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Did Dionysius of Fourna Follow the Material Recipes Described in His Own Treatise? A First Analytical Investigation of Four of His Panel Paintings

Thomas Mafredas [1], Eleni Kouloumpi [2] and Stamatis C. Boyatzis [1,*]

[1] School of Applied Arts and Culture, Campus 1, University of West Attica, 11521 Athens, Greece; tmafredas@uniwa.gr
[2] National Art Gallery, Alexandros Soutsos Museum, 11525 Athens, Greece; ekouloumpi@gmail.com
* Correspondence: sboyatzis@uniwa.com; Tel.: +30-2105385464

Abstract: A research protocol based on imaging techniques and physicochemical analyses was designed and carried out in order to investigate the construction technology of four panel paintings produced by a very important 18th century artist, hieromonk Dionysius from Fourna. Dionysius was the first painter of the post-Byzantine period who wrote an artists' manual for the Eastern Orthodox painting art: he recorded and described in his treatise 'Hermeneia of Art Painting' the materials and construction techniques of the 18th century Christian painting. The contribution of Dionysius and his 'Hermeneia of the Painting Art' is decisive because it gathers all the previously scattered advice and guidelines about the construction of panel paintings and the information quoted by him is probably the only official recorded source of Eastern Orthodox art technology. In this context, four panel paintings signed by Dionysius were selected for scientific research: it is the first time that an effort is made to analytically characterize the materials used by the hieromonk, to recognize the construction technology, and examine whether it follows the recipes included in his manuscript or not.

Keywords: Dionysius of Fourna; painting materials; X-ray fluorescence; SEM-EDX; optical microscopy; infrared spectroscopy

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1. Introduction

The scholars of post-Byzantine art often use 'Hermeneia of the Painting Art', a book authored between 1729 and 1732 by hieromonk and religious painter Dionysius of Fourna (1670–1744/5), as a reference point. As an artist's manual, the book has been of continuing interest to those seeking to discover the traditions and practices of Byzantine and Post-Byzantine painting art [1] because it is a complete treatise concerning the way and the rules by which icon painters should construct and paint their panel paintings [1,2], following the Byzantine painting practices, as they were introduced by a famous icon painter, named Panselinos [1,3,4].

Dionysius' treatise 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 the painting technique, including, among others, recipes for colors, gilding and varnishes, and steps on how to prepare materials for painting. The other five sections of his book deal with the iconographical depiction of various religious subjects [3].

The 'Hermeneia of the Painting Art' manual is decisive because it gathers all the previously scattered information about the construction of panel paintings. This treatise has become a historical reference point and there are various versions in the greater Balkan region [2].

Especially, the construction technology section, is probably the only recorded source about the creation stages of post-Byzantine art. In this context, particularly informative is the text on construction materials, such as the preparation layer, the gilding technique, the pigments and the varnishes. In addition, valuable recipes about glue, acids, medium and recipes on how to construct pigments, as cinnabar, crimson lake, and blue from frayed clothes, are also included.

Furthermore, it is essential to study and certify whether Dionysius, despite of being the author of this book, did follow the instructions cited in his text; this can be achieved by studying the construction technology and identifying the component materials used in his actual work and compare it with the recipes described in the 'Hermeneia' treatise.

A research protocol including a series of imaging techniques and physicochemical analytical methods was applied in order to identify the materials used and to study, at the same time, the construction technology of four of his panel paintings.

Research Aim

In 1737, Dionysius created four panels, Christ as King of the Kings and Great High Priest (panel painting 1, or PP1), Zoodochos Pigi—the Phaneromeni (PP2), Saint John the Baptist—the Forerunner (PP3), and The Apostles Peter and Paul (PP4), to dedicate them to Zoodochos' Pigi monastery, which he had founded in his native region, Fourna (central Greece). After the collapse of the Zoodochos Pigi monastery in 1906, these four panel paintings (Figure 1) were kept in the church of Transfiguration at the village of Fourna until today.

Figure 1. Dionysius' four panel paintings (1737) from the church of Transfiguration, Fournas, Evrytania, Greece. (**a**) PP1, Christ as King of the Kings and High Priest, (**b**) PP2, Zoodochos—PigiThe Phaneromeni, (**c**) PP3, St. John the Baptist, the Forerunner, and (**d**) PP4, The Apostles Peter and Paul. Colored dots depict non-invasive XRF analysis spots, while white dots show invasive sampling spots. Plates (**e**–**h**) show IR reflectographs of corresponding panels.

Considering that the panel paintings under study were constructed around 1737, a few years after Dionysius had completed his treatise (1732), this research aims to investigate his painting technique and evaluate whether he applied the guidelines described in his 'Hermeneia'.

The physicochemical analysis of the materials used to create the four 18th century panel paintings of Dionysius aims at providing important novel information about him as an artist. In addition, the availability of such analytical results would be beneficial for a better understanding of his painting technology, in general, and the materials that he used, including pigments, binders, and varnishes [5]. Previous research studies [6–9] are based on art treatises and physicochemical analysis, but none is a comparative study of his written work and artistic expression. Other studies, such as those by Kakavas [1], Ferens [10], and Homar [11] deal by following a similar kind of research but from a purely theoretical point of view.

2. Materials and Methods

2.1. Non-Invasive Analyses

2.1.1. Imaging Techniques

Visible observation and photographic documentation were achieved using a Nikon Coolpix L120 equipped with a Nikon R21× wide optical zoom lens 4.5–94.5 mm. Digital microscopy (DM) was achieved using a Dino-Lite AM 413T portable digital microscope in different magnification ranges (50× up to 250×).

IR reflectography and UV photography were applied by using a Canon EOS 50/50E SLR analog camera, equipped with a UV and NIR manually removable cut-off filters, respectively, a Canon Zoom Lens EF-S 28–80 mm with Kodak Highspeed IR film. The following filters were used: Hoya Infrared R72 (52 mm) filter in 720 nm (NIR zone); B+W (37 mm), and UV (403 nm) Black filter.

2.1.2. pXRF

In situ elemental analysis was performed by a Brucker Tracer III SD portable X-ray fluorescence spectrometry system, with a beam diameter of 3 mm. The apparatus consists of a rhodium source used in low- and high-energy excitation mode. In low energy mode, voltage was set at 15 kV and current at 24 μA, both with unfiltered, and Al/Ti filtered (0.012 inches Al plus 0.001 inches Ti) beams, allowing the analysis of major and minor elements (Z 11-26), respectively. High energy mode (voltage set at 40 kV and current at 12 μA) was applied for the analysis of minor and trace elements (Z > 26). Data were collected under atmospheric pressure, with a collection time of 60 seconds per measurement. Data collection, analysis, and quantification were made by S1PXRF software.

In all panels, individual spots were selected for pXRF elemental analysis following the scheme shown in Table 1. The corresponding spots on the panels are shown in Figure 1a–d.

2.2. Microsamples Analyses

2.2.1. Sampling Procedure

Samples were removed (1 × 1 × 0.5 mm, weight up to 2 mg) from damaged areas and were divided in two categories depending on the analysis type: (i) microscopic observation via Optical Microscopy (OM) and Scanning Electron Microscopy (SEM); and (ii) molecular analysis with FTIR. Sampling spots are shown in Figure 1a–d. In category (i) samples were studied in the form of cross-sections (embedded in Nosordyne polyester resin), to investigate the stratigraphy of the artwork. In category (ii) samples (up to 5 mg weight) were detached in the form of powder to identify the preparation material, the possible organic media, and the resins used for varnish coating. Cases that more than one sample was collected from the same spot are stated by adding letters (a, b) next to the number of each sample (Table 2).

Table 1. pXRF point analysis scheme.

Panel Paintings			
1	2	3	4
XRF 1, gold	XRF 18, gold	XRF 30, gold	XRF 44, gold
XRF 2, gold	XRF 19, gold	XRF 31, gold	XRF 45, gold
XRF 3, gold	XRF 20, gold	XRF 32, gold	XRF 46, red
XRF 4, gold	XRF 21, flesh	XRF 33, hand	XRF 47, red
XRF 5, flesh	XRF 22, red	XRF 34, hand	XRF 48, black
XRF 6, red	XRF 23, white	XRF 35, flesh	XRF 49, flesh
XRF 8, white	XRF 24, white	XRF 36, red	XRF 50, flesh
XRF 9, red	XRF 25, green	XRF 37, white	XRF 51, grey
XRF 10, gold	XRF 26, black	XRF 38, white	XRF 52, white
XRF 11, black	XRF 27, brown	XRF 39, green	XRF 53, green
XRF 12, black	XRF 28, ground	XRF 40, green	XRF 54, black
XRF 13, background	XRF 29, ground	XRF 41, ground	XRF 55, green
XRF 14, black		XRF 42, ground	XRF 56, green
XRF 15, brown		XRF 43, black	
XRF 16, ground			
XRF 17, ground			

Table 2. Sampling scheme and coding.

