αναπληρωτή Καθηγητή Νικόλαο Ζαχαριά, Διευθυντή του Εργαστηρίου Αρχαιομετρίας του Τμήματος Ιστορίας, Αρχαιολογίας και Διαχείρισης Πολιτισμικών Αγαθών του Πανεπιστημίου Πελοποννήσου.

Ο κύριος σκοπός τη μελέτης αφορά τον χαρακτηρισμό των υλικών και της τεχνολογίας κατασκευής που εφάρμοσε ο Διονύσιος για την κατασκευή των τεσσάρων εικόνων και η σύγκρισή των αποτελεσμάτων με όσα αναφέρει στο έργο του: «Ερμηνεία της ζωγραφικής Τέχνης», ώστε να διαπιστωθεί πλέον και με την χρήση επιστημονικών μεθόδων, ότι όλα όσα αναφέρει στο έργο του τα εφαρμόζει και ο ίδιος στην πράξη. Για τον σκοπό αυτό η μεθοδολογία που πρόκειται να εφαρμοστεί συνίσταται σε:

- Απεικονιστικές τεχνικές για την ανίχνευση αδιόρατων στοιχείων (φωτογράφιση σε διάφορα μήκη κύματος του φάσματος με τη χρήση πολυφασματικής κάμερας)
- Φορητό XRF (pXRF) για την καταγραφή της παλέτας του Διονυσίου
- Μικροτομές Οπτικής Μικροσκοπίας για την καταγραφή της στρωματογραφίας
- Υπέρυθρη φασματοσκοπία για την καταγραφή του βερνικιού
- Χρωματογραφικές τεχνικές για την καταγραφή του οργανικού συνδετικού μέσου

Για τον λόγο αυτό έχουν επιλεγεί οι τέσσερεις εικόνες που ενθησαυρίζονται στο σκευοφυλάκιο του Ι.Ν. Μεταμορφώσεως του Σωτήρος, στον Φουρνά Ευρυτανίας και είναι ενυπόγραφα έργα του ιερομονάχου Διονυσίου. Οι εικόνες αυτές είναι:

1. Ο Χριστός Μέγας Αρχιερεύς 1734-1737, διαστάσεις: 91x56x5,3cm
2. Ζωοδόχος Πηγή, η Φανερωμένη 1737, διαστάσεις 90x57x5,3cm
3. Ο Άγιος Ιωάννης ο Πρόδρομος 1734-1737, διαστάσεις 90x56x5,3cm
4. Απόστολοι Πέτρος και Παύλος 1734-1737, διαστάσεις 90x56x5,3cm

Τα ερωτήματα που αναμένεται να απαντηθούν με την χρήση των φυσικοχημικών τεχνικών σχετίζονται με καθαρά ζητήματα τεχνολογίας, όπως καταγράφονται σε διάφορες παραγράφους στο τεχνολογικό μέρος της «Ερμηνείας της ζωγραφικής τέχνης» και αφορούν, την αναγνώριση του βερνικιού που έχει χρησιμοποιήσει για κάθε μία από τις τέσσερεις εικόνες, την αναγνώριση του στρώματος προετοιμασίας, την αναγνώριση των συστατικών που χρησιμοποιήθηκαν για το χρύσωμα, την αναγνώριση του συνδετικού μέσου, εάν πρόκειται για συνδετικό πρωτεϊνικής φύσεως ή άλλου είδους κ.α. Παράλληλα θα απαντηθούν ερωτήματα που σχετίζονται με την τεχνική κατασκευής των μορφών, των ενδυμάτων κλπ, ενώ θα αποσαφηνιστεί ένα μεγάλο εύρος θεωριών που σχετίζεται με την τεχνολογία κατασκευής των εικόνων, όπως για παράδειγμα το εάν οι χρωστικές εφαρμόστηκαν με μίξη βερνικιού ή όχι.

Για την απάντηση όλων αυτών των ερωτημάτων που σχετίζονται με την τεχνολογία της κατασκευής και τον χαρακτηρισμό των υλικών είναι απαραίτητη η λήψη μικροδειγμάτων από τις εικόνες. Η δειγματοληψία αφορά στη λήψη δύο τομών ανά εικόνα, σε ήδη βεβαρημένες από την φθορά του χρόνου περιοχές, που δεν θα υπερβαίνει τα 2mm. Οι τομές θα προέρχονται, η μία από χρωματικό στρώμα και η άλλη από στρώμα χρυσώματος. Επιπλέον είναι αναγκαία η λήψη ξύσματος από σημείο στο οποίο είναι εμφανή η παρουσία προετοιμασίας για τον χαρακτηρισμό των υλικών, ξύσμα από χρωματικό στρώμα για την ταυτοποίηση του συνδετικού μέσου και ξύσμα από βερνίκι για την αναγνώριση του βερνικιού. Και στις τρεις αυτές περιπτώσεις το κάθε ξύσμα δεν θα υπερβαίνει σε βάρος τα 3-5mg.

Τα μικροδείγματα που θα ληφθούν από τον αιτούντα και με την συμμετοχή της Δρ. Ελένη Κουλουμπή, με τη χρήση νυστεριού, λαβίδας και οδοντιατρικής σπάθης, θα εξεταστούν ως ακολούθως: θα εγκιβωτιστούν σε ρητίνη (κάθετες τομές) ώστε να εξετασθούν με Οπτική Μικροσκοπία και με Ηλεκτρονικό Μικροσκόπιο με Μικροαναλυτή Ακτίνων Χ (SEM/EDX), στα ξύσματα προετοιμασίας και χρωστικής θα πραγματοποιηθούν χρωματογραφικές τεχνικές, γεγονός που προϋποθέτει την χημική επεξεργασία του κάθε δείγματος-ξύσματος, ενώ στα μικροδείγματα από το στρώμα του βερνικιού, τα οποία θα αναλυθούν με υπέρυθρη φασματοσκοπία, το υλικό θα αναμειχθεί με βρωμιούχο κάλλιο προκειμένου να παρασκευασθεί το σχετικό δισκίο. Οι τεχνικές που θα χρησιμοποιηθούν είναι η φασματοσκοπία υπερύθρου (FTIR), η αέρια χρωματογραφία (GC) καθώς και η υγρή χρωματογραφία υψηλής απόδοσης (HLPC).

Οι αναλύσεις των δειγμάτων και οι παρατηρήσεις των τομών θα πραγματοποιηθούν στο Εργαστήριο Φυσικοχημικών Ερευνών της Εθνικής Πινακοθήκης (FTIR, GC, Οπτική Μικροσκοπία), στο Εργαστήριο Αρχαιομετρίας του Πανεπιστημίου Πελοποννήσου στη Καλαμάτα (Οπτική Μικροσκοπία, SEM/EDX, pXRF) και στο Εργαστήριο Φυσικοχημικών Τεχνικών του ΤΕΙ Αθήνας (FTIR, HLPC GC).

Για την πραγματοποίηση της δειγματοληψίας θα προηγηθεί επικοινωνία με την Εφορεία Αρχαιοτήτων Φθιώτιδας, ενώ τα αποτελέσματα των αναλύσεων και η διπλωματική εργασία θα αποσταλεί προς την Υπηρεσία. Η παρούσα αίτηση συντάσσεται και αποστέλλεται προς την Υπηρεσίας σας σύμφωνα με την εγκύκλιο της Διεύθυνσης Συντήρησης Αρχαίων και Νεωτέρων Μνημείων του με αριθμό πρωτοκόλλου: ΥΠΠΟ/ΣΥΝΤ/ΑΡΧ/Φ30/2268/778/5.3.2004, κατά την οποία η ΔΣΑΝΜ και το Τμ. Εφαρμοσμένης Έρευνας είναι η αρμόδια υπηρεσία για την έγκριση ή μη της δειγματοληψίας, χωρίς την προϋπόθεση για σχετική απόφαση από ΤΣΜ ή από ΚΑΣ, και δεν έχει χορηγηθεί στο παρελθόν άδεια δειγματοληψίας για τις συγκεκριμένες φορητές εικόνες.

Η έγκριση της δειγματοληψίας για τη πραγματοποίηση των προαναφερθέντων φυσικοχημικών τεχνικών σε συνδυασμό με την εφαρμογή απεικονιστικών μεθόδων θα παράσχει την δυνατότητα να εξαχθούν πολύτιμα συμπεράσματα ως προς την τεχνική κατασκευής και τον χαρακτηρισμό των υλικών που εφάρμοσε ο ιερομόναχος Διονύσιος για την δημιουργία τεσσάρων εικόνων. Θα απαντήσει σε ένα βασικό ερώτημα, κατά πόσον εφάρμοσε στη πράξη τα όσα κατέγραψε στο έργο του, την Ερμηνεία της ζωγραφικής τέχνης, ενώ παράλληλα θα αποκαλύψει την τεχνική ενός τόσο σημαντικού αγιογράφου της μεταβυζαντινής περιόδου.

Αθήνα, 03.02.2017

Ο αιτών

Θωμάς Μαφρέδας

Συνημμένα:

1. Προτεινόμενες θέσεις δειγματοληψίας από τέσσερεις εικόνες του ιερομονάχου Διονυσίου (5 σελίδες)
2. Προτεινόμενες αναλυτικές τεχνικές (4 σελίδες)
3. Βεβαίωση από το Πανεπιστήμιο Καλαμάτας, Σχολή Ανθρωπιστικών και Πολιτιστικών Σπουδών, Τμ. Ιστορίας, Αρχαιολογίας και Διαχείρισης Πολιτισμικών Αγαθών, ΠΜΣ: «Master of Science in Cultural Heritage Materials & Technologies». (1 σελίδα)

ΑΚΡΙΒΕΣ ΑΝΤΙΓΡΑΦΟ

Ημ/νία: 16/06/2017
Α.Π.: ΥΠΠΟΑ/ΓΔΑΠΚ/ΔΣΑΝΜ/ΤΕΕ/187327/120532/1959/166
Ημ/νία Έκδοσης 16/06/2017
Απάντηση σε: ΥΠΠΟΑ/ΓΔΑΠΚ/ΔΣΑΝΜ/ΤΕΕ/187327/120532/1959/166

ΕΛΛΗΝΙΚΗ ΔΗΜΟΚΡΑΤΙΑ
ΥΠΟΥΡΓΕΙΟ ΠΟΛΙΤΙΣΜΟΥ & ΑΘΛΗΤΙΣΜΟΥ
ΓΕΝΙΚΗ Δ/ΝΣΗ ΑΡΧΑΙΟΤΗΤΩΝ
ΚΑΙ ΠΟΛΙΤΙΣΤΙΚΗΣ ΚΛΗΡΟΝΟΜΙΑΣ
Δ/ΝΣΗ ΣΥΝΤΗΡΗΣΗΣ ΑΡΧΑΙΩΝ
ΚΑΙ ΝΕΩΤΕΡΩΝ ΜΝΗΜΕΙΩΝ
ΤΜΗΜΑ ΕΦΑΡΜΟΣΜΕΝΗΣ ΕΡΕΥΝΑΣ

Ταχ.Δ/νση : Πειραιώς 81
Ταχ.Κώδικας : 105 53 Αθήνα
Πληροφορίες : Πέτρος Πρόκος
Τηλέφωνο : 210 32 15 548 - 210 32 44 628
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e-mail: tee.dsa@culture.gr

Αθήνα, 16 Ιουνίου 2017

Αρ.Πρωτ. ΥΠΠΟΑ/ΓΔΑΠΚ/ΔΣΑΝΜ/ΤΕΕ/Φ77/
187327/120532/1959/166

ΠΡΟΣ: κ. Θ. Μαφρέδα
δια μέσου της ΕΦΑ Φθιώτιδας και
Ευρυτανίας

ΚΟΙΝ : 1) Δ/νση Βυζαντινών &
Μεταβυζαντινών Αρχαιοτήτων
Τμήμα Εποπτείας Ελληνικών και
Αλλοδαπών Επιστημονικών Ιδρυμάτων
και Συντονισμού Θεμάτων Διεθνών
Συνεργασιών και Οργανισμών
2) ΕΦΑ Φθιώτιδας και
Ευρυτανίας

ΘΕΜΑ: Άδεια δειγματοληψίας από τέσσερις φορητές μεταβυζαντινές εικόνες του ιερομόναχου Διονυσίου, που φυλάσσονται στον Ι. Ν. Μεταμορφώσεως του Σωτήρος στο Φουρνά Ευρυτανίας.

Σχετ: 1) Η από 3-2-17 αίτηση του κ. Θ. Μαφρέδα
2) Το υπ' αριθμ. πρωτ. ΥΠΠΟΑ/ΓΔΑΠΚ/ΕΦΑΦΕΥ/72424/43131/739/ 23-3-2017 έγγραφο
3) Το υπ' αριθμ. πρωτ. ΥΠΠΟΑ/ΓΔΑΠΚ/ΔΙΠΚΑ/ΤΕΕΑΕΙ/ 103289/63870/2181/205/17-5-2017 έγγραφο
4) Το υπ' αριθμ. πρωτ. ΥΠΠΟΑ/ΓΔΑΠΚ/ΕΦΑΦΕΥ/114308/7170/1041/ 2-4-2017 έγγραφο της ΕΦΑ Φθιώτιδας και Ευρυτανίας, με το οποίο μας διαβιβάσθηκε το με αρ. πρωτ. 53/21-5-2017 έγγραφο της Ι.Μ. Καρπενησίου, στο οποίο διατυπώνεται η σύμφωνη γνώμη της Μητρόπολης για την αιτούμενη δειγματοληψία.

Έχοντας υπόψη:

1. Το Ν. 3028/28-6-02 «Περί Προστασίας Αρχαιοτήτων και εν γένει της Πολιτιστικής Κληρονομιάς»
2. Την υπ' αριθμ. πρωτ. ΥΠ.ΠΟ/ΑΡΧ/Α3/2869/79/20-4-93 Υ.Α.
3. Την υπ' αριθμ. πρωτ. ΥΠΠΟ/ΣΥΝΤ/ΑΡΧ/Φ30/22268/778/5-3-2004 εγκύκλιο
4. Την υπ' αριθμ. πρωτ. ΥΠΠΟΑ/ΓΔΔΥ/ΔΟΕΠΥ/275876/40938/377 Υ.Α. (ΦΕΚ 2890/Β/29-10-2014)

χορηγούμε στον κ. Θ. Μαφρέδα, άδεια δειγματοληψίας από τέσσερις φορητές μεταβυζαντινές εικόνες του ιερομόναχου Διονυσίου (όπως αναφέρονται στην αίτηση), που φυλάσσονται στον Ι. Ν. Μεταμορφώσεως του Σωτήρος στο Φουρνά Ευρυτανίας στο πλαίσιο εκπόνησης διπλωματικής εργασίας στο μεταπτυχιακού προγράμματος σπουδών Msc in Cultural Heritage, Materials and Technologies του Τμήματος Ιστορίας, Αρχαιολογίας και Διαχείρισης Πολιτισμικών Αγαθών του Πανεπιστημίου Πελοποννήσου, με σκοπό την ταυτοποίηση των υλικών.

- Να ληφθούν έως δύο τομές ανά εικόνα, μία από χρωματικό στρώμα και μία από στρώμα χρυσώματος που δεν θα υπερβαίνουν τα 2mm. Να ληφθεί επίσης από ένα δείγμα ξύσματος ανά εικόνα από 1) προετοιμασία, 2) χρωματικό στρώμα και 3) βερνίκι βάρους έως 5mg. Τα δείγματα αυτά θα εξεταστούν με τις τεχνικές 1) Οπτική μικροσκοπία, 2) Ηλεκτρονική μικροσκοπία σάρωσης (SEM-EDAX), 3) Φασματοσκοπία Υπερύθρου (FTIR), 4) Αέρια χρωματογραφία (GC) και 5) Υγρή χρωματογραφία υψηλής πίεσης (HPLC) στο εργαστήριο Αρχαιομετρίας του Πανεπιστημίου Πελοποννήσου, στο εργαστήριο φυσικοχημικών ερευνών της Εθνικής Πινακοθήκης και στο εργαστήριο φυσικοχημικών ερευνών του ΤΕΙ Αθήνας.
- Τα δείγματα να αποσπασθούν μηχανικά στις προτεινόμενες περιοχές από τον κ. Θ. Μαφρέδα σε συνεργασία με την δρ. Ε. Κουλουμπή παρουσία συντηρητή της Εφορείας.
- Τα δείγματα θα ληφθούν από περιοχές φθοράς, (π.χ. ακμές απωλειών, ρωγμές κλπ). Δεν θα ληφθούν δείγματα από ακέραιες περιοχές ή από σημεία που διακόπτουν τη συνεχεία των παραστάσεων ή από σημαντικές λεπτομέρειες.
- Οι περιοχές δειγματοληψίας να τεκμηριωθούν με λεπτομέρεια σχεδιαστικά και φωτογραφικά από συντηρητή της Εφορείας και τα τεκμήρια θα ενταχθούν στο φάκελο των εικόνων, ώστε να είναι εφικτή η ανάκληση τους.
- Να διασφαλιστεί η μη εξάντληση του σχετικού υλικού, προκειμένου να υπάρχει διαθέσιμο για μελλοντικές αναλύσεις.
- Σε περίπτωση που εξοικονομηθεί δείγμα μετά το πέρας των αναλύσεων καθώς και τα παράγωγα τους (π.χ. λεπτές τομές), να επιστραφεί στην Εφορεία, κατά τα οριζόμενα στην προαναφερόμενη Εγκύκλιο αναφορικά με τη δημιουργία αρχείων σε ιδρύματα και φορείς εκτός της Αρχαιολογικής Υπηρεσίας, χωρίς έγκριση των αρμοδίων Διευθύνσεων του Υπουργείου Πολιτισμού και Αθλητισμού.
- Η άδεια χορηγείται για δύο χρόνια από την ημερομηνία έκδοσης της απόφασης.
- **Μετά την ολοκλήρωση της μελέτης να κατατεθεί από ένα (1) αντίγραφο των αποτελεσμάτων στην βιβλιοθήκη της ΕΦΑ Φθιώτιδας και Ευρυτανίας και στη Δ/νση Συντήρησης Αρχαίων και Νεωτέρων Μνημείων για ενημέρωση των αρχείων.**

Εσωτερική διανομή
Διεύθυνση Συντήρησης Αρχαίων
και Νεωτέρων Μνημείων

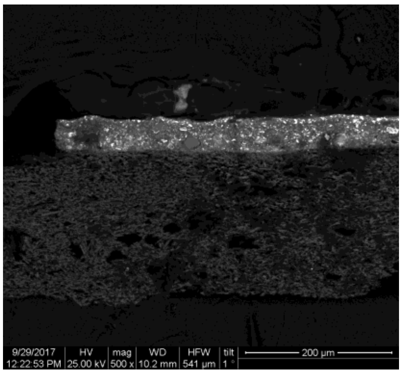
Η Προϊσταμένη της Δ/νσης
Μαρία Μερτζάνη

Ακριβές Αντίγραφο
Κεντρικό Πρωτόκολλο
Μάκα Χαρίκλεια

APPENDIX 2

Obtained Data from SEM/EDX (NCRS Demokritos)

#1, sample: 4



A. Gesso preparation layer

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.82	0.94	0.0015	0.9699	0.2528	1.0021
MgO	1.07	1.88	0.0024	0.9949	0.3659	1.0041
Al2O3	1.20	0.83	0.0031	0.9661	0.5001	1.0078
SiO2	1.22	1.44	0.0036	0.9948	0.6337	1.0141
P2O5	1.18	0.59	0.0038	0.9623	0.7486	1.0246
SO3	54.44	48.19	0.1824	0.9877	0.8380	1.0104
K2O	0.23	0.17	0.0015	0.9465	0.8153	1.0366
CaO	34.99	44.21	0.2100	0.9694	0.8661	1.0001
Fe2O3	0.24	0.10	0.0014	0.8888	0.9482	1.0028
CuO	0.36	0.32	0.0024	0.8615	0.9826	1.0073
HgO2	1.62	0.49	0.0100	0.6839	1.0456	1.0000
PbO	2.65	0.84	0.0172	0.6702	1.0431	1.0000
Total	100.00	100.00				

B. Pigment #1

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.00	0.00	0.0000	1.1701	0.2019	1.0002
MgO	0.00	0.00	0.0000	1.1994	0.2701	1.0005
Al2O3	1.35	2.40	0.0030	1.1639	0.3590	1.0007
SiO2	1.96	5.89	0.0050	1.1974	0.4577	1.0008
P2O5	3.99	5.09	0.0112	1.1573	0.5568	1.0003
K2O	0.27	0.52	0.0012	1.2016	0.4517	1.0016
CaO	3.92	12.64	0.0173	1.2136	0.5099	1.0002
Fe2O3	1.25	1.41	0.0083	1.1068	0.8390	1.0209
CuO	0.97	2.20	0.0082	1.0947	0.9170	1.0628
HgO2	3.61	2.81	0.0283	0.9019	1.0081	1.0000
PbO	82.69	67.04	0.6917	0.8910	1.0114	1.0000
Total	100.00	100.00				

C. Pigment #2 –probably organic

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	1.62	2.85	0.0029	1.0524	0.2306	1.0010

MgO	1.66	4.48	0.0034	1.0792	0.3126	1.0018
Al2O3	1.42	1.51	0.0033	1.0477	0.4149	1.0031
SiO2	2.07	3.74	0.0055	1.0785	0.5274	1.0052
P2O5	0.89	0.68	0.0026	1.0429	0.6324	1.0087
SO3	30.86	41.89	0.0965	1.0700	0.7282	1.0018
K2O	1.46	1.69	0.0074	1.0517	0.5764	1.0047
CaO	8.69	16.84	0.0421	1.0702	0.6336	1.0005
Fe2O3	1.95	1.33	0.0122	0.9793	0.8973	1.0164
CuO	1.18	1.61	0.0090	0.9585	0.9511	1.0480
HgO2	4.62	2.16	0.0317	0.7749	1.0272	1.0000
PbO	43.59	21.23	0.3170	0.7624	1.0276	1.0000
Total	100.00	100.00				

D. Pigment #2

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.97	1.87	0.0019	1.0470	0.2477	1.0011
MgO	1.19	3.53	0.0026	1.0737	0.3386	1.0021
Al2O3	1. 16	1.36	0.0029	1.0424	0.4479	1.0038
SiO2	2.78	5.55	0.0079	1.0730	0.5633	1.0062
P2O5	1.92	1.62	0.0058	1.0376	0.6625	1.0101
SO3	38.39	57.47	0.1228	1.0646	0.7501	1.0000
K2O	0.00	0.00	0.0000	1.0453	0.5604	1.0002
CaO	0.21	0.44	0.0010	1.0640	0.6265	1.0001
Fe2O3	0.40	0.30	0.0026	0.9737	0.9099	1.0217
CuO	0.44	0.66	0.0034	0.9527	0.9598	1.0674
HgO2	47.47	24.46	0.3254	0.7699	1.0326	1.0000
PbO	5.08	2.73	0.0369	0.7574	1.0320	1.0000
Total	100.00	100.00				

