




Article

The Characterization of the Materials Used by Gino Severini in his 20th C Wall Paintings at Semsales in Switzerland

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Abstract: The modern decoration of the Saint Nicolas de Myre Church at Semsales (1924–1926), is the first by renowned Italian artist Gino Severini in Switzerland. Following archival research and visual examination, the materials and the techniques used by Severini for the wall paintings of this church were examined through a multi-technique analytical approach that included both non-invasive and invasive investigations. Archival research revealed lists of some of the materials purchased for the church and notes of the artists. In situ investigations included imaging methods and point analyses (X-ray fluorescence and reflection FT-IR spectroscopy). Based on non-invasive results, a limited number of representative samples were collected for laboratory invasive analyses (SEM-EDS, FTIR-FPA imaging, μ -Raman and GC-MS) to characterize the stratigraphy and the composition of the paintings. Results were coherent with artist's notes and revealed protein-based binders, i.e. animal glue and casein, exclusively on the *Trinity* mural (in the apse) confirming the use of a *secco* technique. All the other wall paintings analyzed at Semsales are painted without the use of organic binders. These findings, integrated with archival researches and the visual examination by conservators, provided significant insights into the materials and techniques used by Gino Severini in his first Swiss murals.

Keywords: Gino Severini; Semsales; wall painting; *a secco*; *a tempera*; *a fresco*; organic binder; analytical investigation; non-invasive techniques; laboratory invasive methods



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1. Introduction

In the Romand region of Switzerland, between 1924 and 1947, the well-known Italian artist Gino Severini (Cortona, 1883–Paris, 1966) decorated five churches in the context of a Catholic art renewal promoted by the Groupe de Saint-Luc [1,2]. Despite Severini's fame as cubist and futurist easel painting artist [3], his murals in Switzerland are not well known and have never been studied from the technical point of view. To fill this gap, a 4-year multidisciplinary research project (2018–2022) entitled “Gino Severini in Switzerland: mural paintings and Catholic art revival of the Groupe de Saint-Luc” is ongoing. This project is coordinated by the University of Applied Sciences and Art of Southern Switzerland (SUPSI), in collaboration with the Bern University of the Applied Sciences and the University of Lausanne [4,5]. Through an interdisciplinary approach that involves historical and archival research, visual examination, and scientific investigations, the project aims to provide a comprehensive and systematic study of the religious wall paintings by Gino Severini in Switzerland [6,7].

The first engagement of Severini in Switzerland was in 1924 for the decoration of the Church of Saint Nicolas de Myre at Semsales in the Canton Fribourg (Figure 1) [8]. Severini

used different media to decorate this church: paintings on walls and on wood, mosaics, stone carving and ceramics. This research focused on the figurative wall paintings: the *Trinity* (in the apse), the *Eucharist* (in the presbytery), the monumental figures of *Saint Nicolas* and *Saint Sebastian* (on the north and south sides of the triumphal arch), the *Virgin and Child* and the *Holy Family* (on the end walls of aisles) (Figure 2). A thorough description of Severini's artistic processes provided by the technical examination of the wall paintings integrated with archival research is presented in Iazurlo et al. [9].



Figure 1. Exterior views of the Church of Saint Nicolas de Myre at Semsales in the Canton Fribourg. (a) Rural location of the church; (b) entrance with the *Crucifixion* in ceramic glazed tiles and carved stone portal by G. Severini.



Figure 2. (a) Church plan with indication of the wall paintings' locations: 1. *Trinity* (6.7 m \times 5.6 m) (b); 2. *Eucharist* (6 m \times 2.2 m) (c); 3. *Saint Nicolas* (1.7 m \times 4 m) (d) 4. *Saint Sebastian* (1.7 m \times 4 m) (e); 5. *Virgin and Child* (2.5 m \times 1.8 m) (f); 6. *Holy family* (2 m \times 2.6 m) (g). Orthophotos by Archéotech SA ©SUPSI.

Severini was very interested in, and often adopted, the traditional and challenging *a fresco* technique to paint on walls. Strictly speaking, this technique does not involve the use of organic binders, but pigments are bound by the process of carbonation of a freshly applied lime plaster patch (*giornata*). To paint *a fresco* requires practice, skills and often artists would complete their works by painting portions *a secco*, i.e., after the lime plaster has set and using an additional binder: either lime, an organic material such as

oil, animal glue, casein, egg or a mixture of these, or in combination. On wall paintings, organic materials are usually added in small amounts and are the hardest to identify as compared to the inorganic ones. At the same time, they are the materials most susceptible to deterioration and alteration.

The background archival research clearly indicated that although Severini preferred the *a fresco* technique, he was forced to decorate the apse of the Semsales church *a secco* because of the presence of a pre-existing gypsum-based plaster. Severini writes: “... L'enorme volta, che copriva l'ambiente, era costituita da un amalgamo resistentissimo di gesso, colla e rena, chiamato “rabitz”; ma su questa superficie non si potevano stendere che colori a tempera. ... cominciai il mio lavoro al Coro con una “Trinità” ispiratemi da quella dipinta da Fouquet nel “Libro d'Ore” di Chantilly. Dovetti dipingerla a tempera, perché i muri della volta erano in “rabitz” e non vi si poteva dipingere a fresco.” [10]. Instead, he painted the other wall paintings either *a fresco*, with a lime-based technique, or both. The different paint technique used by Severini is associated with the condition of the paintings: either the *a fresco*, lime-based portions, or both are in excellent condition, while some deterioration is visible on the *Trinity*.

This article describes the results of the analytical investigations carried out to characterize the artist's materials and provides, in particular, information on the organic materials identified in the wall paintings at Semsales. The methodology adopted for the analytical research follows that developed in the OMWP project [11] and includes a strong integration of previously collected data from background bibliographical and archival research and from the visual examination work by wall painting experts. The analytical study begins with in situ investigations with non-invasive techniques followed by, and integrated with, laboratory invasive analyses on micro-samples. The data collected for each wall painting allowed obtaining a good understanding of the stratigraphy and of the chemical composition of the paint and plaster components (i.e., pigments, binders, fillers, additives and aggregates). Overall, most of the findings were coherent with Severini's notes and other archival information [7,9,10,12,13].

The opportunity to analyze Severini's work in Semsales permitted us to obtain a set of information that, combined with the conservators' observations and the historical and archival documents, provided a full understanding of the materials and the technical painting process followed by the artist during this, his first mural experience, in Switzerland.