Microsamples							
PP1		PP2		PP3		PP4	
# Sample	Sample type	# Sample	Sample type	# Sample	Sample type	# Sample	Sample type
1	preparation powder	7	preparation powder	11	cross section	16	preparation powder
2	varnish powder	8	pigment powder	12	preparation powder	17	varnish powder
3	cross section	8a	varnish (removed with acetone-loaded cotton swap)	13	cross section	19a	cross section
4	cross section	9	cross section	14	varnish powder	19b	cross section
6	cross section	10	cross section				
		10a	varnish powder				

2.2.2. Optical Microscopy and Microchemical Testing

Cross-sections (Figure 2) were photographed under reflected Vis and UV light for the following: color, particle size and shape, binding medium indication, thickness of paint layers, admixtures of pigments, and paint layer stratigraphy. This offers a useful 'pictorial' guide when interpreting data from elemental analyses [12].

For microchemical testing Naphthol Blue-Black 10B was used (also known as Amido Black or Noir Amide-NA), in solutions of varying pH (pH2 and pH3) [13]. The OM and staining tests on cross sections were performed at the National Gallery of Athens' Laboratory of Physicochemical Research. The OM setup consists of a Leica DM/LM Microscope with a double source of visible and UV light and integrated DC 300F infrared camera [14].

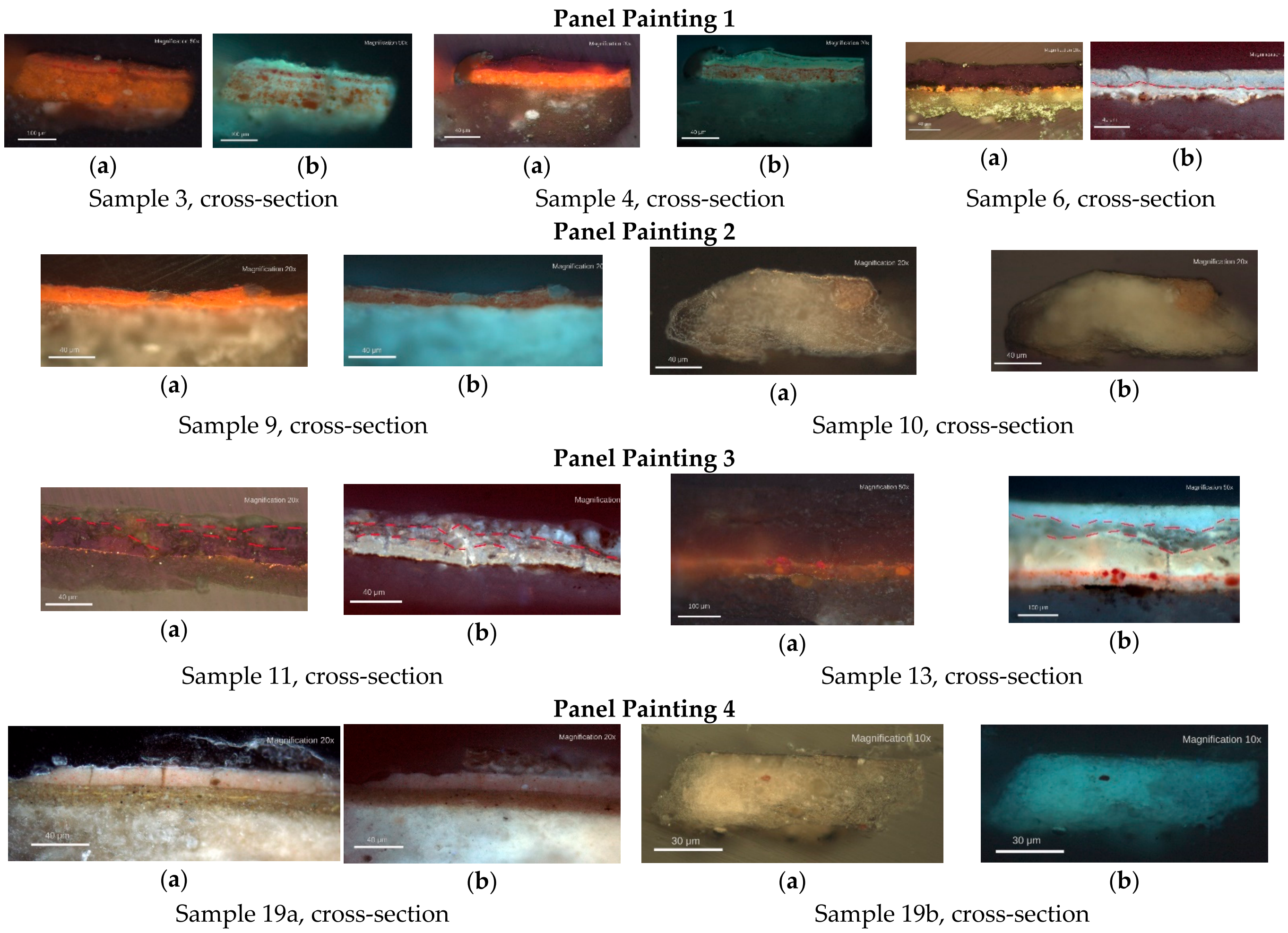


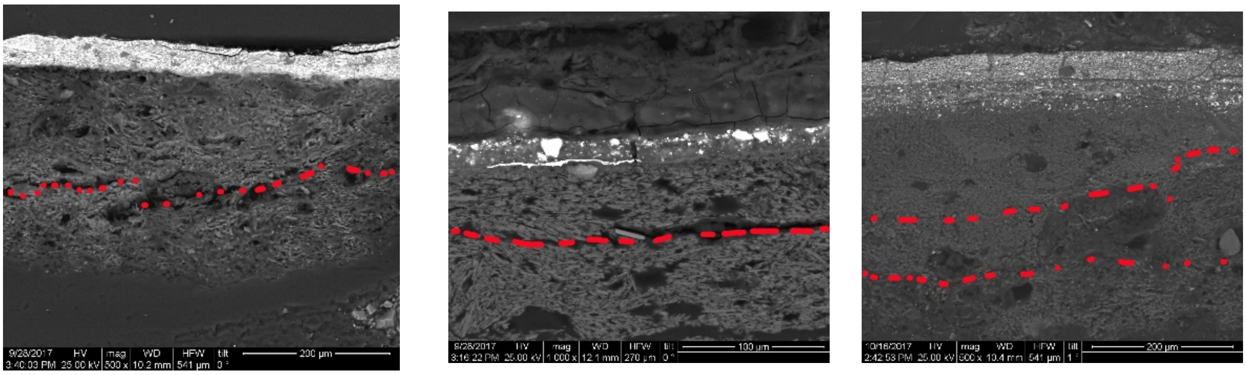
Figure 2. Optical Microscope images obtained under (**a**) visible light and (**b**) UV of the cross-sections from microsamples of each panel painting. Original magnification with scale is shown on each plate.

2.2.3. SEM-EDX

Microelemental analysis in cross-sections was performed by a Scanning Electron Microscopy with Energy-Dispersive X-ray analysis (SEM/EDX) at the National Center for Scientific Research (NCSR) "Demokritos" (Aghia Paraskevi, Athens) using a FEI, model Quanta Inspect D8334, INN-NCSR "D", SEM/EDX system integrated with a super ultra-thin window (sutw) EDX detector. The apparatus was operated under 25kV, while sample surfaces were examined using backscattered electrons (BSE mode) [15].

Cross-section samples were pre-coated with a thin layer of conductive carbon powder deposited on their surface using an appropriate apparatus manufactured by Balzers (model CED 030, INN-NCSR "D") for ionizing the sample.

By SEM/EDX technique, it was easy to investigate the layers of the samples, to recognize the quality of the construction technique—especially for the gesso preparation and to identify the ingredients constituting the bole layer and the different pigment layers, as well as the metal leaf used for the gilding technique (Figure 3).



P.P.2 Sample 9, cross section SEM | P.P.3 Sample 13, cross section, SEM | P.P.4 Sample 19a, cross section, SEM

Figure 3. SEM microphotography of microsamples from panel paintings 2, 3 and 4.

2.2.4. FTIR (or Infrared Spectroscopy)

Fourier Transformed Infrared Spectroscopy (FTIR) was carried out at the Department of Conservation Antiquities and Works of Art, University of West Attica, Greece. A Perkin-Elmer Spectrum GX-FTIR system in standard transmission mode for KBr powder samples using Spectrum v5.1 software was employed.

Samples from the preparation and varnish layers, aimed at FTIR analysis, were mixed with potassium bromide (KBr), accordingly pulverized, and pressed into suitable 13 mm discs for analysis [16]. Specifically, for varnish-aimed analysis, scraped powdered samples were carefully detached from the surface of all panels, except panel 2, where the varnish was extracted using an acetone-soaked cotton swab.

