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RESEARCH ARTICLE



Traditional and modern pigments in Gino Severini's Swiss murals

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Abstract

Between 1924 and 1947, Gino Severini decorated five churches in the Romand region of Switzerland with monumental religious wall paintings. This mural art played an important role in the Italian artist's career despite being mostly unknown and not easily found. The painting methods and materials of these modern Swiss murals were characterized by combining historical and archival research with onsite visual and scientific examination. Most pigments were identified with noninvasive methods integrating mapping techniques (i.e., technical photography and digital microscopy) with point analysis (x-ray fluorescence and reflection FT-IR spectroscopy). The results of these portable techniques were completed with SEM-EDS, µFT-IR FPA imaging, and µRaman analyses on micro-samples which provided stratigraphic and compositional information to complement the noninvasive results. Overall, the data obtained show that Severini used both traditional pigments (e.g., Sangiovanni white and ochres/earths of various color) and modern ones, such as cadmium-based pigments, with different painting techniques (e.g., zinc white was applied exclusively a secco). Apart from cerulean blue (cobalt stannate) and Naples yellow (lead antimonate) found only in two locations, the same set of pigments was documented in all of Severini's Swiss murals. The characterization of the artist's palette is important to understand the technical painting process followed by Severini, his interest on new painting materials available on the market and, at the same time, loyalty towards traditional painting methods, such as painting a fresco.

KEYWORDS

Gino Severini, mural art, noninvasive/invasive investigation, pigments, wall paintings

INTRODUCTION 1

During the early 1920s, the famous Italian painter Gino Severini (Cortona, 1883-Paris, 1966) began to explore mural art as an additional means of expression to mosaic and easel paintings. He created his first mural in 19211922 at Montegufoni Castle, in Tuscany, where he decorated an entire room, the studiolo, with characters of the Commedia dell'Arte. This was Severini's first experience with mural painting, the complexity of painting on plaster and the use of new paint materials. He followed Cennini's medieval treatise² on the instruction for traditional a fresco

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technique, but his workmanship, the accuracy of details and the chiaroscuro effects reveal a style close to that of easel painting. Two years after this experience, Severini's next work on wall painting is in Switzerland, where he approached sacred art in the framework of the activities promoted by the Catholic society known as the Groupe de Saint-Luc.^{3,4} In this context, over two decades (from 1924) until 1947), the Italian artist painted religious subjects in five churches of the French-speaking part of Switzerland: St. Nicolas de Myre in Semsales (FR, 1924-1926), Notre-Dame-de-l'Assomption in La Roche (FR, 1927-1928), St. Pierre in Fribourg (FR, 1933), Notre-Dame du Valentin in Lausanne (VD, 1934), and the church of the Couvent des capucins in Sion (VS, 1947). Although mural art was an important phase in Severini's artistic development, a comprehensive technical and stylistic study of his wall paintings is missing. The lack of this knowledge led to the 4-years SNF research project (2018–2023) entitled "Gino Severini in Switzerland: mural paintings and Catholic art revival of the Groupe de Saint-Luc."5,6 This project aims at understanding Severini's expressive intentions and his technical choices in terms of both materials and painting procedures through an interdisciplinary approach. With this focus, historical and archival research⁸ has been integrated with onsite visual and scientific examination 9,10 of Severini's wall paintings.

This contribution presents the results obtained by the research project focusing on Severini's pigment choice. Most of the pigments used by Severini in the Swiss murals were characterized by noninvasive techniques. Specifically, preliminary, and fundamental information about surface distribution and optical behavior of the paint layers emerged from the sets of images collected by technical photography in various spectral ranges (visible, infrared, and ultraviolet). Optical properties and morphology of the painted surfaces were explored at the micrometer-scale using a digital microscope (with visible and UV illumination). These mapping data guided and were combined with point analyses performed using X-ray fluorescence (XRF) and reflection FT-IR spectroscopy to understand the chemical composition of the painting materials. Additional information on the nature of specific pigment formulations and binder materials was gained by analytical investigation on micro-samples mounted in cross-sections associated with light microscopy (LM), scanning-electron microscopy with elemental analysis and mapping (SEM-BSE/-EDS), micro-Fourier-transform infrared spectroscopy with focal plane array imaging (µFT-IR FPA imaging) and µRaman spectroscopy (RS). Table 1 provides information on the wall paintings examined within each church, the number of areas and points analyzed with noninvasive techniques, and the number of samples taken. This table shows that thanks to the use of noninvasive methods, sampling is reduced to the minimum compared to investigations carried out a few decades ago where sampling was the first operation.

Overall, the analytical results obtained revealed that Severini's palette mostly matches his personal notes as well as historical and archival information. 11 In the case of the church in Semsales, thanks to the finding of the original pigment purchase invoices, it was possible to confirm the correlation between the analytical results and the painting materials acquired for the church decoration.¹⁰ The research findings allow retracing Severini's wall painting execution process and his experiments to combine traditional painting materials with modern synthetic ones available on the market. In the Swiss churches, Severini painted mostly a fresco and/or with a lime-based technique. Only the wall decorations of the Fribourg church (Angels and Tribune decoration) and the Trinity on the apse of the Semsales church, 9,10 were made with a secco technique using organic paint binders.

2 | EXPERIMENTAL

The investigation of the painting materials in Severini's Swiss murals was guided by and integrated with the results of visual examination by wall painting conservators who studied the painted surface with visible and UV lamps for several days prior to the arrival on site of the scientific team. The analytical study started onsite using noninvasive techniques. First, mapping investigations were performed by collecting images at the macro- and micro-scale by technical photography and digital microscopy, respectively. The mapping results, combined with observations by wall painting conservators, guided the selection of the areas to be examined with noninvasive point analyses carried out through portable x-ray fluorescence and FT-IR spectrometers. Based on the results of noninvasive campaigns, the work onsite (undertaken in each Swiss church) was completed collecting a limited number of representative micro-samples to confirm and visualize the stratigraphy and obtain with invasive investigation the chemical composition of each layer. For this purpose, most of the micro-samples were mounted in cross-sections and analyzed in laboratory by microscopy (optical and electron microscopy SEM-BSE/-EDS) and vibrational micro-spectroscopy (µFT-IR FPA imaging and µRaman) techniques.

