

Article

Degradation Products Assessment of the Wooden Painted Surfaces from a XVIIth Heritage Monastery

Rodica-Mariana Ion ^{1,2,*} , Lorena Iancu ¹, Ramona Marina Grigorescu ¹ , Sofia Slamnoiu-Teodorescu ³, Ioana Daniela Dulama ³  and Ioan Alin Bucurica ³ 

¹ National Institute for Research, Development in Chemistry and Petrochemistry—ICECHIM, Research Group “Evaluation and Conservation of Cultural Heritage”, 202 Splaiul Independentei, 060021 Bucharest, Romania

² Doctoral School of Materials Engineering Department, “Valahia” University of Targoviste, 35 Lt. Stancu Ion, 130105 Targoviste, Romania

³ Institute of Multidisciplinary Research for Science and Technology, Valahia University of Targoviste, 130004 Targoviste, Romania

* Correspondence: rodica_ion2000@yahoo.co.uk or rodica.ion@valahia.ro

Abstract: Currently, approximately 70% of paintings in museum collections are affected by the presence of metallic soaps, evidenced by spherical globules visible on the surface of the paintings. They are responsible for altering the paintings’ surface through processes such as exfoliation and cracking, or even in the form of surface “skins” that appear in the pictorial layers. The objective of this study is the investigation of the icon paintings from Saint Mary Monastery, Techirghiol, Romania, which underwent some restoration procedures. This study is so important/significant, due to the presence of efflorescence that is correlated with the conversion of some fatty acids, as palmitic acid, stearic acid and azelaic acid, in the so-called metallic soaps through the reaction of the metals contained in the pigments from the painting layer and the binder. The investigated paintings are strongly affected by zinc carboxylate aggregation, and for this, the sample was embedded in polyester resin and the obtained cross-section, after polishing, was investigated by microscopic techniques (optical microscopy (OM), stereomicroscopy, and scanning electron microscopy with electronic dispersion spectroscopy (SEM-EDS), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, and gas-chromatography with mass spectrometry (GC-MS) in good agreement with data from the literature. The potential result of this study is the identification and quantification of the metallic soap generated as a white deposit (probably salts, a kind of white efflorescence), from the binding medium of the metal carboxylate ionomer, by the crystallization of saturated fatty acids, through polymerization in oil. Six pigments (calcite, lithopone, carbon black, red ochre, vermilion, and ultramarine), present in the sublayers of the samples were identified.

Keywords: painting alteration; FTIR; GC-MS and SEM-EDS



Citation: Ion, R.-M.; Iancu, L.; Grigorescu, R.M.; Slamnoiu-Teodorescu, S.; Dulama, I.D.; Bucurica, I.A. Degradation Products Assessment of the Wooden Painted Surfaces from a XVIIth Heritage Monastery. *Appl. Sci.* **2023**, *13*, 2124. <https://doi.org/10.3390/app13042124>

Academic Editor: Ion Sandu

Received: 27 December 2022

Revised: 21 January 2023

Accepted: 26 January 2023

Published: 7 February 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Works of art generally contain inorganic and/or organic compounds combined in complex ways. This is the case of traditional oil paintings, in which inorganic and/or organic pigments are mixed with a drying oil, after which the resulting mixture is applied to a canvas, wood, or metal support, and a protective organic coating is applied on top. Icons on wood are generally executed by using an artistic egg tempera technique on a grounded wooden panel (or support) [1].

The support can be of lime tree or fir and consists of two or more tabletops glued animal glue, while the painting layer consists of primer, color film and varnish [2].

The deterioration process of the painting layer (ground, strip, and varnish) is a very complex one, the main effects being: erosion and scratches, crackles, fissures, cracks, detachments, exfoliation, gaps, flight holes and galleries mold stains, candle wax spots, carbonization, spots of dirt adherence, brown-red lacquer, varnish erasing, agglomerations,

and carbonization [3]. Certainly, wood could contribute at the painting degradation process, by deformations of the wooden countertop, cracks, and fractures [4,5].

The metal soap observed in paintings from the 17th to the 20th centuries is the most aggressive degradation form occurring on many paintings, focusing on changes in surface appearance, notably implicating lead, zinc, or other metal soaps in the formation of insoluble efflorescent crusts [6,7]. Although they are found in most old paintings, the action mechanism of metallic soaps is unclear, primarily due to subsequent restorations that took place [8–10]. Various publications have reported that the particularities of the materials, as well as the artists' techniques, can be responsible for the formation of metallic soaps, or the conservation procedures to which the respective paintings were subjected, or the environmental conditions in which they were stored: relative humidity, high temperature, or solar radiation [11,12].

Built in the 17th century by the peasants of Maiorești (Mureș district), the wooden Saint Mary monastery, Techirghiol, Constanta (Figure 1), dedicated to “St. Apostles Peter and Paul” was moved in 1934 by King Carol II to the Pelișor Castle in Sinaia, where, after the establishment of Communism, it remained in vain until Patriarch Justinian brought it and restored it at Techirghiol, Constanta county (Figure 1). The church walls are made of oak beams of varying thickness between 25–30 cm, horizontally superimposed and joined by a technique specific to the Transylvanian wooden lodges called “dovetail tail” and in some places by wooden nails. On the painted scenes on the walls, no original inscriptions were preserved, some of which being rebuilt in the first part of the 19th century. It is one of the few wooden churches that has preserved its entire painting. Between 1965 and 1967, Patriarch Justinian initiated renovations and expansion of the fireplace (the wing extended and overcrowded) and between 1975–1977 the left wing of the complex was built and the perpendicular part joining the two wings gave the complex the appearance of traditional monasteries (especially of the Brancoveanu dynasty).



Figure 1. The photo of St. Mary Church, Techirghiol (personal photo).

Wooden icons represent the most common image of interest in religious worship. They can be made of deciduous (linden) or coniferous (fir) wood, and sometimes they are made of successive tops, glued together with animal glue. The wooden panel is prepared by applying several layers of white gesso (a thick layer of plaster), because this leads to the smoothness of the surface and minimal roughness [13]. The paint layer consists of primer, colored paste, and varnish. After drying, the icon is covered with a varnish such as olipha (a mixture of linseed oil and turpentine).

The old wooden paintings found in the Orthodox churches were made using the tempera or oil technique, being later varnished or not, applied to the wooden panels prepared as mentioned previously. In the tempera technique, mineral pigments are mixed with water and egg yolk. Common pigments were used, as follows: iron oxide for red, iron oxide-hydroxide for yellow, and lapis lazuli for blue [14–17]. Taking into account all the identified species, the mechanism of metallic soap formation is the following: the polymerization of the oil and the binding of the carboxyl group to the pigment used, following these steps: the migration of metal ions in the network of polymerized oil; the binding of the carboxylate ion to the metal; the crystallization of the metal soap determined by the presence of saturated fatty acids; the diffusion of metal ions and fatty acids to the core of the metal soap, and its migration to the painted surface [18].

In the case of zinc soap, the zinc-containing pigments and drying varnishes readily react with fatty acids in oil-based paints to form zinc carboxylates. Through the formation of these carboxylates, processes such as severe cleavage, the loss of paint, disfigurement due to some agglomerated formations, increased transparency and surface efflorescence occur, are to list only a few problems associated with zinc soaps. As they crystallize, zinc soaps can cause severe delamination - both between and within layers of paint—resulting in the loss of structural integrity of the painting [19]. Different phases were identified during zinc soap formation: amorphous zinc soaps, considered as the intermediate stage, and crystalline zinc soaps, as the final stage in the degradation process, which causes delamination and increased brittleness of the paint [20,21].

There are many studies related to the deterioration of paintings associated with the aggregation of metallic soaps. In general, zinc-based aggregates contain soaps formed from palmitic and stearic acids [22,23]. By oxidation, the paint becomes more polar, and the zinc stearate and palmitate formed become less compatible with the paint matrix and form a separate phase [14–17]. However, the azelaic acid, a product of oxidative degradation of the predominant C18 unsaturated fatty acids in dried oils, is identified near the perimeter of the aggregates [24].

The white crusts that appear on paintings from the 17th–18th century can be caused by humidity gradients and capillarity as factors responsible for migration to the surface. The oleic acid levels could be an indicator of embrittlement in zinc oxide paints, due to the oxidation of oleic acid (C18:1) to azelaic acid during paint curing, by comparison with the modern paints, where the formation of fatty acid soaps immobilizes and prevents migration of stearic and palmitic acids to the surface [25].

Metal soaps are complexes of metal ions from pigments with long-chain fatty acids. The adoption of ZnO by the paint industry in artists' paints in France appeared as early as 1784 [26], and in Great Britain, zinc-white watercolor paints appeared in 1834 [27]. The first occurrence of zinc white in oil tubes was only reported in 1860. There is documentary evidence that zinc oxide was progressively incorporated into prepared paints and pigment materials, often undeclared [28].

The characterization of the materials and degradation products (metal soaps) found in this type of artwork, and how metal soaps influence the appearance of the artwork and the selection of the restoration procedures, have to be investigated. Additionally, the paint layers' deterioration based on lead pigments appears as craters (holes with 100 µm diameter and protrusions), as whitish protruding materials [15].

For the identification of the components of the painting layer, among the most used specific analytical techniques are: scanning electron microscopy with energy dispersive

spectroscopy (SEM-EDS), which allows the elemental analysis of the pigments and additives used, gas chromatography coupled with mass spectrometry (GC-MS), the latter allowing the identification of chemical changes in paints during oil drying [29]. In some cases, the GC-MS technique involves a specific preparation of the sample by hydrolysis and methylation of fatty carboxylic groups, leading to esters, free acids, and metal carboxylates [30]. In addition to these techniques, Fourier transform infrared spectroscopy (FTIR) is also used, which allows the identification of metal soaps in paints, the metal associated with the carboxylate group (through peaks attributed to asymmetric CO ($\nu_{as}(\text{CO})$) and symmetric CO ($\nu_s(\text{CO})$) [31]. As an example, lead, calcium, and copper carboxylates from 15th century paintings were identified by $\nu_{as}(\text{CO})$ frequencies 1540 and 1513, 1576 and 1539, and 1585 cm^{-1} . Metal soap chains can also be identified by Raman spectroscopy [32]. Last, but not least, the elemental distribution of metals and the new formed metal carboxylates can be obtained by X-ray fluorescence (XRF) [33] and, respectively, by X-ray diffraction (XRD) [34,35]. All these techniques allow the identification of the morphology, the elemental composition, and the crystalline phases of the metallic soaps.