3. Results

3.1. Investigation Scheme

Visible, IR reflectography and UV fluorescence imaging and macro-imaging, were employed for non-invasive, in situ examination of the panels. In selected spots of the surface, digital microscopy was used to investigate details, and portable XRF (pXRF) analysis allowed surface elemental screening of all four (4) panels.

The stratigraphy of the samples was revealed through microscopic examination of cross-sections (shown in Figure 2) [17,18]; in all cross-sections preparation layers, paint layer(s) and a varnish layer were detected. Finally, a powder sample from the same sampling area was prepared for applying Fourier Transform infrared spectroscopy, where main organic and inorganic components were detected.

3.2. Underdrawings

Infrared reflectography provided detailed features concerning the artist's underdrawing; infrared images of whole panels are shown in Figure 1e–h, while selected details are shown in Figure 4. Not-easily recognizable details due to the deterioration of the varnish, such as the edges from Christ's garments (Figure 4e), the perimetric decoration of the pedestal at Christ's feet, and the Evangelists' symbols (Figure 4i), were identified. Traces of initial drawing (Figure 4a,d–i,l), were also detected by infrared photography and surface digital microscopy (DM). Characteristic is the finding in the inscription section of Panel 4, where a grid for the writing of the inscription was detected (Figure 4d–h).

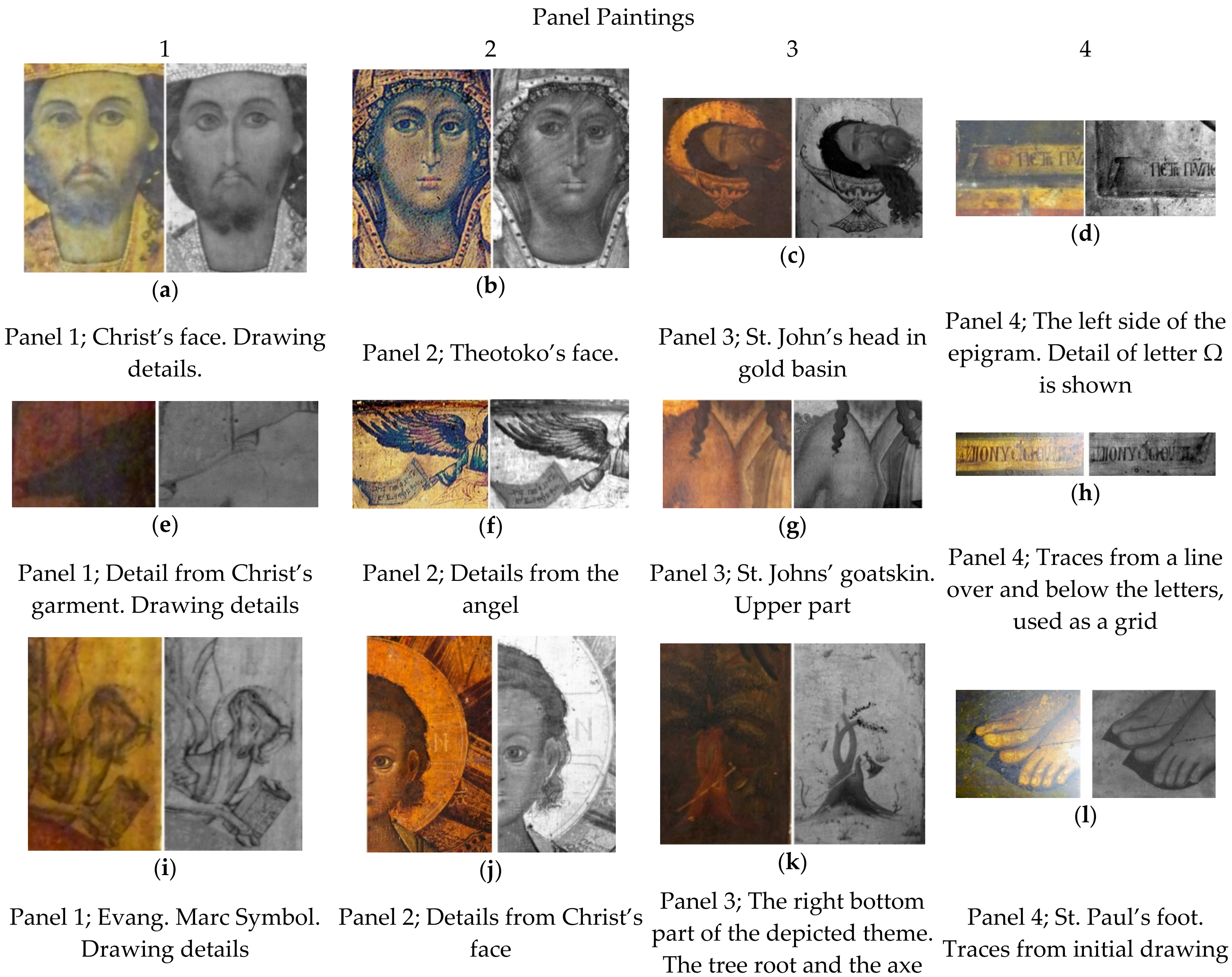


Figure 4. (**a**–**l**) Surface DM images (visible and infrared) showing details of underdrawings.

3.3. Preparation Layers

SEM investigation of the ground layer from the panel paintings showed two or three preparation layers (Figure 3, layer edges accentuated by dotted lines). In addition, elemental analysis with EDX spectroscopy identified calcium and sulfur, indicating calcium sulfate (Table 3).

Infrared spectroscopy (results listed in Table 4) applied in powder samples from PP1, and PP3 detected the presence of calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$, gypsum) due to the characteristic sulfate bands at 1139, 1115, 669, 602 cm^{-1} and the crystalline water peaks at 3551, 3402, 1622, and 1687 cm^{-1} [16,19]; these are shown in Figure 5a,c).

On the other hand, in the samples from painting panels 2 and 4, besides gypsum, the additional bands at 1542, 1458, and the shoulder at 1654 cm^{-1} suggest the presence of proteinaceous material (Figure 5b,d). Furthermore, subtracting a pure gypsum spectrum (i.e., the one in Figure 5c) from spectrum 5d shows proteinaceous material due to the characteristic amide I and II bands at 1655 and 1542 cm^{-1} (Figure 5e). This result suggests the use of *gesso*, as described in "Hermeneia," (a mixture of gypsum and animal glue) in PP2 and PP4. Finally, in the preparation sample from PP2, the presence of a band at 1385 cm^{-1} (Figure 5b) corresponds to the presence of nitrates ($NO_3{}^-$), possibly as the result of microbial action in wet environments [20].

Table 3. Elemental analysis results in the four panel paintings.

Layer/Area	Panel Paintings			
	1	**2**	**3**	**4**
	Surface analysis (pXRF) [1]			
Preparation layer	Spot 16, 17	Spot 28, 29	Spot 41, 42	Spot 44, 45
	Ca, S, Pb	Ca, S, Pb	Ca, S	Ca, S
Gold background	Spot 1–4, 10	Spot 18-20	Spot 30–32	Spot 44, 45
	Au, Ca, Fe, Pb, Cu, Hg (occasionally)	Au, Ca, Pb, Fe, Cu, Hg (occasionally)	Au, Ca, Fe, Pb	Au, Hg, Ca, Fe, Pb, Cu
Red area	Spot 6, 9	Spot 21, 22	Spot 36	Spot 46
	Pb, Hg, Fe	Pb, Hg	Pb, Hg, S	Pb, Hg
White pages from books	Spot 8	Spot 23, 24	Spot 37	
	Pb	Pb	Pb	
Flesh	Spot 5	Spot 21	Spot 34–36, 39	Spot 49–51
	Pb, Fe	Pb, Hg, Fe	Pb, Hg, Fe	Pb, Cu, Fe
Brown area	Spot 15	Spot 26, 27		Spot 48, 54
	Pb, Cu	Pb, Cu, Fe, Mn		Pb, Hg, Fe, Cu
Green area	Spot 13		Spot 40, 43	Spot 53, 55–56
	Pb, As, Fe, Cu		Pb, As, Fe, Cu	Cu, As, Pb, Fe
Blue area		Spot 25		
		Pb, Cu, Fe		
White garment			Spot 38	Spot 52
			Pb	Pb, Fe
	Micro-analysis of cross-section (SEM/EDX)			
Preparation	Ca, S	Ca, S	Ca, S	Ca, S
Bole layer	Ca, S, Al, Si, Mg, Fe	Ca, S, Al, Si, Mg, Fe	Ca, S, Al, Si, Mg, Fe	
Red pigment	Hg, S, Pb	Hg, S, Pb	Hg, S, Pb	
Flesh				Ca, Al, Si, Mg, Pb, Fe, Cu

[1] Spot numbers refer to point analysis spots shown in Figure 1.