2.1 | In situ noninvasive techniques

2.1.1 | Technical photography

On each wall painting, several sets of images at different spectral range were taken using a Nikon D800 digital

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Noninvasive investigation and sampling

Technical photography: 38 sets

Digital microscopy: 36 areas

Sampling: 11 micro-samples

XRF: 310 points FT-IR: 154 points

TABLE 1 Severini's wall paintings studied in each Swiss church with indication of the number of areas and points analyzed with noninvasive techniques, and the number of samples taken.

Church

St. Nicolas de Myre Semsales (1924-1926)



Wall paintings

Trinity $(6.7 \text{ m} \times 5.6 \text{ m})$



Eucharist (6 m \times 2,2 m)





St. Nicolas $(1,7 \text{ m} \times 4 \text{ m})$



St. Sebastian $(1,7 \text{ m} \times 4 \text{ m})$



Virgin and Child $(2,5 \text{ m} \times 1,8 \text{ m})$



Holy family $(2 \text{ m} \times 2,6 \text{ m})$

Technical photography: 37 sets Digital microscopy: 64 areas XRF: 201 points

FT-IR: 94

Sampling: 15 micro-samples

Notre-Dame de l'Assomption



Last Supper (5 m \times 3 m)



The Pietà (8,8 m \times 3,4 m)





Angels (4,3 m \times 1,5 m)



Tribune decoration (10,2 m \times 2,5 m)

Technical photography: 7 sets Digital microscopy: 89 areas

XRF: 118 points FT-IR: 68 points

Sampling: 8 micro-samples

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TABLE 1 (Continued)

Church

Notre-Dame du Valentin Lausanne (1934)



Wall paintings



Apse decoration (15 m \times 10,2 m)

Noninvasive investigation and sampling

Technical photography: 38 sets Digital microscopy: 91 areas

XRF: 320 points FT-IR: 127 points

Sampling: 20 micro-samples





St. Francis receiving stigmata (6,5 m \times 4,3 m)



St. Felix $(1.9 \text{ m} \times 3.5 \text{ m})$



St. Anthony $(1,9 \text{ m} \times 3,5 \text{ m})$

Technical photography: 8 sets Digital microscopy: 84 areas

XRF: 214 points FT-IR: 102 points

Sampling: 13 micro-samples

Source: Photos ©SUPSI.

camera with the built-in UV/IR block filter removed and different types of illuminators and filters. 10 Each set consists of the following types of photographic recordings:

- 1. Visible-reflected (Vis)
- 2. Raking light (Rak)
- 3. Infrared-reflected (IRr)
- 4. Ultraviolet-reflected (UVr)
- 5. Ultraviolet-induced visible luminescence (UVL)
- 6. Visible-induced infrared luminescence (VIL)

Digital microscopy 2.1.2

Optical properties and morphology of the painted surfaces were examined at high magnifications (50X and 200X) through a portable digital microscope. The device used is a Dino-lite Premier AM4115T-FUW equipped with 4 visible and 4 UV (375 nm) LEDs, controlled by the DinoCapture 2.0 software. This allowed the recording of both visible and UVL images with a scale bar included.

X-ray fluorescence 2.1.3

The elemental composition of the painting materials was determined using a portable NitonTM XL3t 900 x-ray fluorescence (XRF) spectrometer (Thermo Scientific) that allows the detection of chemical elements with atomic number $Z \ge 16$ (from sulfur). The instrument consists of an x-ray tube (max. voltage: 50 kV), a silver (Ag) anode and a semiconductor detector Si-PIN with a resolution of 195 eV. Each XRF spectrum was collected from a sampling area of ca. 3 mm \emptyset with an acquisition time of 30 s.

2.1.4 Reflection FT-IR spectroscopy

The portable Bruker ALPHA II spectrometer equipped with an external reflectance module (specular optics-22"/22") was used to collect noninvasive (noncontact) infrared spectra at a working distance of \sim 1 cm. The spectrometer is composed of a CenterGlowTM source, a RockSolidTM interferometer (with

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gold mirrors) and a temperature controlled DTGS detector. The reflection FT-IR spectra were collected in the broad spectral window ranging from 8000 to 350 cm^{-1} wavenumbers, at a resolution of 4 cm^{-1} and 3 min. of acquisition time. A spectrum acquired from a flat gold mirror was used for the background correction. The data was visualized as pseudo-absorption spectra (A' = Log [1/R]; R = reflectance) through the *OPUS 8.1* software, while the view of the sampling area (ca. 3 mm \emptyset) was provided by an integrated USB video camera.

2.2 | Laboratory invasive methods

Micro-samples coming from the five Swiss churches were studied as is and selected portions were embedded in the two-component epoxy resin Araldite 2020 (CTS Europe) and polished with MicroMesh® abrasive cloths to obtain cross-sections.

2.2.1 | Optical microscopy

The micro-samples (fragments and cross-sections) were observed with the optical Leica DM2700M microscope equipped with Vis (LED) and UV (CoolLED PE-300) illumination. Two long pass filters at 430 and 515 nm were used to collect (UV- and blue excitation resp.) luminescence images.

2.2.2 | Scanning electron microscopy

Cross-sections were coated with a carbon-evaporation coater for SEM-EDS elemental analyses. The instrument used was a Zeiss EVO MA 10 (2014) equipped with a Thermo NORAN System 7 (2014) EDS with a Peltier cooled ULTRADRY detector for energy dispersive spectrometry measurements. EDS analyses were performed in high vacuum mode, at an acceleration voltage of 20 kV, 100 pA beam current, an acquisition time of 30 s per spectrum, while element maps were collected at 20 kV and 300 pA excitation and recorded at 512 \times 384 pixel resolution. Data and phase analysis was performed using COMPASS & XPHASE software.

2.2.3 | μFT-IR FPA imaging

FT-IR imaging measurements were carried out on a Bruker[®] Hyperion 3000/Tensor 27 infrared spectrometer equipped with a Ge-ATR crystal and a multi-element FPA 64 \times 64 detector (32 \times 32 μ m² area). The measuring depth is approx. 0.2–0.7 μ m and the FT-IR spectra were

recorded in the spectral range from 4000 to 900 cm⁻¹, at spectral resolution of 4 cm⁻¹ and 64 scans.