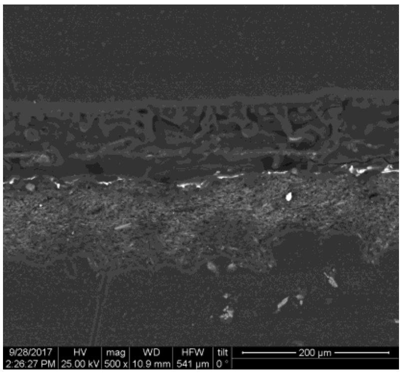
E. Pigment #2

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.46	0.93	0.0009	1.0589	0.2367	1.0009
MgO	0.17	0.54	0.0004	1.0858	0.3242	1.0019
Al2O3	0.42	0.52	0.0010	1.0541	0.4336	1.0035
SiO2	1.60	3.33	0.0045	1.0850	0.5502	1.0060
P2O5	1.67	1.47	0.0050	1.0492	0.6545	1.009
SO3	37.53	58.62	0.1203	1.0764	0.7433	1.0002
K2O	0.17	0.22	0.0008	1.0606	0.5469	1.0006
CaO	1.03	2.31	0.0049	1.0786	0.6108	1.0002
Fe2O3	0.87	0.68	0.0055	0.9867	0.8991	1.0200
CuO	0.63	0.99	0.0049	0.9667	0.9531	1.061
HgO2	29.57	15.90	0.2054	0.7830	1.0287	1.0000
PbO	25.88	14.50	0.1905	0.7707	1.0288	1.0000
Total	100.00	100.00				

F. Pollutants layer

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	1.33	1.56	0.0028	0.9822	0.2836	1.0039
MgO	0.09	0.16	0.0002	1.0074	0.3956	1.0077
Al2O3	11.01	7.88	0.0308	0.9783	0.5332	1.0118
SiO2	64.89	78.80	0.1836	1.0073	0.6006	1.0005
P2O5	0.00	0.00	0.0000	0.9744	0.4618	1.0008
SO3	2.03	1.85	0.0047	1.0001	0.5745	1.0007
K2O	0.89	0.69	0.0052	0.9613	0.7319	1.0019
CaO	1.59	2.07	0.0088	0.9837	0.7880	1.0011
Fe2O3	2.99	1.37	0.0185	0.9017	0.9699	1.0108
CuO	1.22	1.11	0.0086	0.8754	0.9905	1.0267
HgO2	4.07	1.28	0.0257	0.6969	1.0485	1.0000
PbO	9.89	3.23	0.0656	0.6833	1.0454	1.0000
Total	100.00	100.00				

#1, sample: 6A

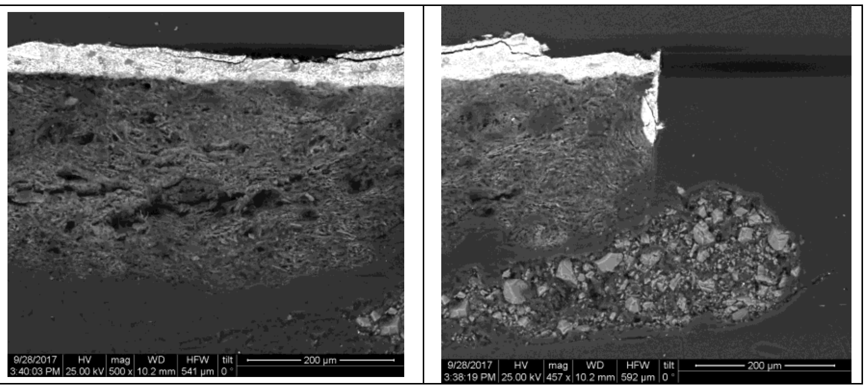


A. Gesso preparation

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.32	0.35	0.0006	0.9652	0.2487	1.0021
MgO	0.42	0.71	0.0009	0.9900	0.3646	1.0043
Al2O3	0.98	0.66	0.0025	0.9614	0.5048	1.0083
SiO2	1.42	1.61	0.0043	0.9900	0.6419	1.0151
P2O5	0.25	0.12	0.0008	0.9577	0.7565	1.0269
SO3	54.70	54.70	0.1856	0.9830	0.8508	1.0133
K2O	0.35	0.26	0.0025	0.9403	0.8525	1.0478
CaO	39.95	48.66	0.2474	0.9635	0.8989	1.0004
Fe2O3	0.96	0.41	0.0056	0.8835	0.9506	1.0011
CuO	0.65	0.56	0.0044	0.8558	0.9832	1.0000
I	100.00	100.00				

B. Bolo layer

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.37	0.43	0.0007	0.9652	0.2602	1.0027
MgO	0.17	0.31	0.0004	0.9900	0.3802	1.0056
Al2O3	9.83	6.88	0.0264	0.9615	0.5243	1.0083
SiO2	15.31	18.20	0.0434	0.9900	0.6061	1.0100
P2O5	0.71	0.36	0.0020	0.9578	0.6501	1.0167
SO3	43.23	38.55	0.1296	0.9831	0.7555	1.0080
K2O	0.59	0.45	0.0040	0.9396	0.8382	1.0302
CaO	25.80	32.85	0.1576	0.9629	0.8864	1.0013
Fe2O3	3.54	1.58	0.0212	0.8830	0.9670	1.0009
CuO	0.44	0.39	0.0030	0.8552	0.9888	1.0000
Total	100.00	100.00				



#2, sample: 9

A. Thick ground preparation

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.00	0.00	0.0000	0.9803	0.2346	1.0019
MgO	0.88	1.32	0.0018	1.0055	0.3437	1.0037
Al2O3	0.37	0.22	0.0009	0.9764	0.4741	1.0073
SiO2	18.80	18.92	0.0545	1.0053	0.6115	1.0077
P2O5	1.07	0.45	0.0029	0.9724	0.6389	1.0129
SO3	1.03	0.78	0.0031	0.9980	0.7303	1.0222
K2O	0.44	0.28	0.0034	0.9591	0.8960	1.0949
CaO	68.92	74.31	0.4504	0.9817	0.9299	1.0017
TiO2	2.65	2.00	0.0110	0.8986	0.7693	1.0006
Fe2O3	0.83	0.31	0.0048	0.8998	0.9163	1.0025
CuO	0.42	0.32	0.0029	0.8728	0.9644	1.0063
Au2O3	1.16	0.16	0.0075	0.7016	1.0364	1.0000
HgO2	1.29	0.34	0.0080	0.6937	1.0361	1.0000
PbO	2.13	0.58	0.0139	0.6800	1.0353	1.0000
Total	100.00	100.00				

B. Ground preparation/ Pb from the pigment layer

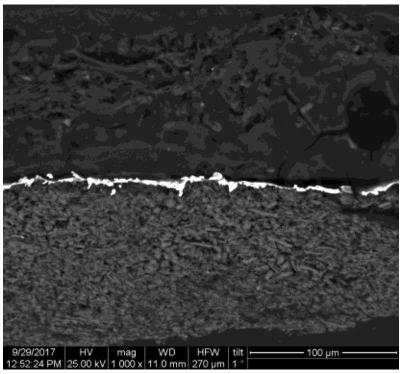
Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.00	0.00	0.0000	0.9892	0.2435	1.0016
MgO	0.75	1.44	0.0016	1.0145	0.3506	1.0032
Al2O3	0.90	0.68	0.0022	0.9852	0.4777	1.0060
SiO2	2.30	2.96	0.0067	1.0143	0.6073	1.0103
P2O5	0.30	0.17	0.0009	0.9811	0.7145	1.0181
SO3	45.67	44.12	0.1449	1.0069	0.7805	1.0077
K2O	0.63	0.52	0.0039	0.9711	0.7437	1.0262
CaO	31.56	43.52	0.1785	0.9930	0.7966	1.0005
TiO2	0.53	0.51	0.0023	0.9079	0.7948	1.0008
Fe2O3	0.71	0.34	0.0042	0.9100	0.9307	1.0080
CuO	0.68	0.66	0.0048	0.8843	0.9721	1.0229
Au2O3	2.49	0.44	0.0165	0.7130	1.0402	1.0000
HgO2	2.15	0.71	0.0136	0.7052	1.0396	1.0000
PbO	11.33	3.93	0.0755	0.6918	1.0380	1.0000

Total	100.00	100.00	

C. Red (HgS) pigment layer

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.91	1.79	0.0017	1.0530	0.2454	1.0011
MgO	1.02	3.10	0.0022	1.0797	0.3350	1.0020
Al2O3	1.24	1.49	0.0031	1.0482	0.4433	1.0037
SiO2	3.11	6.32	0.0088	1.0790	0.5572	1.0058
P2O5	2.04	1.75	0.0061	1.0434	0.6547	1.0094
SO3	36.30	55.32	0.1155	1.0705	0.7423	1.0001
K2O	0.00	0.00	0.0000	1.0531	0.5522	1.0003
CaO	0.45	0.98	0.0021	1.0713	0.6176	1.0001
TiO2	0.07	0.10	0.0003	0.9738	0.7463	1.0001
Fe2O3	0.28	0.21	0.0018	0.9802	0.9043	1.0206
CuO	0.00	0.00	0.0000	0.9598	0.9568	1.0658
Au2O3	0.00	0.00	0.0000	0.7840	1.0312	1.0000
HgO2	40.36	21.17	0.2787	0.7766	1.0312	1.0000
PbO	14.22	7.78	0.1040	0.7642	1.0309	1.0000
Total	100.00	100.00				

#3, sample: 11A



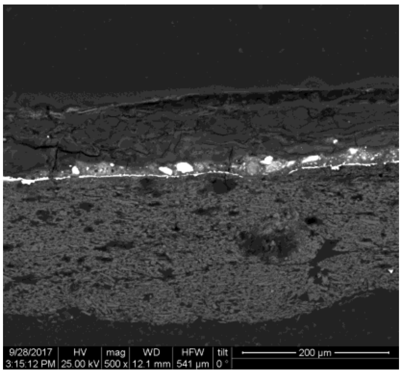
A. Gesso preparation

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.74	0.82	0.0013	0.9662	0.2528	1.0022
MgO	1.31	2.24	0.0029	0.9911	0.3679	1.0042
Al2O3	1.10	0.74	0.0029	0.9625	0.5025	1.0081
SiO2	2.00	2.29	0.0060	0.9911	0.6381	1.0145
P2O5	1.22	0.59	0.0039	0.9587	0.7491	1.0253
SO3	53.46	45.90	0.1789	0.9840	0.8391	1.0120
K2O	0.35	0.26	0.0024	0.9417	0.8407	1.0432
CaO	37.72	46.23	0.2311	0.9648	0.8884	1.0002
Fe2O3	0.39	0.17	0.0023	0.8847	0.9508	1.0015
CuO	0.45	0.39	0.0030	0.8571	0.9839	1.0022
HgO2	0.59	0.18	0.0036	0.6796	1.0462	1.0000
PbO	0.67	0.21	0.0043	0.6659	1.0436	1.0000
Total	100.00	100.00				

B. Bolo layer

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.87	1.09	0.0017	0.9762	0.2633	1.0030
MgO	0.44	0.84	0.0010	1.0013	0.3769	1.0059
Al2O3	16.72	12.65	0.0446	0.9724	0.5143	1.0071
SiO2	23.20	29.80	0.0609	1.0012	0.5578	1.0057
P2O5	2.37	1.29	0.0058	0.9686	0.5768	1.0089
SO3	26.58	25.62	0.0723	0.9941	0.6801	1.0045
K2O	0.71	0.58	0.0045	0.9530	0.7890	1.0169
CaO	16.39	22.55	0.0963	0.9759	0.8411	1.0018
Fe2O3	5.17	2.50	0.0314	0.8948	0.9667	1.0056
CuO	0.84	0.82	0.0058	0.8676	0.9864	1.0126
HgO2	3.69	1.22	0.0229	0.6891	1.0469	1.0000
PbO	3.02 0	1.04	0.0197	0.6754	1.0442	1.0000
Total	100.00	100.00				

#3, sample: 13



A. Gesso preparation

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.29	0.33	0.0005	0.9683	0.2475	1.0019
MgO	0.32	0.56	0.0007	0.9932	0.3616	1.0040
Al2O3	0.50	0.35	0.0013	0.9645	0.5005	1.0077
SiO2	0.87	1.02	0.0026	0.9932	0.6395	1.0142
P2O5	0.71	0.35	0.0023	0.9607	0.7568	1.0251
SO3	55.11	48.41	0.1801	1.0115	0.8183	1.0115
K2O	0.37	0.27	0.0025	0.9443	0.8332	1.0418
CaO	37.47	46.99	0.2284	0.9673	0.8814	1.0005
Fe2O3	1.09	0.48	0.0064	0.8869	0.9494	1.0032
CuO	1.00	0.88	0.0068	0.8595	0.9823	1.0050
Au2O3	2.28	0.36	0.0147	0.6897	1.0460	1.0000
Total	100.00	100.00				

B. Bolo layer

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.55	0.69	0.0011	0.9765	0.2738	1.0034
MgO	0.47	0.91	0.0011	1.0016	0.3930	1.0067
Al2O3	21.16	16.24	0.0584	0.9727	0.5324	1.0073
SiO2	31.92	41.56	0.0823	1.0016	0.5490	1.0036
P2O5	0.55	0.30	0.0013	0.9689	0.5369	1.0057
SO3	19.74	19.29	0.0462	0.9944	0.5853	1.0031
K2O	0.78	0.64	0.0049	0.9532	0.7826	1.0118
CaO	11.36	15.84	0.0662	0.9761	0.8347	1.0018
Fe2O3	5.30	2.60	0.0325	0.8950	0.9724	1.0074
CuO	0.59	0.58	0.0042	0.8678	0.9893	1.0190
Au2O3	7.58	1.34	0.0495	0.6972	1.0501	1.0000
Total	100.00	100.00				

C. External pollutants layer

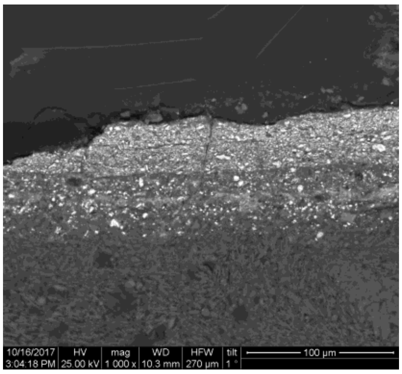
Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.00	0.00	0.0000	0.9732	0.2691	1.0036
MgO	2.83	5.31	0.0067	0.9983	0.3909	1.0067

Al2O3	15.83	11.72	0.0423	0.9695	0.5161	1.0087
SiO2	39.48	49.60	0.1042	0.9983	0.5638	1.0036
P2O5	4.40	2.34	0.0097	0.9657	0.5201	1.0046
SO3	13.18	12.43	0.0309	0.9912	0.5889	1.0034
K2O	3.75	3.01	0.0241	0.9487	0.8073	1.0093
CaO	7.56	10.17	0.0443	0.9718	0.8426	1.0030
Fe2O3	8.23	3.89	0.0505	0.8912	0.9806	1.0053
CuO	0.94	0.89	0.0065	0.8636	0.9901	1.0096
Au2O3	3.79	0.65	0.0246	0.6930	1.0502	1.0000
Total	100.00	100.00				

D. Thin pigment layer over the gold leaf

Elem	**Wt %**	**Mol %**	**K-Ratio**	**Z**	**A**	**F**
Na2O	0.14	0.29	0.0003	1.0586	0.2395	1.0009
MgO	0.37	1.15	0.0008	1.0855	0.3298	1.0018
Al2O3	1.93	2.35	0.0048	1.0538	0.4399	1.0032
SiO2	3.57	7.37	0.0100	1.0847	0.5501	1.0048
P2O5	1.17	1.02	0.0035	1.0489	0.6460	1.0079
SO3	31.58	48.96	0.0951	1.0761	0.6986	1.0006
K2O	0.10	0.13	0.0005	1.0600	0.5523	1.0019
CaO	3.61	7.99	0.0172	1.0781	0.6167	1.0003
Fe2O3	1.19	0.92	0.0075	0.9863	0.9001	1.0212
CuO	0.45	0.71	0.0036	0.9661	0.9534	1.0655
Au2O3	4.04	1.13	0.0293	0.7897	1.0288	1.0000
HgO2	38.11	20.34	0.2646	0.7823	1.0290	1.0000
PbO	13.75	7.65	0.1011	0.7700	1.0291	1.0000
Total	100.00	100.00				

#4, sample: 19A



A. Gesso preparation layer

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.43	0.47	0.0008	0.9636	0.2549	1.0022
MgO	0.91	1.53	0.0020	0.9884	0.3737	1.0045
Al2O3	1.29	0.86	0.0034	0.9599	0.5127	1.0085
SiO2	2.16	2.44	0.0066	0.9884	0.6480	1.0153
P2O5	0.61	0.29	0.0020	0.9562	0.7575	1.0269
SO3	55.73	47.30	0.1885	0.9814	0.8497	1.0127
CaO	38.88	47.11	0.2401	0.9617	0.8984	1.0000
Total	100.00	100.00				

B. Flesh

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.30	0.47	0.0005	1.0675	0.2146	1.0007
MgO	1.72	4.16	0.0034	1.0946	0.2969	1.0012
Al2O3	2.18	2.09	0.0049	1.0626	0.3957	1.0020
SiO2	7.00	11.37	0.0181	1.0937	0.5035	1.0019
P2O5	0.96	0.66	0.0026	1.0575	0.5900	1.0031
CaO	32.14	55.91	0.1639	1.0884	0.6551	1.0010
Fe2O3	5.75	3.51	0.0356	0.9955	0.8766	1.0136
PbO	49.95	21.83	0.3683	0.7777	1.0213	1.0000
Total	100.00	100.00				

C. Yellow line

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.25	0.45	0.0004	1.1011	0.2141	1.0007
MgO	4.21	11.89	0.0084	1.1289	0.2916	1.0008
Al2O3	2.00	2.24	0.0044	1.0957	0.3764	1.0013
SiO2	5.65	10.71	0.0143	1.1276	0.4797	1.0010
P2O5	0.75	0.60	0.0020	1.0902	0.5698	1.0016
CaO	19.00	38.57	0.0910	1.1295	0.5929	1.0006
Fe2O3	3.97	2.83	0.0252	1.0321	0.8645	1.0164
PbO	64.16	32.71	0.4946	0.8154	1.0184	1.0000

Total	100.00	100.00	

D. Flesh over the yellow line

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.00	0.00	0.0000	1.0854	0.2142	1.0007
MgO	1.69	4.54	0.0033	1.1129	0.2946	1.0012
Al2O3	2.87	3.06	0.0064	1.0803	0.3905	1.0018
SiO2	8.29	14.96	0.0213	1.1118	0.4931	1.0013
P2O5	0.71	0.54	0.0019	1.0750	0.5739	1.0021
CaO	23.43	45.31	0.1151	1.1103	0.6181	1.0008
Fe2O3	5.11	3.47	0.0321	1.0151	0.8710	1.0153
PbO	57.90	28.13	0.4373	0.7979	1.0198	1.0000
Total	100.00	100.00				

E. Over layer of sample

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	0.00	0.00	0.0000	1.1506	0.2092	1.0006
MgO	0.46	1.87	0.0009	1.1795	0.2809	1.0011
Al2O3	5.40	8.66	0.0122	1.1446	0.3714	1.0011
SiO2	8.11	22.05	0.0204	1.1777	0.4581	1.0002
P2O5	0.66	0.76	0.0018	1.1384	0.5373	1.0011
CaO	1.57	4.59	0.0070	1.1899	0.5244	1.0003
Fe2O3	2.36	2.41	0.0155	1.0858	0.8494	1.0196
PbO	81.44	59.66	0.6674	0.8701	1.0145	1.0000
Total	100.00	100.00				

APPENDIX 3

Sampling positions from 4 panel paintings

SAMPLING POSITIONS FROM 4 PANEL PAINTINGS OF DIONYSIUS FROM FOURNA

# sample	# Panel	Kind of sample	Area	Kind of Analysis	Technique	Comments
1	1	Gesso preparation powder	Bottom Left, low, in the horizontal frame of the panel	Investigation for protein elements	GC	
1α	1	Gesso preparation powder	Bottom Left, low, in the horizontal frame of the panel	Investigation for protein elements	**FTIR**	
2	1	Varnish powder	Bottom right, 1/4 of the image from below	Characterization of varnish	**FTIR**	
3	1	Cross section	Bottom center, low, in the horizontal frame of the panel	Study of the pigment layer	**OM SEM/EDX**	The sample was failed
4	1	Cross section	Bottom Left, low, in the horizontal frame of the panel	Study of the pigment layer	**OM SEM/EDX**	Cross section for painting layer
4a	1	Cross section	Bottom Left, low, in the horizontal frame of the panel	Study of the pigment layer	OM SEM/EDX	Cross section for painting layer
5	1	Pigment powder	Bottom left, 1/4 of the image from below	Study of the pigment layer	GC	
5a	1	Pigment powder	Bottom left, 1/4 of the image from below	Study of the pigment layer	GC	
6	1	Cross section	Bottom Left, low, in the horizontal frame of the panel	Study of gilding technique	OM SEM/EDX	
6α	1	Cross section	Bottom Left, low, in the horizontal frame of the panel	Study of gilding technique	**OM SEM/EDX**	
7	2	Gesso preparation powder	Bottom Left, low, in the horizontal frame of the panel	Investigation for protein elements	GC	
7α	2	Gesso preparation powder	Bottom Left, low, in the horizontal frame of the panel	Investigation for protein elements	**FTIR**	
8***	2	Pigment powder	Bottom left, near to the end of the vertical frame	Study of the pigment layer	**FTIR**	

8a	2	Pigment powder	Right vertical frame, at the half of the panel	Study of the pigment layer	GC	
9	2	Cross section	Bottom Left, low, in the horizontal frame of the panel	Study of the pigment layer	**OM** **SEM/EDX**	
9α	2	Cross section	Bottom Left, low, in the horizontal frame of the panel	Study of the pigment layer	OM SEM/EDX	
10	2	Cross section	Upper horizontal frame. On the middle of the panel	Study of the pigment layer	**OM** SEM/EDX	
10a	2	Varnish powder	Upper horizontal frame. On the middle of the panel	Characterization of varnish	**FTIR**	
11	3	Cross section	Right up, in the vertical frame of panel	Study of gilding technique	OM SEM/EDX	
11a	3	Cross section	Bottom right, in the horizontal and vertical frame joint	Study of gilding technique	**OM** **SEM/EDX**	
12	3	Gesso preparation powder	Bottom right, in the horizontal and vertical frame joint	Investigation for protein elements	**FTIR**	
12a	3	Gesso preparation powder	Bottom right, in the horizontal and vertical frame joint	Investigation for protein elements	GC	
13	3	Cross section	Bottom right, in the horizontal and vertical frame joint	Study of the pigment layer	**OM** **SEM/EDX**	The sample consisted also of red pigment and gold leaf
14	3	Varnish powder	In the middle of the painting surface, under the scroll	Characterization of varnish	**FTIR**	
14a	3	Varnish powder	Bottom left, in vertical frame of panel, near to Forerunners' head	Characterization of varnish	GC	
15	3	Pigment powder	Bottom left, in vertical frame of panel, near to Forerunners' head	Study of the pigment layer	GC	