In this paper, the presence of metallic soaps, as well as the degradation processes related to several icons painted on wood from the Romanian church (Sf. Maria Monastery, Techirghiol) are analyzed. In order to comply with the cultural heritage protection criteria, only small, detached fragments were used for the experiments, with no heritage value and no possibility of reuse. Prepared as cross-sections, the samples were examined using optical microscopy (OM), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, wavelength-dispersive X-ray fluorescence spectroscopy (WDXRF), and gas chromatography with mass spectrometry (GC/MS).

2. Materials and Methods

2.1. The Church Painting Samples

The photographs of the painted surfaces from where the samples have been taken (0.5–1 mm) can be seen in Figure 2.



Figure 2. The interior of church nave—eastern part used for sampling.

2.2. Characterization Methods

Optical microscopy (OM) images were obtained with a Novex Microscope BBS trinocular microscope (EUROMEX Microscopen, Arnhem, The Netherlands) (magnifications: 40 $\times$, 100 $\times$, 400 $\times$, 1000 $\times$). The microscope is equipped with a digital video camera (EUROMEX-HOLLAND), through the microscope software (ZenPro), allowed the acquisition of data in real time. The images were processed using the ImageJ 1.50 software (free soft). Additionally, the optical microscopy was recorded by a ZEISS Primo Star optical microscope working at 4 $\times$ and 100 $\times$ magnifications. The equipment is equipped with a digital video camera (AxioCam 105) that allows the acquisition of data in real time.

For the cross-section investigations, the damaged paint fragments, with sizes between 0.5 and 1 mm were embedded in polyester resin, dried at room temperature, and then microtomed with a tungsten knife. After the resin cured, the samples were dry polished using Micromesh™ polishing cloths.

For stereomicroscopy, a Stereo trinocular stereomicroscope (EUROMEX Microscopen B.V., BD Arnhem, Holland), model 1903, was used (magnification degrees of 7–45 $\times$).

For Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) a SU-70 (Hitachi, Japan) microscope was used with a magnification range: 30 $\times$ –800,000 $\times$. This microscope has an energy dispersive spectrometer (EDS) device for a qualitative and quantitative elemental analysis.

The wavelength dispersive X-ray fluorescence (WDXRF) was carried out on a Rigaku ZSX Primus II spectrometer (Rigaku, The Woodlands, TX, USA) equipped with an X-ray tube with Rh anode, 4.0 kW power, with front Be window (30 μ m thickness). The measurements were carried out under vacuum atmosphere on pressed pellets.

FTIR spectra (ATR-FTIR) were recorded on paint cross-sections using a Vertex 80 spectrometer (Bruker Optik GmbH, Ettlingen, Germany) in the range 4000–400 cm^{-1} , 32 scans, resolution 4 cm^{-1} , with the attenuated total reflectance mode, ATR, equipped with a germanium crystal. Data were processed and interpreted using Bruker Opus 7.5 software. Additionally, the spectra were interpreted by comparison with references in the material collection of the Database of ATR-FT-IR spectra of various materials.

Raman spectra have been measured with a Raman wavelength portable analyzer (Rigaku, The Woodlands, TX, USA) equipped with a 785 and 1064 nm stabilized laser, providing high sensitivity. A resolution of 4 cm^{-1} with a laser power of 252 mW was used for measurements. The data were collected and processed with the Opus 7.0 software (Bruker Optics GmbH, Ettlingen, Germany).

For the chromatic parameters' measurements, a CR-410 colorimeter (Konica Minolta, Tokyo, Japan) was used. By applying the CIELAB standard [36,37], the following parameters were measured:

L^* -brightness ($L^* = 0$ (black) to 100 (white));

a^* -red/green variation (a^* -red/green coordinate, with + a^* meaning red and - a^* meaning green),

b^* -yellow/blue variation (b^* -yellow/blue coordinate, with + b^* meaning yellow and - b^* meaning blue).

For gas chromatography with mass spectrometry (GC-MS) analysis, a GC/MS Triple Quad Agilent chromatograph has been used with the following parameters; DB-WAX column ($L = 30$ m, $D = 250$ μ m, $d = 0.25$ μ m); Oven Program: 50 $^{\circ}\text{C}$ for 5 min, 4 $^{\circ}\text{C}/\text{min}$ at 150 $^{\circ}\text{C}$, 10 $^{\circ}\text{C}/\text{min}$ at 320 $^{\circ}\text{C}$; carrier gas: He, Flow = 1 mL/min; QQQ Collision Cell: Quench Flow Gas (He) = 2.2 mL/min; Collision Flow Gas (N_2) = 1.5 mL/min; Source: EI, Electron Energy: 70 eV, Temperature: 230 $^{\circ}\text{C}$, auxiliary temperature: 280 $^{\circ}\text{C}$.

The samples collected from the paintings was prepared in the following way: 100 mL of dichloromethane and 100 mL of 2 M KOH solution were mixed with the sample (<0.1 mg). The obtained solution was stirred for about 2 min and left for 15 min at 60 $^{\circ}\text{C}$. After that, 500 mL of a solution of HCl and CH_3OH (1:1) were added and the final product was extracted three times using with 100 mL of dichloromethane. The solution was evaporated to 150 mL under a mild flow of N_2 , and finally analyzed by GC-MS.

3. Results and Discussion

In oil painting conservation, the occurrence of metal soaps through the reaction between metallic ions and saturated fatty acids is currently a growing concern. In the case studied in this paper, large deposits of metallic soaps were found on the exposed surface of the paintings, visible by optical microscopy and stereomicroscopy. However, some case studies have been reported where saturated fatty acids migrated from the paint layer and crystallized on the paint surface. All these processes affect both the oil painting aspect and their structural integrity. Additionally, the formation of metallic soap created a painted surface with protrusions, visible by optical microscopy, in good agreement with the specialized literature [24].

For identifying the metallic soap and the degradation products of these icons, the following directions are followed in this work:

(1) The study of macro and microscopic aspects that reveal the current state of icon paintings. In this sense, discussions are addressed about the visible changes of the painting and the related microscopic findings: stratigraphy, the presence of efflorescence and all defects detected using optical microscopy and SEM analysis;

(2) The characterization of the materials used, original pigments and binders, but also those added during the previous restoration procedures;

(3) The identification of degradation products (metallic soaps and other efflorescence).

The stratigraphic layers of representative paint fragments from each sampling location were examined with an optical microscope and stereomicroscope. All samples contained a colored layer (blue, green, or red) and a white base layer, with possible intermediate layers of gray or black paint. The collected samples are composed of several layers of paint, most likely due to the repeated interventions that took place over time.

The pigments and the places where they were taken are shown in Table 1. In this table are also attached the related chromatic parameters, as useful data in classifying these pigments in the color classes.

The granular texture observed in the images provided by optical microscopy can be a first explanation for the formation of metallic soaps. In Figure 3, images of the variously painted areas are presented, and aggregates of metallic soaps that have penetrated/protruded through the paint surface, have been identified.

Metallic soap efflorescence, observed by OM, appears as transparent or whitish opaque masses, with a circular shape, with a diameter between 10 and 200 μm and can reach up to 500 μm or even larger [17]. In our case, the opaque mass has the size of 30–50 μm . This metallic soap can penetrate the surface of the pictorial layer, migrate to the surface of the painting and lead to the formation of crusts of lead carbonates, hydroxy chlorides, sulfates and sometimes oxalates, increase the transparency of the pictorial layer, affect the wooden support allowing artists to become visible in some paintings in oil [25].

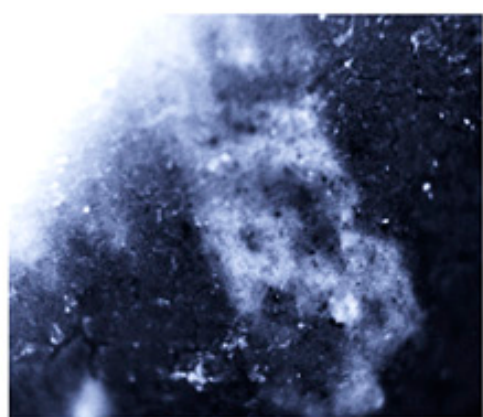
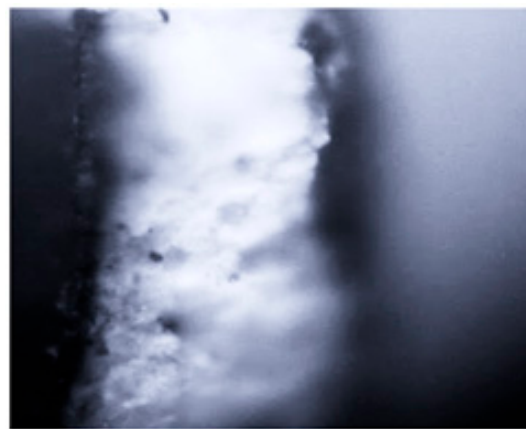
Aggregates with small dimensions are possible and lead to an expansion of the volume, in order to later pierce the surface layers and erupt on the surface. In some cases, the damage caused by metallic soaps appears as dark spots, most likely attributed to preservation treatments and can be due to the accumulation of dirt and layers of aging varnishes and coatings, and some pustules appeared on the surface.