Table 4. FTIR analysis showing the main components detected in the samples from the four panel paintings.

Material	Vibration [1]	Varnish Samples [1]				Notes
		PP1	**PP2**	**PP3**	**PP4**	
Gypsum	νO-H	3551 3402	3410	3551 3496 3407	3550 3408	Preparation layers Crystalline water
	δO-H	1687, 1622	1685, 1627	1687, 1622	1688, (1655) 1622	
	νS-O	1139 1115	1116	1140 1116	1144 1116	Preparation layers. Sulfate peaks
	δS-O	669, 602	670, 601	669, 602	670, 602	

Table 4. *Cont.*

Material	Vibration [1]	Varnish Samples [1]				Notes
Nitrates	νN-O		1385			Preparation layers. Biogenically formed
Proteinaceous material	Amide I (vC = O)		1655		1655	Preparation layers. Found as add-on in gypsum
	Amide II (vC = O + vC-N)		1542		1542	
	δCH_2		1458		1456	
Diterpenic resin	νO-H	3425	3442	3433	3451	Varnish layers
	ν C-H	30762935 2873	30762935 2873	30762935 2873	307429352873	
	νC=O	1709 1644	1720 (sh) 1710 1641	1721(sh) 1711 1644	1716(sh) 1706 1644	
	δC-H	1462 1451 1391	1462	1462 1451 1391	145813921377	
	δ_{ip}C-O-H	1413	1413	1413	1415	
	νC-O	1255	1250–1241	1246 1178	1239 1178	
	δ_{oop}C-O-H	890			890	
Triterpenic resin	O-H		3425		3425	Varnish layers
	νC-H		2959 (sh) 2874		2959 (sh) 2874	
	νC=O		1720		1716	
	δC-H		1462 1384		1458 1376	
	νC-O		1241		1239	
Oil binder	νC-H		2926 2855			Paint layers
	νC=O		1733			
	δC-H		1463 1377			
	νC-O		1250 1181			
	ρCH_2		721			
Carboxylates	νC-H		2925 2859		2932	Paint layers
	δC-H		1458		1461	
	νCOO^-		1542		1547	

[1] ν: stretching vibration; δ: bending vibration; δ_{oop}: out-of-plane bending vibration; δ_{ip}: in-plane bending vibration; ρ: rocking vibration.

3.4. Pigments, Gilding and Binders

For the characterization of Dionysius' color palette, pXRF on selected spots from the panel paintings was performed, along with EDX elemental microanalysis of cross-sections of microsamples (see Tables 1 and 3). These are shown in the following tables, separately, for each panel painting. Additionally, the binding medium was possible to investigate from a sample of PP2.

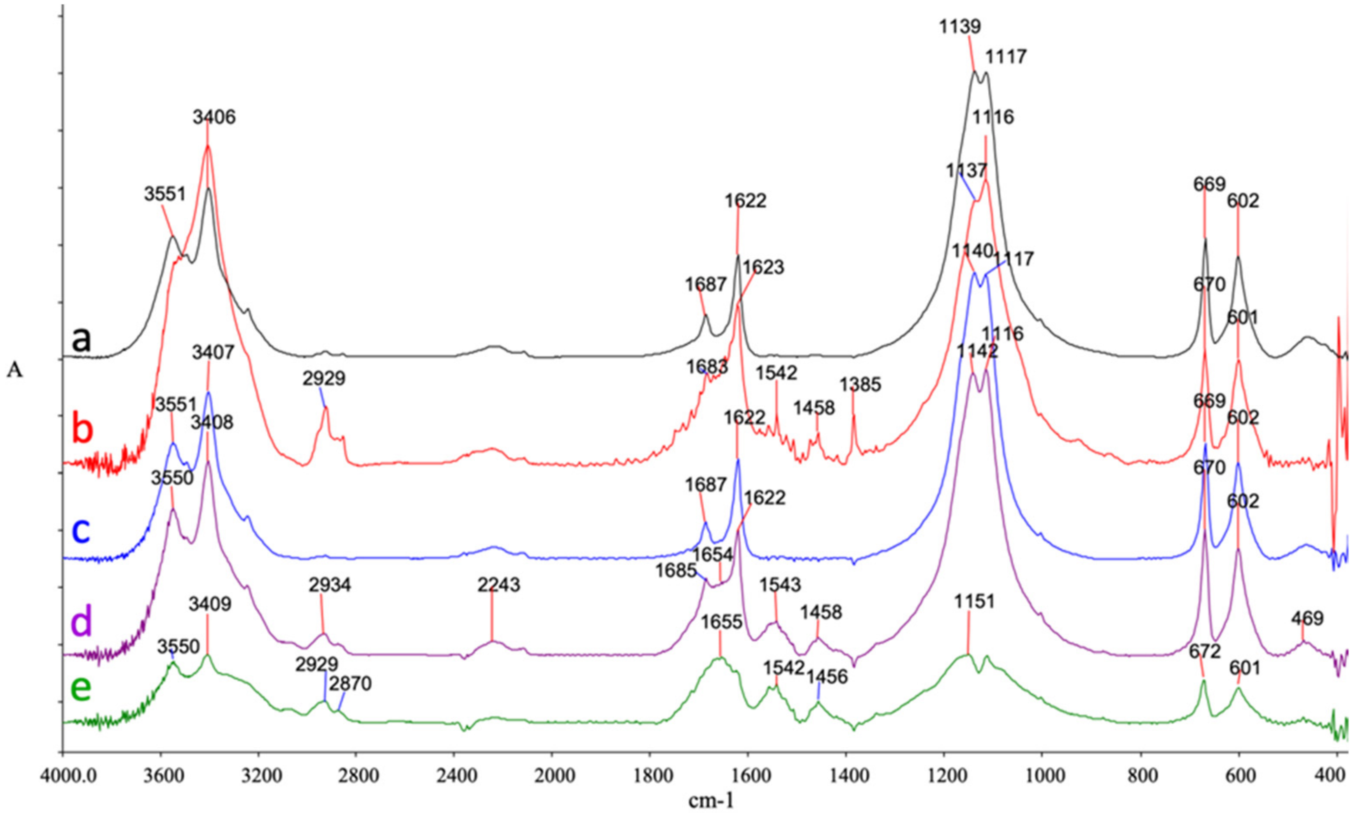


Figure 5. FTIR spectra of micro-samples from preparation layers of panel paintings (**a**) 1; (**b**) 2; (**c**) 3; and (**d**) 4; (**e**) difference spectrum: obtained from the subtraction of line c with line d.

3.4.1. Panel Painting 1: Christ as King of the Kings and Great High Priest

In situ XRF analysis: Surface elemental analysis showed the presence of lead in white areas (e.g. spot 5), suggesting the use of lead white ($2PbCO_3{\cdot}Pb(OH)_2$); lead, iron, and mercury in red areas, assumed the presence of red lead (Pb_3O_4), and red ochre (Fe_2O_3) along with cinnabar (HgS); finally copper and arsenic were detected in green areas, presumably, assumed the mixing of blue (azurite $2CuCO_3.Cu(OH)_2$), with a yellow pigment. The standard mixing of blue and yellow for obtaining green color was followed by Dionysius, even though there is no related reference in his treatise [3].

Cross-section analysis: The OM examination of the cross-section sample from the red perimetric frame of the panel revealed the existence of two overlapping red pigment layers with different grain sizes (Figure 2). EDX analysis detected the presence of lead (Pb) in the first layer, while the presence of cinnabar (HgS) in combination with lead red was identified in the second pigment layer (Figure 6a–d).

Gilding: Concerning the gilding technique, various pigment grains under the gold leaf were detected. According to EDX analysis, Al and Si are both indicative of the bole layer, Fe indicates the presence of ochre, while Hg and Pb signify the presence of cinnabar and, possibly, lead white, respectively (data not shown).

3.4.2. Panel Painting 2. Zoodochos Pigi—The Phaneromeni

In situ XRF analysis: Surface elemental analysis detected lead (in white and red areas), iron, and mercury (in red areas), while copper was identified in brown and blue areas. According to the above, it could be assumed that red lead (Pb_3O_4), red ochre (Fe_2O_3), and cinnabar (HgS) were the red pigments employed, while lead white ($2\ PbCO_3{\cdot}Pb(OH)_2$) was the white pigment used. In addition, azurite ($2CuCO_3{\cdot}Cu(OH)_2$) could be attributed to the blue pigments, while cuprite (Cu_2O) for the brown areas. Furthermore, the presence of manganese and iron in brown areas (spot 27), is an indication of brown pigments, such as umber [21], in variable quantities in order to achieve the right hue (elemental data are analytically listed in Table 3).