16	4	Gesso preparation powder	Upper horizontal frame of panel, next to Christ's glory.	Investigation for protein elements	GC	
16a	4	Gesso preparation powder	Upper horizontal frame of panel, next to Christ's glory.	Investigation for protein elements	**FTIR**	
17	4	Varnish powder	Bottom left low, in the vertical frame of the panel	Characterization of varnish	**FTIR**	Powder from the edge of the area
18	4	Pigment powder	Bottom right. At 1/3 from below, on the vertical side of the panel	Study of the pigment layer	GC	Red pigment layer
19	4	Cross section	Bottom left low, in the vertical frame of the panel	Study of the pigment layer	OM SEM/EDX	
19α	4	Cross section	At the foot of Apostle Peter	Study of the pigment layer	**OM** **SEM/EDX**	
19β	4	Cross section	In the garment of St. Peter	Study of the pigment layer	**OM** **SEM/EDX**	
20	4	Cross section	Upper horizontal frame of panel, next to Christ's glory	Study of the pigment layer	OM SEM/EDX	

Comments during sampling process

1. During sampling process it was observed that the painting layers were very thins
2. In panel painting #2 the painting layer is extremely thin
3. In panel painting #3 the painting layer (sampling position no 13) is thicker than the pigment layers in the other panel paintings
4. From sampling position 8 of panel #2 was received varnish which removed with cotton swap in Acetone solution. A refining process was performed to obtain the varnish in order to be characterized through FTIR analysis

PANEL PAINTINGS SAMPLING POSITIONS

Panel #1 Sampling positions *(personal archive Th. Mafredas)*

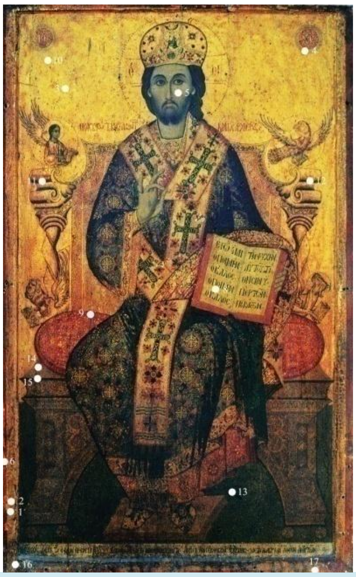
Panel #2 Sampling positions *(personal archive Th. Mafredas)*

Panel #3 Sampling positions *(personal archive Th. Mafredas)*

Panel #4 Sampling positions *(personal archive Th. Mafredas)*

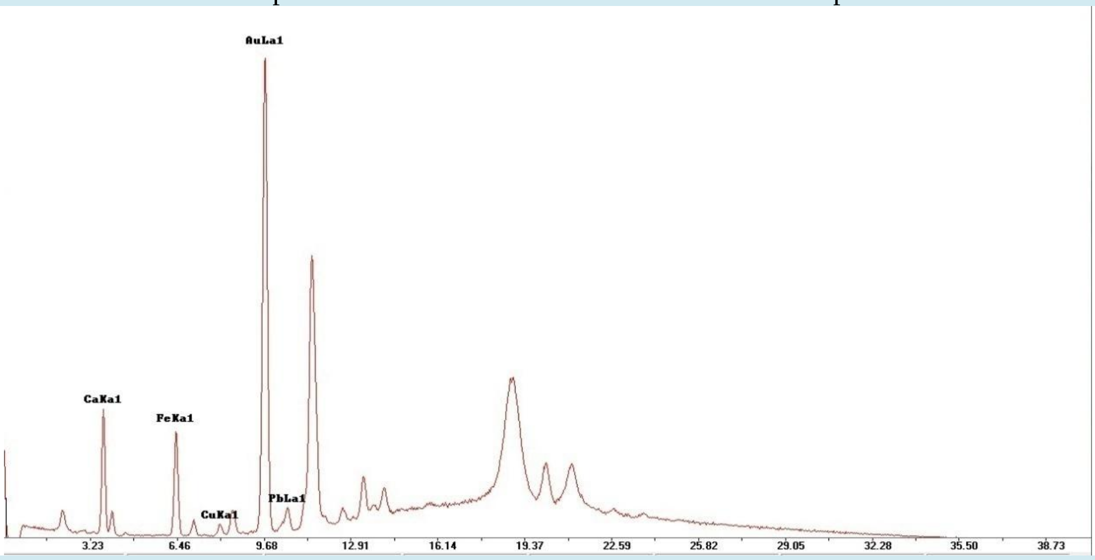
APPENDIX 4

Obtained XRF spectra from Dionysius' Panel paintings

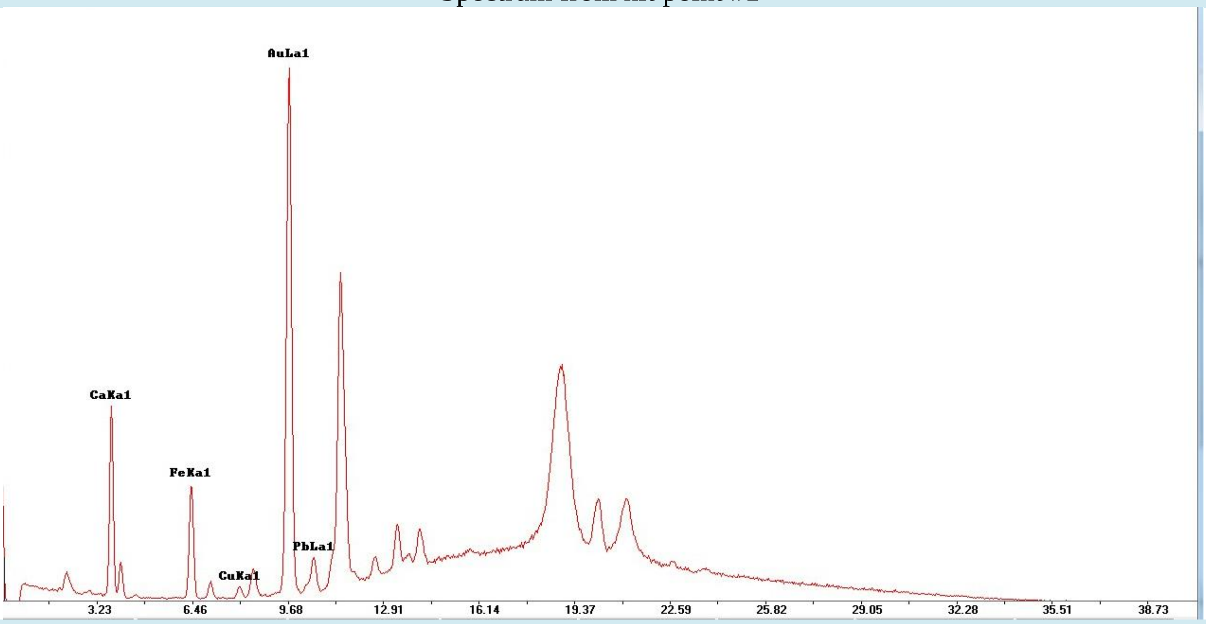


Panel #1 XRF Hit points

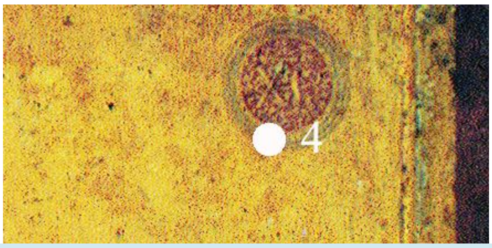
Panel #1. Hit points 1-2



Spectrum from hit point #1

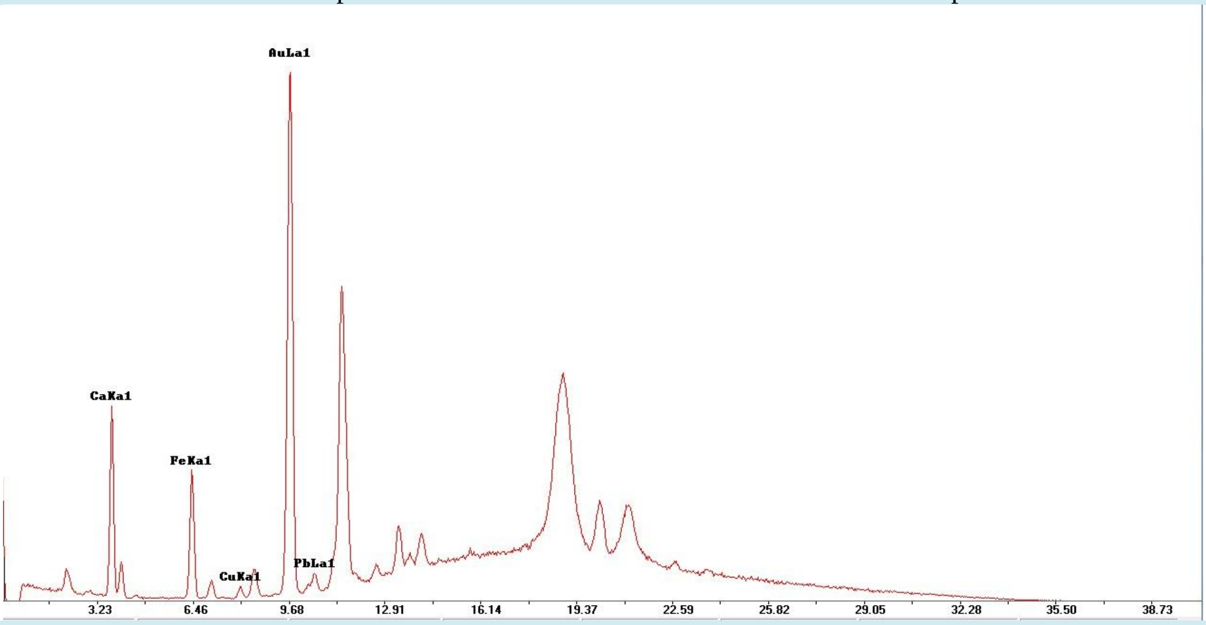


Spectrum from hit point #2

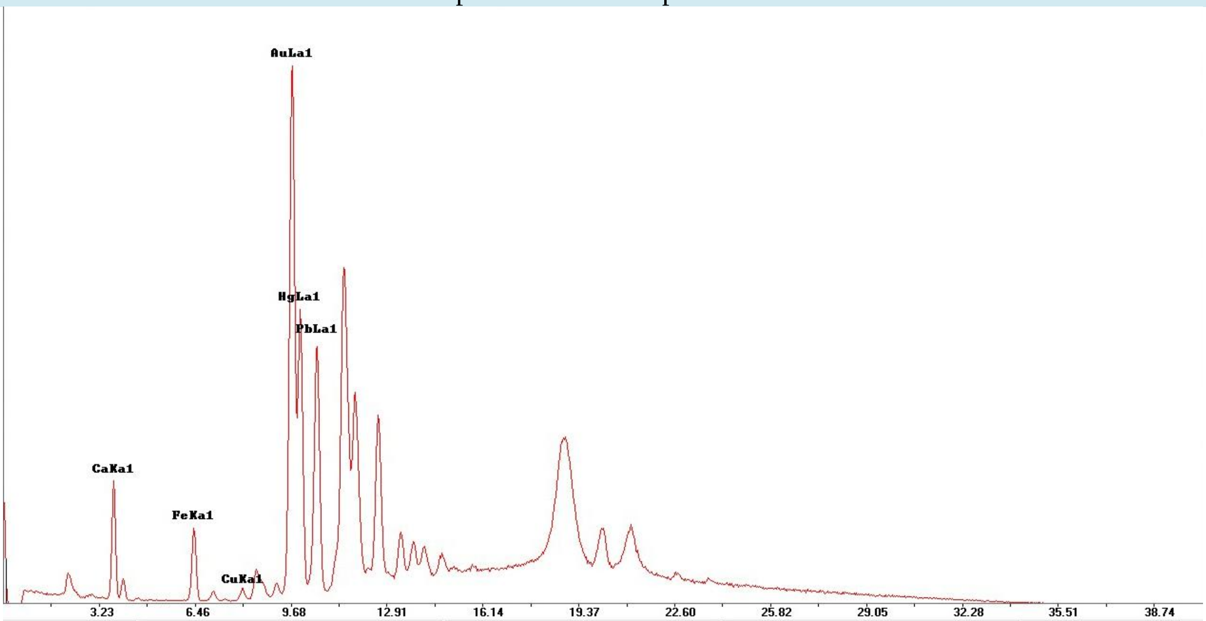


Panel #1. Hit point 3

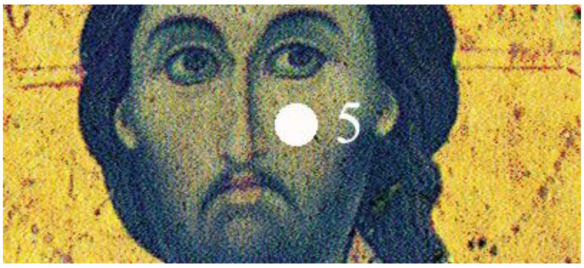
Panel #1. Hit point 4



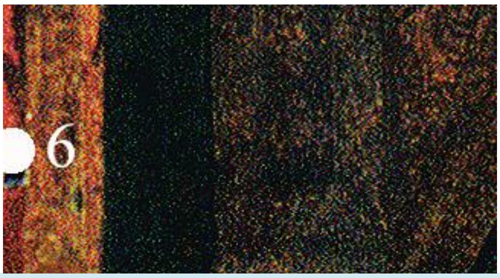
Spectrum from hit point #3



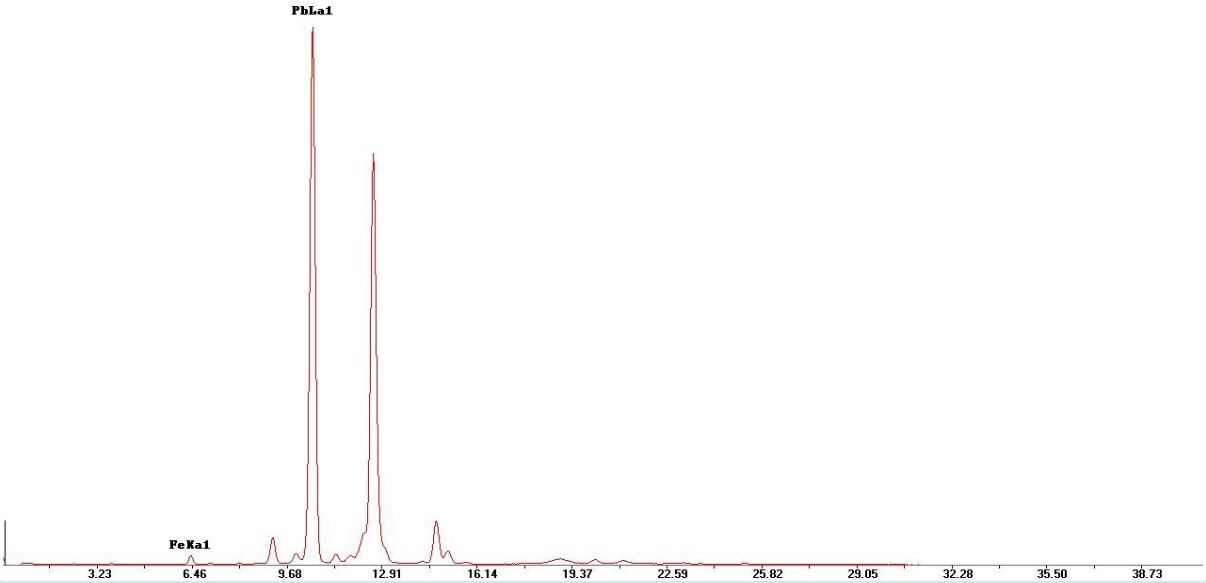
Spectrum from hit point #4



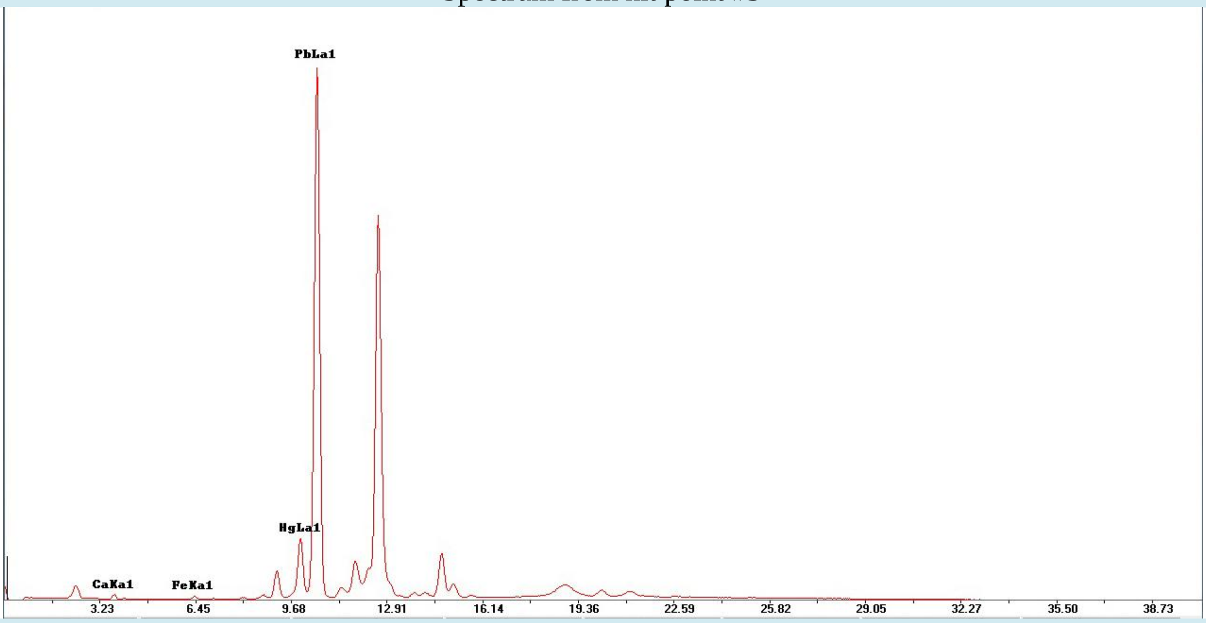
Panel #1. Hit point 5



Panel #1. Hit point 6

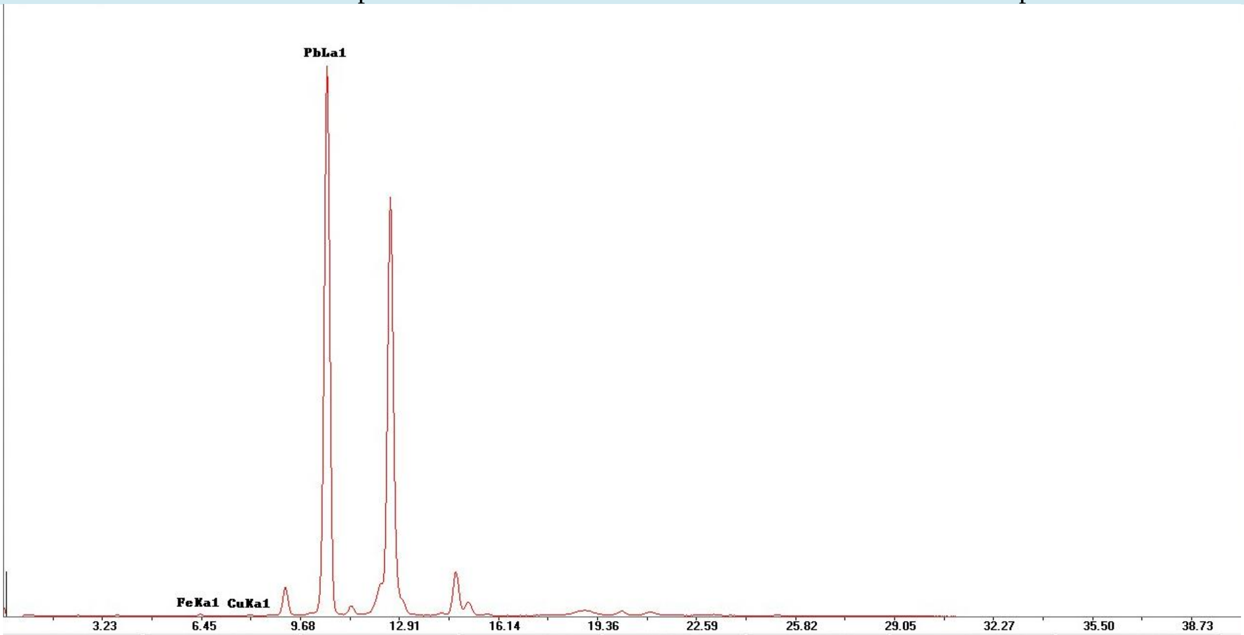


Spectrum from hit point #5

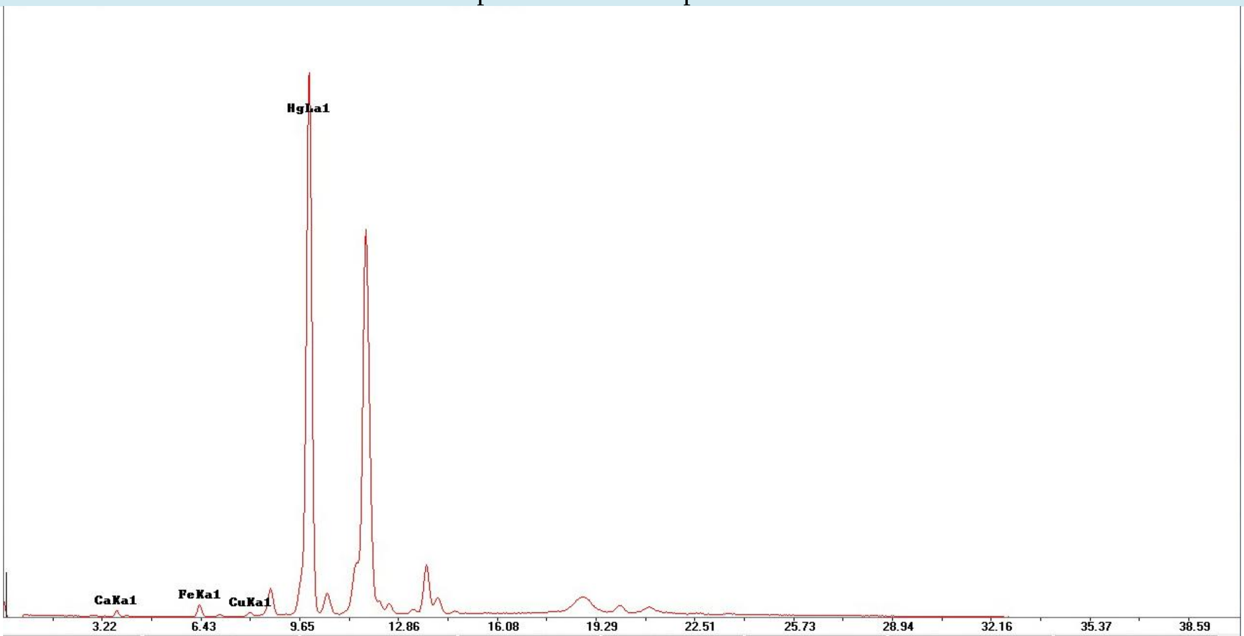


Spectrum from hit point #6

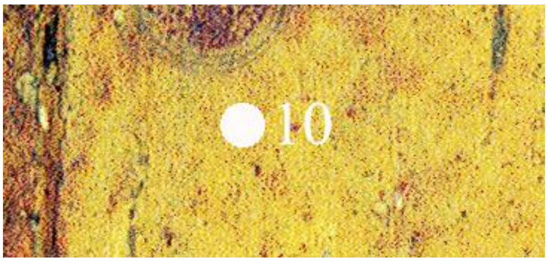
Panel #1. Hit point 8 | Panel #1. Hit point 9