The microscopic analysis of the paint samples detached from these icons corroborated with WDXRF and EDS results, and highlighted the presence of zinc soap as a fluffy deposit formed at the painting surface; this being the cause of the deterioration of hundreds of oil paintings dating from the 15th to the 20th centuries [38,39].

OM is completed with stereomicroscopy, which allows to clearly observe the white layer of metallic soaps formed at the pigment surface, Figure 4. Additionally, by using the microscope tool it was possible to measure the size of the white deposit from the surface painting.

Table 1. The description of the samples collected from Techirghiol church (Church Naos–eastern part).

Sampling Site	Sampling Point	Sample Name, Description and Analysis
St. Nichifor and St. Dimitrie Icon 1 ($L^* = 48.12$; $a^* = 5.15$; $b^* = 27.67$)		Green decoration FTIR, SEM-EDS, OM, GC-MS, colorimetry
Pilda Slăbănogului Icon 2 ($L^* = 19.06$; $a^* = -4.01$; $b^* = 14.27$)		Red decoration FTIR, SEM-EDS, OM, GC-MS, colorimetry 3 ($L^* = 40$; $a^* = 35.92$; $b^* = 36.60$) 4 ($L^* = 69.88$; $a^* = 4.25$; $b^* = 37.61$)
St. Nichifor and St. Dimitrie Icon		Blue decoration FTIR, SEM-EDS, OM, GC-MS, colorimetry 5 ($L^* = 27.49$; $a^* = -2.73$; $b^* = 10.92$) 6 ($L^* = 46.29$; $a^* = 28.05$; $b^* = -29.76$)

50.20 μm 50.20 μm **Figure 3.** The optical microscopy of the efflorescence generated by blue pigments.

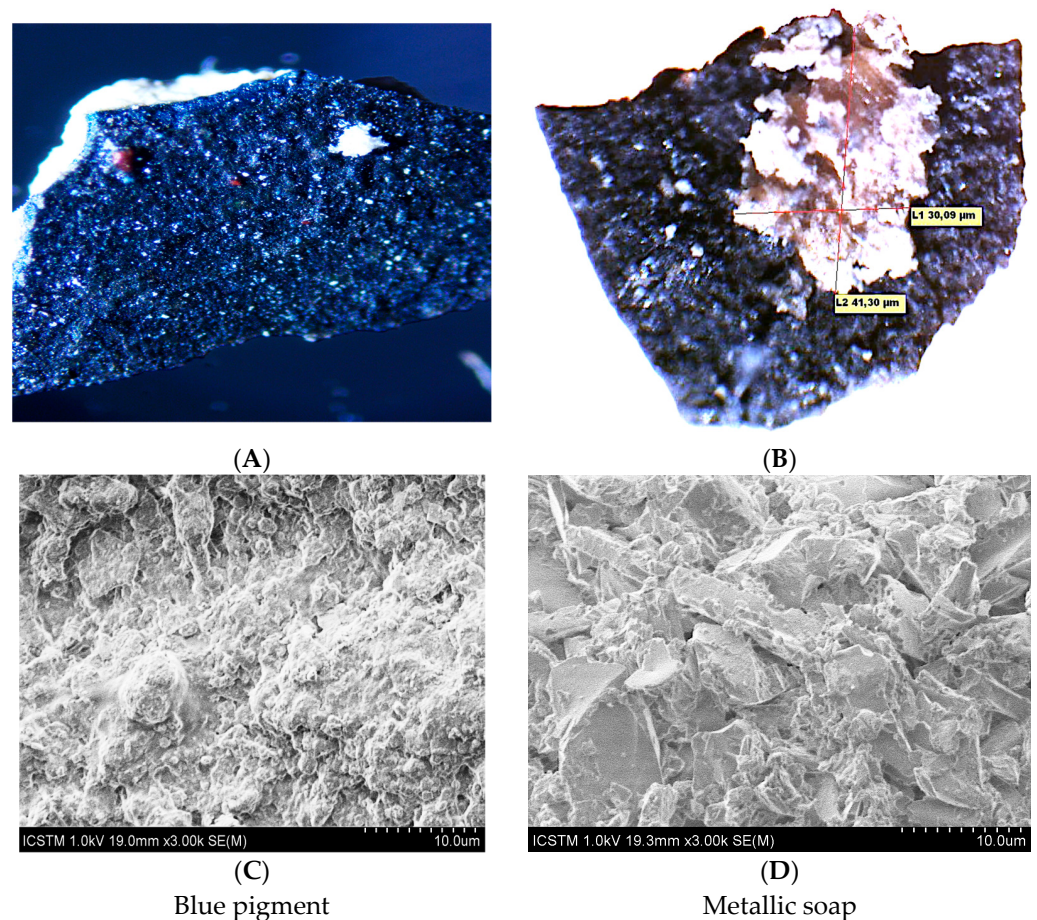


Figure 4. Stereomicroscopy of blue pigment with white deposit (A,B) images and SEM images of blue pigment (C) and of the white deposit (D).

In the case of optical microscopy, whitish points and small fragments of metallic soap or varnish are visible in all the investigated fragments, as a sign of the metallic soaps generation or subsequent conservation procedures, Figure 5. A fractally aggregated distribution of the metallic soaps is visible and these images are a conclusive image of the damage propagation. It is known that the zinc oxide is a pigment that readily reacts with fatty acids in oil-based paints to form zinc carboxylates. Zinc stearate and zinc palmitate aggregates are associated with deterioration in late 19th and 20th century paintings, following the fractal aggregation theories [40].



Figure 5. The optical microscopy of the metallic soap generated by the pigments.

In this context, for a better visualization, SEM images are used to identify the material structure aspect, degradation processes, or conservation additions. Effects such as porous

film, cracks and an irregular surface, holes in and under the surface, and overlapping layers of paint could be observed. Further, the additional white area is seen in Figure 6, attributed to the plaster used to cover the holes, or missing part of this icon.

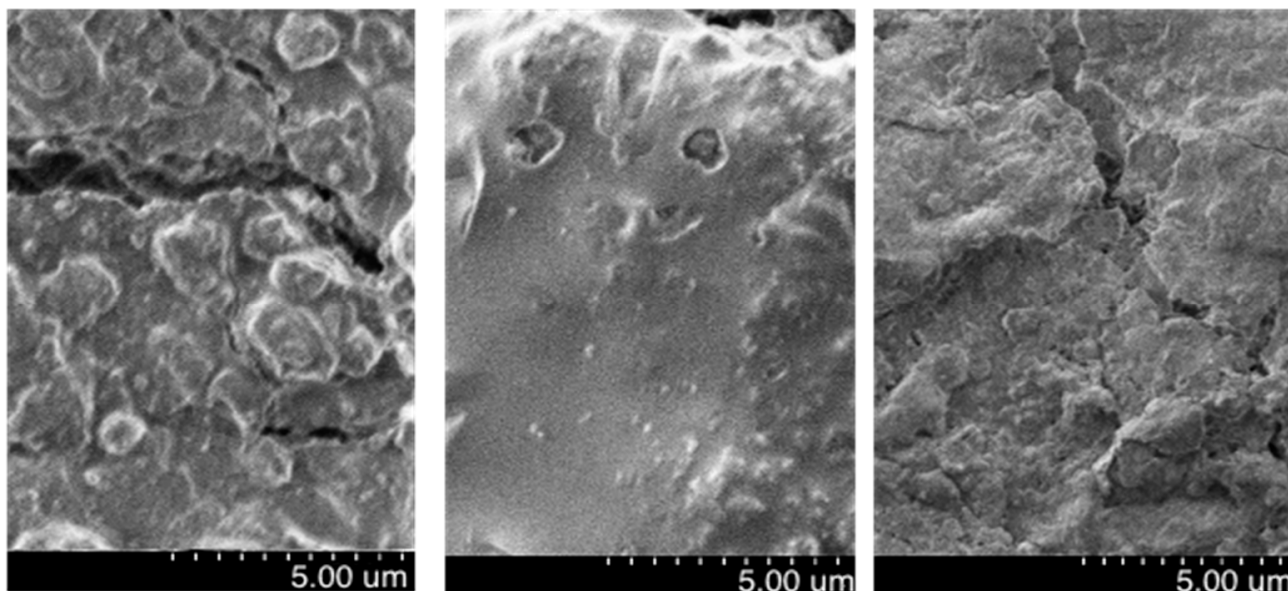


Figure 6. SEM images of green, red and blue colored samples (from left to right).

SEM images show that the soap exhibits several small (semi-)crystalline domains, each with a coordinated layered structure of 50–100 nm in size, without a specific orientation. The newly formed structures are organized in successive layers that formed a 3D flower-like structure generated by the initial precipitation of the zinc soaps. The distribution of these domains is quite homogeneous, thus confirming the hypothesis that the nucleation processes take place in the binding environment and not at the level of the pigment particles [41]. This finding suggests that zinc soaps can be present as amorphous zinc carboxylates, bound to the network of oxidized, cross-linked oil, as well as crystalline zinc soaps, generated by paint degradation [42].

The WDXRF analysis, of the pigments Table 2, reveals that the common contributing elements detected in the red layer were Fe, Ca, Al, and Si (EDS analysis display similar semi-quantitative results). Additionally, Ba is present, but not P, which could mean that black bone has not been used. It is suggestive of a Fe-based pigment such as an ochre possibly mixed with calcium carbonate or sulphate (sulphur has a high concentration), possibly from the gypsum identified on the restored part of the painting, Figure 7.

The EDS analysis reveals the presence of sulfur (S), which can be bound to both calcium (Ca) and barium (Ba). Barium is generally present in the paint layers as barium sulfate (BaSO_4), a white thinner commonly used for pigments, or as lithopone (BaSO_4 and ZnS). Indeed, synthetic barium sulfate was developed in the early 19th century. Lithopone is a white pigment produced since 1874 and widely used in soil layers or as filler [43]. The calcium could be related to the presence of calcium sulfate (gypsum, CaSO_4), which was commonly used as a preparation layer from early medieval times to modern times [44]. The analysis also highlighted the presence of zinc in the primer layer, confirming the use of zinc oxide (Zinc White). Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was rarely found and used alone or in combination with ZnO .