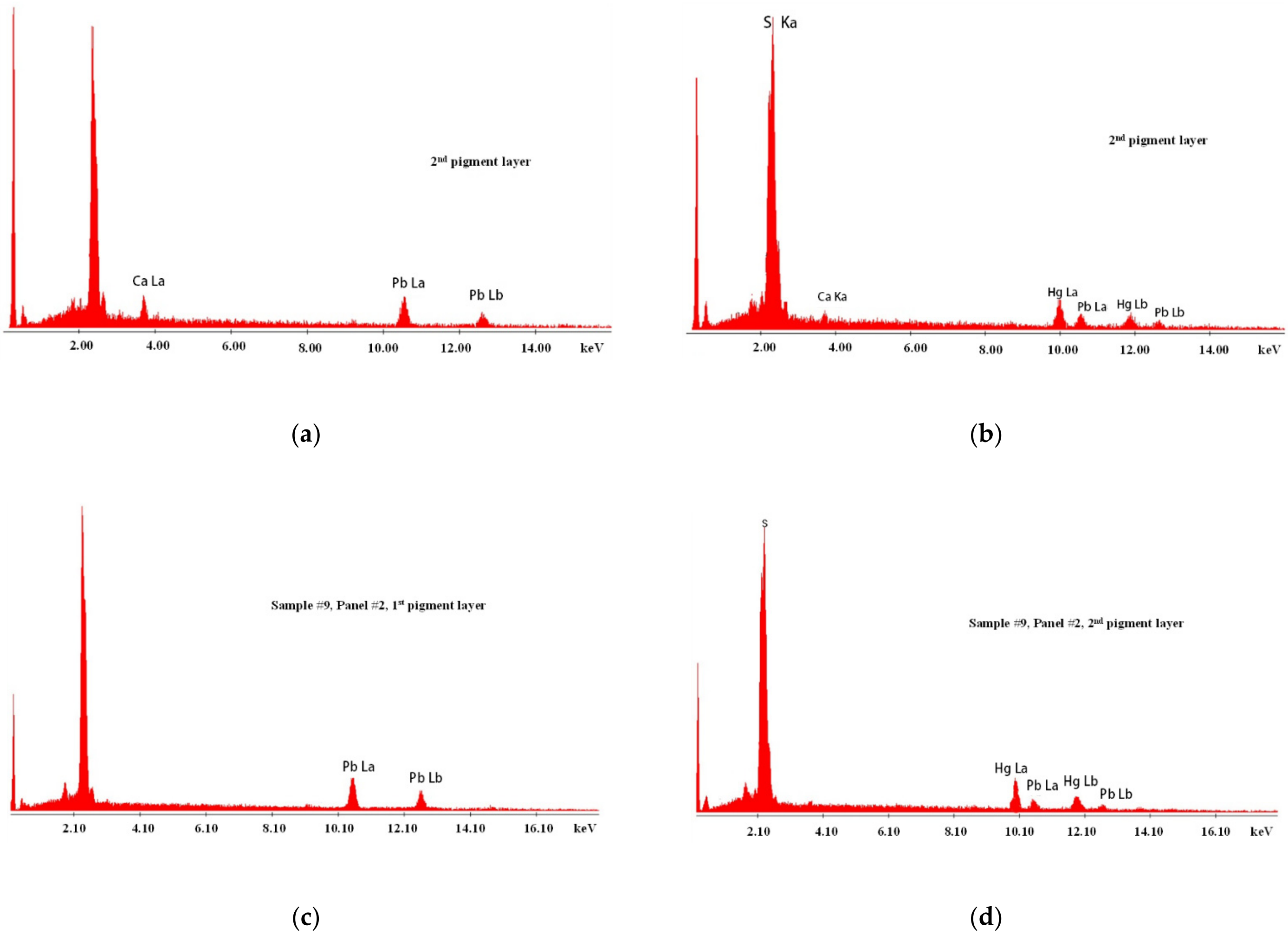


Figure 6. EDX spectra collected in the first pigment layer (**a**,**c**) and second pigment layer (**b**,**d**) of the cross-sections that belong to PP1 and PP2, respectively.

Cross-section analysis: OM examination of a cross-section sample from the lower part of the panel, and, more specifically, from the red perimetric frame, revealed the presence of two different red pigment layers (Figure 2); EDX analysis showed that the bottom layer of red contained lead (Pb_3O_4), while the upper layer, contained cinnabar (HgS) (Figure 6b).

Gilding: Concerning the gilding technique, DM and OM observation of the cross-sections revealed three layers in total. The first two were thin layers and these included the bole preparation (4.49 µm) and the gold leaf layer (2.9 µm) and a significantly thicker (85.35 µm), which was the gesso preparation layer.

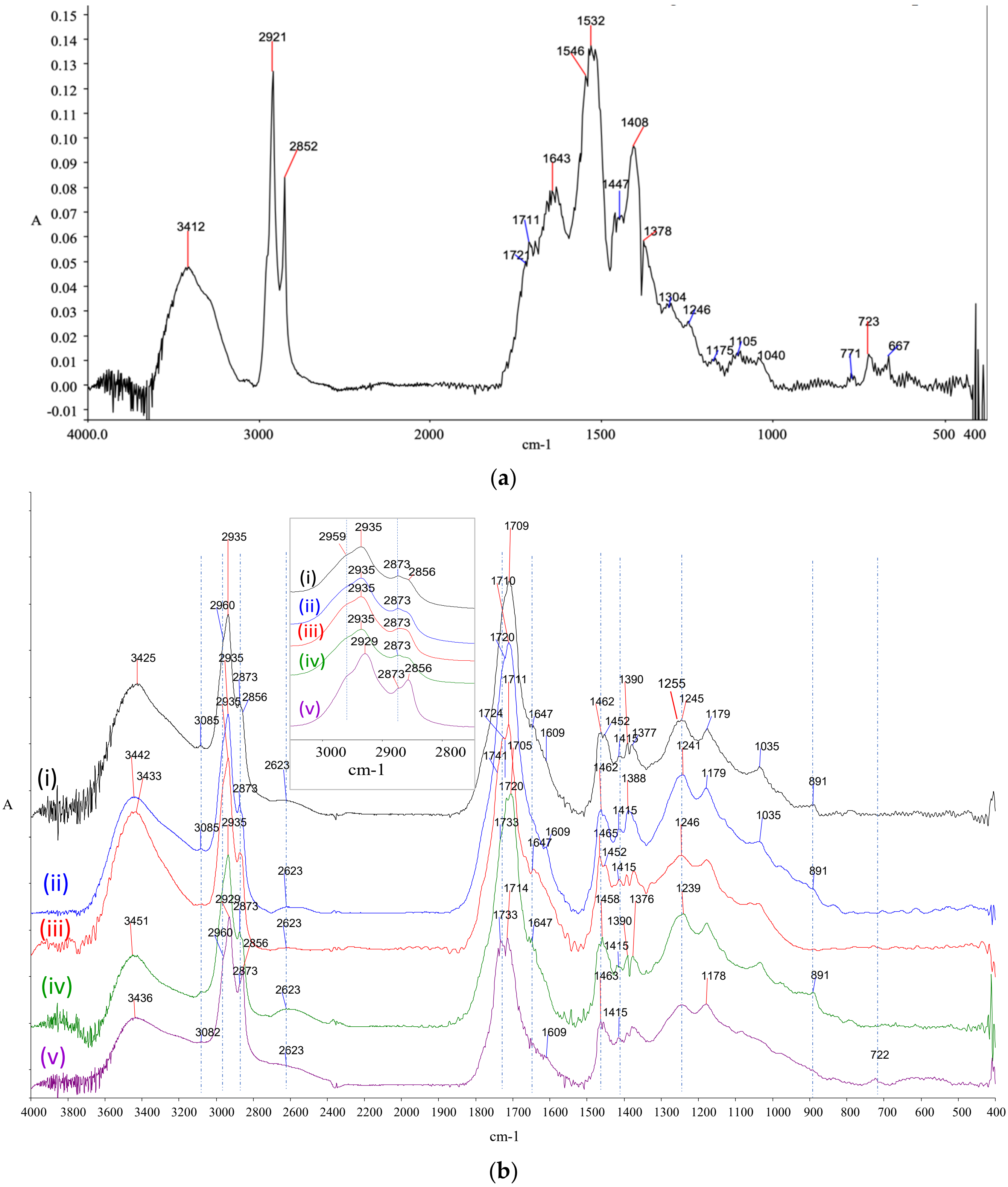


Figure 7. Infrared spectra of (**a**) powder sample from paint layer (spot 8); and (**b**) varnish layers of (i) PP1, (ii) PP2, (iii), PP3, (iv) PP4, and (v) acetone extract from varnish of PP2. Inset in 6b: Zoom in the C-H stretch region.