2.2.4 | μRaman spectroscopy

A few selected micro-samples (fragments and crosssections) were analyzed by a Renishaw InVia dispersive Raman spectrometer (2007) equipped with a Leica DM LM microscope. The laser used was the 785 nm laser (diode-type), Renishaw HP NIR785 (300 mW) with a 1200 L/mm grating. The Raman spectra were acquired in the spectral range 120-2200 cm⁻¹ with 0.1-1.2 mW power on sample at a spectral resolution of 2 cm⁻¹. The interaction volume depends on the objective and the laser wavelength used. Using the $100 \times$ objective (NA = 0.9), the lateral spot size is approximately 1 um with a penetration depth of 2 um. The maximum spectral resolution achievable (depending on wavelength and grating) is ca. 1-0.5 cm⁻¹. Prior to each measurement, the instrument was calibrated on the internal Si-reference standard to 520.6 $\pm 0.1 \text{ cm}^{-1}$.

3 | RESULTS

The analytical results concerning the characterization of the pigments used by Severini in his Swiss murals are presented and discussed by colors. Each color section includes the description of both traditional and modern pigments as well as references to the paint binder used for their application. The data are illustrated starting from the noninvasive results (mapping and point analyses) and completed with results of invasive investigations performed on micro-samples (fragments and cross-sections).

3.1 | Yellow and orange pigments

In the Swiss murals examined, all the yellow pigments used for the haloes showed an intense orange UV-induced visible luminescence (UVL) that in combination with the visible-induced infrared luminescence (VIL) suggested the presence of cadmium-based pigments. ^{12–16} In Figure 1, an example of these optical properties is visible in the UVL and VIL images (Figure 1C,D) of the Christ's halo of the lunette mural in the Sion church. The UV response of the yellow paints was explored also at the micron-scale with digital microscopy (Figure 1E–G). The correlation of this optical behavior with the presence of cadmium-containing pigments was clearly confirmed

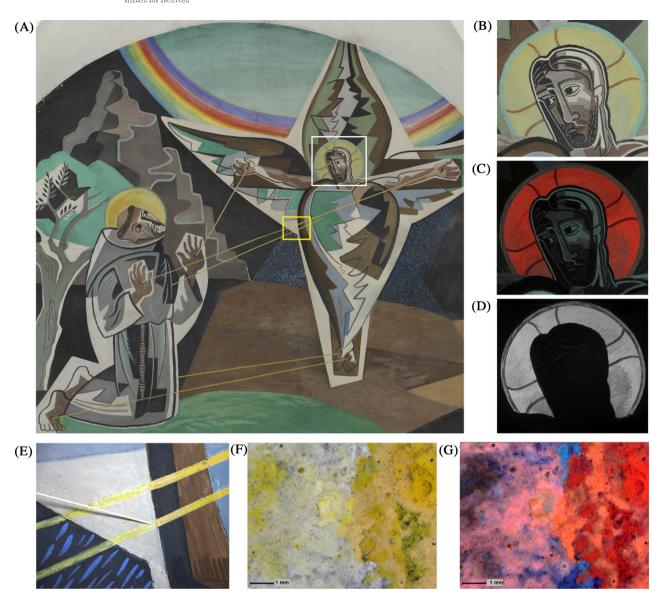


FIGURE 1 Couvent des Capucins, Sion: (A) picture (central area) of the lunette mural Saint Francis receiving the stigmata with indication of the areas examined by technical photography (white rectangle) and digital microscopy (yellow rectangle). (B) Vis, (C) UVL and (D) VIL photographic records by Ottaviano Caruso, ©SUPSI. (E) Picture of the area investigated by Dino-Lite: (F) Vis and (G) UV images collected.

by XRF analyses (Figure S1). In fact, XRF spectra of most of the areas with these optical properties showed abundant presence of cadmium (Cd) in combination with low counts of barium (Ba) and zinc (Zn). XRF findings suggest the use of a cadmium lithopone variety composed of a mixture of cadmium sulfide (CdS) and barium sulfate (BaSO₄) and sometimes also zinc sulfide (ZnS)¹⁷ and μRaman investigation confirmed barium sulfate (BaSO₄) on a micro-sample coming from the *Saint Nicolas* mural (yellow floral decoration of the Saint's shoe) in Semsales. On a few of the orange areas located in the *Trinity* mural of the Semsales apse, cadmium was detected in combination with mercury (Hg), suggesting a mixture of cadmium yellow (CdS) and vermilion (HgS) or the possible use of a pigment such as cadmium/mercury sulfide

(CdS-HgS). Further analyses are ongoing to clarify the nature of this color reported in the literature to be unavailable before 1955. 17

According to Severini's notes, 9 cadmium yellow was mixed with ochres to obtain color tones varying from dark yellow to orange. This procedure was confirmed by the analytical investigation. For example, the UVL and VIL images taken from two apostles of the *Eucharist* scene in the Semsales church (Figure 2A–C), showed the presence of a cadmium-based pigment on the orange dress and, in this case, the XRF analysis (Figure 2D,E) revealed high counts of iron (Fe) in addition to those of cadmium suggesting the mixing of pigments.

In addition to synthetic cadmium-based pigments, Severini used traditional yellow ochre, alone, or mixed

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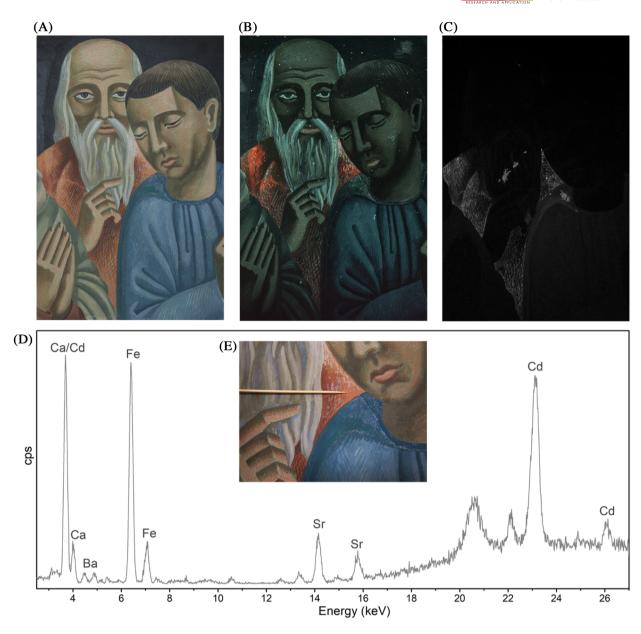