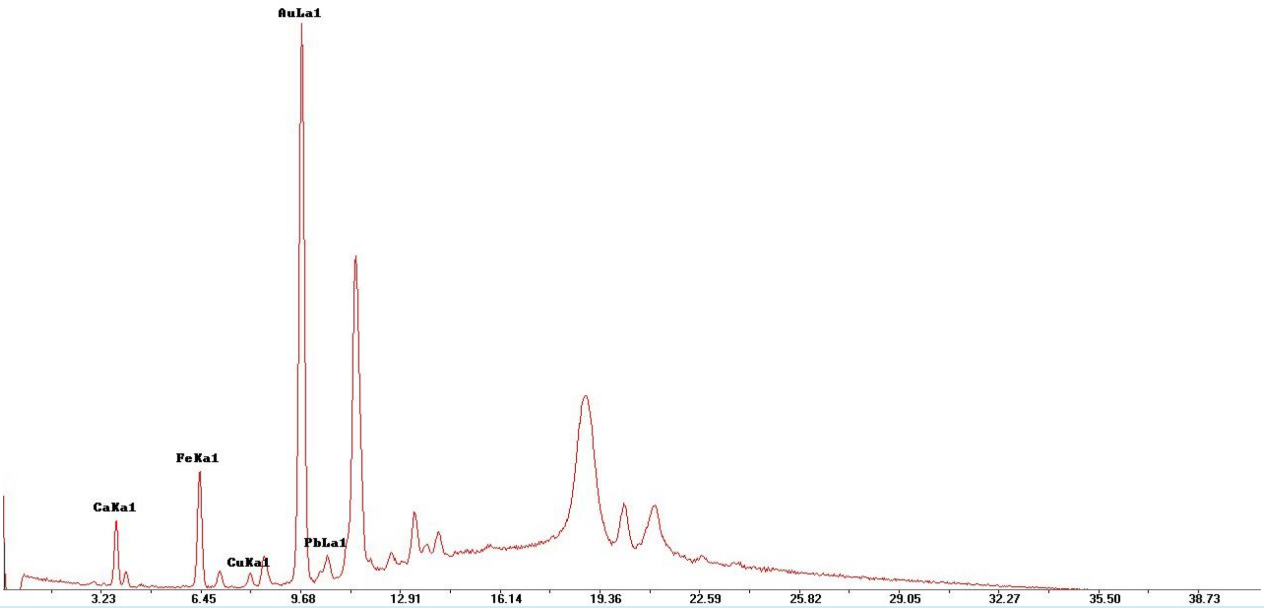
Spectrum from hit point #8



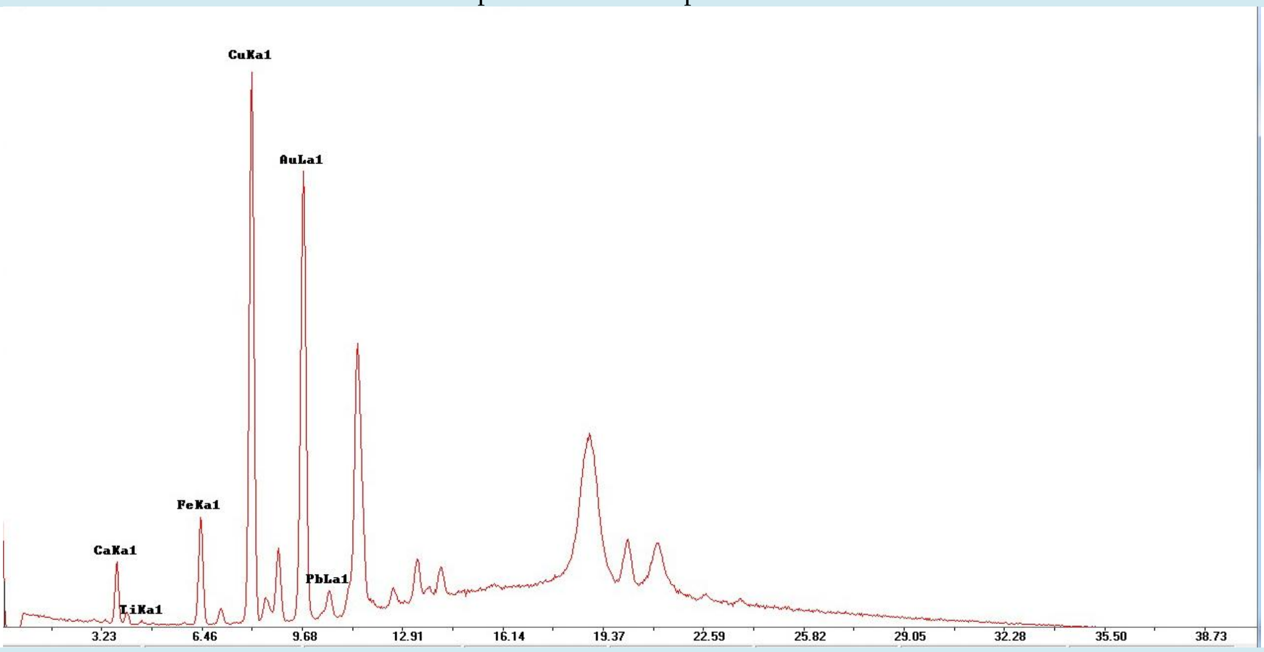
Spectrum from hit point #9



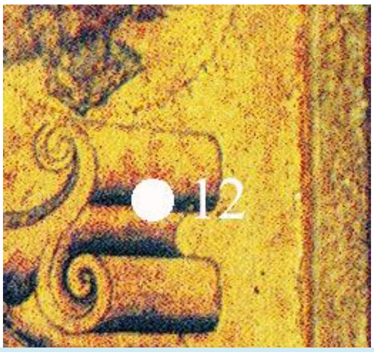
Panel #1. Hit point 10 | Panel #1. Hit point 11