Binder: FTIR analysis of a sample detached from the paint layer of this panel showed oil binder maxima at 2921, 2852, 1711, 1447, and 723 cm^{-1} (see Figure 7a and Table 4 for assignments). In addition, intense carboxylate peaks at 1532 and 1408 cm^{-1} were detected, possibly, the result of interaction between either degraded oil medium (free fatty acids) or natural resin acids [22] and the metal ions (possibly, Zn^{2+}) from the pigments within the same layer [22–25]. Finally, the peaks at 1643, 1546 (shoulder) and 1246 cm^{-1} correspond to the amide I, II and III bands, respectively, typical of a proteinaceous material; for a more secure identification, however, further investigation is needed at this point [26–28].

3.4.3. Panel Painting 3. Saint John the Baptist—The Forerunner

In situ XRF and micro-samples analysis: Surface elemental analysis (Table 1) showed the presence of lead, mercury, iron, and copper. The assignment was assisted through the cross-section OM analysis, showing two different red pigment layers identified through EDX microanalysis. These contained mercury for the larger-grain layer, suggesting the presence of cinnabar (HgS), and lead for the smaller grain, possibly, lead red (Pb_3O_4). The presence of iron was also confirmed through EDX microanalysis of cross-section sample 11 (see Table 3).

Gilding: OM and SEM studies of the gilding, from a cross-section removed from the lower part of the panel (Figure 8) (the joint point of the vertical and the horizontal frame) confirmed the presence of relatively thin layers. For example, the bole layer of Al, Si, and Fe, was measured at 3.56 µm, while the gold layer, showing a discontinuity, was measured at 2.63 µm (Figure 7b).

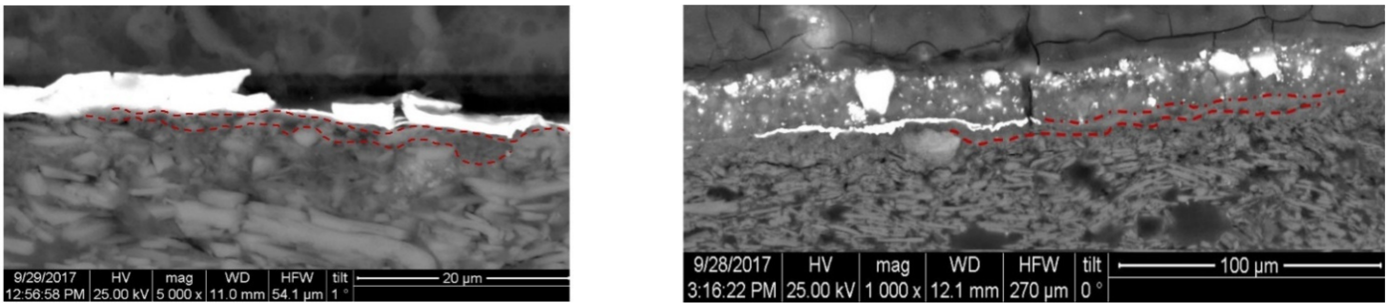


Figure 8. The thickness of the bole layer along with the discontinuity of the gold leaf; (**a**) sample 11 and (**b**) sample 13 (referring to samples in Figure 2).

3.4.4. Panel Painting 4. The Apostles Peter and Paul

In situ XRF and micro-samples analysis: Surface elemental analysis of PP4 showed the presence of lead, mercury, iron, and copper, similarly to the other panels. The assignment was assisted through the cross-section OM analysis of sample 19a, (St Peter's right foot), where two different painting layers (Figure 2) were observed; micro-elemental analysis identified the presence of iron, aluminum, manganese along with lead and copper (see Table 3). At the first pigment layer, according to the identified elements, it seems that terra verde pigment (Fe^{2+}/Fe^{3+} and Al^{3+}, Mg^{2+}, K^+ silicate) [21,29–32] was used, while micro-elemental analysis from the second painting layer, identified the presence of lead (Pb), possibly indicative of lead white.

In addition, lead, iron and copper were detected on St. Peter's (spot 49, 51) and St. Paul's faces (spot 50), which could be the result of mixing lead white and a yellow/red ochre with a small quantity of green, pigments corresponding to Hermeneia's guidelines for the proplasmos and the flesh areas [3]. Finally, the pXRF elemental analysis at the red area in spot 47 (Figure 1 and Table 1), at St. Paul's garment showed no other element besides gold, suggesting the possible presence of an organic pigment.

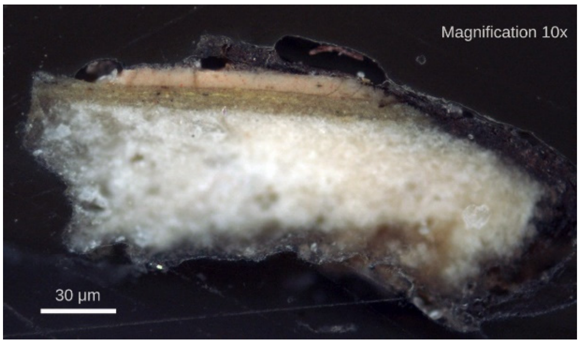
Binder: Concerning the characterization of binder, microchemical staining tests on cross-sections were performed. In particular, staining with Noir Amide 2 (positive test indicates proteinaceous materials [14,33]) in all the cross-section samples showed low selective staining, suggesting that the binder is weak in proteinaceous material.

In addition, the staining test from the cross-section sample 19A of PP4 showed low-intensity staining, especially at the pigment layer, in contrast to the gesso layer, which could confirm the hypothesis that the artist combined two different binders (Figure 9).

3.5. Organic Protective Coating

The examination of the cross-section samples from the four panel paintings under OM, revealed the presence of two and occasionally three, successive organic coating layers (Figure 2).

Powder samples, detached from each panel painting (sampling spots shown in Figure 1a–d) were analyzed with infrared spectroscopy (Table 4) showing in all cases maxima at 2938, 2850, 1706–1697, 1462/1452 (doublet), 1380, 1255–1241, 1178, 1035, 890 cm^{-1}, and shoulders at 3076, 1644 and 1415 cm^{-1}, assignable to a diterpenoid resin, probably, sandarac [16,34], with the possible addition of an another resin, possibly, triterpenoid, due to additional peaks or shoulders at 2959, 2873, ~1720, 1458–1460, 1245, 1170–1160, and 1115 cm^{-1} [16,35]. Spectra are shown in curves i–iv of Figure 7b, while assignments of main infrared peaks are listed in Table 4. Furthermore, an acetone extract of the sample from painting panel 2 (Table 2) shows mostly in Figure 7b (curve v) the diterpenic fraction as the more soluble to this solvent, with the possible addition of an oily material with maxima at 2929, 1731, and 720 cm^{-1}.



(**a**)

(**b**)

Figure 9. OM image showing Noir Amide staining test in cross-section 19A from PP4 (cf. with Figure 2): (**a**) before, and (**b**) after staining.

The above results for the use of more than one resin type are in accordance with the OM-observed overlapping layers of varnish (Figure 2) and may well support the hypothesis that either two different types of varnishes were used by the artist instead of one, also in agreement with Dionysius' text [16,34,35], or a second varnish layer was applied through conservation at unspecified time. Further analysis employing chromatographic techniques is needed to elucidate the varnish issue better.

4. Discussion

To summarize the analytical results (Table 5), optical microscopic inspection showing plaster extending at various depths across the preparation shows that the layers were applied quickly, not clearly, and without diligence. Furthermore, this study shows that significantly fewer (two) preparation layers than those suggested through the 'Hermeneia' text [3] were practically applied.

Table 5. Results obtained for each panel painting.

Materials	PP 1	PP 2	PP 3	PP 4
Gesso layer				
Calcium sulfate ($CaSO_4$)	Dihydrate	Hydrate	Dihydrate	Dihydrate
Bole Layer				
2nd or 3rd recipe	√	√	√	√
Gold layer				
Gold leaf, Au with Cu impurities	√	√	√	√
Pigments				
White lead [$2PbCO_3 \cdot Pb(OH)_2$]	√	√	√	√
Orpiment [As_2S_3]	√		√	√
Cinnabar [HgS]	√	√	√	√
Red lead [Pb_3O_4]	√	√	√	√
Red Ochre [Fe_2O_3+$SiO_2Al_2O_3$+SiO_2]	√	√		√
Umber [Fe_2O_3+$Al_2O_3SiO_2$+MnO_2(8-16%]		√		
Hematite [Fe_2O_3]	√	√		√
Verdigris [$Cu(CH_3COO)_2 \cdot 2Cu(OH)_2$]	√	√	√	
Terra Verde [Fe^{2+}/Fe^{3+} and Al, Si, Mg, and K]				√
Azurite [$CuCO_3 \cdot Cu(OH)_2$]	√	√	√	√
Binding media				
Proteinaceous materials	√	√	√	√
Lipids		√		
Varnish				
Mastic	√	√	√	√
Sandalwood	√	√	√	√
Oil		√		

The 'Hermeneia' text mentions three different recipes for the gilding technique [3] (Table 6). The implementation of microscopic techniques, such as OM and SEM, helped to locate the bole layer. Results from microelemental and molecular spectroscopic analysis suggest that the artist applied mainly the second recipe, while for the metal foil, the use of gold foil was confirmed.