FIGURE 2 St. Nicolas de Myre, Semsales: (A) Vis, (B) UVL, and (C) VIL images collected by Ottaviano Caruso, ©SUPSI, from two figures of the Eucharist. (D) XRF spectrum collected from (E) an orange area with active UVL and VIL.

with other red and brown ochres/earths (umbers and siennas) on several occasions. These pigments were identified on darker yellow/orange areas combining XRF data (detection of iron) with noninvasive infrared spectra characterized by the IR bands of components such as kaolinite and/or gypsum often present in the ochre formulations.¹⁸ The detection of kaolinite (an example is shown in Figure 3) suggest the use of a French yellow ochre as reported in the study by Genestar and Pons. 19 This material is listed among the painting materials purchased for Severini for the decoration of the Semsales church.¹⁰

Rarely, in addition to cadmium yellows and ochres, Severini used a yellow pigment not commonly found in modern wall paintings, namely lead antimonate yellow

also known as Naples yellow (Pb₂Sb₂O₇). This pigment was identified as part of this research exclusively on the Angels depicted in the church of St. Pierre in Fribourg where high counts of lead (Pb) and antimonate (Sb) emerged from the in situ XRF investigation and their concurrent presence in the yellow paint was confirmed by both point and map SEM-EDS data (Figure 4).

Pink, red, and brown pigments 3.2

In addition to the luminescence phenomena due to the presence of cadmium-based pigments, a pink-reddish visible luminescence induced by ultraviolet radiation was

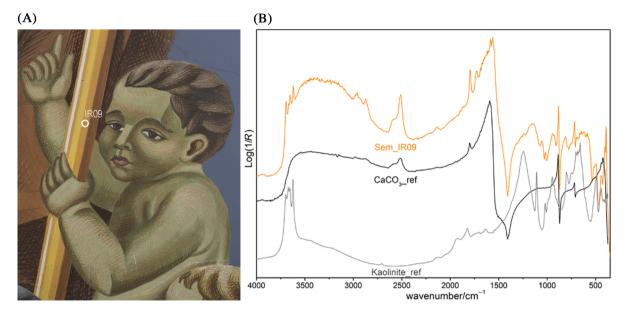


FIGURE 3 St. Nicolas de Myre, Semsales: (A) detail of one of the children in the *Saint Nicolas* mural. The circle indicates the point IR09 analyzed by portable FT-IR spectroscopy. (B) Reflection FT-IR spectrum collected from the point IR09 compared with reference spectra of calcium carbonate (black profile) and kaolinite (gray profile).

noticed in some details, mostly on pink floral decorations. This phenomenon suggested the presence of a red lake, 12 which was identified as alizarin by µRaman analysis on a micro-sample from a pink flower on the crozier of Saint Nicolas in Semsales. 10 Considering the time of use, first half of 20th century, it is probably synthetic alizarin and not the natural one. In fact, Raman investigation detected only pure alizarin and no other components, and this is typical of the synthetic one.²⁰ This finding most likely corresponds to the purchased "laque de Garance" listed in the invoices of painting materials for Semsales decoration. 10 Indeed, in the early 20th century the term "laque de Garance" was used to indicate both natural and synthetic red lakes.²¹ The same alizarin dve was identified in a micro-sample of the purple rainbow stripe depicted in the lunette mural of the Sion church (Figure 5). Here, alizarin (dark red grains) is mixed in the same paint layer with red-orange vermilion grains. The Raman spectrum (Figure 5c) shows alizarin marker bands at ca. 1485, 1331, and 1296 cm⁻¹, while the bands at ca. 343, 285, and 253 cm⁻¹ are characteristic markers for vermilion.22

Severini obtained delicate pink shades by mixing a red lake (probably alizarin) with *Sangiovanni* white (CaCO₃) or zinc white (ZnO) depending on the binder used. He mixed the lake with *Sangiovanni* white to paint *a fresco*/lime-based technique (e.g., in the *St. Nicolas* figure at Semsales), while to paint *a secco* (e.g., in the floral decoration at Fribourg) he mixed the lake with zinc white. Most commonly, to obtain pink colors, Severini

used a red iron-based pigment instead of a red lake. For example, in the *Angels* of the Fribourg church a red pigment containing iron was detected in association with lithopone (a co-precipitate of ZnS and BaSO₄) and a low content of a protein-based binder (paint layer n.2 of the cross-section shown in Figure 4). On other pink areas such as the angels of *The Pietà* in La Roche church (Figure 6), there is no organic material and the iron-based pigment is simply bound with lime (see SEM-EDS data obtained for the cross-section shown in Figure 6) following a very traditional painting method.

In terms of red paints, pure red iron-based pigments and pure vermilion were identified only in few cases (Figures S2 and S3). For example, vermilion was found on the lips and on the robes of some figures in Semsales¹⁰ and on the red band of the rainbow depicted on the lunette mural in Sion (Figure S3). All tones from dark red to brown were obtained with mixtures of traditional earths, namely raw and burnt Sienna, and raw and burnt umber (Figure S4). Umber was promptly recognized through the XRF detection of manganese (Mn).¹⁸

3.3 | Blue pigments

In the wall paintings examined, two different kinds of blue hues were predominant and clearly distinguished: synthetic ultramarine blue (ideal formula $Na_{7.5}[Al_6Si_6O_{24}]S_{4.5}$) and Thénard's or cobalt blue (CoAl₂O₄). Both pigments were identified noninvasively

collected in (A). Stratigraphy: 1. plaster; 2. pink paint layer; 3. yellow paint layer. (C) Vis-UV optical images, SEM-BSE image, and SEM-EDS phase maps (element combinations) of the area marked in (B) with a dashed white rectangle.

combining the XRF analyses with the FT-IR investigation. Representative FT-IR spectra obtained from these two blues on the Eucharist scene in Semsales are shown in Figure 7. Specifically, the inverted bands at ca. 1010 and 450 cm⁻¹ visible in the blue spectrum (Figure 7B) correspond to the silicate framework characteristic of the ultramarine blue (see the comparison with a reference

spectrum in black). 23,24 A cobalt-containing pigment, instead, was identified by the broad inverted band visible in the infrared region (bluish-green spectrum in Figure 7D), which is due to the d-d electronic transition of cobalt (II) tetrahedrally coordinated.²⁵ This data, supported by the detection of cobalt (Co) by XRF (see XRF spectrum in Figure 7C), confirmed the use of cobalt blue.