Spectrum from hit point #10

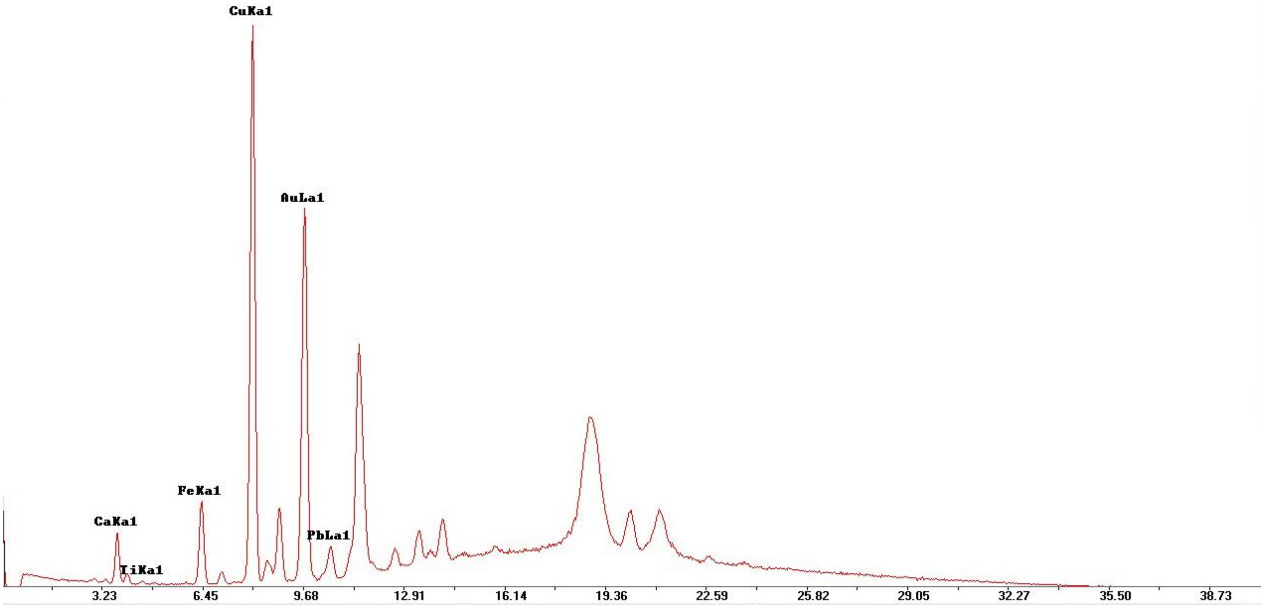


Spectrum from hit point #11

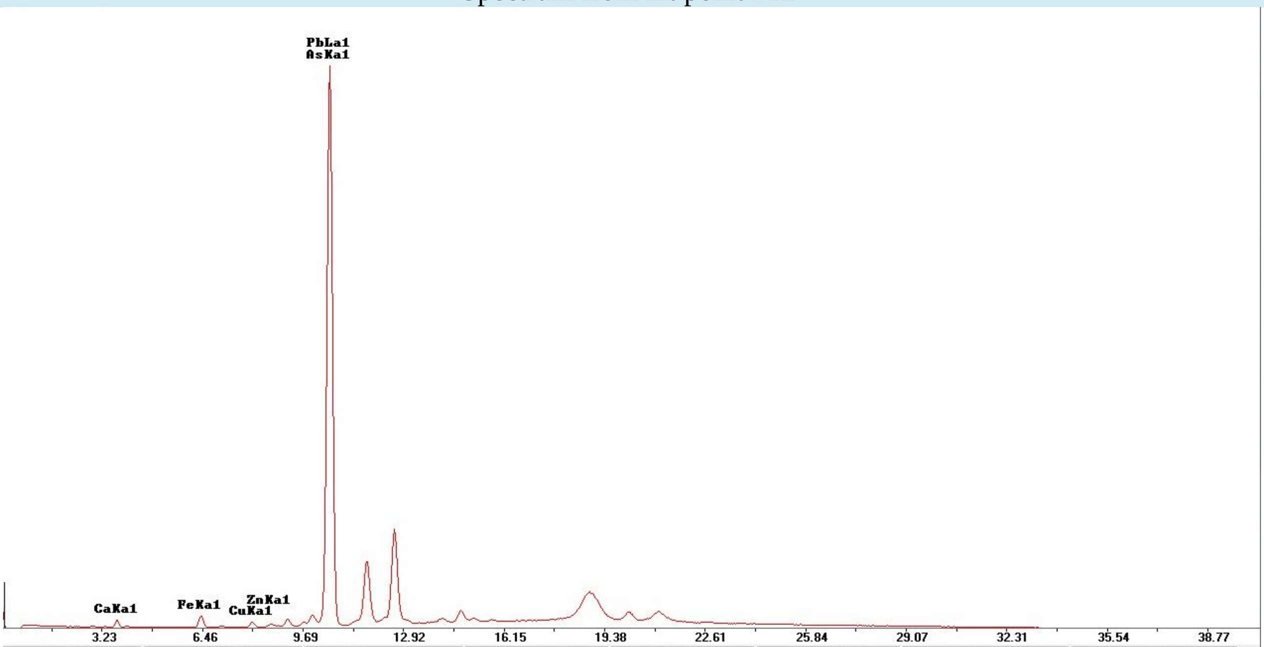


Panel #1. Hit point 12

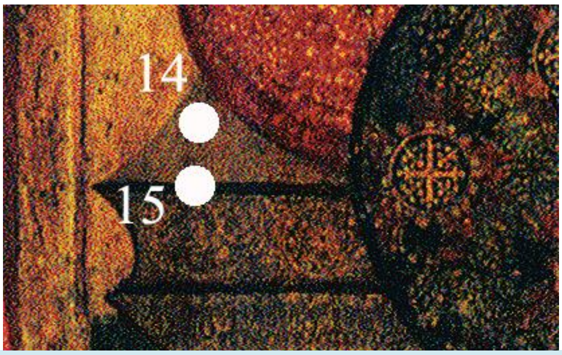
Panel #1. Hit point 13



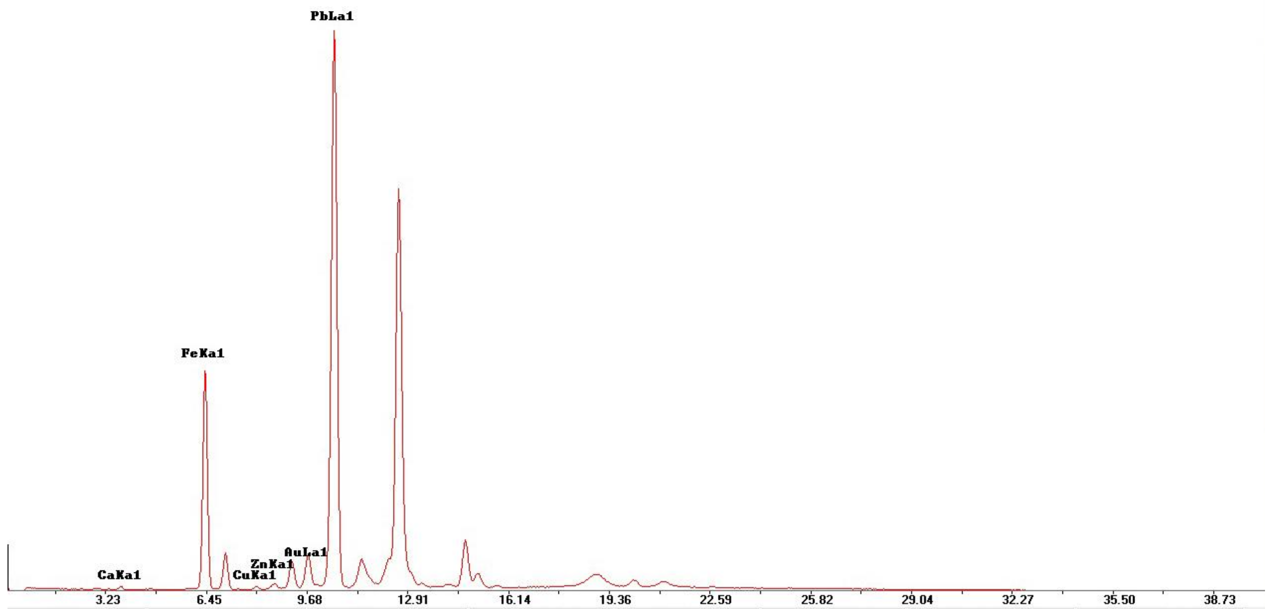
Spectrum from hit point #12



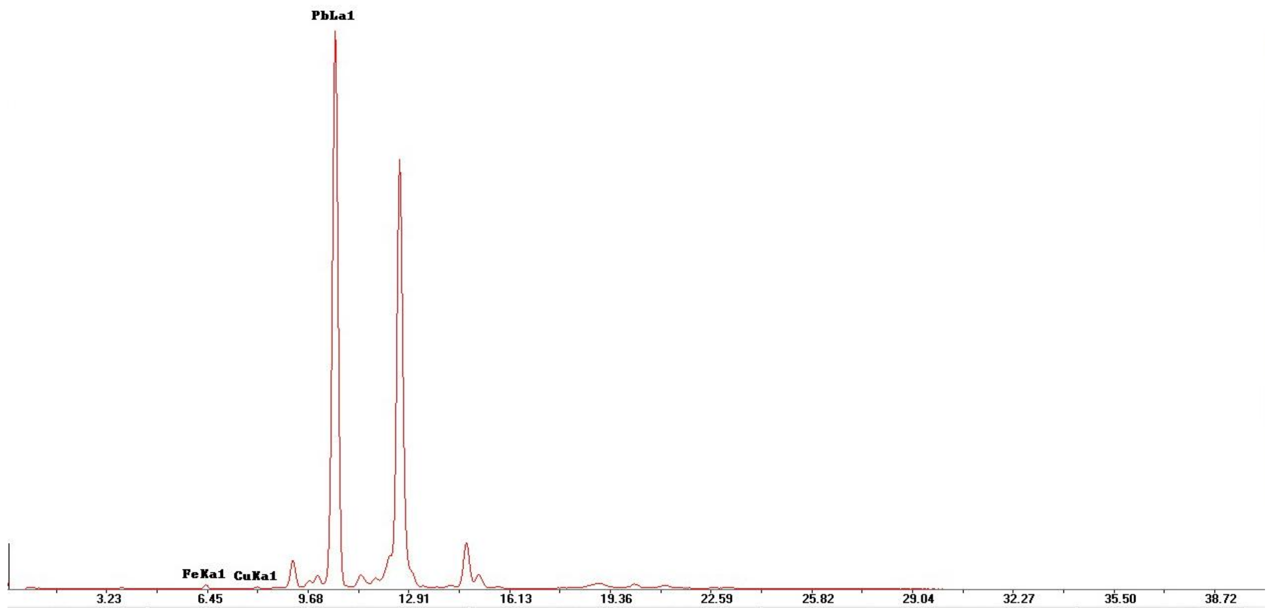
Spectrum from hit point #13



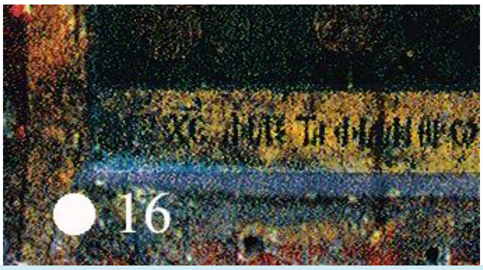
Panel #1. Hit point 14-15

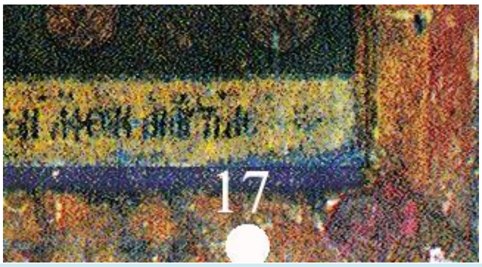


Spectrum from hit point #14



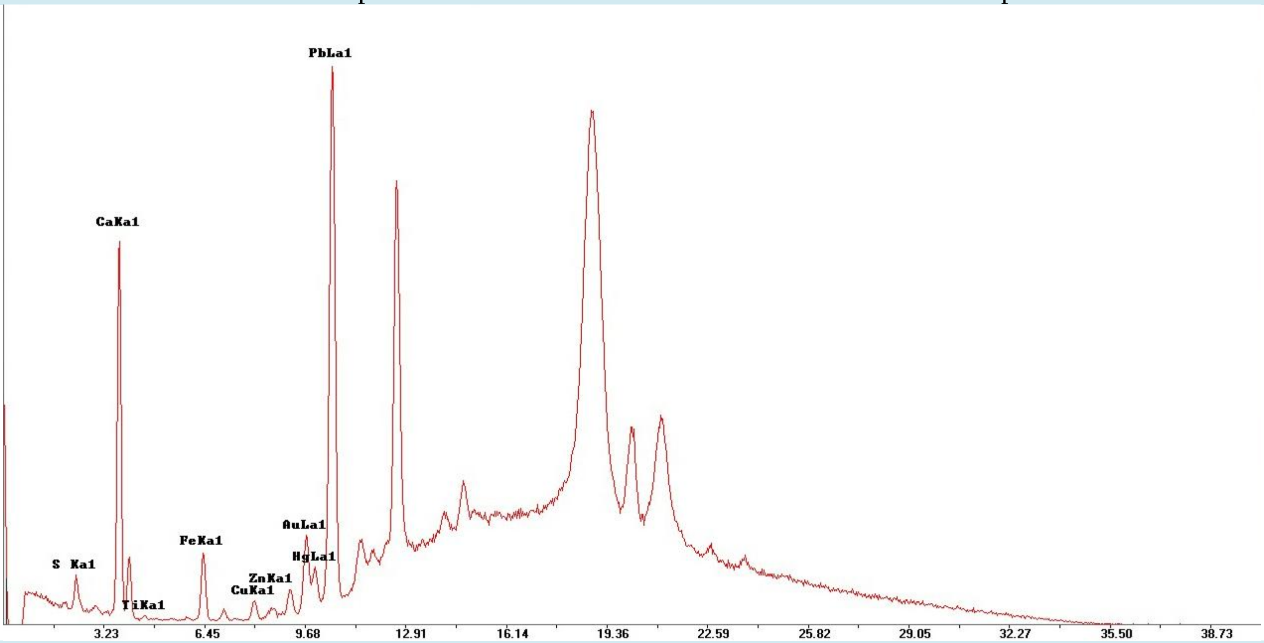
Spectrum from hit point #15



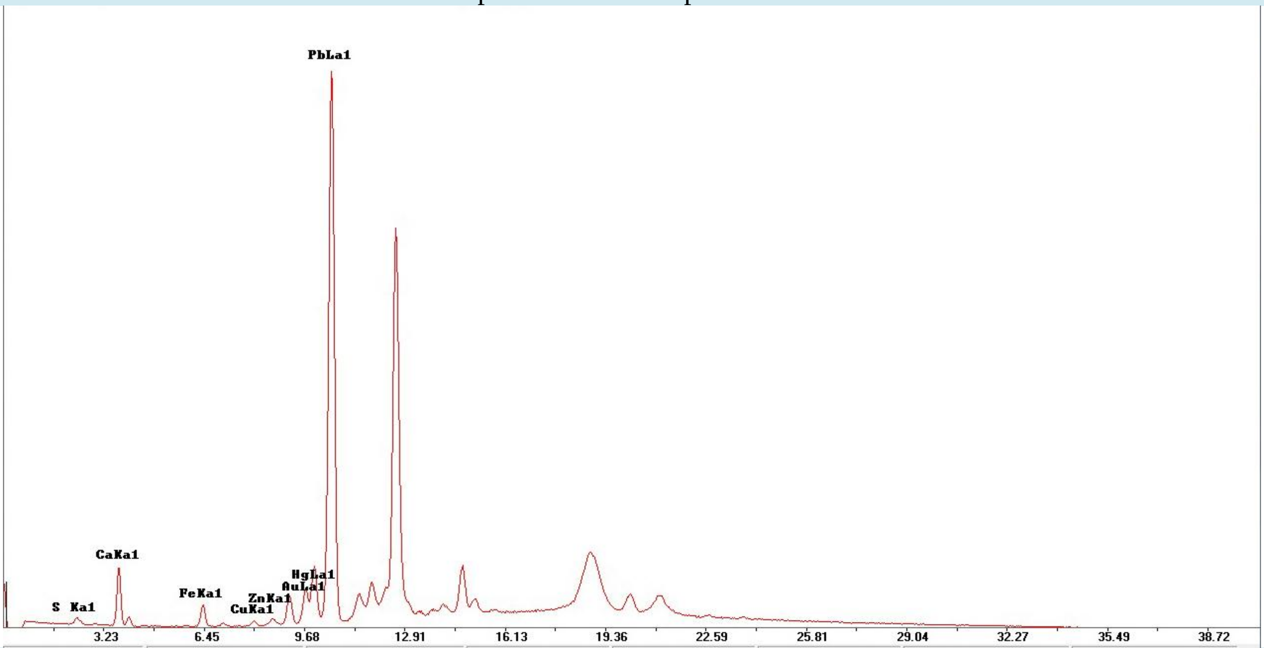


Panel #1. Hit point 16

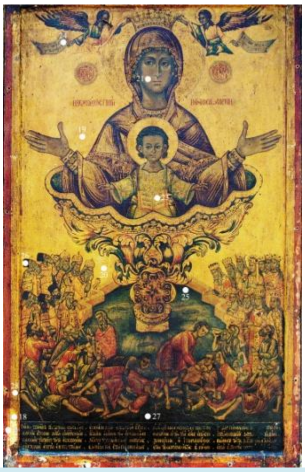
Panel #1. Hit point 17



Spectrum from hit point #16

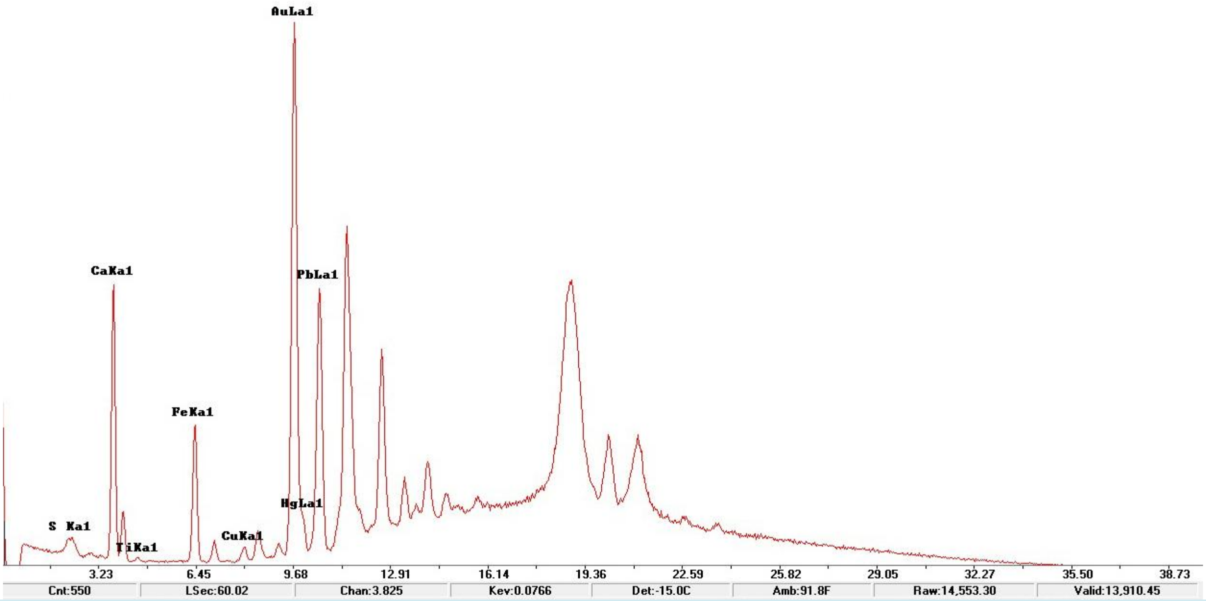


Spectrum from hit point #17



Panel #2 XRF Hit points

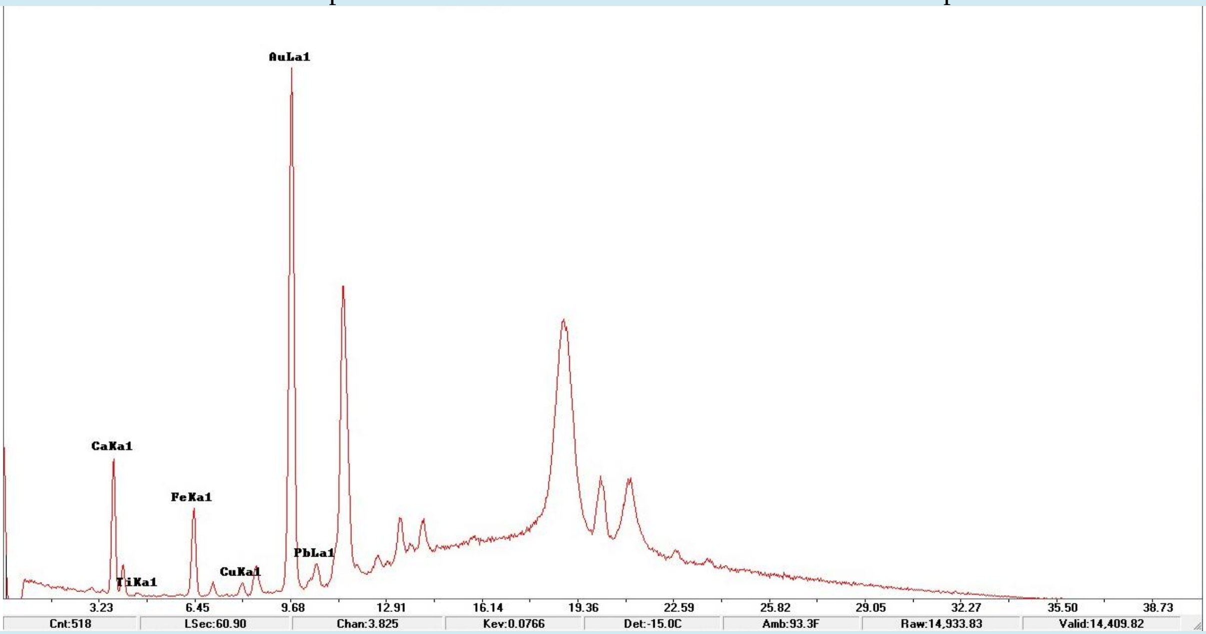
Panel #2. Hit point 18



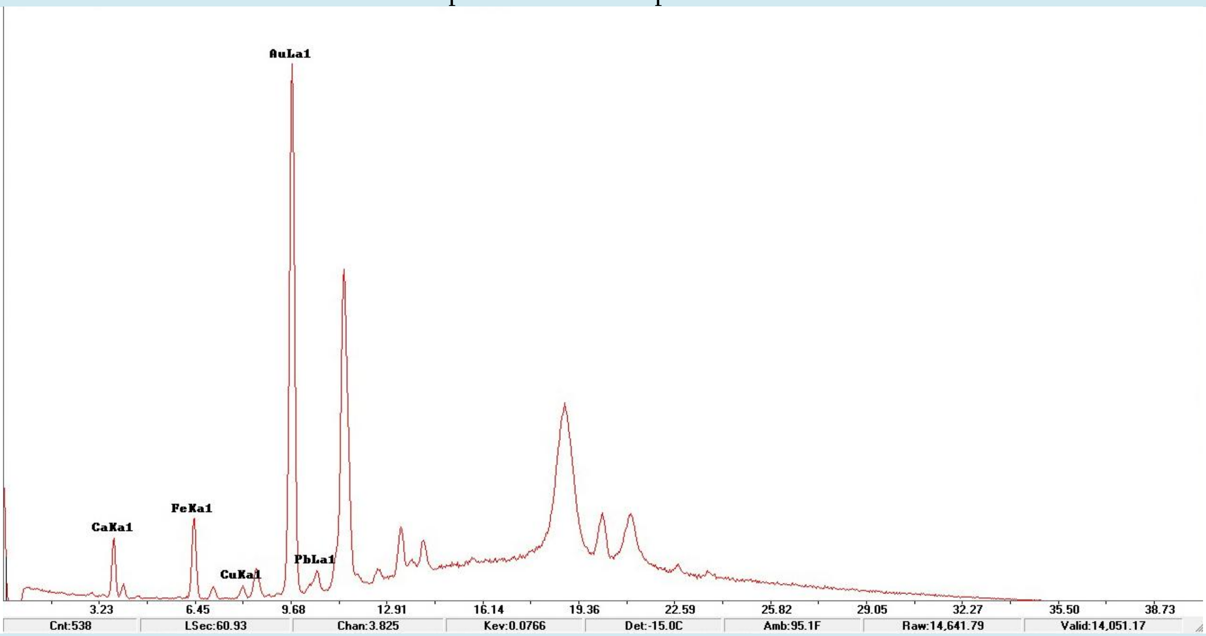
Spectrum from hit point #18

Panel #2. Hit point 19

Panel #2. Hit point 20



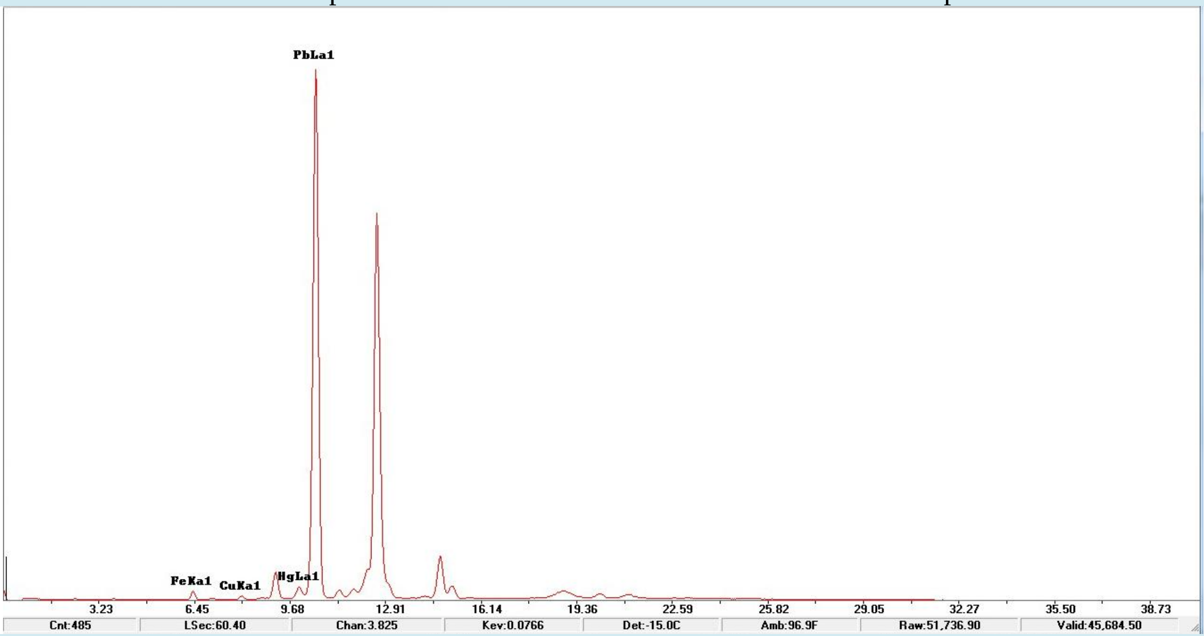
Spectrum from hit point #19



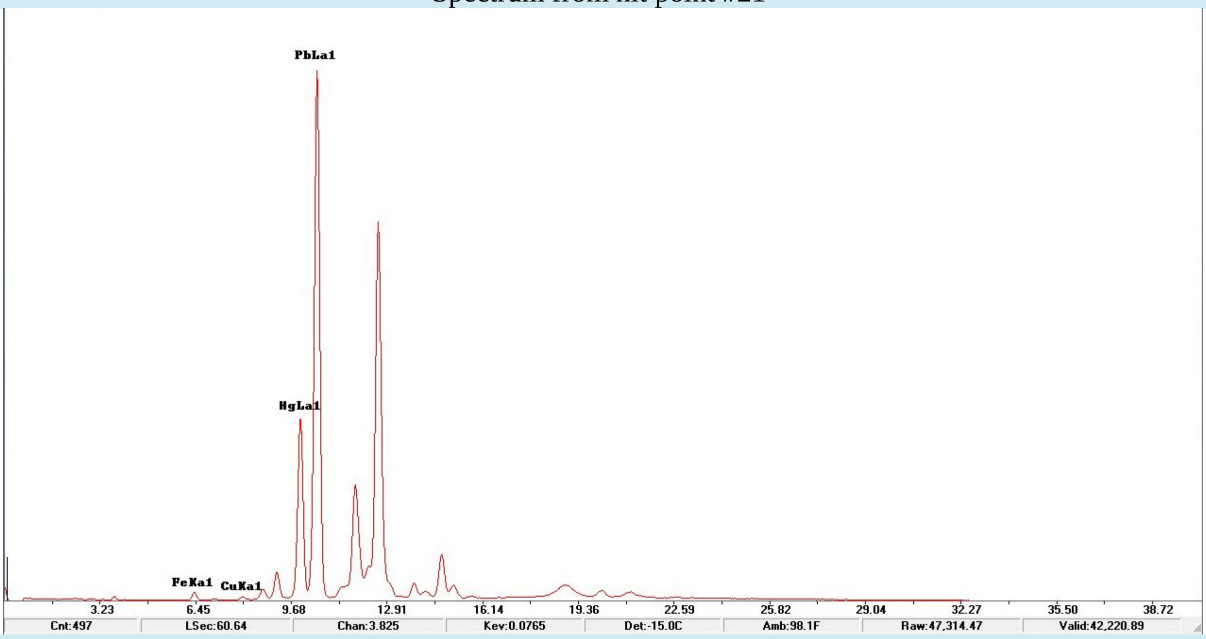
Spectrum from hit point #20

Panel #2. Hit point 21

Panel #2. Hit point 22