Table 2. The elemental analysis (WDXRF) of the investigated pictural layers.

Element	Sample		
	Green	Red	Blue
C	43.43 ± 0.21	25.25 ± 0.13	38.26 ± 0.19
O	42.17 ± 0.73	49.21 ± 0.25	39.15 ± 0.56
Na		0.34 ± 0.01	
Mg	0.20 ± 0.01	0.03 ± 0.01	0.25 ± 0.01
Al	0.56 ± 0.01	0.13 ± 0.01	0.64 ± 0.01
Si	1.09 ± 0.01	0.28 ± 0.01	1.35 ± 0.01
P	0.35 ± 0.01		0.74 ± 0.01
S	1.09 ± 0.01	11.31 ± 0.04	1.60 ± 0.01
Cl	0.19 ± 0.01	0.19 ± 0.01	0.14 ± 0.01
K	0.14 ± 0.01	0.18 ± 0.01	0.15 ± 0.01
Ca	6.84 ± 0.03	11.10 ± 0.05	5.17 ± 0.03
Ti	0.32 ± 0.02		0.05 ± 0.01
Cr	0.70 ± 0.02		0.15 ± 0.01
Fe	1.68 ± 0.03	0.17 ± 0.01	4.83 ± 0.04
Zn	0.73 ± 0.05		7.54 ± 0.07
Ba		1.92 ± 0.05	0.44 ± 0.02

**Figure 7.** The presence of gypsum on painting layer.

The presence of silica (Si), aluminum (Al), magnesium (Mg) and iron (Fe) suggests the use of green earth in the first layers of paint [45]. This could be partially responsible for the bluish-green color of the paint layer, along with the presence of chromium (Cr), which could be attributed to either green chromium oxide, viridian (hydrated chromium (III) oxide) [46]. The presence of magnesium, silica, and calcium, may indicate calcium and magnesium silicates in all blue pastels.

Iron oxide pigments were also used to produce the red shades [47]. Iron oxide paints are durable and resistant to light and weather. The intensity of their color depends on the amount of the present chromophore: hematite (red), hydrohematite (mummy or red-brown), goethite (yellow), etc. The brown and red-brown paints were found to contain impurities of baryta white. The black pigment is most likely bone black, with such a finding being indicated by the presence not only of carbon, but also of magnesium and calcium phosphates [48].

Depending on the ratio of the components involved, for blue colors the hues vary from blue-green to violet, which, when mixed with white pigments, emit hues ranging

from pale blue (paleo) to grey-blue [49]. In this context could be the $L^*a^*b^*$ value for each color collected and measured from the icons (Table 1). At temperatures above 250 °C (candlelight), the pigment may darken, sometimes acquiring a greenish tint.

The aspects of FTIR spectra of the main components that could be identified for all the present pigments from both icons, are shown in Figure 8.

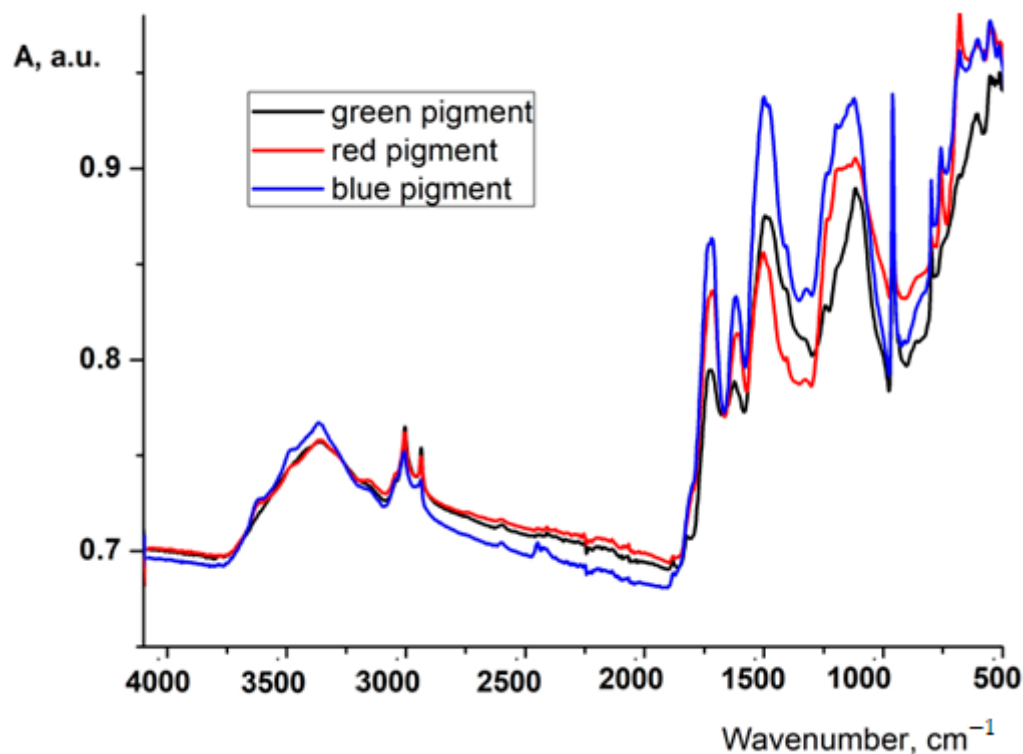


Figure 8. ATR-FTIR spectra of the analyzed samples (green color pigment, blue color pigment, red color pigment).

The red layer displayed a pronounced broad band between 990 and 1290 cm^{-1} . Such spectral regions host features compatible with those of a sulfate (983, 1087, 1116, and 1182 cm^{-1}), probably barite (BaSO_4), to which the two uncertain peaks at 611 and 638 cm^{-1} also appear to be assigned. Barite could be present as a natural impurity, since its identification as an artist's pigment occurred long after the making of this icon [50–53]. Small amounts of anhydrite (CaSO_4) and arcanite (K_2SO_4) were detected, and their presence can be attributed to interactions with environmental pollutants. The presence of hematite supports the EDS results, through Fe content. Additionally, calcite could be identified by the bands from 1440, 875, 712 cm^{-1} , because usually calcite is used as mix or as substrate for painting [54,55].

By separating the white deposit from the pigment surface (in this case blue pigment), the FTIR spectrum reveals the main specific bands of the components, Figure 9.

The most obvious characteristic for the detection of metal soaps in oil paint layers is the intense asymmetric stretching vibration of the carboxylate head group, for Zn soaps this band is at 1547 cm^{-1} [56].

Interestingly, the IR spectra of zinc oleate and zinc azelate also show a split carboxylate band structure, similar to the short-chain zinc soaps, Figure 10.

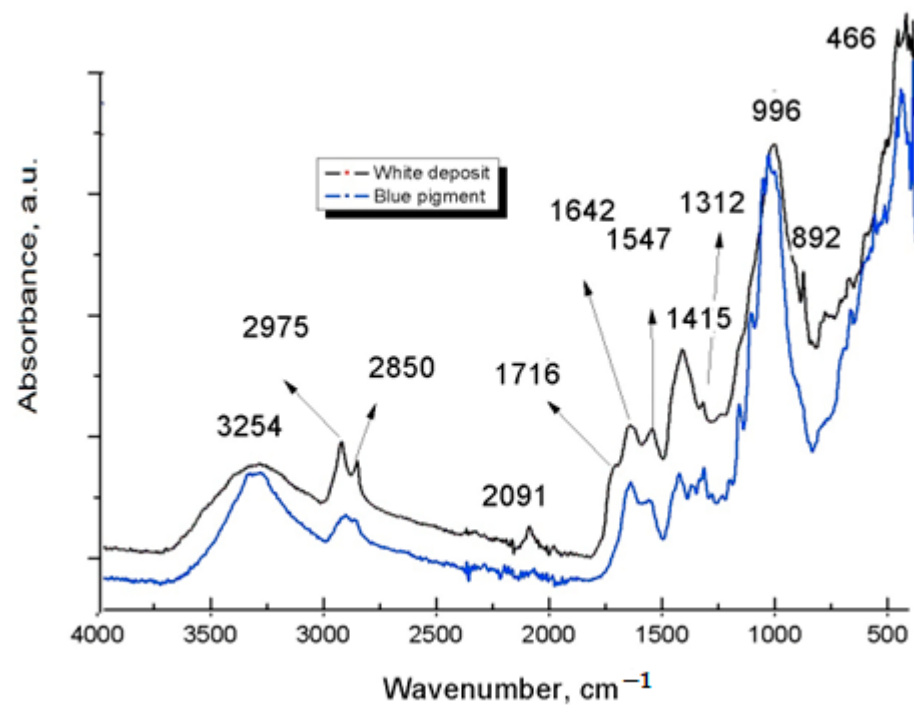


Figure 9. FTIR spectra of blue pigments and white deposits.