2. Materials and Methods

2.1. Analytical Approach

The cycle of Severini's wall paintings in Semsales was examined by the integrated use of both non-invasive and invasive analytical techniques. Firstly, in situ mapping investigations were performed by collecting images in macro- and micro-scale by imaging methods and digital microscopy, respectively. Specifically, the use of different radiations (Vis, UV and IR) and high magnifications (in the case of the digital microscope) allowed us to evaluate and compare optical behavior, such as the presence of UV-induced visible luminescence, the morphology and overlapping of the paint layers. The results of this mapping investigation, interpreted and combined with observation by wall painting conservators, guided a preliminary selection of the areas to be studied with non-invasive point analysis. In this study, point analyses were carried out by X-ray fluorescence and reflection infrared spectroscopy to determine elemental and molecular composition of the materials, respectively, on the six wall paintings examined (Figure 2). The data emerged from the non-invasive measurements and the hypothesis formulated permitted the development of a targeted sampling strategy. Considering that the purpose of the study is understanding the original painting technique, sampling focused on well-preserved areas. A set of 11 representative samples was collected and mounted in cross-sections to characterize the stratigraphic sequence of paint layers and analyze the components of each layer by invasive laboratory methods (optical microscopy, SEM-EDS, FTIR-FPA imaging and μ -Raman). Gas chromatography/mass spectrometry (GC/MS) analyses of

three selected micro-samples provided additional accurate information on the nature of the organic materials in the *Trinity*.

2.1.1. Imaging Techniques

Technical photography was performed using a modified Nikon D800 digital camera (inbuilt UV/IR block filter removed) equipped with a CMOS detector (FX format $36 \times 24 \text{ mm}^2$) with 36.3 mega pixel nominal full range from 350 to 1000 nm (Nital certified/Profilocolore s.r.l.). On the Semsales wall paintings, a total of 36 set of images were collected as follows: 11 for the *Trinity*, 12 for the *Eucharist*, 2 for *Saint Nicolas*, 2 for *Saint Sebastian*, 5 for the *Virgin and Child* and 4 for the *Holy family*. Specifically, each set consists of 6 types of photographic recordings (Vis, Rak, IRr, UVr, UVL and VIL) acquired by modifying radiation source and filters as necessary (see Table 1 for radiation source and filters used).

Table 1. Description of the radiation source and filters for the different imaging methods and in parenthesis the abbreviation used in the text to indicate the type of image.

Imaging Method	Radiation Source	Filters
1. Visible-reflected (Vis)	Flash SB-910 Nikon *	Hot mirror + UV/IR CUT
2. Raking light (Rak)	Flash SB-910 Nikon *	Hot mirror + UV/IR CUT
3. Infrared-reflected (IRr)	Flash SB-910 Nikon *	Kodak Wratten 87
4. Ultraviolet-reflected (UVr)	CR500 LED Madatec	B + W 403 UV pass filter Hot mirror Kolari
5. Ultraviolet-induced visible luminescence (UVL)	CR500 LED Madatec	Hot mirror Better Light UV cut Schott KV418
6. Visible-induced infrared luminescence (VIL)	LED visible	IR Pass 850 nm

* Flash modified by removal of covering filter.

2.1.2. Digital Microscopy

The digital portable microscope used to collect micro-images of the painting surfaces with high magnification ($50\times$ and $200\times$) is a Dino-lite Premier AM4115T-FUW equipped with 4 white and 4 UV (375 nm) LED lights switched by software (*DinoCapture 2.0*).

2.1.3. X-ray Fluorescence (XRF)

XRF analyses (a total of 310 measurements) were carried out with the Niton XL3t 900 X-ray spectrometer produced by Thermo Scientific. The instrument is equipped with an X-ray tube (maximum voltage 50 kV), an Ag anode and a semiconductor detector Si-PIN which allows a resolution of 195 eV. Acquisition time was 30 s. This instrumental set-up, with a sampling area of ca. 3 mm \varnothing , is suitable for the detection of chemical elements with atomic number $Z \geq 16$ (from sulfur; S).

2.1.4. Reflection FT-IR Spectroscopy

Non-invasive infrared spectra (a total of 142 measurements) were acquired through the compact portable Bruker ALPHA II spectrophotometer. This instrument is equipped with a dedicated external reflectance module with specular optics ($22^\circ/22^\circ$) which allow contactless analyses. The system consists of a CenterGlow source, a RockSolid interferometer (with gold mirrors) and a temperature controlled DTGS detector. An integrated USB video camera provides the view of the sampling area of ca. 3 mm \varnothing . The reflection FT-IR spectra were recorded in the spectral range of $8000\text{--}350 \text{ cm}^{-1}$ (medium and partially near infrared region), with a resolution of 4 cm^{-1} and using an average of 186 scans (few minutes of acquisition time). Background correction was performed employing a spectrum collected from a flat gold mirror. Data are shown as pseudo-absorption spectra ($A' = \text{Log}(1/R)$; R = reflectance). The use of a wide IR spectral range that includes NIR radiations

allows obtaining the chemical composition not only at the surface, but also from deeper layers of the paintings.

2.2. Invasive Methods

2.2.1. Optical microscopy

For microscopy, the samples were cast in Araldit 2020 epoxy resin and polished with micro mesh polishing cloths. The optical examinations were performed with a Leica DM270M microscope. The examinations were carried out in bright field and dark field with crossed polarizers. UV fluorescence images were taken with long pass filters at 430 and 515 nm.

2.2.2. Scanning Electron Microscopy (SEM-EDS)

SEM-EDS on cross-sections were carried out with a Zeiss EVO MA 10 scanning electron microscope (2014) coupled with a Thermo NORAN System 7 (2014) EDS system with a Peltier cooled ULTRADRY detector for energy dispersive spectrometry measurements. The measurements were performed with an acceleration voltage of 20 kV and with an acquisition time of 60 s.

2.2.3. FTIR-FPA Imaging

FTIR imaging was performed by a Bruker Hyperion 3000/Tensor 27 infrared spectrometer with a germanium attenuated total reflectance (ATR) crystal (diameter: 250 μm). The spectral resolution achievable with the Cassegrain optics (NA 0.6) and the ATR Ge-crystal (Ge: nD 4.0) is between 0.6 and 2.5 μm . The pixel resolution with pixel binning was 1 μm , covering an area of $32 \times 32 \mu\text{m}^2$. The measuring depth is approx. 0.2–0.7 μm and the FT-IR spectra were recorded in the spectral range of 4000–900 cm^{-1} , with a resolution of 4 cm^{-1} and using an average of 64 scans.