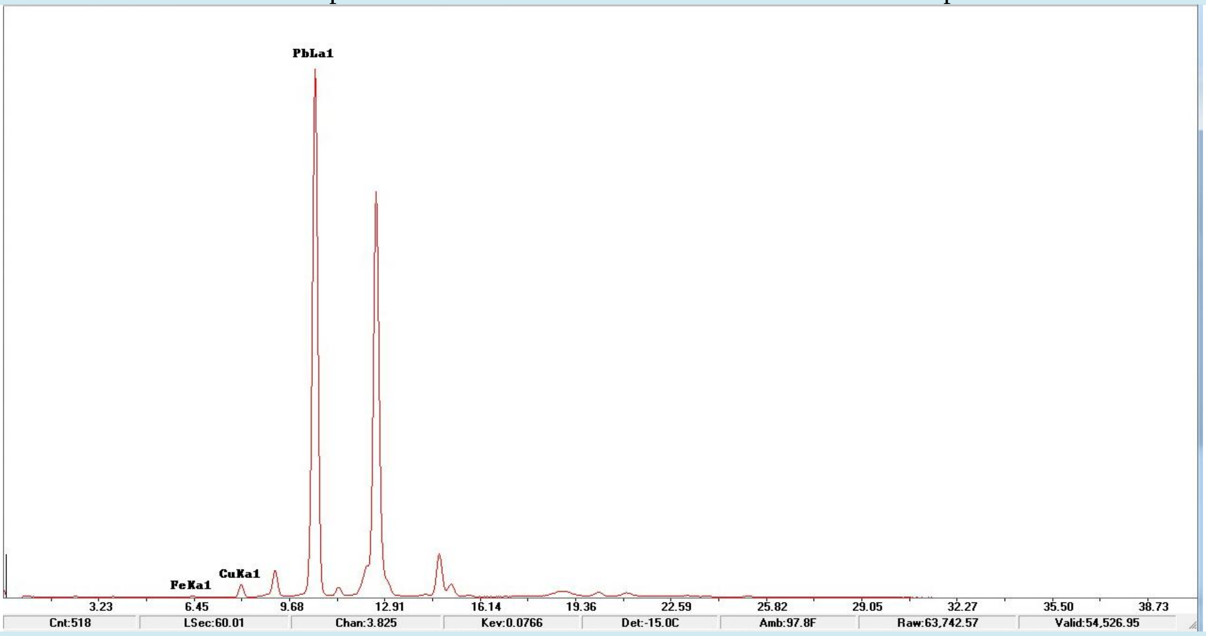


Spectrum from hit point #21

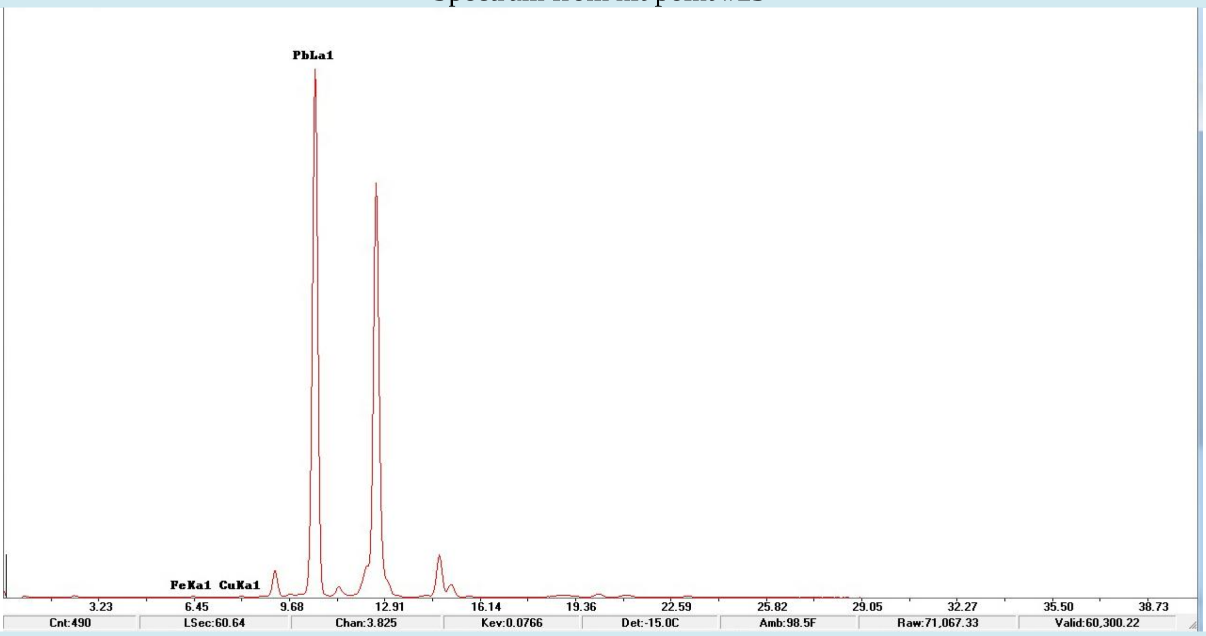


Spectrum from hit point #22

Panel #2. Hit point 23 | Panel #2. Hit point 24



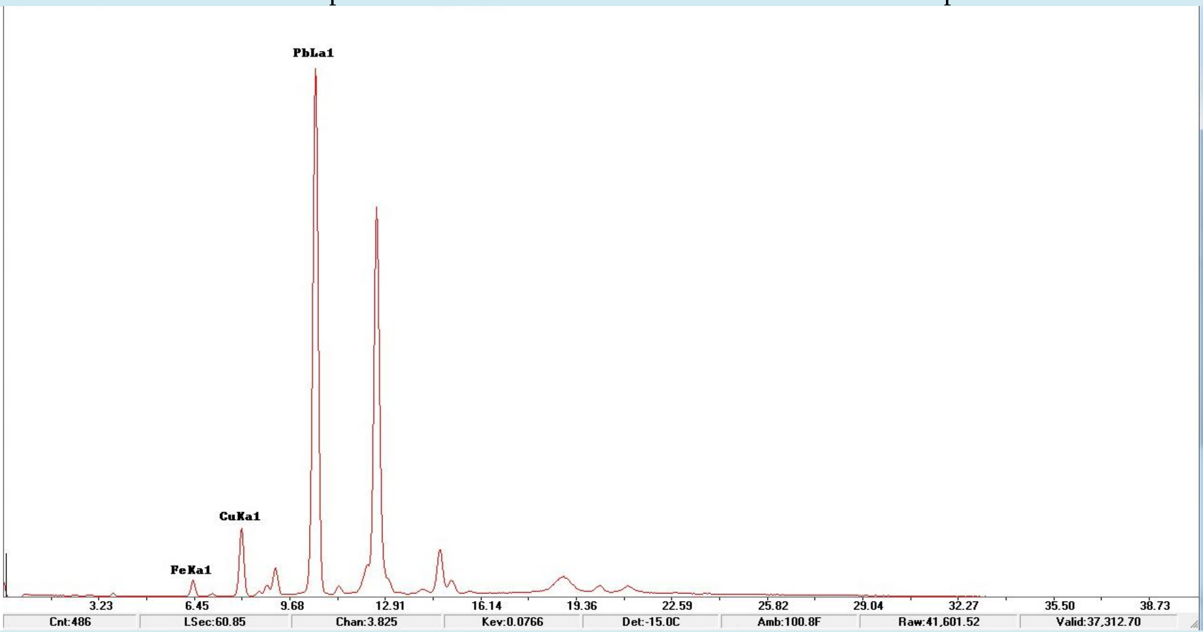
Spectrum from hit point #23



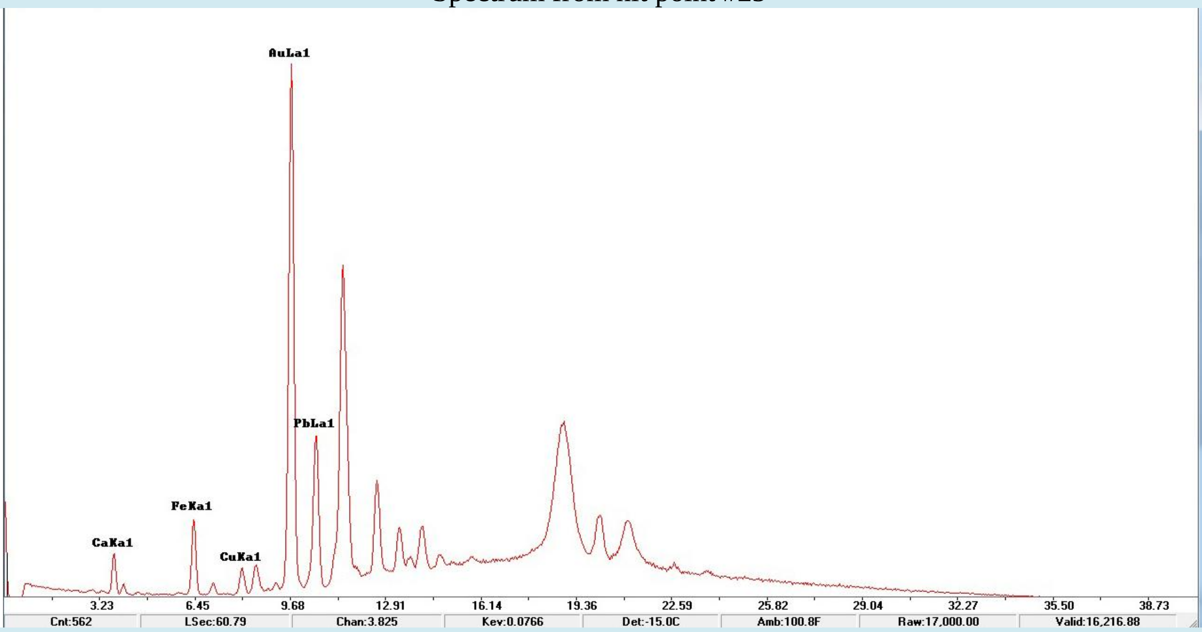
Spectrum from hit point #24

Panel #2. Hit point 25

Panel #2. Hit point 26



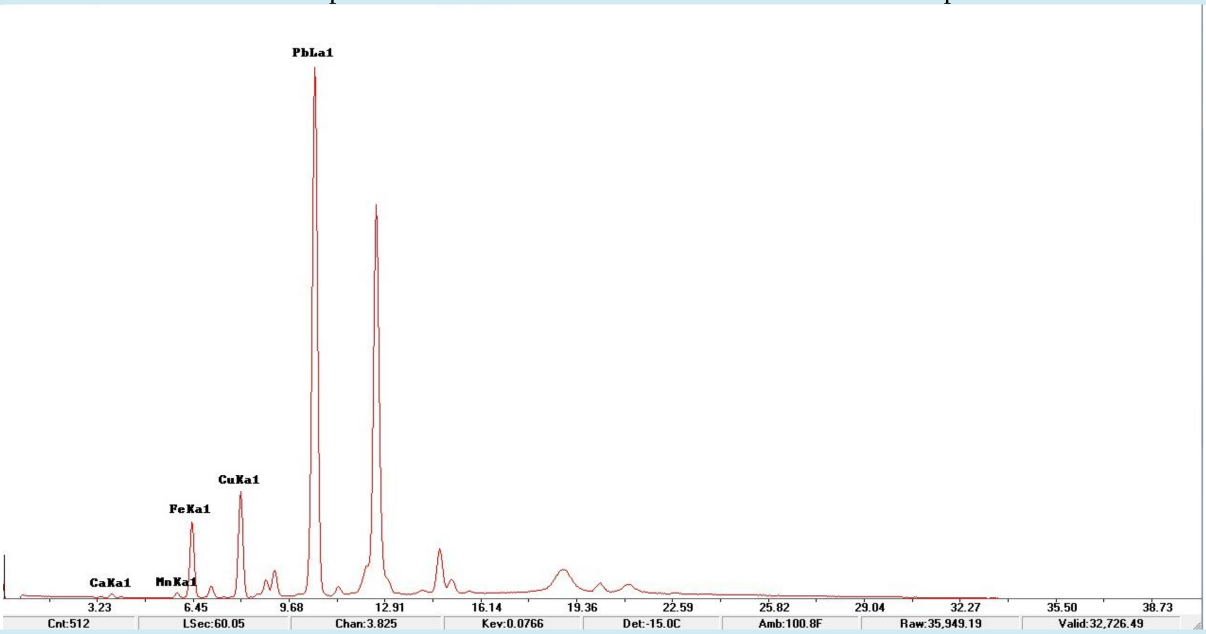
Spectrum from hit point #25



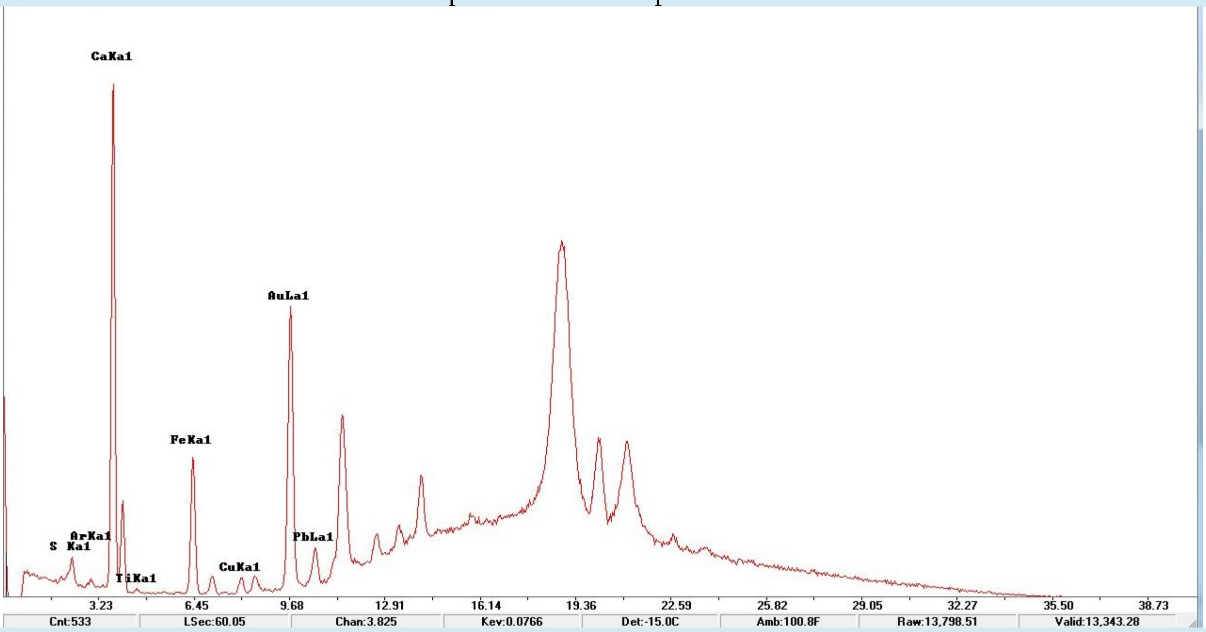
Spectrum from hit point #26

Panel #2. Hit point 27

Panel #2. Hit point 28

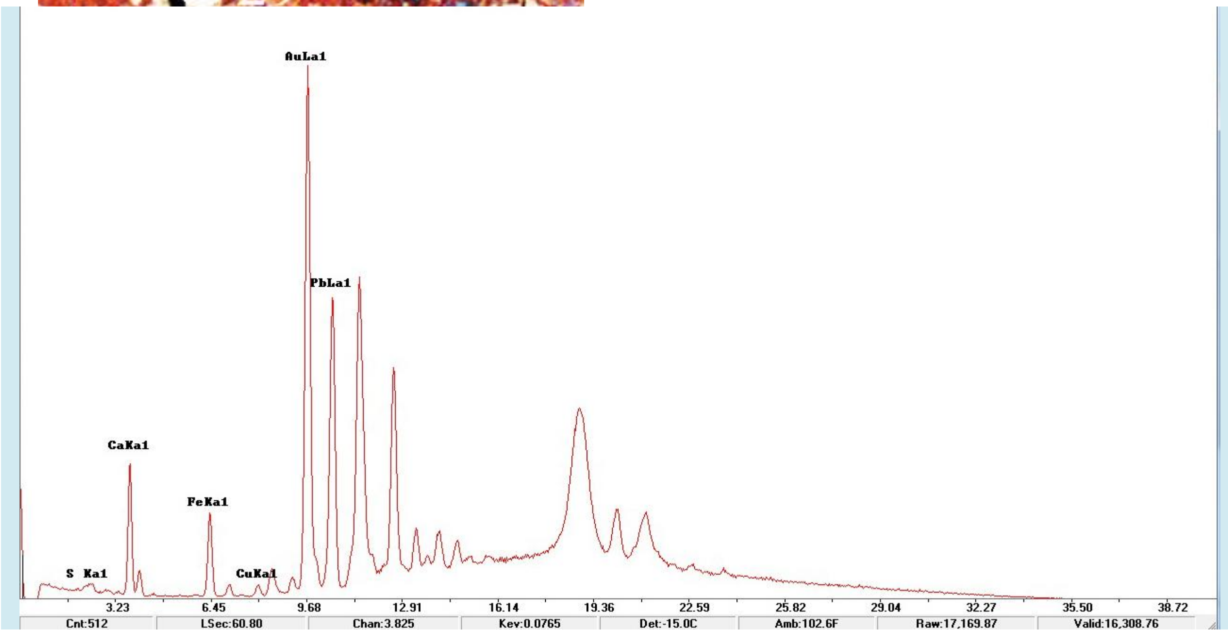


Spectrum from hit point #27

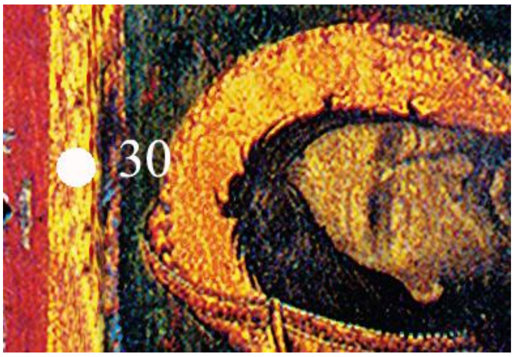


Spectrum from hit point #28

Panel #2. Hit point 29

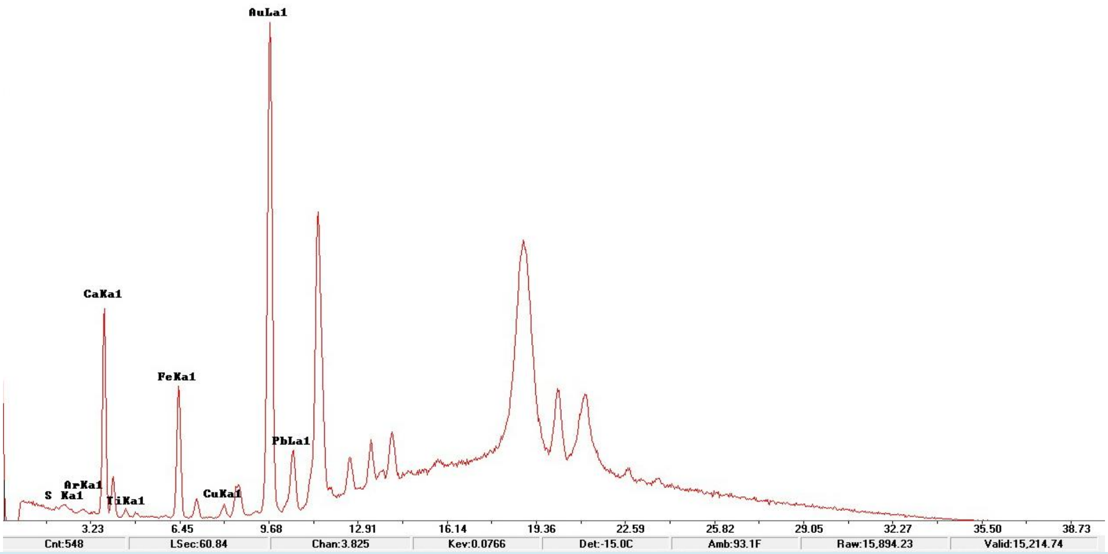


Spectrum from hit point #29



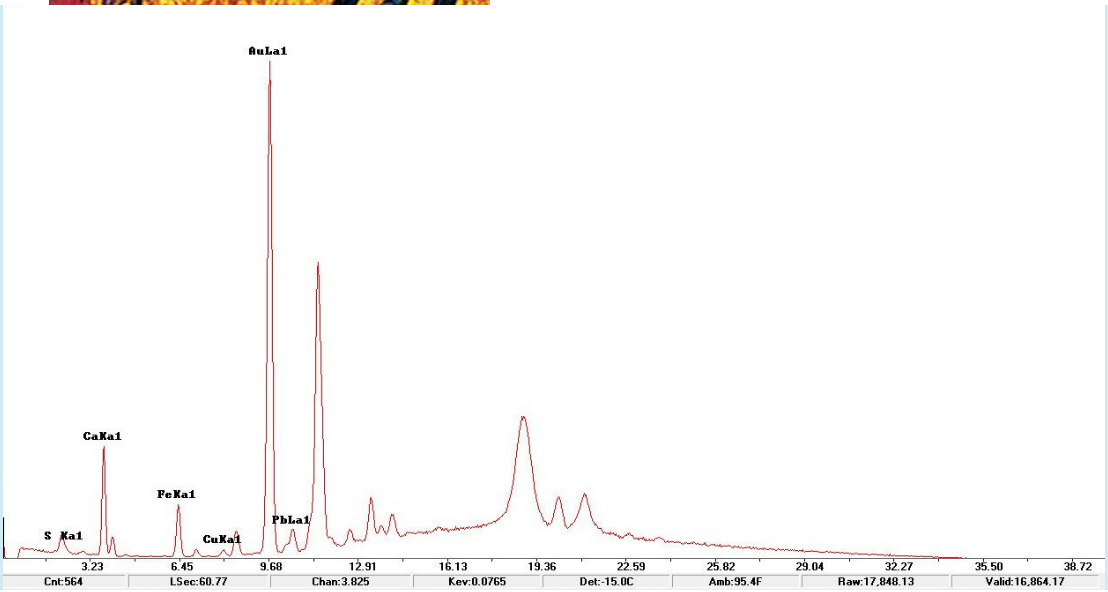
Panel #3 XRF Hit points

Panel #3. Hit point 30



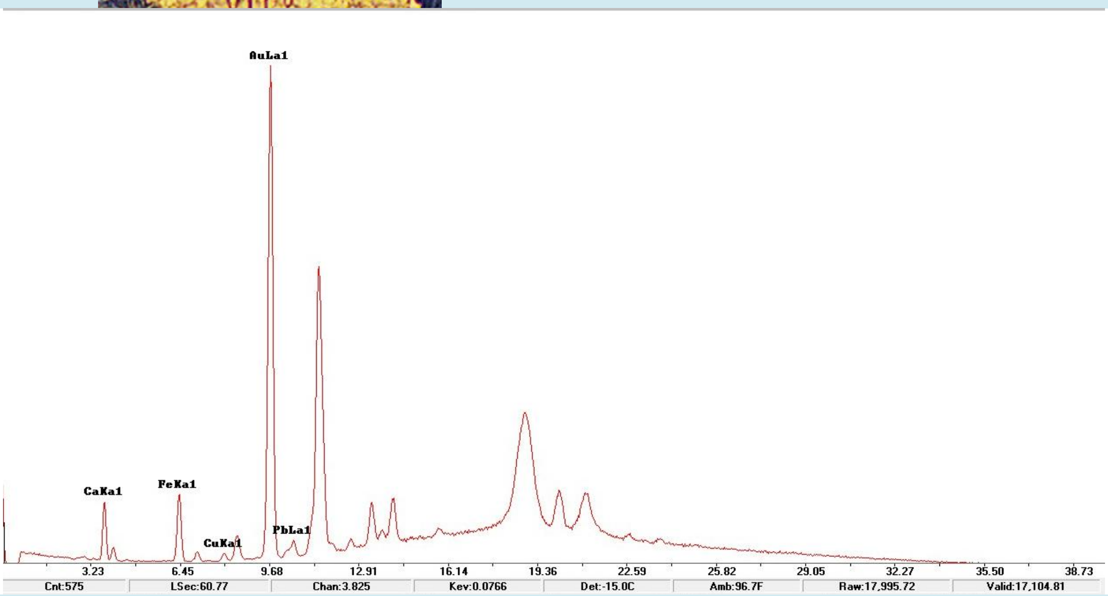
Spectrum from hit point #30

Panel #3. Hit point 31

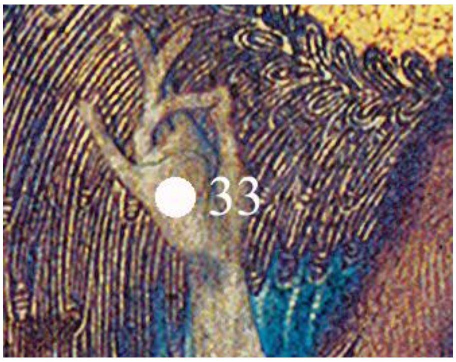


Spectrum from hit point #31

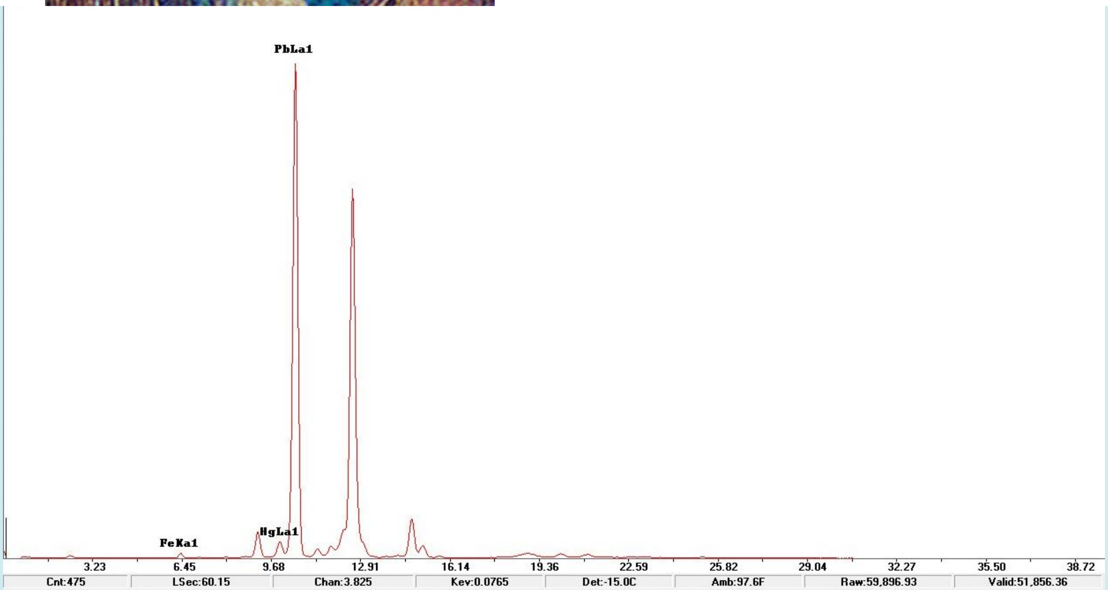
Panel #3. Hit point 32



Spectrum from hit point #32

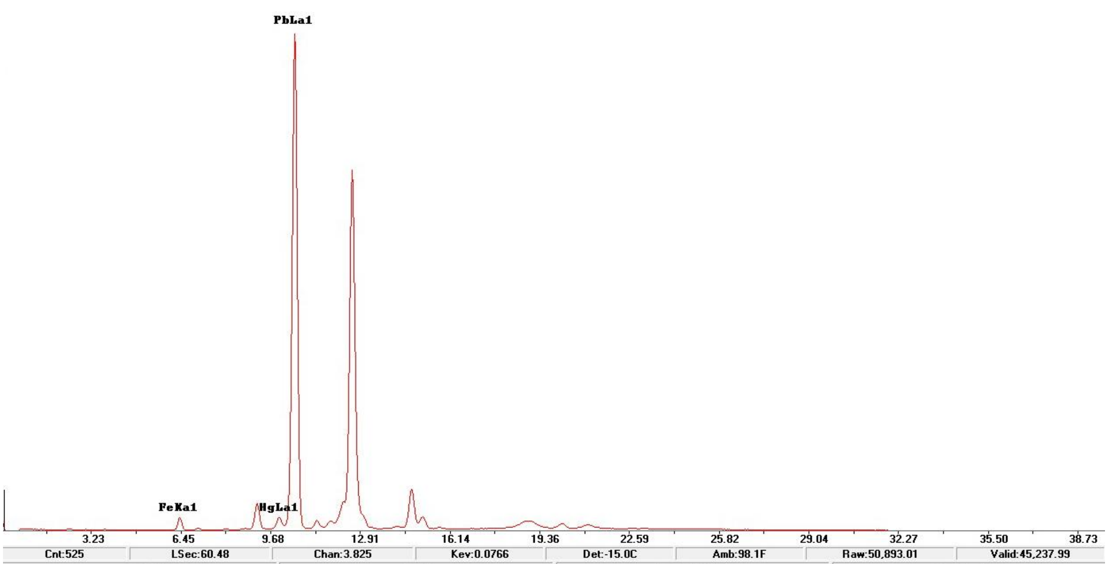


Panel #3. Hit point 33