Table 6. Hermeneia's recipes for the bole layer.

Recipes for Bole	
1st recipe	Bole (=clay) pale red, ochre, red lead, wax, burned paper, mercury
2nd recipe	Bole (=clay) pale red, ochre, soap, egg white
3rd recipe	Bole (=clay) pale red, ochre, red lead, cinnabar, egg white, gal, wax, mercury

According to the elemental analysis (pXRF and SEM-EDX) of selected pigments, it could be assumed that a variety of pigments was used, all of which are mentioned in Dionysius' treatise [3]. However, since XRF is an elemental analytical method, the addition of a molecular method, such as μRaman, would be useful for the safer characterization of the artist's palette [36–39]. In particular, red lead (Pb_3O_4), red ochre (Fe_2O_3) and cinnabar (HgS) were the red pigments used, and white lead ($2PbCO_3{\cdot}Pb(OH)_2$) was the white pigment found. For blue pigments, azurite ($2CuCO_3{\cdot}Cu(OH)_2$) was most likely used, while verdigris $Cu(CH_3COO)_2{\cdot}2Cu(OH)_2$) and terra verde ($Fe^{2+}/Fe^{3+}$, Al^{3+}, Mg^{2+}, and K^+ silicate) were utilized for green pigments and orpiment (As_2S_3) for yellow pigments. Furthermore, concerning the red pigments, OM and SEM showed that the artist typically used a first layer of red lead followed by a consecutive, thin layer of cinnabar. Additionally, it seems that he used a combination of pigments in order to achieve the right color hue. Concerning the pigment mixture for *proplasmos* (or flesh), the elemental analysis in different spots confirmed that Hermeneia's guidelines were followed [3].

Concerning the binding medium of the pigments, it was difficult to discern a specific instruction about the exact use of a binding medium. For example, Hermeneias' guidelines mention one kind of binding medium made from glue, potash solution, white wax, or garlic juice, for applying gold as a pigment. Furthermore, the use of egg medium is mentioned for the pigments and the use of egg white as a binding medium for the bole layer. Infrared spectroscopy results of PP2, sample 8, showed the presence of lipids in deteriorated condition; the possibility of proteinaceous material (Figure 6a), may suggest egg as medium. In addition, the weakly positive staining tests in combination with the FTIR results favor the hypothesis that Dionysius possibly used a proteinaceous binding medium in a mixture with an oily binder.

Concerning the binding media for the gesso layer, 'Hermeneia' guidelines mention the use of animal glue-gypsum mixtures. In addition, intense staining was observed in a preparation layer cross-section from PP4 (Figure 9), suggesting the presence of proteinaceous materials; its intensity, however, could be the result of the gesso preparation layer's porous structure.

The need for a more sophisticated, chromatography-based research protocol is here pointed out in order to achieve secure answers concerning the organic binding media of both the paint and the preparation layers.

Finally, regarding the organic protective coating, five different recipes for varnish are proposed by Hermeneia's author [3]. During spectroscopic analysis by FTIR, mastic and sandarac were detected with the possible addition of drying oil. Again, chromatographic analysis is also proposed for more precise identification of the varnish components and the possibility of drying oil. Furthermore, studying the cross-section samples by OM and SEM, different varnish layers were observed. Even though bibliography points out that the most widely used varnish (from the 9th c. A.D. till the late 17th c. A.D.) was made by dissolving mastic, or both mastic and sandarac in linseed oil [40], the results suggest that a sandarac-mastic mixture is not a possibility; instead, it is safer to assume that these are two different kinds of varnish applied on the panels at different times. Nevertheless, in any case, both these resins are mentioned in Hermeneias' treatise as ingredients for the varnish layer.

5. Conclusions

The use of the above-mentioned research protocol in Dionisius' four panel paintings revealed, for the first time, the artist's materials and techniques. Most of the data obtained from the research protocol show that Dionysius presented a more conservative approach in the Hermeneia than the actual execution of his artistic works. For example, it seems that he did not follow the instructions concerning the application of the gesso layer to the four (4) 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. For example, pXRF spectra obtained from Theotoko's face, showed the presence of cinnabar, along with the pigments for proplasmos, showing the relevance between instructions in Hermeneia and Dionysius' painting technique. Furthermore, OM clarified the presence of two overlapping pigment layers, while SEM helped study the preparation layer. Interestingly, although Hermeneia's text instructs for seven different plaster layers, the examined panel paintings showed only two or three (Figure 3).

From our data, it appears that Dionysius followed the given instructions in Hermeneia's text for two panels: Christ as King of the Kings and Great High Priest (PP1) and Zoodochos Pigi—The Phaneromeni (PP2) [1,3]. Concerning PP3, even though there are abundant references to Saint John the Forerunner that could be found in many sections of Dionysius' treatise [3], none of them describe his physical appearance and features. The iconography of PP4, with Apostles St. Paul and Peter holding a church model, is also remarkable, as it is not included among suggested subjects in the text [3]. 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 Hermeneia, even though Dionysius suggested many other epigrams to accompany these types of depicted themes for panel paintings. This can be explained by considering that the epigrams for these particular panel paintings were composed specifically for these themes and after completing his treatise [1].

The implementation of the research protocol in the studied panel paintings allows us to reach some further conclusions concerning the construction technique and compare his works with the text of his treatise. For example, it was possible to perceive Dionysius' color palette compared to his instructions in a particular part of the treatise [3]. Furthermore, through analytical techniques as FTIR, it was possible to identify the varnishes and compare the results with Hermeneia's text, 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. Additionally, the materials analysis provided information concerning the conservation history of these four panel paintings. Even though no previous conservation record has been found, some of the obtained data indicate previous conservation treatment which might have compromised the paintings' material integrity. Nevertheless, the results of this work suggest possible interventions, as shown through the FTIR spectra from PP2 (Table 4, Figure 5b), and from the cross-sections' observation for the organic protective coating, where overlapping layers of varnish were observed (Figure 2).

Giving a specific answer to the question 'did Dionysius follow the instructions of Hermeneia's text in his artistic work?' is challenging. The scientific examination from these panel paintings has offered some answers concerning the identity of materials. However, answering the above question requests a deeper understanding of the construction technology, which can be gained by broader coverage of Dionysius' work and a more extended research protocol; the latter could include GS/MS analysis techniques for identifying the varnish and the binders in the preparation and paint layers, and μRaman for confirming the pXRF results of pigments. Nevertheless, further research will offer more supporting data to better document Dionysius' technique and understand post-Byzantine painting. Furthermore, it will offer more convincing clues for the reform period of post-Byzantine painting (starting in the 18th century), for which Dionysius is accredited.

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Glossary

Bole	a generic term used for a velvety-smooth reddish earth composed of clay and red iron oxide (Fe_2O_3). It was used in gilding to temper the color and size.
Forerunner (or Prodromos)	refers to St. John the Baptist, as the person that precedes the coming of Christ.
Hermeneia	Greek word meaning "interpretation".
Phaneromeni	refers to religious icons (often of Virgin Mary) miraculously appeared.
Proplasmos	skin shown in painting.
Theotokos	Greek word meaning the "mother of God".
Zoodochos Pigi	Greek word meaning the Life-giving fountain, referring to Virgin Mary.

Abbreviations

DM	Digital Microscopy.
EDX	Energy Dispersive X-ray analysis.
FTIR	Fourier Transform Infra-Red spectroscopy.
GC/MS	Gas Chromatography-Mass Spectrometry.
OM	Optical Microscopy.
PP	Panel Painting.
pXRF	portable X-ray Fluorescence.
SEM	Scanning Electron Microscopy.