2.2.4. Micro-Raman Spectroscopy

The Raman spectroscopy measurements were performed using a Renishaw InVia (2007) system, with a 250 mm focal length. The maximum spectral resolution is $\sim 1\text{--}0.5 \text{ cm}^{-1}$ achievable (depending on wavelength and grating). The system is coupled with 3 lasers; a 785 nm laser (diode-type): Renishaw HP NIR785 (300 mW), grating 1200 L/mm, edge filter, 110–3200 cm^{-1} , a 633 nm laser (He-Ne-type): Renishaw RL633 (17 mW), grating 1800 L/mm, std edge filter, 100–4000 cm^{-1} and a 514 nm laser (Ar-type): Spectra-Physics (24 mW), grating 1800 L/mm, sup edge filter, 100–4000 cm^{-1} . The spectra were acquired with different power and a spectral resolution of 2 cm^{-1} . The measuring field size depends on the lens and the laser used. Normally (with 100 \times objective) this is approximately 1 μm . with a penetration depth of 2 μm .

3. Results

The results are presented in two sections following the known technical differences between the wall painting *a secco* of the *Trinity* in the apse (Section 3.1) and either the *a fresco*, lime-based wall paintings or in combination, in the rest of the church (Section 3.2).

In each section, the results are presented according to the investigation protocol, i.e., data from non-invasive investigations followed by those obtained by lab-analyses. Specifically, the non-invasive techniques provided information concerning the optical behavior (imaging methods) and the molecular composition (reflection FT-IR spectroscopy) of the surface paint materials. The chemical elements identified by XRF arise from the deeper layers too, but it is not possible to define their specific stratigraphic distribution. For this purpose, SEM-EDS and FTIR-FPA imaging analyses of micro-samples mounted in cross-sections were fundamental. Moreover, the examination of the cross-sections by both optical and scanning electron microscopy provided the aspect, color and morphology of each layer, as well as a better distinction between layers and the identification of thin intermediate layers.

Overall, the set of information obtained from the non-invasive multi-technique analytical approach, verified and implemented by the study of the samples, allowed formulating a hypothesis about the paint composition and the process of execution of the murals. Generally, this interpretation process can lead to formulating different options and identifying questions to be addressed by future researches.

Although this paper focuses on Severini's original painting technique, some information is also provided on the materials identified for the limited retouching found on the paintings.

3.1. The Trinity: A Secco Wall Painting

The in situ non-invasive investigations on the *Trinity* mural promptly confirmed the *a secco* nature of this wall painting as described by Gino Severini [10]. UV-induced visible luminescence images, as part of the imaging methods, showed intense luminescence in many wall painting portions (examples of Vis and UVL images of mural portions are shown in Figure 3a,b). Several optical behaviors could be observed, in particular UV-induced visible luminescence which could be attributed to both organic material and inorganic pigments, typically synthetic pigments [14]. For example, a very bright yellow-green UVL emission corresponding to white areas (Figure 3b) suggested the presence of zinc white (ZnO). This was confirmed non-invasively by the XRF detection of zinc (Zn) (Figure S1) and with the molecular composition emerged from the in situ infrared analyses (Figure 3c). Zinc white was only identified in the painting of the *Trinity* at Semsales.

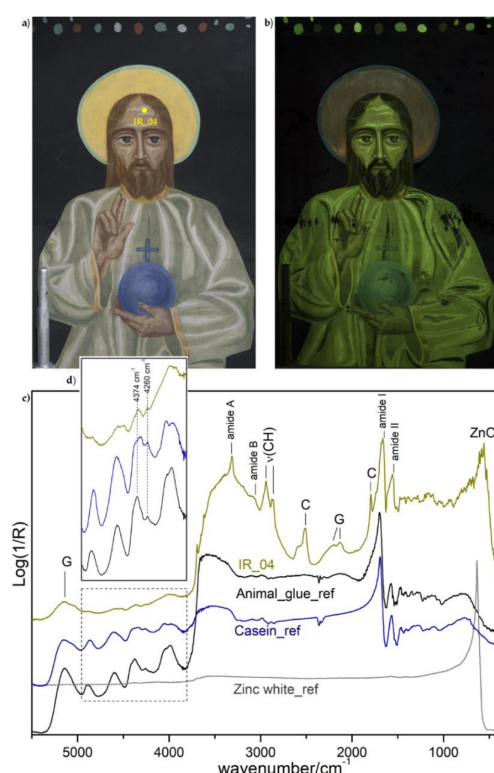


Figure 3. (a) Vis and (b) UVL images of the central figure (image size ca. 90 cm × 90 cm) of the *Trinity* shown in Figure 2b. The UV-induced visible luminescence in (b) is related to the presence of zinc white (ZnO) and cadmium-based pigments (Cd in the halo). (c) Reflection FT-IR spectrum collected from the point IR_04 (location shown in (a)) in comparison with reference spectra of animal glue, casein and zinc white. Marker bands of calcium carbonate (C) and gypsum (G). (d) Magnification of the spectral range between ca. 3750 and 5000 cm^{−1} showing better match with the FT-IR spectrum of animal glue than with that of casein.

Another group of luminescent pigments identified are cadmium-based yellow and orange (CdS). In this case, UV-induced visible luminescence appears bright red-orange [15] (see the halo of Christ in Figure 3b) and the presence of the element cadmium (Cd) was confirmed by XRF (Figure S1). Interestingly, in some orange areas the element mercury (Hg) was found along with cadmium (Figure S2) suggesting the possible presence of a cadmium/mercury sulfide (CdHgS_2) pigment [16] or a mixture of cadmium yellow and vermilion (HgS). However, the exclusive use of vermilion is limited to a few specific red portions of the painting (e.g., lips of the central figure, Figure S2).

Overall, by combining the imaging data with the XRF and the FT-IR analysis it was possible to characterize Severini's palette in a completely non-invasive way. In addition to the already discussed materials, pigments identified include: ultramarine blue, chrome-based green, ivory black, red/brown and black earths. Kaolinite and gypsum, probably used as fillers in the formulation of these iron-based pigments, were found by FT-IR in most of samples analyzed.

More detailed information on the chemical formulation of some pigments emerged from the invasive analysis of micro-samples. For example, chromium hydroxide green "Guignet green" was recognized by micro-FT-IR on a micro-sample coming from the background decoration (green dots). This pigment is a variation of viridian produced by calcination, as documented by the presence of the by-product chromium borate [17]. Moreover, on the *Trinity* dark background two different black pigments were found: ivory black on the homogenous base and an iron-rich black pigment (i.e., black earth) used for the retouches applied by Severini himself to modify the shape of some colored dots.