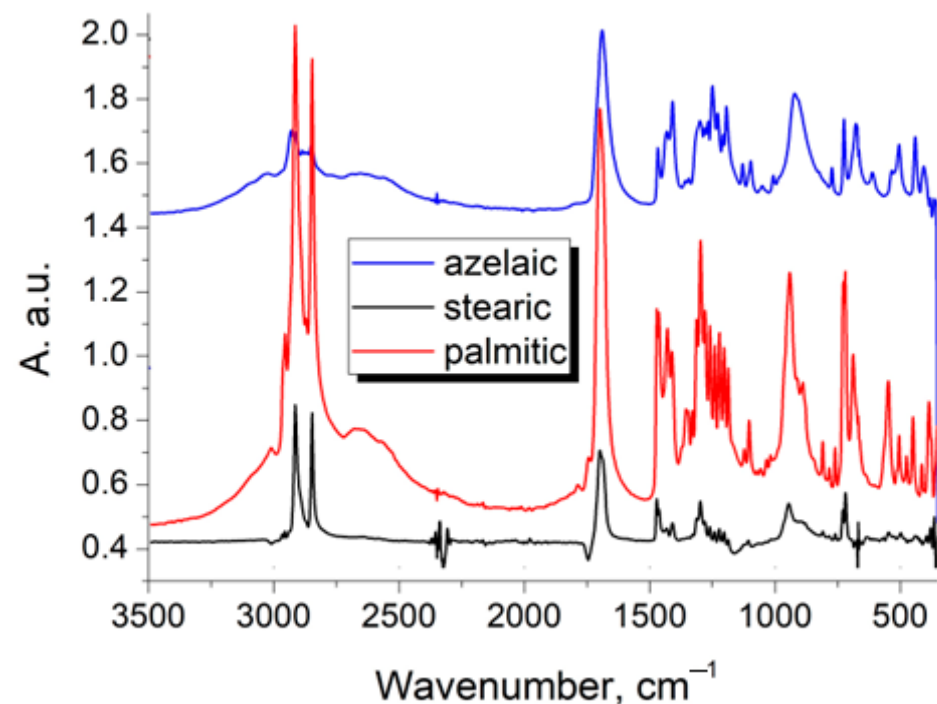


Figure 10. The FTIR spectra of fatty acids.

By analyzing all these results, it could be observed that in FTIR spectra of all icons' pigments, the bands of acids could be identified, in very good agreement with literature [57].

The pigments used in painting are mineral, natural, or synthetic minerals: colored clays with hydrated iron oxide (ochre) or anhydrous iron oxide (red ochre), Fe, Al, Mg, and K hydro silicate (green), silicates (blue enamel), lazurite, calcium carbonate (calcite). To obtain more shades, these pigments were blended with white, probably calcite or titanium dioxide (from previous restoration), remaining from some previous restorations' procedures, or as impurity from natural raw materials used for pigments preparation.

The red pigment is a red inorganic pigment as Fe_2O_3 (hematite). Hematite is identified by the FTIR spectrum that highlights the bands characteristic of hematite ($\alpha\text{-Fe}_2\text{O}_3$) located at 467 cm^{-1} and 534 cm^{-1} . At the same time, for the purpose of obtaining different shades, the masters probably used the white Tarigrad pigment containing a natural aluminum silicate- $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ -white, and the white lime pigment constituted by calcium hydroxide. According to FTIR spectra, gypsum from the painting can be identified (1627 cm^{-1} and 1126 cm^{-1}) and the proof of its application has been shown above, by visual photo taken from the church. Quartz is generally indicated by the typical doublet at $779\text{--}800\text{ cm}^{-1}$ [32].

For the blue pigments, based on WDXRF, EDS, and FTIR, could be identified a mixture between ultramarine $(\text{Na, Ca})_8(\text{AlSiO}_4)_6(\text{SO}_4, \text{S, Cl})_2$, and lazurite $(\text{Na, Ca})_8(\text{AlSiO}_4)_6(\text{S, SO}_4)$, with very small concentrations of $\text{Cr}_2\text{O}_3\text{-Fe}_3\text{O}_4$ and ZnO. Lazurite, as an aluminosilicate, is the essential ingredient of lapis lazuli and the mineral that gives it the blue color. Lazurite is a sodium, calcium, aluminosilicate mineral that contains sulfur: the color is due to a charge transfer between sulfur atoms.

(<https://www.minerals.net/mineral/lazurite.aspx>, accessed on 10 December 2022).

The “green earth” pigment is a mixture of Fe, Mg, Al, K (mainly minerals as celadonite and glauconite). Additionally, $\text{Cr}_2\text{O}_3\text{-Fe}_3\text{O}_4$, viridian, hydrated chromium oxide, like green zinc or green Rinmann’s green (CoZnO_2), and iron oxide, are present in this pigment. The presence of all these elements could be identified by elemental analysis.

The green pigments based on chromium, such as viridian and chromium oxide, did not exist in the 18th century, so it can be presumed that these pigments could be sourced from different restoration procedures which occurred in time.

Figure 11 shows the FTIR spectrum of the ZnS nanoparticles. The spectra exhibit strong bands appearing in the 1114 , 1259 , 1384 assigned to ZnS nanoparticles [58]. The peaks at 612 cm^{-1} are assigned to the ZnS band (i.e., corresponding to sulphides) [59,60]. The O–H bending region due to absorbed water appears at 1620 cm^{-1} . The stretch vibration adsorption of ZnO at $420\text{--}460\text{ cm}^{-1}$ is not detected, which indicates that ZnS was not oxidized to ZnO during the preparation as reported by She Yuan-Yuan et al. [61].

Metallic soaps contain pigments based on heavy metals, such as lead or zinc, which react with the fatty acids resulting from the hydrolysis of glycerides in the oil binding medium or from the protective layers [62]. Soap inclusions in oil paintings, studied by gas chromatography-mass spectrometry (GC-MS) and Fourier transform infrared spectroscopy (FTIR), concluded that they contain saturated C16 (palmitic) and C18 (stearic) zinc carboxylates, and relatively small amounts of zinc azelate (C9) [63,64].

In Raman spectra, Figure 12, a strong band near 545 cm^{-1} , along with a weaker band near 1098 cm^{-1} , are the features of Ultramarine pigment (artificial Lapis lazuli) [65–68]. By EDS and WDXRF, were identified the four key elements (apart from oxygen) of this pigment, Na, Al, Si, and S.

The band near 1085 cm^{-1} is arising from calcite, and the presence of BaSO_4 is evidenced by the band near 987 cm^{-1} . The presence of Ba, S, and Zn above identified indicate that the main component is lithopone ($\text{BaSO}_4 + \text{ZnS}$). Additionally, the presence of Ca indicates the presence of CaCO_3 (calcite) near 1085 cm^{-1} was observed in the spectra from the same area obtained.

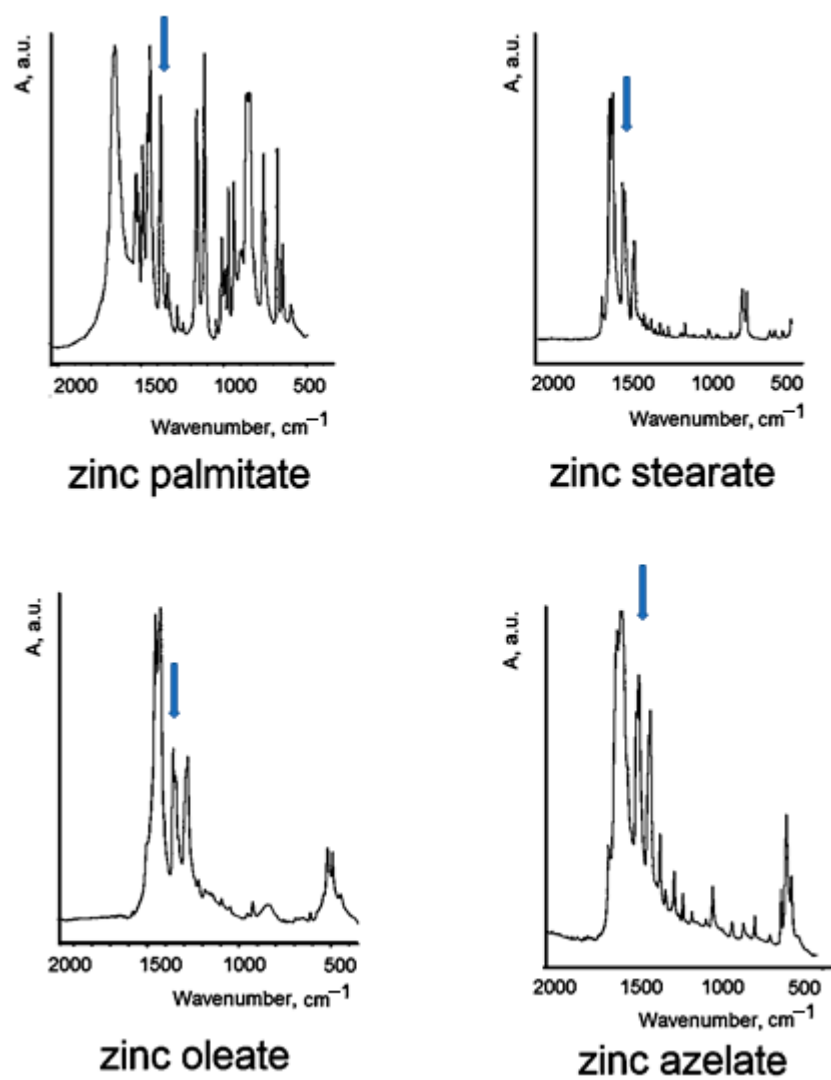


Figure 11. The FTIR spectra for zinc carboxylates.

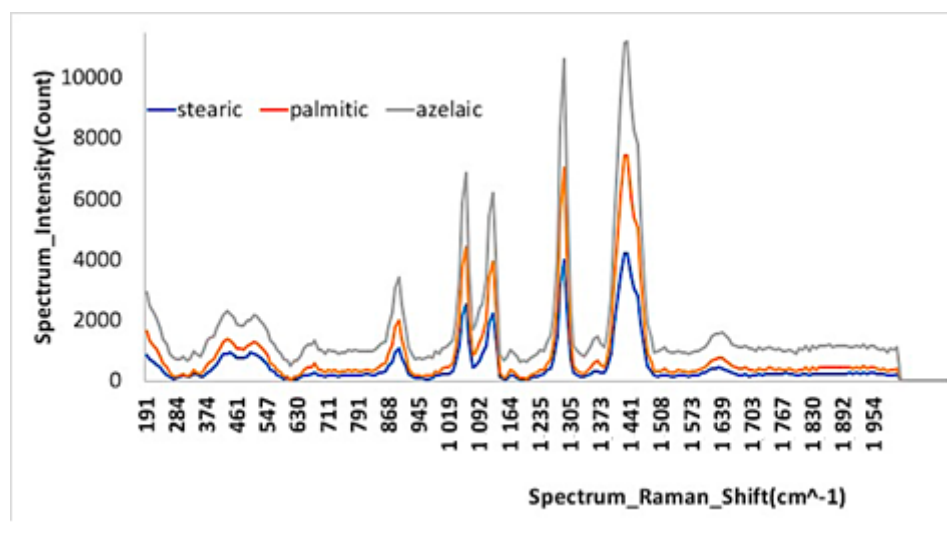


Figure 12. The Raman spectrum of fatty acids.