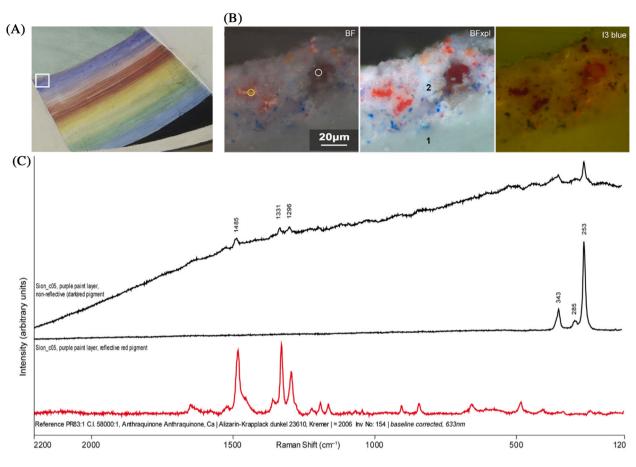


FIGURE 5 Couvent des Capucins, Sion: (A) detail of the rainbow in the lunette mural *Saint Francis receiving the stigmata* with indication of the sampling area (white rectangle). (B) Optical images of the cross-section of the sample collected in (A). Stratigraphy: 1. plaster; 2. purple paint layer. (C) Raman spectra collected from the red-orange (yellow circle) and dark red (white circle) grains of the purple paint layer compared with a reference spectrum (red profile) of synthetic alizarin lake (PR83; 1,2-dihydroxyanthraquinone).

In blue-greenish areas, such as in the Apostle's robe shown in Figure 7A, XRF spectra (Figure 7C) showed the presence of cobalt along with chromium (Cr) suggesting a mixture or an overlapping of paint layers containing cobalt blue and a chromium-based green.

A mixture of chromium green and ultramarine blue, instead, emerged only on the background of the decorated tribune in the Fribourg church (Figure S5). On other blue backgrounds, Severini applied ultramarine blue mixed with bone black⁹ or *Sangiovanni* white (e.g., backgrounds of the saints depicted on the triumphal arch of the Sion church) obtaining darker or lighter blue tones, respectively.

In addition to ultramarine and cobalt blue, Severini occasionally used cerulean blue $(CoO \cdot nSnO_2)$ or Co_2SnO_4 , which was found only on the lunette mural in the Sion church, his last wall painting. Interestingly, the blue "drops" depicted on the black background behind the Christ's figure were made of two different pigments: ultramarine blue in the area under

the Christ's right hand, and cerulean blue on the other side (Figure S6). Both cerulean blue and ultramarine blue were applied with lime, probably using a magnesium lime (see the SEM-EDS phase maps of dolomite and calcium carbonate in Figure 8). The SEM-EDS maps of the cerulean blue cross-section sample (Figure 8), show the distribution of cobalt (Co), tin (Sn) and magnesium (Mg) in the blue paint layer suggesting the presence of a magnesium-tin-cobalt oxide type (Mg_{2-v}Co_vSnO₄). Magnesium, indeed, was commonly found in the cerulean blue formulations, probably added as magnesium sulfate to obtain different hues of the pigment. 26,27 It is interesting to notice that several of the blue "drops" under the Christ's right hand, not on the other side, were overpainted with darker tones continuing with ultramarine blue, but applied a secco in oil paint, perhaps an artists' oil tube. Considering that Severini returned to Sion in 1948,8 it is likely that he made these retouchings to improve the apperance of his paintings.

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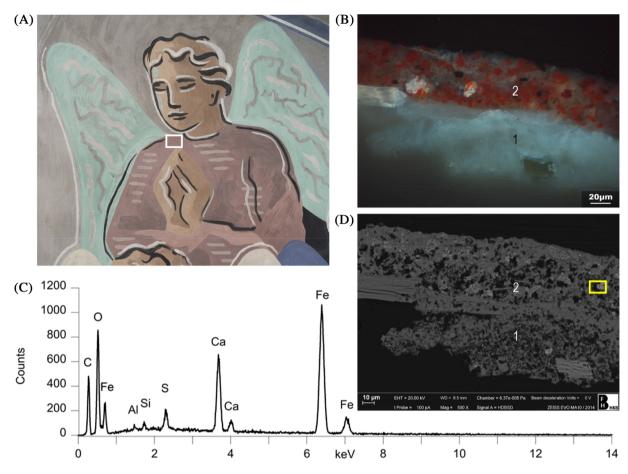


FIGURE 6 Notre-Dame de l'Assomption, La Roche: (A) detail of one of the angels in *The Pietà* mural with indication (white rectangle) of the sampling area. (B) Vis optical microscope image of the cross-section of the micro-sample collected in (A). Stratigraphy: 1. plaster; 2. pink/red paint layer; (C) SEM-EDS spectrum acquired on the yellow marked (yellow rectangle) in the (D) SEM-BSE image.

3.4 | Green pigments

Most of the green areas examined on the Swiss wall decorations showed the presence of chromium (Cr) revealing the use of the modern synthetic chromium-based pigments, namely chromium oxide (Cr₂O₃) and chromium oxide hydrate (Cr₂O₃·2H₂O) also known as Viridian. Both these chromium-greens are listed in the invoices related to the purchases for Semsales decoration 10 where Viridian is indicated with the French term "vert émaraude." 28 However, analysis revealed that in several green areas the pigment known as Guignet's green was used. This pigment is a variation of the Viridian obtained by calcination of a mixture of boric acid and potassium dichromate. Analytically, the presence of Guignet's green can be determined by the infrared bands at ca. 1288 and 1252 cm⁻¹ due to the insoluble chromium borate produced as a synthesis residue.²⁹ In this study, the IR borate marker bands were identified mostly on bright green paint layers by both noninvasive (Figure S7) and invasive

analyses. For example, the μ FT-IR FPA imaging results obtained for the sample (cross-section) coming from the green robe of the Virgin in the Lausanne church, shows the stratigraphic distribution of the Guignet's green (Figure 9) through the integration of chromium oxide hydrate (1073–1053 cm $^{-1}$) and chromium borate (1296–1269 cm $^{-1}$) spectral signals. These two Cr-based green pigments are in the green paint layer together with gypsum. It is unclear if gypsum was present in the pigment formulation as filler/extender or if Severini himself added it. In the surface layer, instead, the μ FT-IR FPA map collected confirmed the polyvinyl acetate (PVAc) applied over almost the entire painted surface of the Lausanne apse during the 1970s restoration.