In several cases, UV-induced visible luminescence was linked to the presence of organic materials, i.e., the *a tempera* paint mentioned in Severini's unpublished manuscript [10]. Luminescence of organic material is attenuated by specific types of colors, blacks and dark browns, while others pigments (Cu-based) significantly reduce/eliminate the UV-induced visible luminescence [18]. However, FT-IR spectra confirmed the presence of organic material in all the 47 spectra acquired for the *Trinity* mural (a representative spectrum is shown in Figure 3c). The protein-based nature of the binder is suggested by detection of amide infrared bands at ca. 3313 (amide A), 3064 (amide B), 1658 (amide I) and 1565 (amide II) cm^{-1} [19]. Although, it is not possible to identify the type of protein exclusively by non-invasive FT-IR [20], a tentative assignment to an animal glue can be formulated considering the signals at ca. 4374 and 4260 cm^{-1} of the methylenic *stretching* and *bending* combination bands [21] (Figure 3d). However, the broad shape of the bands and the co-presence of other compounds makes the protein discrimination difficult. Gypsum and calcium carbonate present in either the plaster, preparatory layers or both (marker IR bands depicted with C and G, respectively, in Figure 3c) are among these interfering compounds.

The stratigraphic distribution of the compounds identified non-invasively, was examined through the study of micro-samples selectively taken from the mural and mounted in cross-sections. An example of the data set collected for a sample coming from the *Trinity* background is provided in Figure 4. Firstly, the microscope examination (Figure 4b) allowed the distinction of two preparatory layers characterized by different properties and morphological aspect as clearly visible in the SEM-BSE images (Figure 4c). The micro-FT-IR measurements across the entire stratigraphy of the sample (Figure 4d) permitted the detection of gypsum exclusively in the plaster (layer 1) with a possible weak contribution of an organic material (carbonyl band between 1711 and 1750 cm^{-1} localized in a thin line of layer 1—Figure 4e). On the top of the gypsum-based plaster, the identification of amide I band (1695–1615 cm^{-1}) suggested the presence of a primer (layer 2) composed of a proteinaceous material and followed by a lime-based preparatory layer (layer 3). In the latter, the weak protein component observed (Figure 4e) is probably penetrated from the upper protein bound paint layer (layer 4) containing ivory black (see phosphate group bands between 1061 and 992 cm^{-1} [22] in Figure 4e). A representative IR spectrum of layer 4 is shown in Figure S3.

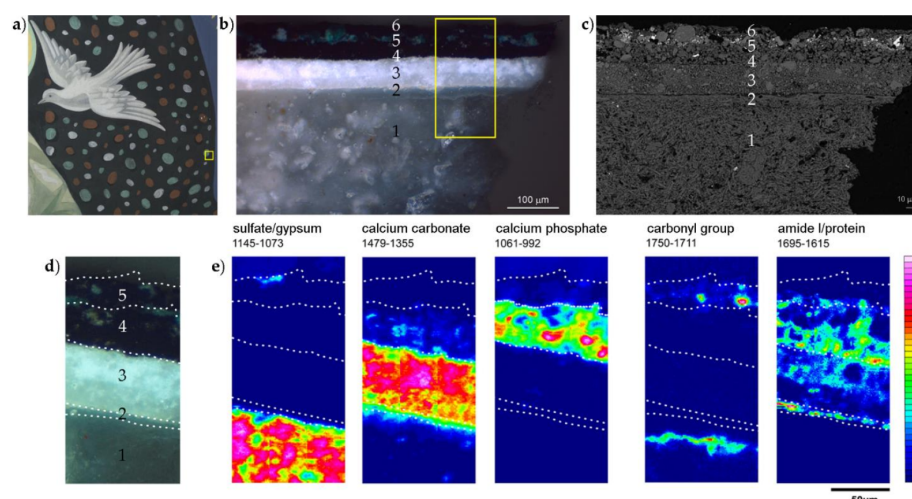


Figure 4. (a) Detail of the Trinity background (image size ca. 80 cm × 80 cm) with indication (yellow square) of the sampling area (black edge of a green dot); (b) optical microscope image and (c) SEM-BSE image of the cross-section of the micro-sample collected in a; (d) cross-section area analyzed by FTIR-FPA imaging (the location is shown in b with a yellow rectangle); (e) FTIR-FPA imaging results with integration of the following spectral range: 1145–1073 cm⁻¹ (sulfate/gypsum), 1479–1355 cm⁻¹ (calcium carbonate); 1061–992 cm⁻¹ (calcium phosphate/ivory black); 1750–1711 cm⁻¹ (carbonyl group); 1695–1615 cm⁻¹ (amide I/protein).

Concerning the lime-based preparatory layers, it is important to point out that in the cross-sections obtained from two samples coming from the upper part of the vault, an additional yellow lime-based layer (Figure 5b, layer 4) is visible above the white lime-based layer (Figure 5b, layer 3). The yellow preparatory layer consists of a blend of yellow ochre and cadmium yellow mixed with calcium carbonate. The presence of cadmium yellow in this underlayer explains the element cadmium found in all the XRF spectra, a total of 39 spectra, acquired on the two angels in the upper part of the vault (Figure 2b), particularly where the color of the paint layer is a dark blue or black, i.e., not associable with a cadmium-based pigment. This yellow preparatory layer does not seem to be present in the rest of the *Trinity*. In the sample shown in Figure 5, over this yellow preparatory layer, the paint layer is visible in multiple applications (layer 5). The paint layers contain zinc white, yellow ochre, cadmium yellow, ivory black and an organic red pigment, all mixed with a protein-based binder. On the sample surface, the last layer (layer 6) is a non-original application of an acrylic resin. The cross-section shows that the yellow preparatory layer is broken and lifting, probably due to the application and the shrinkage upon drying of the acrylic surface coating.

Overall, high protein amounts were found in correspondence with the paint layer in each *Trinity* sample examined, confirming the data emerged from the in situ infrared investigations. Moreover, in addition to protein signals, most of the non-invasive FT-IR spectra contained the signal at ca. 1740 cm⁻¹ related to carbonyl stretching mode and sharp CH bands between 3000–2700 cm⁻¹ that suggest the possible presence of a lipid component. These infrared features were particularly pronounced in spectra acquired from areas with a different appearance in the UVL images. For example, in situ FT-IR on a cloud (Figure 6) revealed that this UVL difference could be related to an additional diluted paint or glaze application containing a lipid component. In order to identify the nature of this component and that of the protein-based binder, a micro-sample representative of the measuring point IR_42 (Figure 6b) was analyzed by gas chromatography/mass spectrometry (GC/MS). Regarding the proteins, GC/MS identified a mixture of animal glue and probably casein. The results did not help to clarify the lipid component as they revealed a diterpenoid resinous material such as pine resin, and excluded the presence of a siccative oil. These results, as well as the presence of small amounts of pine resin,

were also confirmed by GC/MS analysis in the other two *Trinity* samples analyzed by this method, however, pine resin was in much higher amounts in the area of cloud identified by UVL [23].