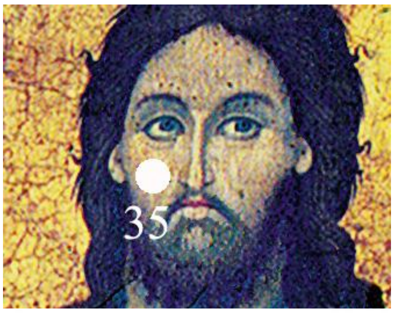


Spectrum from hit point #33

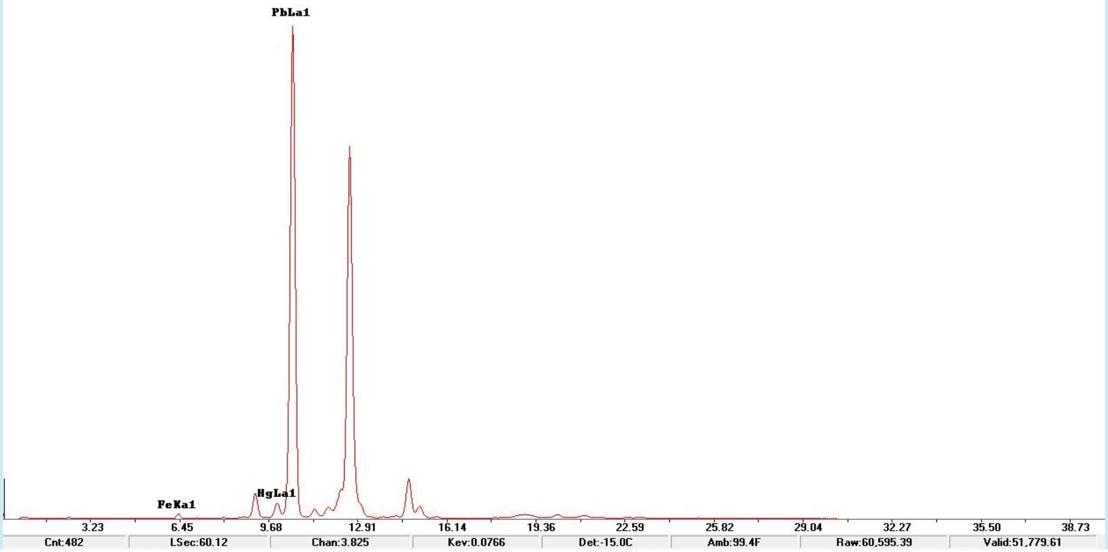
Panel #3. Hit point 34



Spectrum from hit point #34

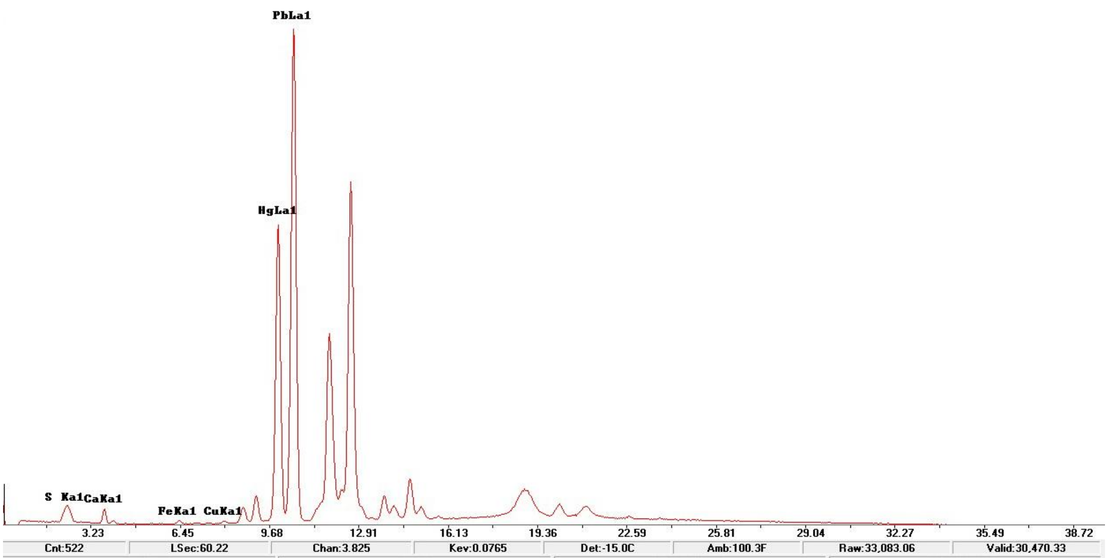


Panel #3. Hit point 35



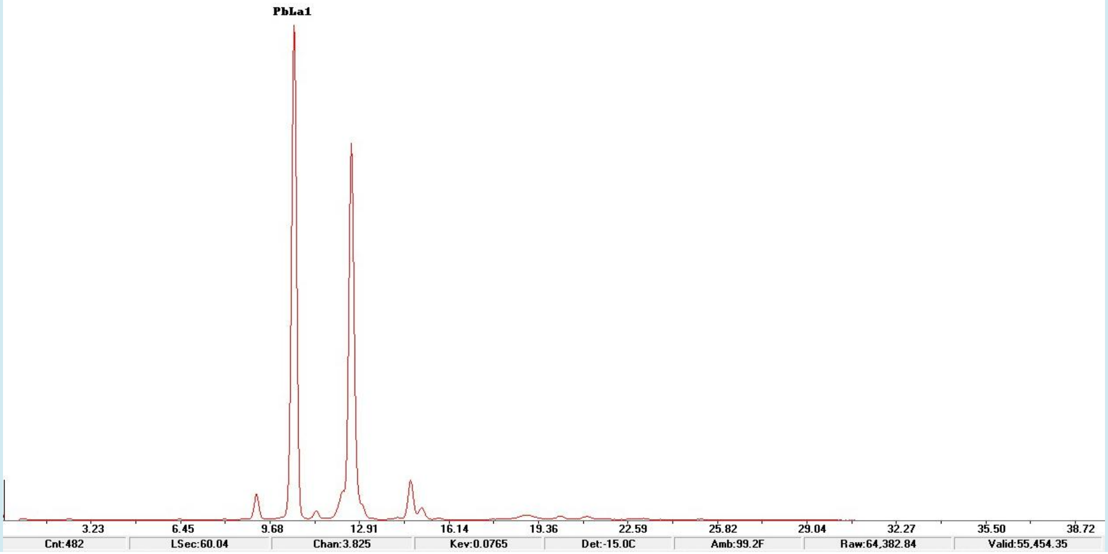
Spectrum from hit point #35

Panel #3. Hit point 36



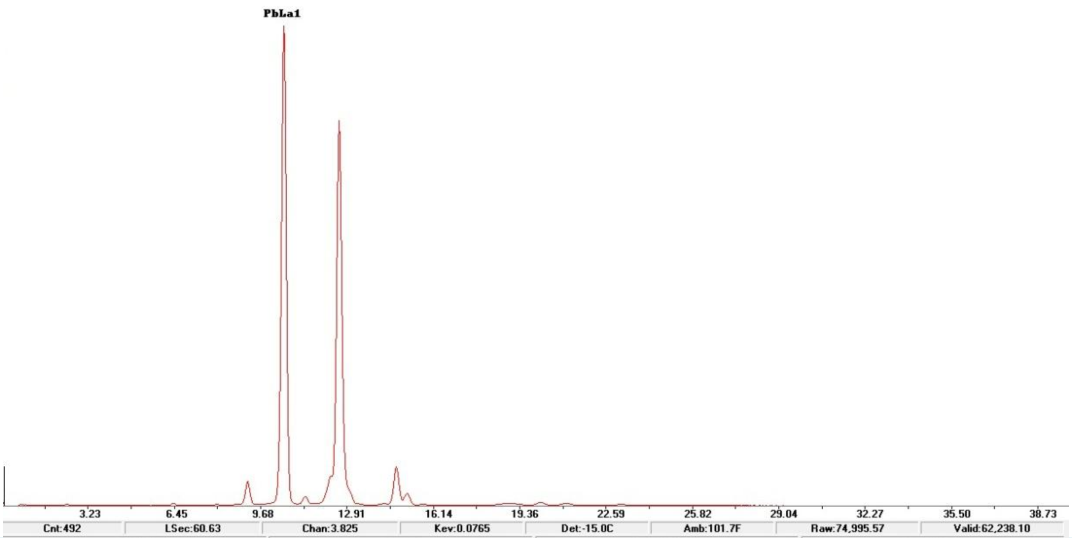
Spectrum from hit point #36

Panel #3. Hit point 37



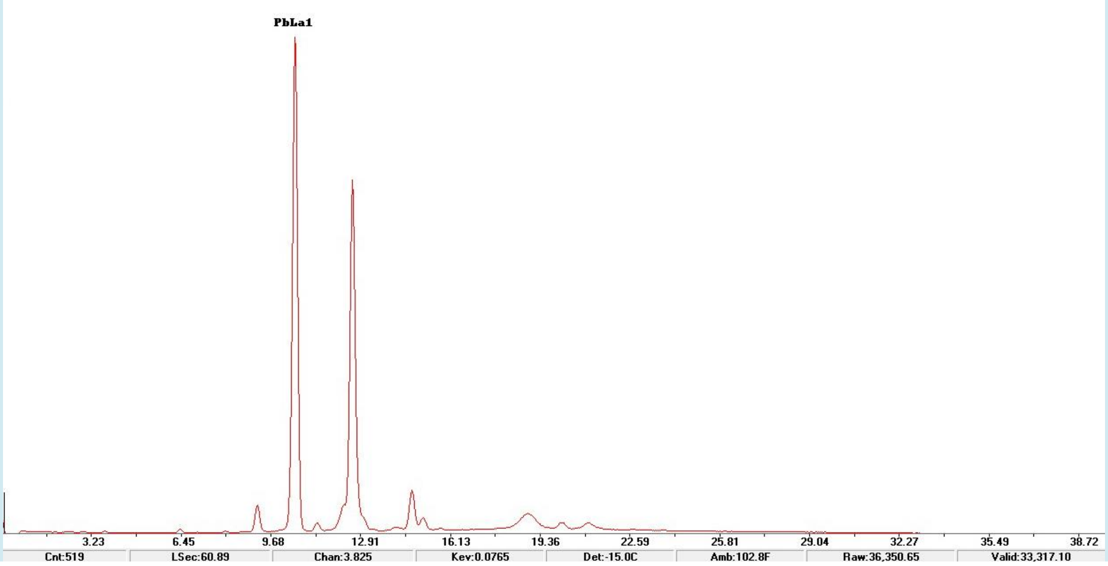
Spectrum from hit point #37

Panel #3. Hit point 38

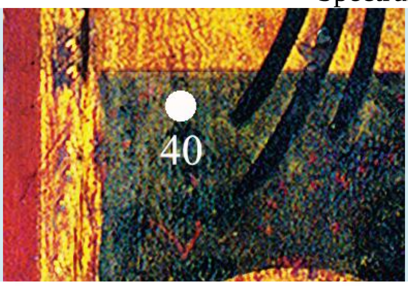


Spectrum from hit point #38

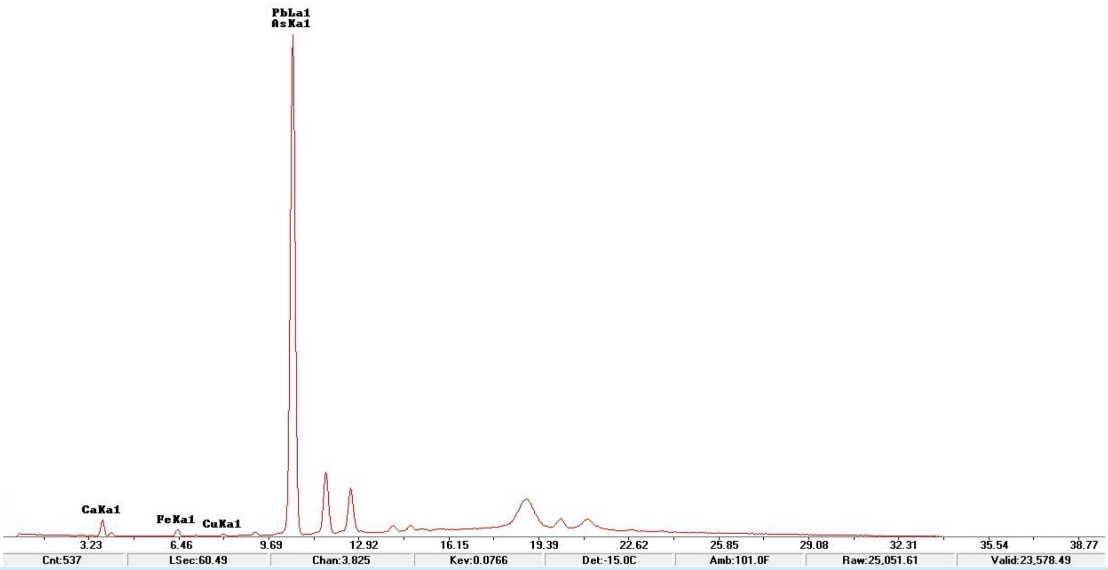
Panel #3. Hit point 39



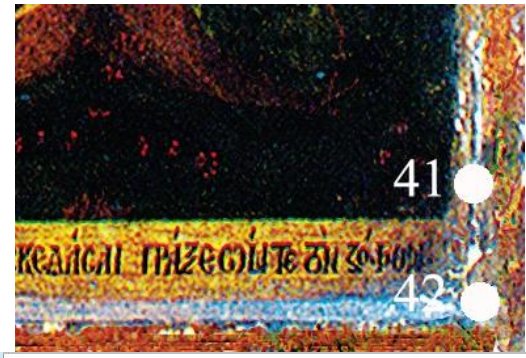
Spectrum from hit point #39



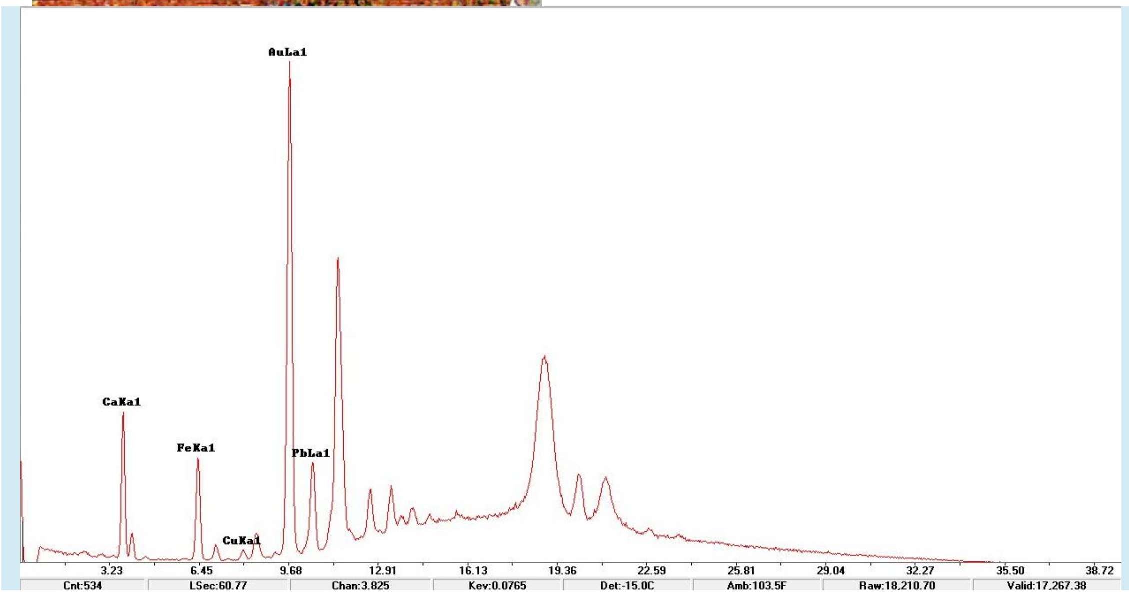
Panel #3. Hit point 40



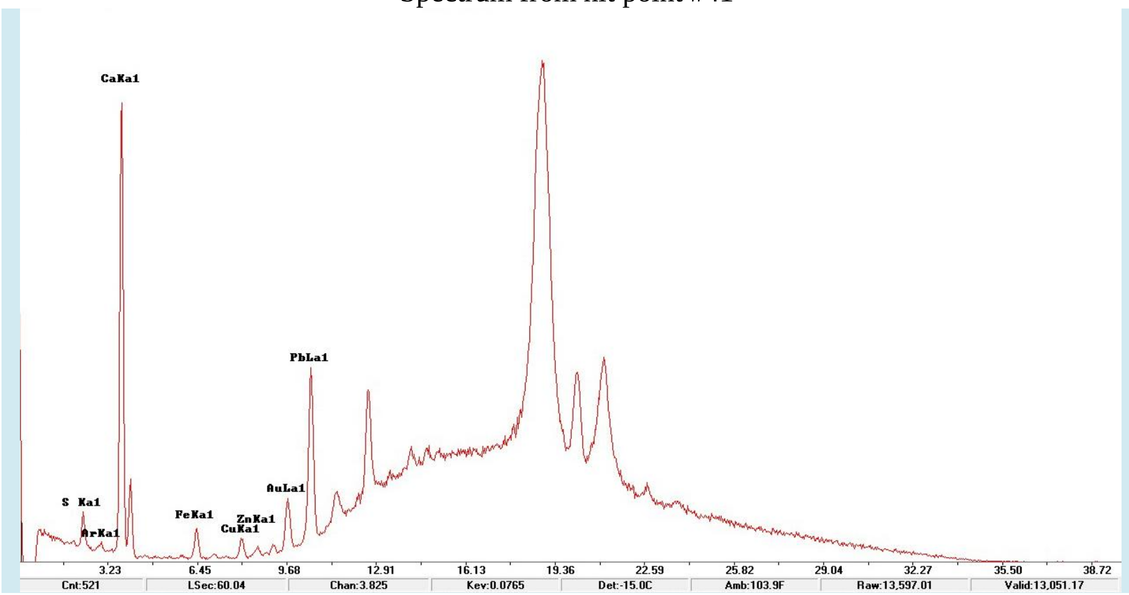
Spectrum from hit point #40



Panel #3. Hit points 41-42

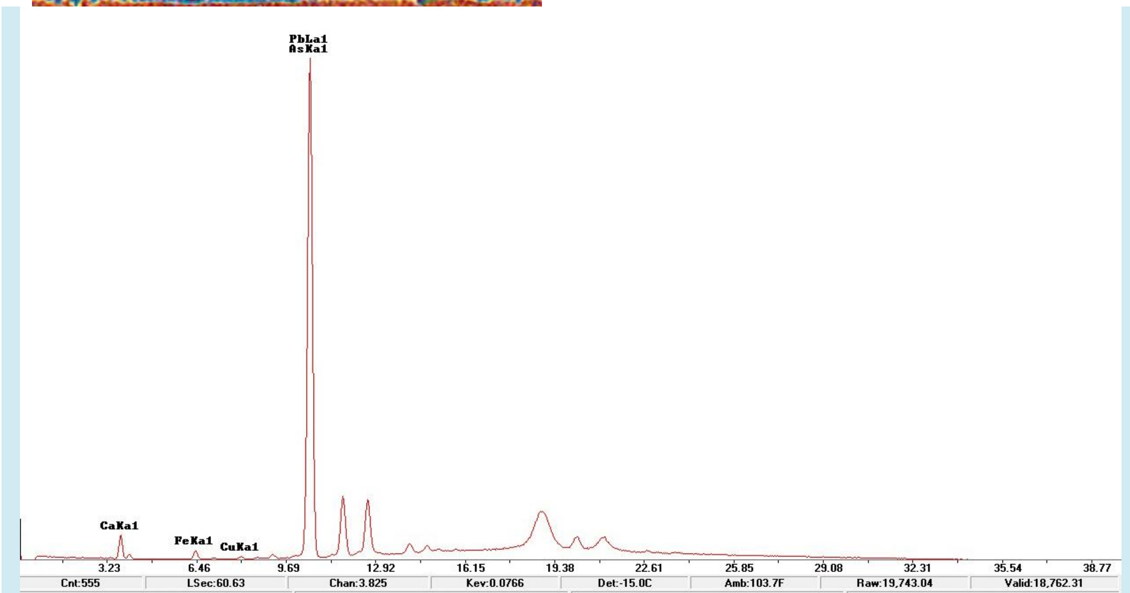


Spectrum from hit point #41



Spectrum from hit point #42

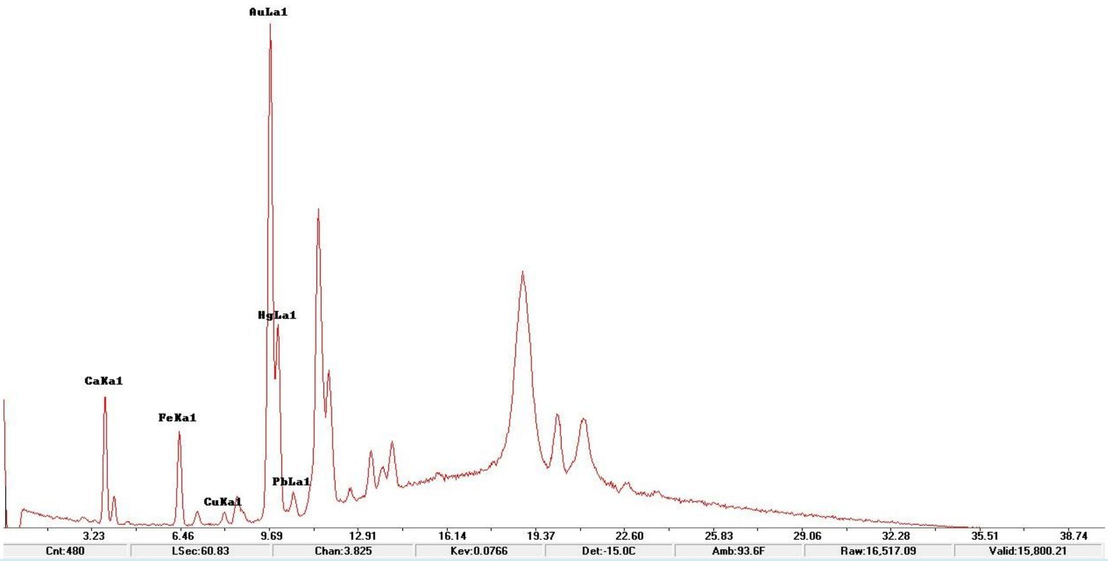
Panel #3. Hit point 43



Spectrum from hit point #43

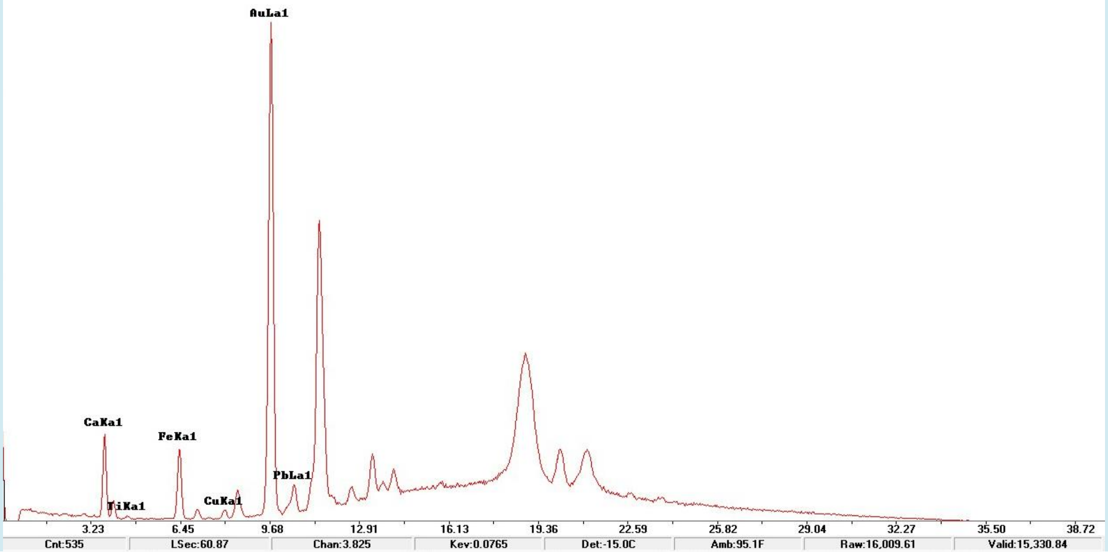
Panel #4 XRF Hit points

Panel #4. Hit point 44



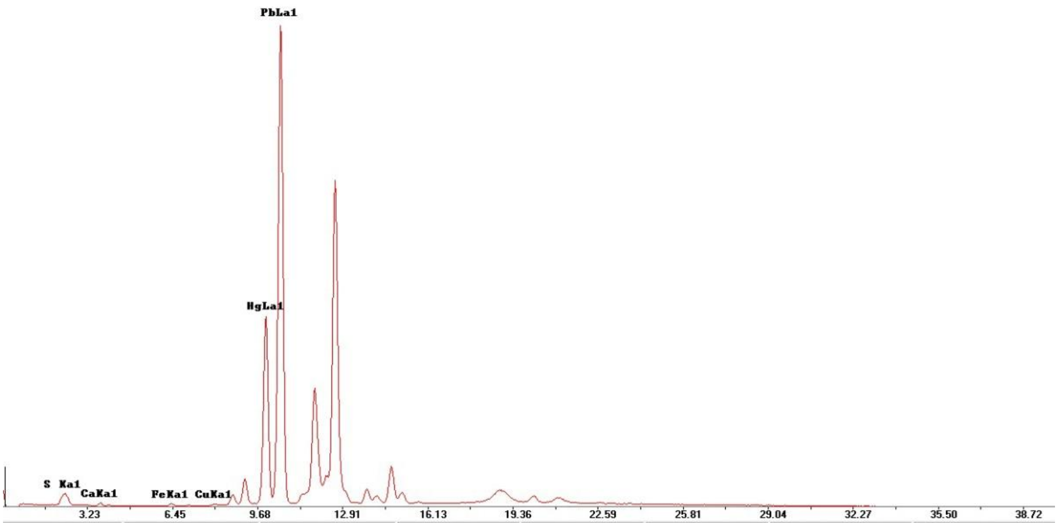
Spectrum from hit point #44