The three bands near 224 cm^{-1} , 291 cm^{-1} , and 408 cm^{-1} , and the weaker band from 611 cm^{-1} , are indicative of the presence of red ochre ($\text{Fe}_2\text{O}_3 + \text{clay}$). Of the known red pigments, only haematite (the basic component of red ochre) contains iron.

The two peaks near 1725 cm^{-1} ($\nu(\text{C}=\text{O})$) and 1600 cm^{-1} ($\nu(\text{C}=\text{C})$) are assigned to the presence of triglycerides, basic constituents of the binding material. The relatively broad carbonyl band is arising from the contribution of oxidation products of triglycerides (aldehydes, ketones, and carboxylic acids). The band from 1600 cm^{-1} ($\nu(\text{C}=\text{C})$) is partly due to unsaturated triglycerides present in the binding materials. Because of the sample constraints mentioned previously, it is rather difficult to make unequivocal assertions about the organic substances present in the sample on the basis of the Raman spectra alone.

The zinc ions from the pigments bind to the carboxylate ions in the polymerized oil network as an intermediate step in paint aging [69], a process in which the diffusion of metal ions and fatty acids takes place to explain the appearance of metal soaps in the paint structure oil. The use of a protein binder by master painters is demonstrated by the presence of linoleic, stearic, azelaic, and palmitic fatty acids, according to GC-MS measurements, Figure 13. Azelaic acid is a marker of the use of drying oil.

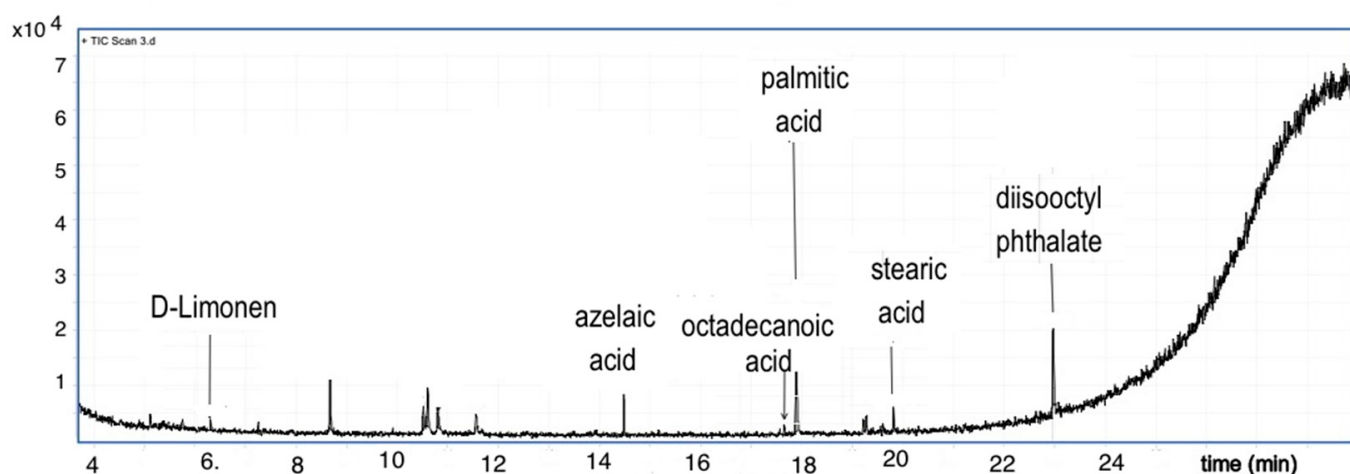


Figure 13. The main components from pictorial layer.

Additionally, long-chain hydroxycarboxylic fatty acids could be derived from waxes, such as beeswax, and has been used as a binder in a painting technique called encaustic. The use of a protein binder by master painters is demonstrated by the presence of linoleic, stearic, azelaic, and palmitic fatty acids, according to GC-MS measurements [70].

Monocarboxylic and dicarboxylic saturated fatty acids (azelaic and palmitic acid are the most abundant), indicate the presence of a lipid material, and are found in all the analyzed samples [71].

Phthalates are also identified in the chromatogram in Figure 13; they are a sign of the microbial population present in the painting layer. The peaks corresponding to phthalate derivatives can be easily observed in the investigated samples.

Regarding the lipid content, palmitic acid, stearic acid, and azelaic acid, are present in all the analyzed samples, Table 3. Special attention was paid to the determination of the azelaic acid content, because of its high level in the drying oil. In fact, it has been determined that if a sample has a ratio of azelaic acid to palmitic acid (A/P) greater than 1, a drying oil is present in the sample, while an A/P ratio close to 0.1 suggests that it may be egg material present [72]. The paint layer contains a binding medium prepared from an emulsion of egg and walnut oil. Egg is the most commonly used bonding medium for base coat application (present in chromatogram at retention time 8–12).

Table 3. Summary of the main compounds and materials identified in the chromatograms of the lipid-resinous fraction of the samples.

Sample	Lipid Material	Drying Oil	Pine Resin Markers	Related Pine Resin Compounds	Phthalate Derivatives	Long Chain Hydroxycarboxylic Acids
Green	yes	Yes	Yes	Yes	yes	yes
Red	Yes	Yes	No	No	Yes	yes
Blue	yes	yes	no	no	yes	yes

Based on the results obtained in this work, it can be concluded that in this church only a few species of pigments were identified, and mainly the traditional ones, such as vermilion, lazurite, green earth, bone black, and red/yellow ochre. Other pigments are synthetic pigments, such as ultramarine blue, and synthetic iron pigments.

However, it should be mentioned that not all these pigments are original. Some of them appeared during subsequent restoration interventions and complicated the composition of the pictorial stray.

The analysis of the binding media from the investigated samples highlighted their organic nature [73]. Moreover, in the restoration processes that took place in churches over time, alkyd resins and even pine resins were used as surface coatings.

In addition to pigments, varnishes were used in restorations for protection against wear, against the action of different environmental factors, and to improve the appearance of a painting by saturating the color and imparting gloss [74]. Until the 16th century, dry oils (e.g., linseed or walnut oil) and resins (e.g., sandarac or mastic) were practically the only means of varnishing paintings. From the end of the 16th century, varnishes produced by dissolving resins appeared [75]. Apart from these, there was an intermediate group, namely those containing both resins and oleoresins (e.g., Venetian turpentine), known as “mixed varnishes”. Apart from varnishes containing oil and/or resin, egg white (often combined with gums) was also occasionally used for varnishing purposes [76].

The diagnostic procedures and chemical analyses are very important now, in order to know the most useful procedure to save and keep alive such monuments. Before cleaning and applying the restoration measures, some microscopic examinations of the paint surface are recommended. The study of painting layers raises major problems, due to the difficulty of separating these layers of micrometric thickness (1–200 μm), as well as due to their heterogeneity (components, impurities and/or degradation products resulting from aging processes). The identification and characterization of pictorial layers is an essential aspect in the conservation and restoration of paintings.

4. Conclusions

Based on the pigment’s analysis from the pictorial layers of the icons in the Church of Saint Mary in Techirghiol, the appearance of the degraded surface and the forms of degradation due to the metallic soaps were highlighted in this paper through analytical techniques. Pigments, binders, and varnishes were investigated, for the metallic soaps formed. Through FTIR, the broadening of the absorption region associated with carbonyl groups was highlighted as a result of the formation of new bands in the region 1800–1700 cm^{-1} , respectively, the formation of metal salts - the region 1600–1500 cm^{-1} . At the level of binders, it was observed that many of the diagnostic bands disappear due to the aging processes. Complementary to the spectral and microscopic techniques, GC-MS analyzes were carried out. The presence of monocarboxylic and dicarboxylic saturated fatty acids (azelaic, stearic, and palmitic acid), indicated the presence of a lipid material, which is found in all the analyzed samples.

The high level of azelaic acid could be a marker of the presence of the drying oil. If a sample has a ratio of azelaic acid to palmitic acid greater than 1, it can be concluded that drying oil is present in the sample; if the sample contains a ratio between azelaic

acid and palmitic acid less than 1, it can be proof of the existence of egg material. In the investigated case, the A/P ration is very small, so the egg is present in these icons (present in chromatogram at retention time 8–12).

The binding medium used for the paint layer contain egg and walnut oil. Phthalates are identified and are a sign of the microbial population present in the paint layer.

The signs of previous restoration procedures have been evidenced by gypsum presence and by elements discovered after 1900.