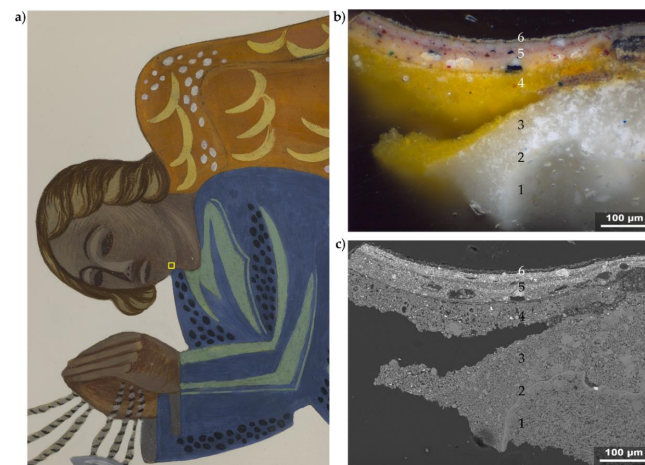


Figure 5. (a) Detail of one of the two angels (image size ca. 70 cm × 100 cm) above the *Trinity* in the south portion of the upper part of the vault with indication of the sampling area (yellow square); (b) optical microscope image and (c) SEM-BSE image of the cross-section of the micro-sample taken in the area shown in (a).

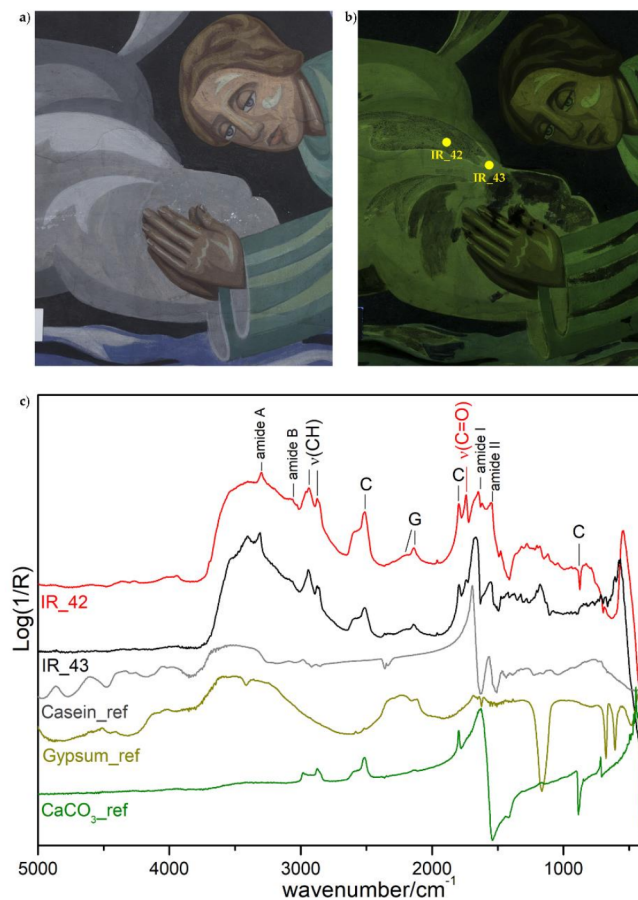


Figure 6. (a) Vis and (b) UVL images of a detail of cloud and angel (image size ca. 55 cm × 70 cm) in the lower south portion of the *Trinity* in the apse. (c) Reflection FT-IR spectra collected from the points IR_042 and IR_43 (location shown in (b) in comparison with reference spectra of casein, gypsum and calcium carbonate). Marker bands of calcium carbonate (C) and gypsum (G).

Later addition, repainting and non-original areas were promptly recognized in the UVL images mainly for their lack of UV-induced visible luminescence. The element titanium (Ti) was detected exclusively in some of these repainted areas and similarly the synthetic resins identified, acrylic, styrene/n-butyl acrylate (Sty/n-BA) copolymer and vinyl, were all in non-original paint and coatings applications.

3.2. A Fresco and/or Lime-Based Wall Paintings

The analytical study of the Severini's murals in the presbytery (*Eucharist*), triumphal arch (*Saint Nicolas* and *Saint Sebastian*) and aisles (*Virgin and Child* and *Holy Family*) of the Semsales church confirmed that Severini painted in either the *a fresco*, lime-based technique, or both.

Optical and SEM-BSE microscope images of a sample taken from the *Virgin and Child* (Figure 7) show a typical stratigraphy of a lime-based painting consisting of a relatively thick paint layer (layer 2) on a plaster (layer 1) characterized by aggregates of different color, shape and size. SEM-EDS (Figure 7c) and FTIR-FPA imaging analyses (Figure S4) revealed the presence of calcium carbonate in the paint layer. In addition, the upper part of the plaster is visibly enriched in calcium carbonate (as a sinter layer, Figure S4). These morphological and chemical characteristics suggest a lime-based technique rather than a *fresco* [24].



Figure 7. (a) Detail of the *Virgin and Child* (image size ca. 50 cm × 60 cm) with indication of the sampling area (yellow square); (b) optical microscope image and (c) SEM-BSE image of the cross-section of the micro-sample collected in (a). SEM-BSE image corresponds with the area indicated with a white rectangle in (b).

UVL images allowed us to hypothesize the presence of pigments such as Cd-based pigments, red lakes and also zinc white in small areas of retouching in the *Eucharist* mural. The floral decorations on the cloak and the crozier of *Saint Nicolas* showed a pink UV-induced visible luminescence (Figure 8a,b) different from the orange one due to the presence of cadmium yellow (see also the visible-induced infrared luminescence showing the distribution of the cadmium yellow in Figure 8c). The white pigment used by Severini in these wall paintings was the Sangiovanni white (CaCO_3). In addition to the pigments detected in the *Trinity*, Severini added pigments commonly used and compatible with either the *a fresco*, lime-based technique, or both, such as green earth and yellow ochre.