Panel #4. Hit point 45



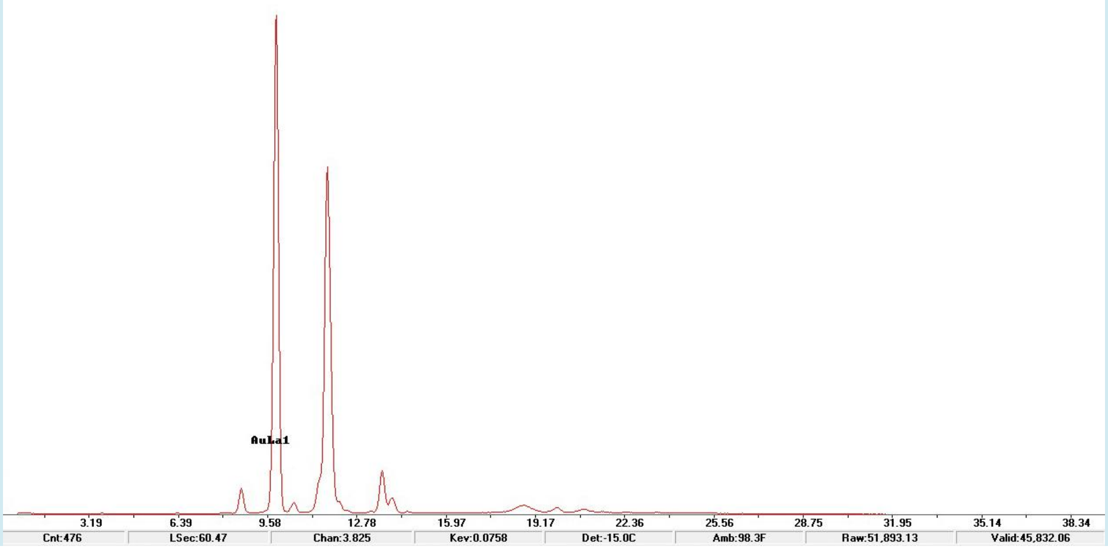
Spectrum from hit point #45

Panel #4. Hit point 46



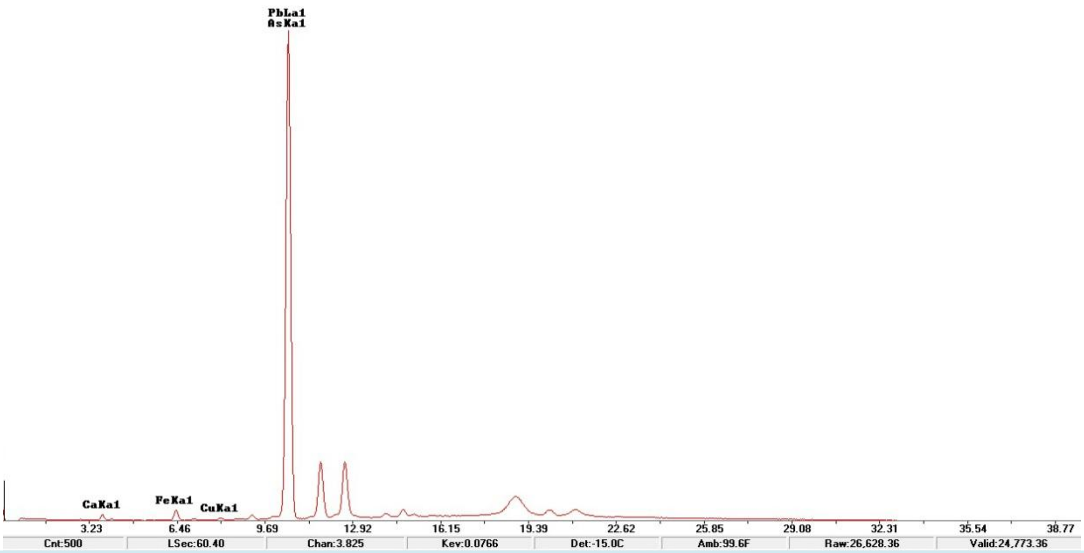
Spectrum from hit point #46

Panel #4. Hit point 47

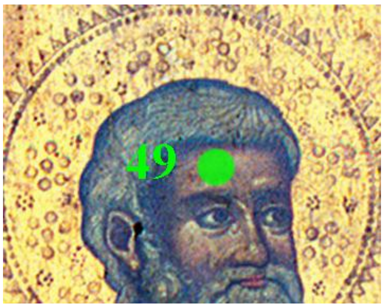


Spectrum from hit point #47

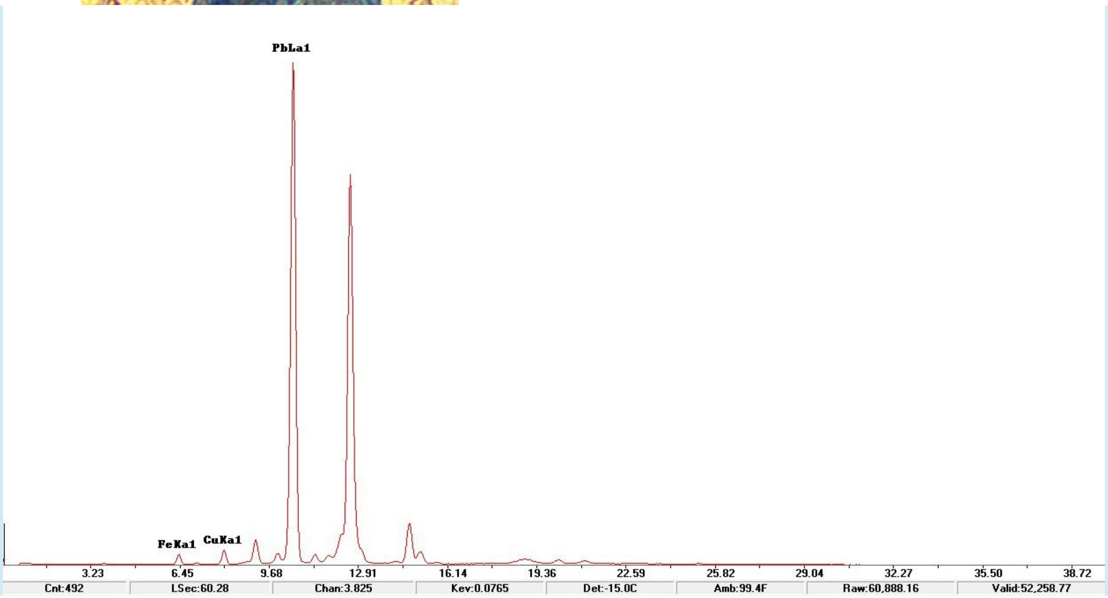
Panel #4. Hit point 48



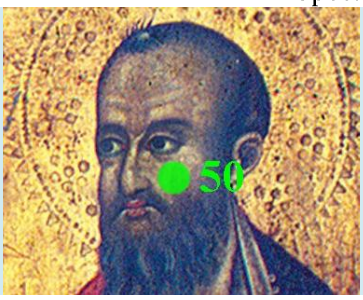
Spectrum from hit point #48



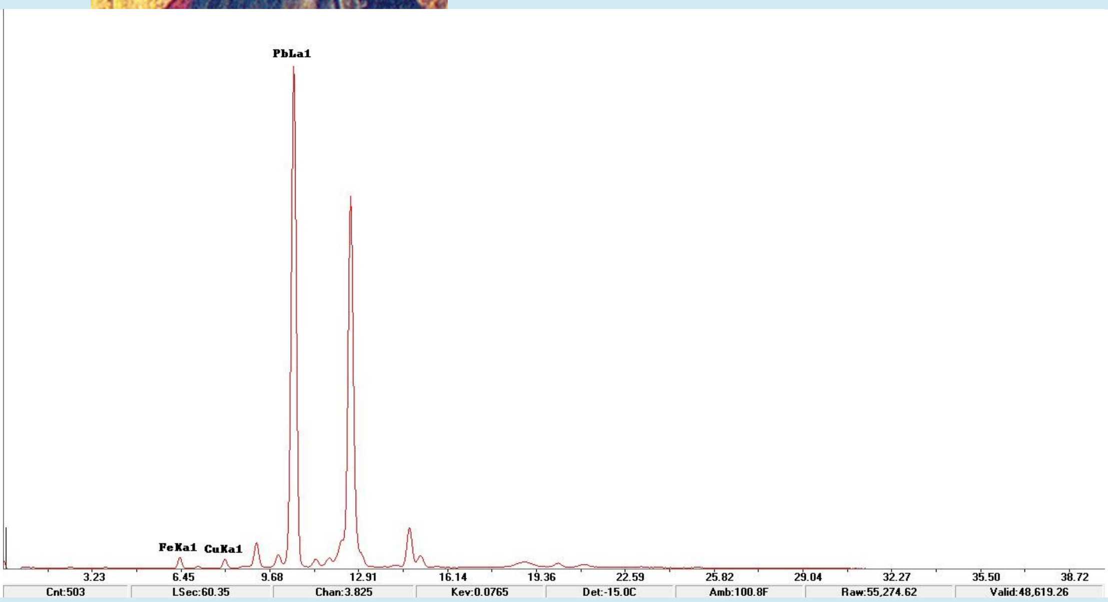
Panel #4. Hit point 49



Spectrum from hit point #49

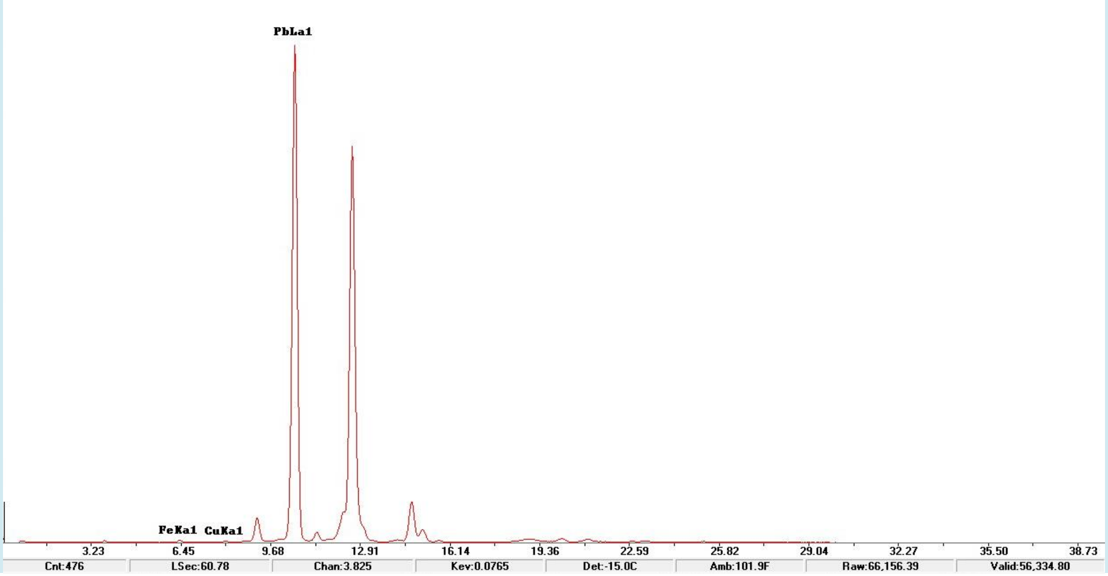


Panel #4. Hit point 50



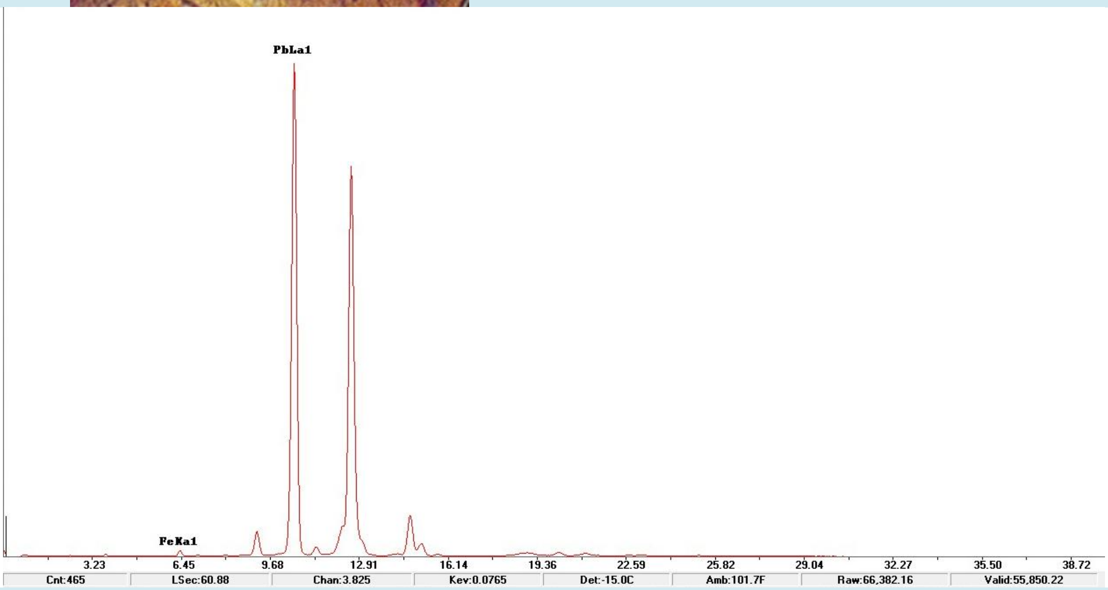
Spectrum from hit point #50

Panel #4. Hit point 51

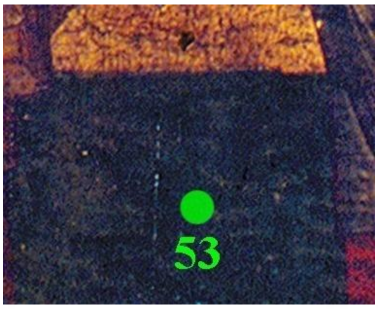


Spectrum from hit point #51

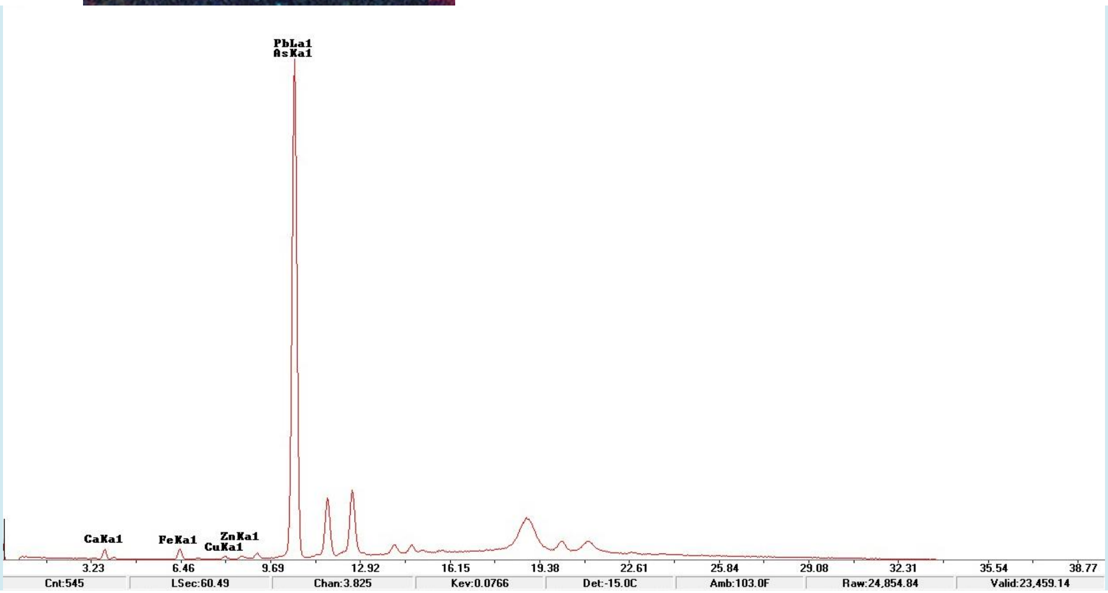
Panel #4. Hit point 52



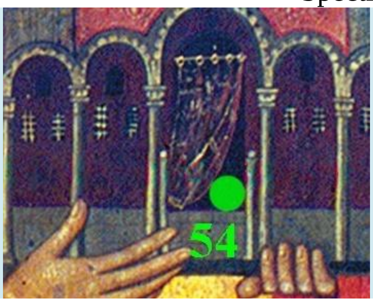
Spectrum from hit point #52



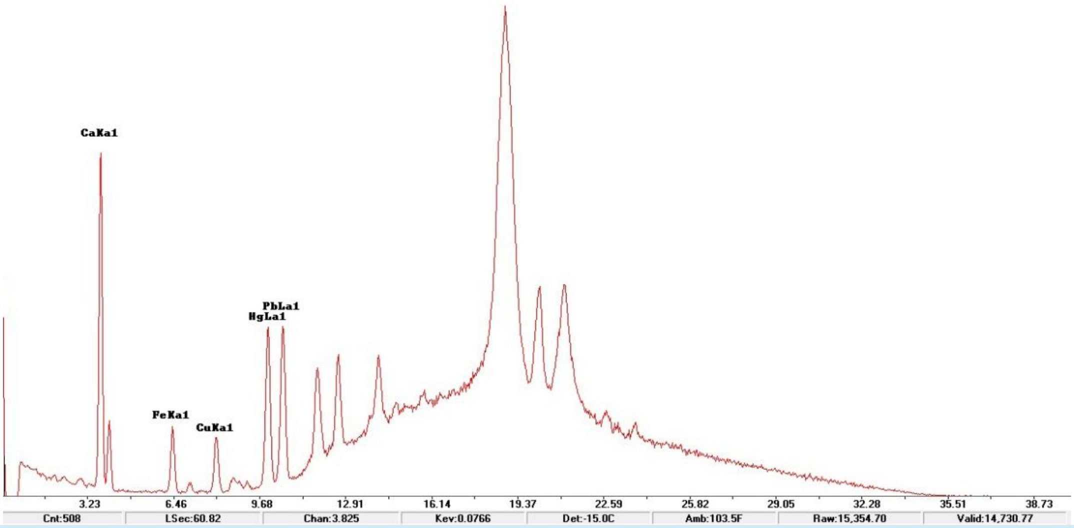
Panel #4. Hit point 53



Spectrum from hit point #53

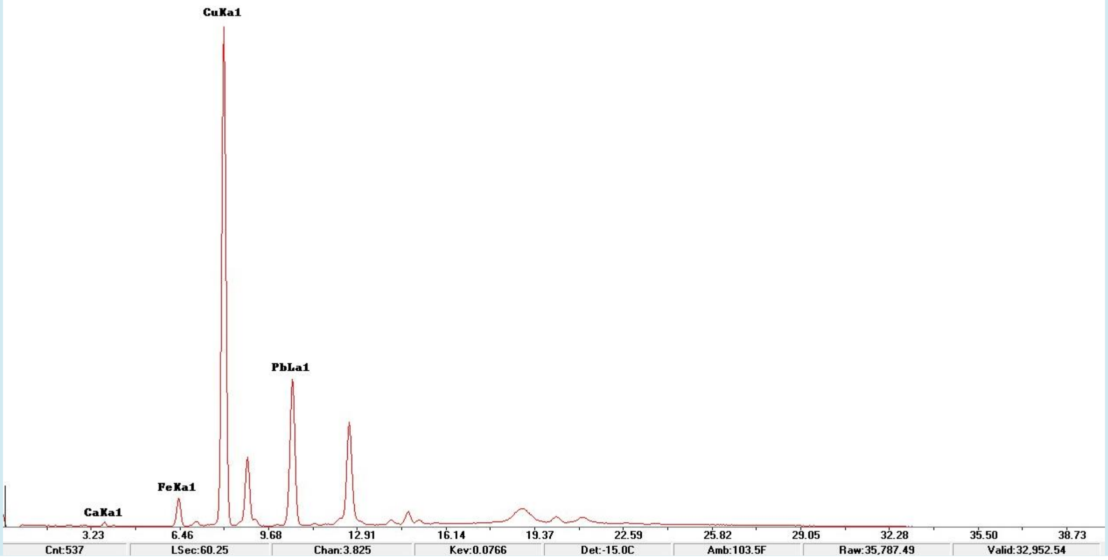


Panel #4. Hit point 54



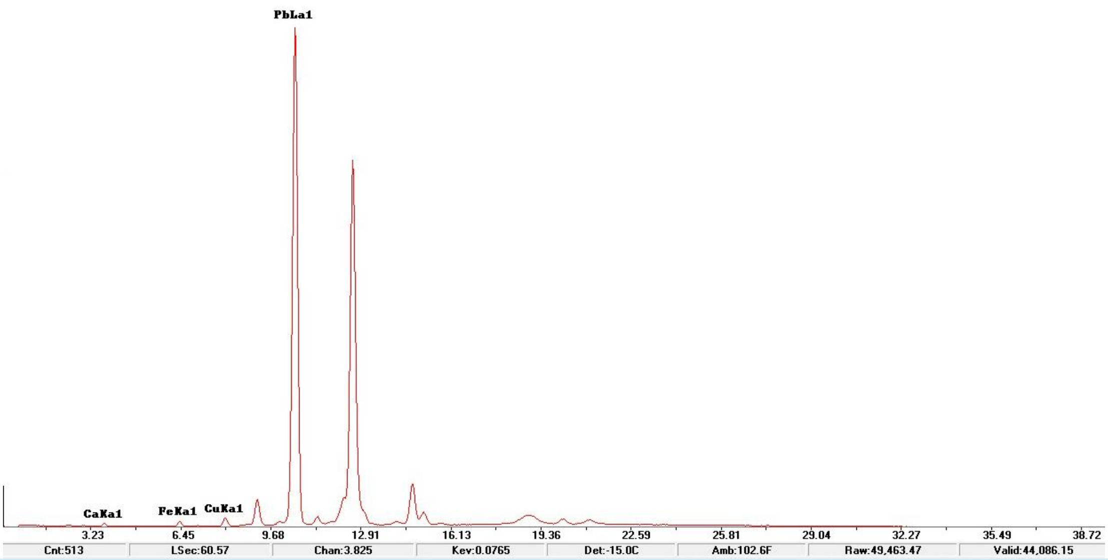
Spectrum from hit point #54

Panel #4. Hit point 55



Spectrum from hit point #55

Panel #4. Hit point 56



Spectrum from hit point #56