References

1. Kakavas, G. *Dionysios of Fourna (c. 1670–c. 1745): Artistic Creation and Literary Description*, 1st ed.; Alexandros Press: Leiden, The Netherlands, 2008.
2. Moutafov, E. Post-Byzantine Hermeneia zographikes in the eighteenth century and their dissemination in the Balkans during the nineteenth century. *Byz. Mod. Greek Stud.* **2006**, *30*, 69–79. [CrossRef]
3. Papadopoulos-Kerameas, A. *Dionysius of Fourna, Hermeneia of the Painting Art and its Main Unpublished Sources*; Russian Imperial Archaeological Society: St Petersbourg, Russia, 1909.
4. Vassilaki, M. Ακολουθώντας τα βήματα του Διονυσίου. *Δελτίο Της Χριστιανικής Και Αρχαιολογικής Εταιρείας* **2012**, *33*, 379–386.
5. Daniilia, S.; Bikiaris, D.; Burgio, L.; Gavala, P.; Clark, R.J.H.; Chryssoulakis, Y. An Extensive Non-Destructive and Micro-Spectroscopic Study of Two Post-Byzantine Overpainted Icons of the 16th Century. *J. Raman Spectrosc.* **2002**, *33*, 807–814. [CrossRef]
6. Diamantopoulos, A.C. Dionysius of Fourna and the practice of Icon painting: A comparative study of his technical treatise and the painting of the Oberlin Icon, St Gregory the Theologian and St. *Artemios. Bull. Allen Meml. Art Mus.* **1993**, *46*, 17–36.
7. Oltrogge, D. Byzantine recipes and book illumination. *Rev. Hist. Arte* **2011**, *1*, 59–61.
8. Mastrotheodoros, G.; Beltsios, K. Sound Practice and Practical Conservation Recipes as Described in Greek Post-Byzantine Painters' Manuals. *Stud. Conserv.* **2018**, *64*, 42–53. [CrossRef]
9. Mastrotheodoros, G.; Beltsios, K.; Bassiakos, Y. On the blue and green pigments of post-byzantine greek icons. *Archaeometry* **2020**, *62*, 774–795. [CrossRef]
10. Ferens, M.J. Dionysius of Fourna: Artistic Identity Through Visual Rhetoric. Master's Thesis, University of California, Riverside, CA, USA, June 2015.
11. Homar, A.R. Analisis, Contexto y Relaciones entre el Manual de Pintura de Dionisio de Fourna y la Pintura Iconografica y Mural de la Peninsula del Monte Athos. Ph.D. Thesis, Universidad de Murcia, Murcia, Spain, 2016.

12. Westlake, P.; Siozos, P.; Philippidis, A.; Apostolaki, C.; Derham, B.; Terlixi, A.; Perdikatsis, V.; Jones, R.; Anglos, D. Studying Pigments on Painted Plaster in Minoan, Roman and Early Byzantine Crete. A Multi-Analytical Technique Approach. *Anal. Bioanal. Chem.* **2012**, *402*, 1413–1432. [CrossRef]
13. Martin, E. Some Improvements in Techniques of Analysis of Paint Media. *Stud. Conserv.* **1977**, *22*, 63–67. [CrossRef]
14. Terlixi, A.V.; Doulgeridis, M.; Ioakimoglou, E. Staining and Fluorescent Staining Techniques for the Characterization of Binding Media within Paint Cross-Sections. Examination of Post-Byzantine Icons from the National Gallery of Athens—Alexandros Soutzos Museum's Collection as a Case Study. In Proceedings of the International Meeting. Icons: Approaches to Research, Conservation and Ethical Issues, Athens, Greece, 3–7 December 2006.
15. Mastrotheodoros, G.P.; Beltsios, K.G.; Bassiakos, Y.; Papadopoulou, V. On The Grounds of Post-Byzantine Greek Icons. *Archaeometry* **2016**, *58*, 830–847. [CrossRef]
16. Derrick, M.R.; Stulik, D.; Landry, J.M. *Scientific Tools. Infrared Spectroscopy in Conservation Science*; Getty Conservation Institute: Los Angeles, CA, USA, 1999.
17. Derrick, M.; Souza, L.; Kieslich, T.; Florsheim, H.; Stulik, D. Embedding paint cross-section samples in polyester resins: Problems and solutions. *J. Am. Inst. Conserv.* **1994**, *33*, 227–245. [CrossRef]
18. Mazzeo, R.; Prati, S.; Sandu, I. Optical Microscopy. In *Scientific Examination for the Investigation of Paintings. A handbook for Conservators-Restorers*; Pinna, D., Galleotti, M., Mazzeo, R., Eds.; Centro Di: Florence, Italy, 2009; pp. 179–183.
19. Melo, H.P.; Cruz, A.J.; Candeias, A.; Mirao, J.; Cardoso, A.M.; Oliveira, M.J.; Valadas, S. Problems of analysis by FTIR of calcium sulphate based preparatory layers: The case of group of 16th century Portuguese paintings. *Archaeometry* **2014**, *56*, 513–526. [CrossRef]
20. Ciferri, O. Microbial degradation of paintings. *Appl. Environ. Microbiol.* **1999**, *65*, 879–885. [CrossRef] [PubMed]
21. Eastaugh, N.; Walsh, V.; Chaplin, T.; Siddal, R. *Pigment Compendium. A Dictionary and Optical Microscopy of Historical Pigments*; Butterworth-Heinemann: Oxford, UK, 2008.
22. Poli, T.; Chiantore, O.; Diana, E.; Riccirillo, A. Drying Oil and Natural Varnishes in Paintings: A Competition in the Metal Soap Formation. *Coatings* **2021**, *11*, 171. [CrossRef]
23. Hermans, J.J.; Keune, K.; Van Loon, A.; Iedema, P.D. Toward a Complete Molecular Model for the Formation of Metal Soaps in Oil Paints. In *Metal Soaps in Art*; Springer: Cham, Switzerland, 2019; pp. 47–67.
24. Hermans, J.J. *Metal Soaps in Oil Paint: Structure, Mechanisms and Dynamics*; University of Amsterdam: Amsterdam, The Netherlands, 2017.
25. Otero, V.; Sanches, D.; Montagner, C.; Vilarigues, M.; Carlyle, L.; Lopes, A.J.; Melo, J.M. Characterization of metal carboxylates by Raman and infrared spectroscopy in works of art. *J. Raman Spectrosc.* **2014**, *45*, 1197–1206. [CrossRef]
26. Riaz, T.; Zeeshan, R.; Zarif, F.; Ilyas, K.; Muhammad, N.; Safi, S.Z.; Rahim, A.; Rizvi, S.; Rehman, I.U. FTIR analysis of natural and synthetic collagen. *Appl. Spectrosc. Rev.* **2018**, *53*, 703–746. [CrossRef]
27. De Campos Vidal, B.; Mello, M.L.S. Collagen type I amide I band infrared spectroscopy. *Micron* **2011**, *42*, 283–289. [CrossRef]
28. Payne, K.J.; Veis, A. Fourier transform IR spectroscopy of collagen and gelatin solutions: Deconvolution of the amide I band for conformational studies. *Biopolymers* **1988**, *27*, 1749–1760. [CrossRef]
29. Feller, R.L. *Artists' Pigments. A Handbook of Their History and Characteristics*; National Gallery of Art: Washington, DC, USA, 1986.
30. Χατζηδάκη, Ν.; Phillipon, J.; Ausset, P.; Χρυσουλάκης, Ι.; Αλεξοπούλου, Α.θ. Συμβολή Των Φυσικοχημικών Μεθόδων Ανάλυσης Στη Μελέτη 13 Εικόνων Του Βυζαντινού Μουσείου. *Δελτίο Της Χριστιανικής Και Αρχαιολογικής Εταιρείας* **1988**, *13*, 215–246. [CrossRef]
31. Fitzhugh, W.E. *Artists' Pigments*; National Gallery of Art: Washington, DC, USA, 1997; Volume 3.
32. Parry, E.J.; Coste, J.H. *The Chemistry of Pigments*; Scott, Greenwood & Co.: London, UK, 1902.
33. Abd el Salam, S. A Binding Media: Methods of Identification: Part 1, Theoretical Work. *J. Phys. Sci. Appl.* **2011**, *1*, 204–215. [CrossRef]
34. Azémard, C.; Vieillescazes, C.; Ménager, M. Effect of photodegradation on the identification of natural varnishes by FT-IR spectroscopy. *Microchem. J.* **2014**, *112*, 137–149. [CrossRef]
35. Bruni, S.; Guglielmi, V. Identification of archaeological triterpenic resins by the non-separative techniques FTIR and 13C NMR: The case of Pistacia resin (mastic) in comparison with frankincense. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2014**, *121*, 613–622. [CrossRef]
36. Clark, R.J. Applications of Raman Spectroscopy to the Identification and Conservation of Pigments on Art Objects. *Handb. Vib. Spectrosc.* **2006**, 2977–2992. [CrossRef]
37. Burgio, L.; Clark, R.J. Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2001**, *57*, 1491–1521. [CrossRef]
38. Burgio, L.; Clark, R.J.; Theodoraki, K. Raman microscopy of Greek icons: Identification of unusual pigments Spectrohim. *Acta A Mol. Biomol. Spectrosc.* **2003**, *59*, 2371–2389. [CrossRef]

39. Bersani, D.; Lottici, P.P. Raman spectroscopy of minerals and mineral pigments in archaeometry. *J. Raman Spectrosc.* **2016**, *47*, 499–530. [CrossRef]
40. Gettens, R.J.; Stout, G.L. *Painting Materials. A Short Encyclopaedia*, 3rd ed.; Dover Publications: New York, NY, USA, 1966.