Overall, Severini used the chromium-greens, alone or in mixture with white (zinc white or *Sangiovanni* white), yellow (cadmium-yellow) or blue (mostly cobalt blue) pigments, for the border of the haloes of all figures, for the robes as well as for decorative vegetal elements. Less bright and paler shades of green were probably obtained

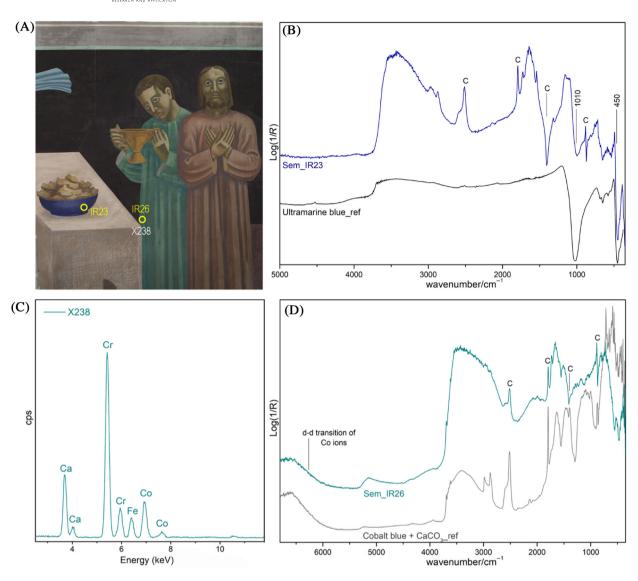


FIGURE 7 St. Nicolas de Myre, Semsales: (A) detail of the *Eucharist* mural with indication of the points IR23 and IR26 analyzed by portable FT-IR spectroscopy. (B) Reflection FT-IR spectrum collected from the point IR23 compared with a reference spectrum of ultramarine blue (black profile); (C) XRF spectrum collected from the point X238/IR26 and (D) reflection FT-IR spectrum compared with a reference spectrum of cobalt blue with calcium carbonate (gray profile). Marker bands of calcium carbonate are indicated by the letter C.

by mixing green earth to the chromium-based green. On these matt tones, XRF analysis revealed a decrease in chromium counts and an increase in iron counts. However, no green earth markers such as potassium (K) or the clay minerals glauconite and celadonite³¹ were found by FT-IR.

3.5 | Black pigments

The black pigment favored and most used by Severini was bone black, which was identified in all the churches except in Sion where only iron-based black was found. Bone black was detected on the apse decoration in Lausanne church, on the tribune decoration in Fribourg

church and on the backgrounds of some scenes painted in both the churches of Semsales (*Trinity, Virgin, and Child* and *Holy family*) 9,10 and La Roche (*Last supper*). For example, the SEM-EDS analysis of a cross-section sample coming from the *Last supper* of La Roche church (Figure 10) shows the presence of calcium (Ca) and phosphorus (P) which are indicative of the main components of the bone black, namely hydroxyapatite (Ca₅[PO₄]₃OH) and calcium carbonate.

In general, the presence and the extensive use of the bone black emerged immediately from the noninvasive FT-IR measurements. All bone black IR spectra showed the phosphate group pattern (inverted band at ca. 1038 cm⁻¹ and doublet at 567 and 604 cm⁻¹) in

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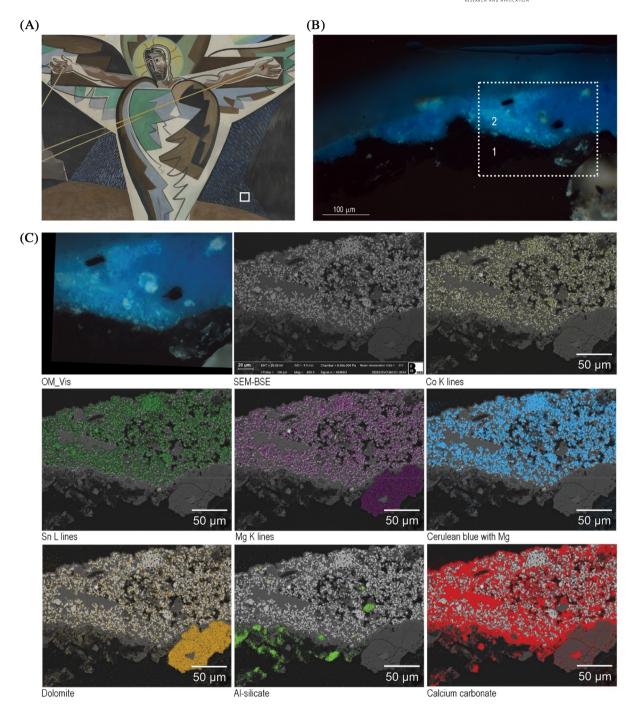


FIGURE 8 Couvent des Capucins, Sion: (A) detail of the lunette mural *Saint Francis receiving the stigmates* with indication of the sampling area. (B) Vis optical microscope image of the cross-section of the sample collected in (A). Stratigraphy: 1. black paint layer; 2. blue paint layer. (C) Vis optical image, SEM-BSE and SEM-EDS maps of the area marked in (B) with a dashed white rectangle.

association with a sharp band at ca. 2013 cm⁻¹³² related to degradation products of proteins such as isocyanate (RNCO), thiocyanate (RSCN), and isothyocianate (RNCS) groups.³³ Figure 11 shows a representative spectrum of bone black detected on the dark background of the *Trinity* mural in Semsales. Here, in addition to bone black, Severini used a black ironcontaining pigment to reshape and retouch some

colored dots on the black background. ^{9,10} The inverted band at ca. 1040 cm⁻¹ visible in the FT-IR spectrum recorded on a black retouching (Figure 11, point IR26) is due to a silicate component (band labeled with Si) of possible clay minerals. This finding combined with high counts of iron suggests the presence of a black earth. ³⁴ On the other hand, the high zinc XRF counts are due to the underlying paint layer (a mixture of