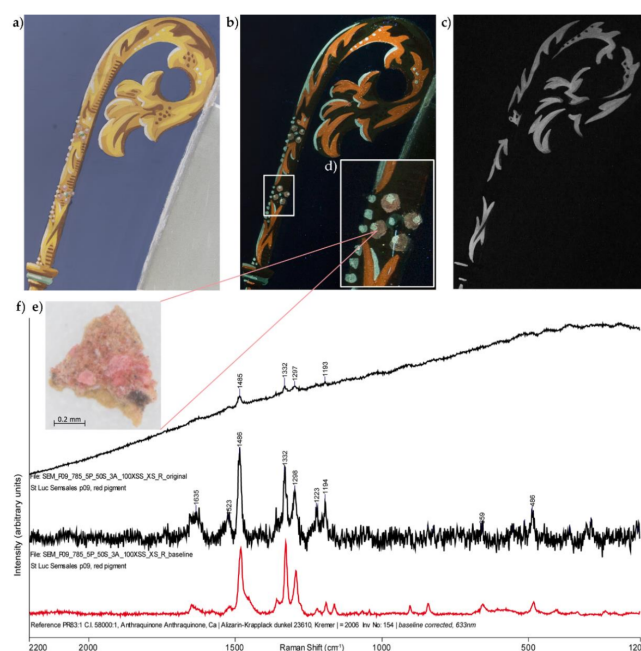


Figure 8. (a) Vis, (b) UVL and (c) VIL images of a detail of the crozier (image size ca. 50 cm × 75 cm) of *Saint Nicolas*; (d) sampling area on a pink portion of the flower; (e) micro-sample analyzed by micro-Raman; (f) Raman spectrum (original and with baseline correction) compared with a reference spectrum of synthetic alizarin lake (PR83).

The micro-Raman analysis performed on a micro-sample taken from a flower (Figure 8d,e) allowed the identification of bands at ca. 1486, 1332 and 1298 cm^{−1} (Figure 8f) ascribable to synthetic alizarin lake (PR83; 1,2-dihydroxyanthraquinone) [25,26] on an aluminum phosphate substrate (Al and P identified by SEM-EDS analysis of the cross-section). The presence of alizarin lake can be correlated with the pink luminescence observed in the UVL image. Similar UVL color was also noticed in some of the flowers of the crown of the angel depicted in the *Holy family* (Figure 9).

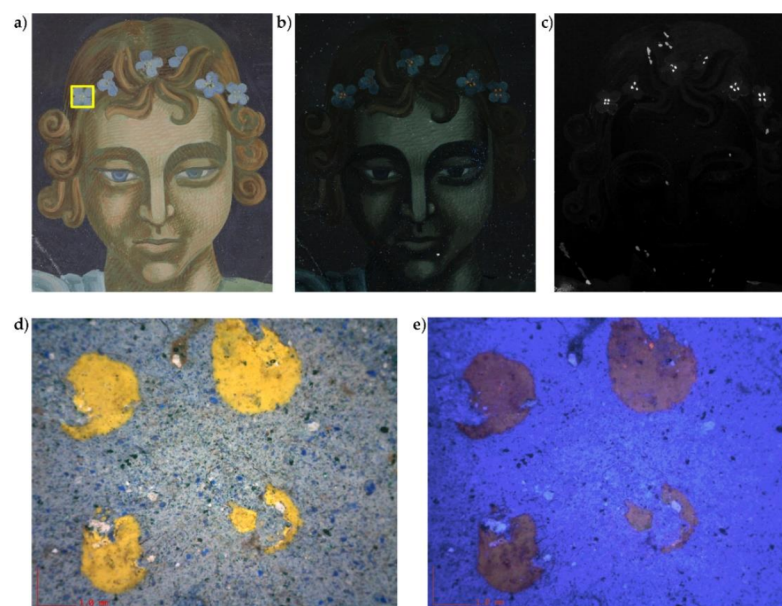


Figure 9. (a) Vis, (b) UVL and (c) VIL images (image size ca. 25 cm × 30 cm) of the angel depicting in the *Holy family*; (d) Vis and (e) UVL images collected by digital microscope (magnification 50×) on the area indicated with a yellow square in (a).

A specific analytical response concerning the characterization of the cadmium yellow pigment widely used by Severini, was provided by Raman investigation of a micro-sample coming from the *Saint Nicolas* (floral decoration of the Saint's shoe, see Figure 10a). The UVL image of the cross-section obtained for this micro-sample (Figure 10c) promptly reveals particles with strong red-orange luminescence ascribable to a cadmium-based pigment. Raman measurements were focused on these luminescent particles. Following Rosi et al. [27], different Raman laser excitations (488, 514, 633 and 785 nm) were used to differentiate the type of CdS-based pigment. However, the Raman spectra obtained (Figure 10d) show that cadmium sulfide emerged exclusively using the 514 nm laser line (marker bands at ca. 302 and 604 cm^{-1}), while the other two lasers used in this work (633 and 785 nm) provided only an enhancement of the Raman bands correlated to calcium carbonate (ca. 1085, 712 and 280 cm^{-1}) and barium sulfate (ca. 988, 461 and 453 cm^{-1}) [28].