Author Contributions: Conceptualization, R.-M.I.; methodology, R.-M.I. and R.M.G.; software: I.A.B. and R.M.G.; validation, R.-M.I.; formal analysis, I.A.B.; investigation, I.A.B., I.D.D., L.I., R.M.G. and S.S.-T.; resources, R.-M.I.; writing—original draft preparation, R.-M.I.; writing—review and editing, R.-M.I.; visualization, I.A.B. and I.D.D.; supervision, R.-M.I. and S.S.-T. project administration, R.-M.I.; funding acquisition, R.-M.I., L.I. and R.M.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: This paper received the financial support of the project: PN-III-P2-2.1-PED-2021-3885 from UEFISCDI-MCID, Romania.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Mayer, R. *The Artist's Handbook of Materials and Techniques*, 4th ed.; Viking Penguin Inc.: New York, NY, USA, 1985; p. 215.
2. Horie, V. *Materials for Conservation. Organic Consolidants, Adhesives and Coatings*, 2nd ed.; Routledge: New York, NY, USA, 2010.
3. Domenech-Carbo, M.T.; Silva, M.F.; Aura-Castro, E.M.; Fuster-Lopez, L.; Martinez-Bazan, M.L.; Mas-Barbera, X.; Mecklenburg, M.F.; Osete-Cortina, L.; Domenech, A.; Gimeno-Adelantado, J.V.; et al. Study of behaviour on simulated daylight ageing of artists' acrylic and poly(vinyl acetate) paint films. *Anal. Bioanal. Chem.* **2011**, *399*, 2921–2937. [\[CrossRef\]](#)
4. Ion, R.M.; Nyokong, T.; Nwahara, N.; Suica-Bunghuez, R.; Iancu, L.; Teodorescu, S.; Dulama, I.D.; Stirbescu, R.M.; Gheboianu, A.; Grigorescu, R.M. Wood preservation with gold hydroxyapatite system. *Herit. Sci.* **2018**, *6*, 37. [\[CrossRef\]](#)
5. Nilson, T.; Rowell, R. Historical wood-structure and properties. *J. Cult. Herit.* **2012**, *13*, S5–S9. [\[CrossRef\]](#)
6. Casadio, F.; Keune, K.; Noble, P.; van Loon, A.; Hendriks, E.; Centeno, S.; Osmond, G. *Metal Soaps in Art*; Springer International Publishing: Berlin/Heidelberg, Germany, 2018.
7. Akerlund, L. Efflorescence: An investigation of selected paintings from the 19th to the 21st century with a preliminary experimental study of the role of moisture in the development of efflorescence. Final year project dissertation, Department of Conservation & Technology, Courtauld Institute of Art. 2012.
8. Church, A.H. *The Chemistry of Paints and Painting*, 3rd ed.; Seeley and Co.: London, UK, 1901.
9. Ferreira, E.S.B.; Boon, J.J.; Marone, F.; Stampanoni, M. Study of the mechanism of formation of calcium soaps in an early 20th century easel painting with correlative 2D and 3D microscopy. In Proceedings of the ICOM Committee for Conservation 16th Triennial Meeting, Lisbon, Portugal, 19–23 September 2011; Bridgland, J., Ed.; James & James Publisher: Lisbon, Portugal, 2011; p. 1604.
10. Noble, P.; Boon, J.J. Metal soap degradation of oil paintings: Aggregates, increased transparency and efflorescence. In Proceedings of the AIC Paintings Specialty Group Postprints, Washington, DC, USA, 16–19 June 2006; AIC: Washington, DC, USA, 2007; Volume 19, pp. 1–15.
11. Chiantore, O.; Scalarone, D. *The Macro- and Microassessment of Physical and Ageing Properties in Modern Paints, Modern PAINTS Uncovered: Proceedings from the Modern Paints Uncovered Symposium May 2006*; Learner, T.J.S., Smithen, P., Krueger, J.W., Schilling, M.R., Eds.; Getty Conservation Institute: Los Angeles, CA, USA, 2007; pp. 96–104.
12. Chiantore, O.; Rava, A. *Conserving Contemporary Art: Issues, Methods, Materials, and Research*, 1st ed.; Getty Conservation Institute: Santa Monica, CA, USA, 2013.
13. Learner, T.J.S. *Analysis of Modern Paints*; Getty Conservation Institute: Los Angeles, CA, USA, 2004.
14. Hermans, J.J.; Keune, K.; Van Loon, A.; Iedema, P.D. , In *Metal Soaps in Art. Cultural Heritage Science*; Casadio, F., Keune, K., Noble, P., Van Loon, A., Hendriks, E., Centeno, S.A., Osmond, G., Eds.; Springer: Cham, Switzerland, 2019.
15. Noble, P.; Boon, J.J.; Wadum, J. Dissolution, Aggregation, and Protrusion. Lead Soap Formation in 17th-century Grounds and Paint Layers. *Art Matters* **2003**, *1*, 46–61.

16. Plater, M.J.; De Silva, B.; Gelbrich, T.; Hursthouse, M.B.; Higgitt, C.L.; Saunders, D.R. The characterisation of lead fatty acid soaps in 'protrusions' in aged traditional oil paint. *Polyhedron* **2003**, *22*, 3171–3179. [\[CrossRef\]](#)
17. Izzo, F.C.; Kratter, M.; Nevin, E.; Zendri, A. A Critical Review on the Analysis of Metal Soaps in Oil Paintings. *ChemistryOpen* **2021**, *10*, 904–921. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Hermans, J.J. Metal Soaps in Oil Paint, Structure, Mechanisms and Dynamics, Amsterdam. Ph.D. Thesis, Faculty of Science, Van't Hoff Institute for Molecular Sciences. University of Amsterdam, Amsterdam, The Netherlands, 2017.
19. Cotte, M.; Checroun, E.; De Nolf, W.; Taniguchi, Y.; De Viguerie, L.; Burghammer, M.; Walter, P.; Rivard, C.; Salomé, M.; Janssens, K.; et al. Lead soaps in paintings: Friends or foes? *Stud. Conserv.* **2017**, *62*, 223–330. [\[CrossRef\]](#)
20. Schilling, M.R.; Khanjian, H.P. Gas Chromatographic Determination of the Fatty Acid and Glycerol Content of Lipids: I. The Effects of Pigments and Aging on the Composition of Oil Paints. In *ICOM Committee for Conservation, 11th Triennial Meeting, Preprints*; Bridgland, J., Ed.; James & James (Science Publishers): London, UK, 1996; pp. 220–227.
21. Robinet, L.; Corbeil, M.-C. The Characterization of Metal Soaps. *Stud. Conserv.* **2003**, *48*, 23–40. [\[CrossRef\]](#)
22. Higgitt, C.; Spring, M.; Saunders, D. Pigment-medium interactions in oil paint films containing red lead or lead-tin yellow. *Natl. Gallery Tech. Bull.* **2003**, *24*, 75–95.
23. Keune, K.; Boon, J.J. Analytical imaging studies of cross-sections of paintings affected by lead soap aggregate formation. *Stud. Conserv.* **2007**, *52*, 161–176. [\[CrossRef\]](#)
24. Boon, J.; Keune, K.; Zucker, J. Imaging analytical studies of lead soaps aggregating in preprimed canvas used by the Hudson River School painter F. E. Church. *Microsci. Microanal.* **2005**, *11* (Suppl. 2), 444–445.
25. Ordonez, E.; Twilley, J. Clarifying the haze: Efflorescence on works of art. *WAAC Newsl.* **1998**, *20*, 1. **1997**, *69*, A416–A422.
26. Gardner, H.A. *Paint Researches and Their Practical Application*; Press of Judd and Detweiler, Inc.: Washington, DC, USA, 1917.
27. Carlyle, L. *The Artist's Assistant: Oil Painting Instruction Manuals and Handbooks in Britain 1800–1900 with Reference to Selected Eighteenth-Century Sources*; Archetype Publications: London, UK, 2001.
28. Townsend, J.; Carlyle, L.; Khandekar, N.; Woodcock, S. Later nineteenth century pigments: Evidence for additions and substitutions. *Conservator* **1995**, *19*, 65–78. [\[CrossRef\]](#)
29. Burnstock, A.; Jones, C. Scanning electron microscopy techniques for imaging materials from paintings. *Radiat. Art Archeometry* **2000**, 202–231. [\[CrossRef\]](#)
30. Tammekivi, E.; Vahur, S.; Vilbaste, M.; Leito, I. Quantitative GC-MS Analysis of Artificially Aged Paints with Variable Pigment and Linseed Oil Ratios. *Molecules* **2021**, *26*, 2218. [\[CrossRef\]](#)
31. van der Weerd, J.; van Loon, A.; Boon, J.J. FTIR studies of the effects of pigments on the aging of oil. *Stud. Conserv.* **2005**, *50*, 3–22.
32. Otero, V.; Sanches, D.; Montagner, C.; Vilarigues, M.; Carlyle, L.; Lopes, J.A.; Melo, M.J. Characterisation of Metal Carboxylates by Raman and Infrared Spectroscopy in Works of Art. *J. Raman Spectrosc.* **2014**, *45*, 1197–1206. [\[CrossRef\]](#)
33. Shugar, A.N.; Mass, J.L. *Handheld XRF for Art and Archaeology*; Leuven University Press: Leuven, Belgium, 2012; Volume 3.
34. Lau, D.; Hay, D.; Wright, N. Micro X-ray diffraction for painting and pigment analysis. *AICCM Bull.* **2007**, *30*, 38–43. [\[CrossRef\]](#)
35. Hradil, D.; Bezdicka, P.; Hradilova, J.; Vašutová, V. Microanalysis of clay-based pigments in paintings by XRD techniques. *Microchem. J.* **2016**, *125*, 10–20. [\[CrossRef\]](#)
36. CIE S 014-1:2006-[ISO 11664-1:2007]; Colorimetry Part 1. CIE Standard Colorimetric Observers. ISO: Geneva, Switzerland, 2007.
37. CIE S 014-2:2006-[ISO 11664-2:2007]; Colorimetry Part 2. CIE Standard Illuminants. ISO: Geneva, Switzerland.
38. 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: Conservation and Research*; Casadio, F., Keune, K., Noble, P., Van Loon, A., Hendriks, E., Centeno, S., Osmond, G., Eds.; Springer: Cham, Switzerland, 2019; pp. 47–65.
39. Keune, K. Binding Medium, Pigments, and Metal Soaps Characterised and Localised in Paint Cross-Sections. Ph.D. Thesis, University of Amsterdam, Amsterdam, The Netherlands, 2005.
40. Mullins, O.C.; Sheu, E.Y.; Hammani, A.; Marshall, A.G. *Asphaltenes, Heavy Oils, and Petroleomics*; Springer: Berlin/Heidelberg, Germany, 2007.
41. Artesani, A. Zinc oxide instability in drying oil paint. *Mater. Chem. Phys.* **2020**, *255*, 123640. [\[CrossRef\]](#)
42. Hermans, J.J.; Keune, K.; van Loon, A.; Iedema, P.D. The crystallization of metal soaps and fatty acids in oil paint model systems. *Phys. Chem. Chem. Phys.* **2016**, *18*, 10896–10905. [\[CrossRef\]](#)
43. Harley, R.D. *Artists' Pigments c.1600–1835: A Study in English Documentary Sources*; Elsevier Pub. Co.: New York, NY, USA, 1970.
44. Picollo, M.; Bacci, M.; Magrini, D.; Radicati, B.; Trumpy, G.; Tsukada, M.; Kunzelman, D. Modern White Pigments: Their Identification by Means of Noninvasive Ultraviolet, Visible, and Infrared Fiber Optic Reflectance Spectroscopy. In *Modern Paints Uncovered*; Getty Conservation Institute: Los Angeles, CA, USA, 2006.
45. Coccato, A.; Caggiani, M.C.; Occhipinti, R.; Mazzoleni, P.; D'Alessio, A.; Russo, A.; Barone, G. The Irreplaceable Contribution of Cross Sections Investigation: Painted Plasters from the Sphinx Room (Domus Aurea, Rome). *Minerals* **2021**, *11*, 4. [\[CrossRef\]](#)
46. Desnica, V.; Furic, K.; Hochleitner, B.; Mantler, M. A comparative analysis of five chrome green pigments based on different spectroscopic techniques. *Spectrochim. Acta Part B At. Spectrosc.* **2003**, *58*, 681–687. [\[CrossRef\]](#)
47. Pfaff, G. *Inorganic Pigments*; Walter de Gruyter GmbH: Berlin, Germany; Boston, MA, USA, 2017.
48. Christie, R. *Colour Chemistry*, 2nd ed.; Royal Society of Chemistry: Cambridge, UK, 2015.
49. Slansky, B. *Technique of Painting, Part I. Painting and Conservation Material*; Technika Malby: Prague, Czech Republic, 1953. (In Czech)