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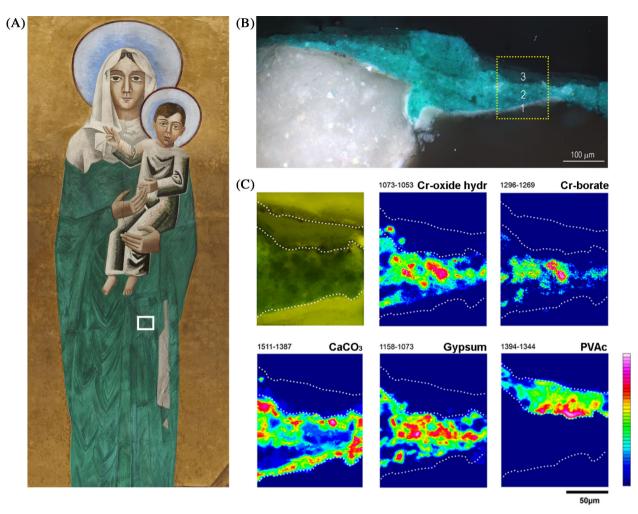


FIGURE 9 Notre-Dame du Valentin, Lausanne: (A) detail of the Virgin with Child with indication (white rectangle) of the sampling area. (B) Vis optical microscope image of the cross-section of the micro-sample collected in (A). Stratigraphy: 1. plaster; 2. green paint layer; 3. repainting/fixative layer. (c) Cross-section area analyzed by µFT-IR FPA imaging (the location is shown in B with a yellow dashed rectangle), µFT-IR FPA imaging results with integration of the following spectral range: 1073–1053 cm⁻¹ (chromium oxide hydrate); 1296– 1269 cm⁻¹ (chromium borate); 1511–1387 cm⁻¹ (calcium carbonate); 1158–1073 cm⁻¹ (gypsum); 1394–1344 cm⁻¹ (polyvinyl acetate).

chromium-based green and zinc white) that was covered by the black retouching.

3.6 White pigments

Regarding white pigments, Severini mostly used Sangiovanni white (CaCO₃). It is the only kind of white pigment detected in the murals in La Roche, Lausanne and Sion. Instead, in the wall paintings in Semsales and in Fribourg, Severini occasionally used also zinc white (ZnO). Zinc white is a modern synthetic white pigment and Severini used it exclusively a secco, that is, mixed with an organic paint binder. Due to the presence of zinc white, the white and light-colored paints on the Trinity mural (at Semsales) showed bright yellow-green UV-induced luminescence typical of this compound. In Semsales, the

zinc white was found in association with protein-based binders (i.e., animal glue and possible casein).¹⁰ Zinc white mixed with a proteinaceous material was identified also on a white portion of the decoration on the tribune in Fribourg. Here, the wall paintings were completely repainted with a vinyl-based paint during a restoration intervention. The UVL photographic images show a yellow-green luminescence located exclusively along thin nonrepainted edges of figures, suggesting the possible presence of zinc white in the original paint below the repainting (Figure 12B). To investigate further, a solventbased cleaning test was performed on a limited white area to remove the repainting and uncover the original materials that could be analyzed by noninvasive FT-IR investigation (Figure 12C-E). The infrared spectrum collected after the cleaning test shows the original paint layer composition which include an intense band at low

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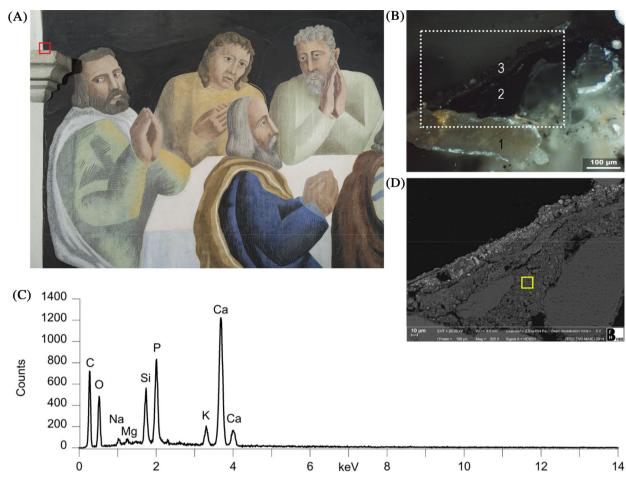


FIGURE 10 Notre-Dame de l'Assomption, La Roche: (A) detail of *Last supper* mural with indication of the sampling area (red square). (B) Vis optical microscope image of the cross-section of the sample collected in (A). Stratigraphy: 1. plaster; 2. black paint layer; (C) SEM-EDS spectrum acquired on the area marked (yellow square) in the (D) SEM-BSE image.

wavenumbers due to the zinc white and the amide infrared bands at ca. 3065 (amide B), 1684 (amide I) and 1560 (amide II) cm⁻¹ due to a protein-based material.³⁵ Instead, the weak carbonyl band at ca. 1748 cm⁻¹ and the signal at ca. 1264 cm⁻¹ are related to residues of the vinyl-based overpaint³⁵ containing titanium white (as suggested by XRF data).

In the same church, the XRF analysis performed on the UV-luminescence areas on the vest of the *Angels* (Figure S8) revealed the presence of zinc often in association with barium (Ba). Furthermore, the SEM-EDS phase maps obtained for the cross-section sample coming from the angel with the yellow dress (see Figure 4), allowed the detection of lithopone (BaSO₄·ZnS) on both yellow and pink paint layers, as well as few grains of calcium fluoride that could be related to the barite formulation. These findings do not justify the intense UV luminescence phenomenon observed which is likely due to the additional presence of zinc white and/or an organic material. Although the paint layers were rich in calcium carbonate, FT-IR analyses revealed the presence of

oxalates and a low protein content (data not shown). Further investigations are in process to clarify this matter.

4 | DISCUSSION AND CONCLUSIONS

This analytical study of Severini's Swiss murals provides a comprehensive characterization of the artist's palette and the pigments used. The study followed a methodology that favors noninvasive investigations and therefore minimized sampling. The results obtained are summarized in Table 2 while further investigations are in progress.