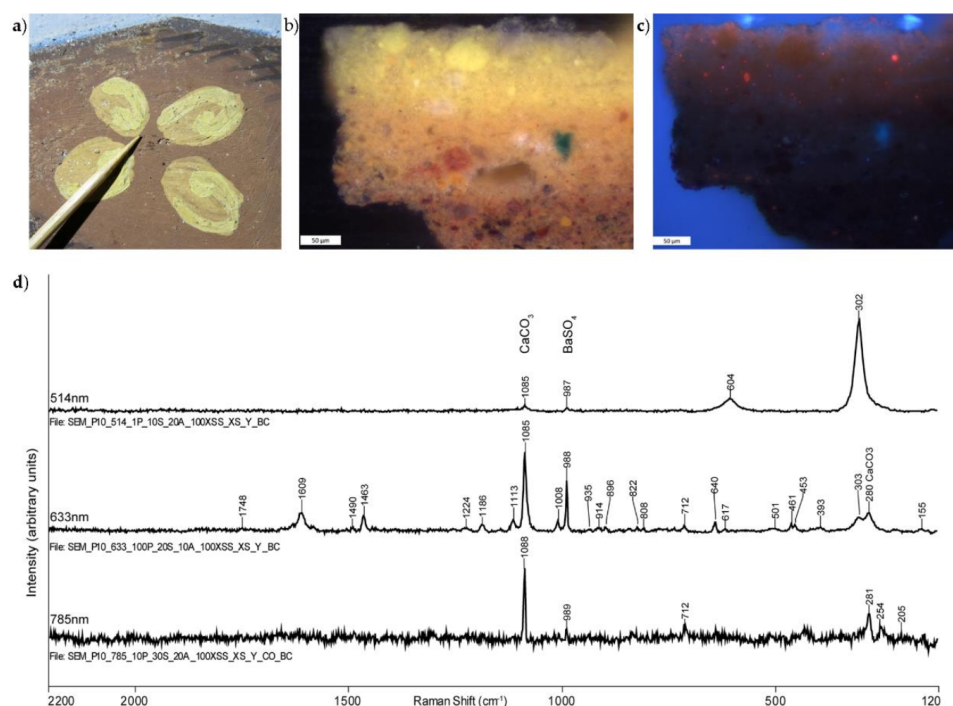


Figure 10. (a) Image of the sampling area (image size ca. 7 × 8 cm) on the floral decoration on the shoe of *Saint Nicolas*; (b) Vis and (c) UVL optical microscope images of the cross-section of the micro-sample; (d) Raman spectra collected on the cross-section using three different laser excitations (514, 633 and 785 nm).

In all the non-invasive FT-IR spectra collected from these wall paintings (95 spectra in total) the marker bands of the calcium carbonate were promptly recognized, in contrast with the results of the *Trinty* (47 spectra in total) where gypsum was largely predominant over calcium carbonate everywhere. In addition, the FT-IR maps of the cross-sections obtained for the micro-samples taken in these areas (see the cross-section in Figure 11), showed that calcium carbonate (ν_3 antisymmetric stretching of CO_3^{2-} in the IR region between 1471 and 1331 cm^{-1} —Figures 11e and S5) is distributed along the full stratigraphy. This evidence, integrated with the visual examination, confirmed the predominant use of either a *fresco*, lime-based painting technique, or both. However, several of the FT-IR spectra acquired on the *Eucharist* and on the figures of the two saints (*Saint Nicolas* and *Saint Sebastian*) presented a weak carbonyl band at ca. 1730 cm^{-1} and possible CH bands in the range between 3000 and 2700 cm^{-1} . These IR features could be correlated to an organic material possibly used in minimal amounts in or over the paintings that may have altered over time producing metal-oxalate complexes. In some FT-IR spectra (Figure S5),

indeed, a weak band at ca. 1320 cm^{-1} , ascribable to $\nu_s(\text{CO})$ vibration of oxalates [29], was recognized.

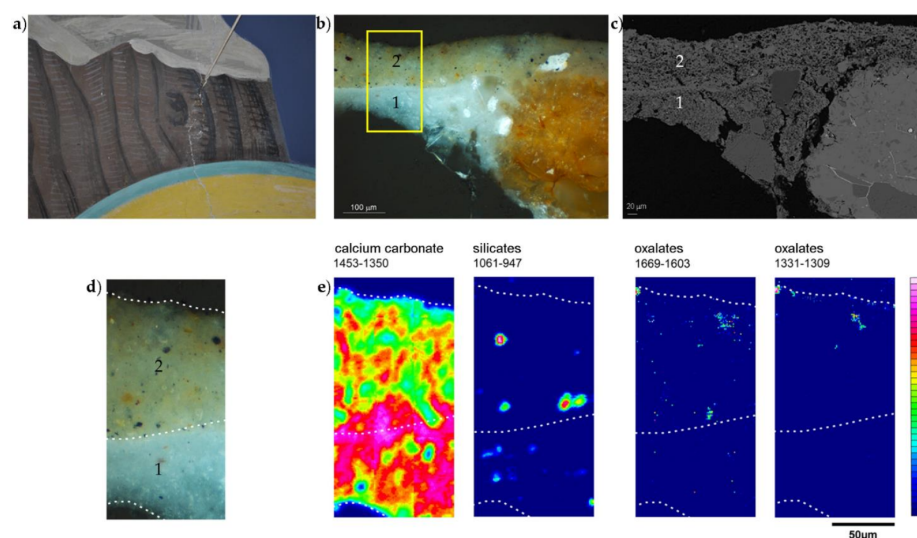


Figure 11. (a) Image of the sampling area (image size ca. $35 \times 20\text{ cm}$) along a fracture in the tree trunk behind the figure of Saint Sebastian; (b) optical microscope and (c) SEM-BSE images of the cross-section of the micro-sample collected in (a); (d) area analyzed by FTIR-FPA imaging (the location is shown in (b) with a yellow rectangle); (e) FTIR-FPA imaging results with integration of the following spectral range: $1453\text{--}1350\text{ cm}^{-1}$ (calcium carbonate); $1061\text{--}947\text{ cm}^{-1}$ (silicates); $1669\text{--}1603\text{ cm}^{-1}$ and $1331\text{--}1309\text{ cm}^{-1}$ (oxalates).

Concerning the detection of non-original materials, only an acrylic resin was found on a glossy retouched area of the *Eucharist* mural (red/brown cloak of 8th apostle from left).

4. Discussion

The analytical results obtained from the study of the wall paintings in the Church of Saint Nicolas de Myre at Semsales summarized in Table 2, provide insights into the painting materials and the techniques used by Severini for his first monumental wall decoration in Switzerland.

Severini started depicting the *Trinity* in the apse by painting *a tempera* on an existing “rabitz” plaster, as he reported in his notes [10]. The term “rabitz” is generally used to indicate a substructure made of woven reeds or wire mesh, which supports a gypsum or cement plaster. The analytical investigations of the *Trinity* have confirmed the presence of a gypsum-based plaster mixed with sand aggregates. However, the “colla” (i.e. the animal glue) described by Severini [10] as part of the “rabitz” mixture was not identified. This layer does not contain any organic material. As clearly revealed by the cross-section analyses, over the gypsum plaster there is a protein-based primer (thickness of ca. $2\text{--}3\text{ }\mu\text{m}$) followed by a lime-based preparatory layer of variable thickness (between 250 and $40\text{ }\mu\text{m}$) not containing any organic binder. It is possible that Severini started by applying the protein-primer on the gypsum and then the lime-based preparatory layer to level the surface. In his notes, contemporary to the work in Semsales, Severini describes several ways to prepare a “rabitz” wall for painting [9]. These recipes could correspond to textural differences revealed by visual examination. However, the stratigraphy and the materials identified in the cross-sections do not correspond exactly to any of these preparation recipes and an extensive invasive sampling campaign would be necessary to characterize them. Another question relates to the presence of an additional yellow preparatory layer visible in the stratigraphy of the two angels over the *Trinity* in the upper most portions of the apse, but missing in the samples from the other areas. This layer contains pigments used by the artist elsewhere, but its role and its presence in the lower portion of the *mandorla*

remains unclear. Regarding the paint layer, the analyses confirm that the *Trinity* mural was painted *a tempera* with a protein-based binder composed of animal glue and possibly casein. Although non-invasive FT-IR investigations identified a lipid component (indicated by the IR ester band at ca. 1740 cm^{-1}), the exact nature of this material remains unknown and the results of chromatographic analyses are inconclusive as only a pine resin was identified. A further sampling campaign would be necessary to clarify the nature of this lipid-based material.