50. Madejová, J. FTIR techniques in clay mineral studies. *Vib. Spectrosc.* **2003**, *31*, 1–10. [\[CrossRef\]](#)
51. Mazzeo, R.; Prati, S.; Quaranta, M.; Joseph, E.; Kendix, E.; Galeotti, M. Attenuated total reflection micro FTIR characterization of pigment–binder interaction in reconstructed paint films. *Anal. Bioanal. Chem.* **2008**, *392*, 65–76. [\[CrossRef\]](#)
52. Müller, C.M.; Pejčić, B.; Esteban, L.; Delle Piane, C.; Raven, M.; Mizaikoff, B. Infrared attenuated total reflectance spectroscopy: An innovative strategy for analyzing mineral components in energy relevant systems. *Sci. Rep.* **2014**, *4*, 6764. [\[CrossRef\]](#)
53. Feller, R.L. Barium sulfate-natural and synthetic. In *Artists' Pigments; A Handbook of Their History and Characteristics*; National Gallery of Art: Washington, DC, USA, 1986; Volume 1, pp. 47–64, M00FCller.
54. Jacobsen, A.; Gardner, W.H. Zinc Soaps in Paints. *Zinc Oleates. Ind. Eng. Chem.* **1941**, *33*, 1254–1256. [\[CrossRef\]](#)
55. Berkesi, O.; Katona, T.; Dreveni, I.; Andor, J.A.; Mink, J. Temperature-dependent Fourier transform infrared and differential scanning calorimetry studies of zinc carboxylates. *Vib. Spectrosc.* **1995**, *8*, 167–174. [\[CrossRef\]](#)
56. Keune, K.; Van Loon, A.; Boon, J. SEM Backscattered-Electron Images of Paint Cross Sections as Information Source for the Presence of the Lead White Pigment and Lead-Related Degradation and Migration Phenomena in Oil Paintings. *Microsc. Microanal.* **2011**, *17*, 696–701. [\[CrossRef\]](#)
57. Domenech-Carbo, M.T.; Domenech-Carbo, A.; Gimeno-Adelantado, J.V.; Bosch-Reig, F. Identification of synthetic resins used in works of art by Fourier Transform Infrared Spectroscopy. *Appl. Spectrosc.* **2001**, *55*, 1590–1602. [\[CrossRef\]](#)
58. Criado, M.; Fernández-Jiménez, A.; Palomo, A. Alkali activation of fly ash: Effect of the SiO₂/Na₂O ratio Part I: FTIR study. *Microporous Mesoporous Mater.* **2007**, *106*, 180–191. [\[CrossRef\]](#)
59. Yang, J.X.; Wang, S.M.; Zhao, X.; Tian, Y.P.; Zhang, S.Y.; Jin, B.K.; Hao, X.P.; Xu, X.Y.; Tao, X.T.; Jiang, M.H. Preparation and characterization of ZnS nanocrystal from Zn(II) coordination polymer and ionic liquid. *J. Cryst. Growth* **2008**, *310*, 4358. [\[CrossRef\]](#)
60. Rema Devi, B.S.; Raveendran, R.; Vaidyan, A.V. Synthesis and characterization of Mn²⁺ doped ZnS nanoparticles. *Pramana-J. Phy.* **2007**, *68*, 679. [\[CrossRef\]](#)
61. She, Y.Y.; Juan, Y.A.N.G.; Qiu, K.Q. Synthesis of ZnS nanoparticles by solid liquid chemical reaction with ZnO and Na₂S under ultrasonic bath. *Trans. Non Ferr. Met. Soc. China* **2011**, *20*, 211. [\[CrossRef\]](#)
62. Sutherland, K. Gas chromatography/mass spectrometry techniques for the characterisation of organic materials in works of art. *Phys. Sci. Rev.* **2018**, *4*. [\[CrossRef\]](#)
63. Meilunas, R.J.; Bentsen, J.G.; Steinberg, A. Analysis of aged paint binders by FTIR spectroscopy. *Stud. Conserv.* **1990**, *35*, 33–51.
64. Keune, K.; Boevé-Jones, G. Its Surreal: Zinc-Oxide Degradation and Misperceptions in Salvador Dalí's Couple with Clouds in Their Heads, 1936. In *Issues in Contemporary Oil Paint*; Springer: Cham, Switzerland, 2014; pp. 283–294.
65. Guineau, B. L'étude des pigments par les moyens de la microspectrométrie Raman. In *Datation-caractérisation des parietales et murals. PACT* **1987**, *17*, 259–294.
66. Devezau De Lavergne, E.; Diatre, O.; Et Vanhuong, P. Caractérisation des pigments picturaux d'une enluminure médiévale par microspectrométrie Raman. In *Pigments et Colorants*; éditions du CNRS: Paris, France, 1990; pp. 143–150.
67. Best, S.P.; Clark, R.J.H.; Daniels, M.; et Withnall, R. A Bible laid open. *Chem. Br. FEBR* **1993**, *29*, 118–122.
68. Yufera, J.F.; Ruiz-Moreno, S.; Mansaneola, M.J.; Munoz, S.; et Jawhari, T. Raman spectroscopy for pigment analysis. In *Proceedings of the LACONA I: Lasers in the Conservation of Artworks, Crete, Greece, 4–6 October 1995*.
69. Bonaduce, I.; Carlyle, L.; Colombini, M.P.; Duce, C.; Ferrari, C.; Ribechini, E.; Selli, P.; Tinè, M.R. New Insights into the Ageing of Linseed Oil Paint Binder: A Qualitative and Quantitative Analytical Study. *PLoS ONE* **2012**, *7*, e49333. [\[CrossRef\]](#)
70. Mills, J.S. The Gas Chromatographic Examination of Paint Media. Part I. Fatty Acid Composition and Identification of Dried Oil Films. *Stud. Conserv.* **1966**, *11*, 92–107.
71. Colombini, M.P.; Andreotti, A.; Bonaduce, I.; Modugno, F.; Ribechini, E. Analytical Strategies for Characterizing Organic Paint Media Using Gas Chromatography/Mass Spectrometry. *Acc. Chem. Res.* **2010**, *43*, 715–727. [\[CrossRef\]](#)
72. Colombini, M.P.; Modugno, F.; Ribechini, E. GC/MS in the Characterization of Lipids. In *Organic Mass Spectrometry in Art and Archaeology*; Colombini, M.P., Modugno, F., Eds.; John Wiley & Sons: Hoboken, NJ, USA, 2009; pp. 191–213.
73. Casoli, A.; Palla, G.; Tavlaridis, J. Gas-Chromatography/Mass Spectrometry of Works of Art: Characterization of Binding Media in Post-Byzantine Icons. *Stud. Conserv.* **1998**, *43*, 150. [\[CrossRef\]](#)
74. Osmond, G.; Boon, J.; Puskar, L.; Drennan, J. Metal Stearate Distributions in Modern Artists' Oil Paints: Surface and Cross-Sectional Investigation of Reference Paint Films Using Conventional and Synchrotron Infrared Microspectroscopy. *Appl. Spectrosc.* **2012**, *66*, 1136–1144. [\[CrossRef\]](#)
75. Dietemann, P.; Kälin, M.; Zumbühl, S.; Knochenmuss, R.; Wülfert, S.; Zenobi, R. A Mass Spectrometry and Electron Paramagnetic Resonance Study of Photochemical and Thermal Aging of Triterpenoid Varnishes. *Anal. Chem.* **2001**, *73*, 2087–2096. [\[CrossRef\]](#)
76. Zumbühl, S.; Soulier, B.; Zindel, C. Varnish Technology during the 16th–18th Century: The Use of Pumice and Bone ash as Solid Driers. *J. Cult. Herit.* **2021**, *47*, 59–68. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.