Table 2. Summary of the analytical results obtained from the study of Semsales wall paintings.

Wall Paintings	Pigments	Organic Materials	Fillers/Extenders
<i>Trinity</i>	Zinc white, Cadmium yellow, Cadmium/mercury orange, Vermilion, Red/brown/black earths, Organic red pigment, Chrome-based greens, Ultramarine blue, Ivory black	Animal glue Casein Acrylic resin * Vinyl resin * Sty/n-BA copolymer *	Kaolinite Gypsum
<i>Eucharist</i>	Sangiovanni white, Cadmium yellow, Yellow/red ochre, Vermilion, Chrome-based greens, Green/brown/black earths, Ultramarine blue, Cobalt blue, Ivory black	Oxalates Acrylic resin *	Kaolinite Gypsum
<i>St. Nicolas</i>	Sangiovanni white, Cadmium yellow, Yellow/red ochre, Alizarine lake, Vermilion, Chrome-based greens, Green/brown/black earths, Ultramarine blue, Cobalt blue	Oxalates	Kaolinite Gypsum
<i>St. Sebastian</i>	Sangiovanni white, Cadmium yellow, Yellow/red ochre, Chrome-based greens, Green/brown/black earths, Ultramarine blue, Cobalt blue	Oxalates	Kaolinite
<i>Virgin and Child Holy family</i>	Sangiovanni white, Cadmium yellow, Yellow/red ochre, Vermilion (only in <i>Virgin and Child</i>), Chrome-based greens, Green/brown/black earths, Ultramarine blue, Cobalt blue, Ivory black Possible alizarine lake (only in <i>Holy family</i>)	Oxalates	Kaolinite Gypsum (only in <i>Holy family</i>)

* non-original added materials.

For the other figurative wall paintings (*Eucharist*, *Saint Nicolas*, *Saint Sebastian*, *Virgin and Child* and *Holy family*), Severini used the traditional *a fresco* and lime-based technique experimented for the first time only a few years earlier in the castle of Montegufoni in Tuscany (1921–1922) [30]. The non-invasive infrared analyses supported and integrated by the study of the cross-sections proved the use of lime as binder. However, the detection of oxalates and weak carbonyl and CH bands indicate a possible addition of small amounts of organic material.

The range of pigments identified in the Semsales murals reveals that Severini combined traditional *a fresco* pigments (e.g., iron-based pigments) with modern ones, i.e., zinc white (only in the *Trinity*), cobalt blue, synthetic ultramarine blue, synthetic alizarin lake, chrome-based greens and cadmium-based yellow and orange pigments (see Table 2 for the complete list). In particular, the cadmium-based pigments are readily identified by technical photography thanks to their characteristic luminescence revealed in both UVL and VIL images [31].

Analytically, the use of modern pigments in the 20th century has been widely explored in easel paintings [32–36], while their application in wall paintings is less known [37–39]. In addition, Semsales is an exceptional example of extensive use of cadmium-based pigments not commonly found in wall paintings, especially the cadmium/mercury sulphide type [40] that probably corresponds to the cadmium orange purchased for the church decoration (see Table S1).

The analytical data are generally in accordance with the results of the archival research. For example, the pigments identified and the casein are listed in the invoices of materials purchased for the church decoration (see Table S1). However, there are some incongruences, and some questions remain open. Notably, the use of potassium silicate, listed among the materials purchased for the decoration of the church and mentioned by Severini in his writings for the silicate paint [41], was not analytically identified with the methods used in any of the wall paintings studied.

This paper is an example of the relevance of the analytical approach that, correlated with the conservator's observations, provides an objective support for the technical study and the interpretation of the historical and archival sources.

The project focused on the study of Severini's wall paintings in Switzerland is ongoing and the findings achieved for the Semsales church represent the basis for the examination of the other religious murals painted by the artist in later years. Currently, the analytical results acquired in Semsales are archived, organized and linked to other information in a specific data management system [42] to be provided in an open access format in future.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/app11199161/s1>. Figure S1. XRF spectra (a and c) collected from a white area on the forehead of the central figure of the *Trinity* (b) and a yellow area of the halo (d). Figure S2. XRF spectra (a and c) collected from an orange area on the wing of an angel of the vault (b) and a red/brown area on the lips of the central figure of the *Trinity* (d). Figure S3. (a) Optical microscope image of the sample shown in Figure 4; (b) FTIR-FPA imaging results corresponding to the spectral range between 1695 and 1615 cm^{-1} (amide I/protein) with indication (black circle) of the acquisition point of the IR spectrum shown in c. In the spectrum are visible the amide bands at ca. 1643 (amide I) and 1531 cm^{-1} (amide II), the signals of the ivory black (2012 and 1030 cm^{-1}), the calcium carbonate marker band at 1417 cm^{-1} and the signals of the casting resin at ca. 1507, 1246 and 1181 cm^{-1} . Figure S4. (a) SEM-BSE image of the cross-section of the sample shown in Figure 7 with indication of the acquisition point of the SEM-EDS spectra reported in d (1) and e (2); (b) optical microscope image of the sample corresponding to the white square marked in a; (c) FTIR-FPA imaging results of the calcium carbonate distribution. Figure S5. (a) Optical microscope image of the sample shown in Figure 11; (b) FTIR-FPA imaging results corresponding to the spectral ranges between 1453 and 1350 cm^{-1} (calcium carbonate) and 1331–1309 cm^{-1} (oxalates) with indication (white circles) of the acquisition points of the IR spectra shown in c (1) and d (2). Spectrum in (c) shows the calcium carbonate marker bands (1396, 1796 and 2512 cm^{-1}), while the oxalate marker band at ca. 1320 cm^{-1} is

weakly visible in the spectrum reported in d. Table S1: Transcription of paintings materials purchased between 1924 and 1926 for the decoration of the Saint Nicolas de Myre Church at Semsales.

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