Severini painted, whenever possible, using the *a fresco* and/or lime-based procedure with a variety of traditional pigments compatible with the alkalinity characteristic of these painting techniques: ochre/earth (i.e., yellow, red, brown, green and black) and *Sangiovanni* white. However, since his earliest wall decoration in the church at Semsales (1924–1926), he also used modern pigments such as zinc white, synthetic

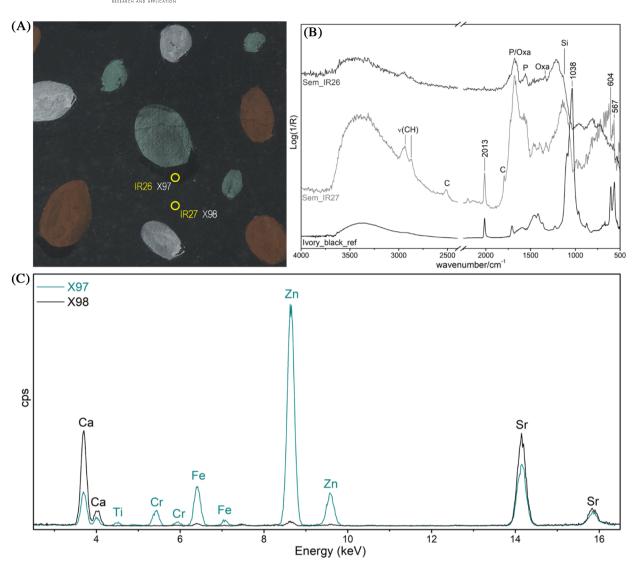


FIGURE 11 (A) Detail of the *Trinity* black background in Semsales church with indication of the noninvasive FT-IR and XRF points analysis. (B) Reflection FT-IR spectra collected from the IR points shown in (A) compared with a reference spectrum of bone black (black profile). Marker bands of calcium carbonate, protein, oxalates and a silicate component indicated with the letter C, P, Oxa, and Si, respectively (C) XRF spectra collected from the X points shown in (A).

ultramarine blue, cobalt-containing blues, chromium greens and cadmium-based pigments. Several of these synthetic pigments, such as ultramarine and cobalt blues, but also chromium-based greens, were available and had been used on wall paintings since the mid-19th century. 37,38 Zinc white and cadmium-based pigments, instead, were synthetized later and are rarely found in mid-20th century murals. 16,39,40 Therefore, in this context, Severini can be considered a pioneer of their introduction in modern mural art. This study shows that the Italian artist adopted specific painting techniques to apply these pigments on the wall. Specifically, zinc white was exclusively applied a secco using protein-based binder/s (Trinity mural in Semsales and wall paintings in Fribourg). In this regard, Severini's choices raise questions about the applicability and stability on wall paintings of this

specific synthetic pigment. For example, zinc white mixed with organic binders (i.e. proteinaceous and polysaccharide media) was also detected in a 1930s mural by Mario Sironi at the Ca' Foscari palace in Venice.³⁹ It is possible, thus, that the artists of the time encountered some difficulties in using zinc white a fresco or with a lime-based technique. Another incongruity is the use of cadmium-based pigments a fresco or with a lime-based technique, while the literature generally discourages it to avoid color alteration.¹⁷ Lime-bound cadmium-based pigments were identified also in other contemporary Portuguese murals. 16,40 No color alteration was noticed in all these cases. SUPSI is currently conducting systematic studies on painted replicas of known composition to better understand the applicability, use and the effective stability of both zinc white and cadmium-based pigments in

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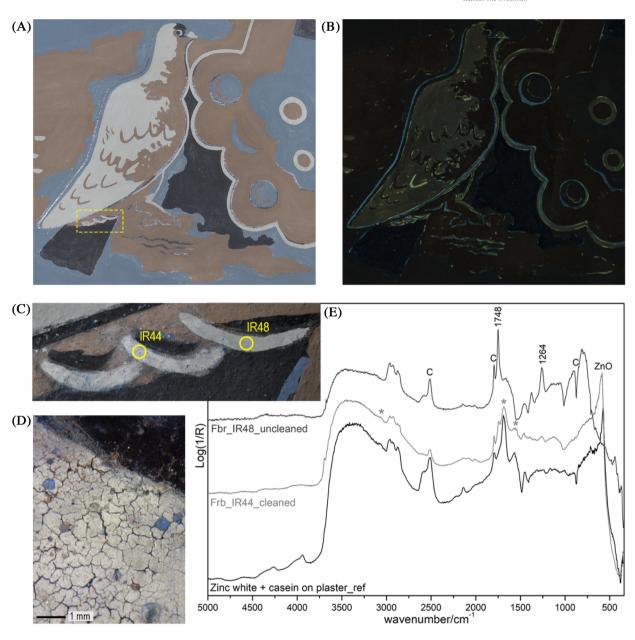


FIGURE 12 St. Pierre, Fribourg: (A) Vis and (B) UVL images of a detail of the tribune decoration. (C) Close-up image of the cleaning test area (dashed yellow rectangle in A) with indication of the noninvasive FT-IR points analysis IR44 (cleaned area) and IR48 (uncleaned area). (D) Vis Dino-Lite image corresponding to the point IR44. (E) Reflection FT-IR spectra collected from the IR points shown in (C) compared with a reference spectrum of a zinc white and casein paint applied on plaster (black profile). Marker bands of calcium carbonate and of a proteinaceous material indicated with the letter C and the simbol (*), respectively.

the alkaline environment typical of the *a fresco* and limebased painting techniques.

The study shows that in a time span of about a quarter of a century, Severini used the same set of pigments for the wall decoration of all five Swiss churches (Table 2). There are a few notable exceptions: bone black used in all churches except at Sion, and the synthetic pigments Naples yellow and cerulean blue used exclusively for the murals in the Fribourg (1934) and Sion (1947) churches. This could be correlated to the commercial

availability of the painting materials in these two places and in different times.

Exceptionally, several invoices of the materials acquired for Severini's wall decorations were found in the archives of the church in Semsales. All the pigments analytically identified in Semsales are listed on the bills of sale. Yellow and red chromium pigments listed on the invoices, but not detected, were probably used for others paint decorations not examined as part of this project (e.g. paint decoration of the choir).



TABLE 2 Summary of the pigments identified on the Severini's Swiss murals.

	Pigments identified on the examined wall painting portions					
Church	Yellow and orange	Pink, red and brown	Blue	Green	Black	White
St. Nicolas de Myre Semsales (1924–1926)	Cd-yellow Cd/Hg orange (?) Yellow ochre	Alizarine lake Vermilion Fe-based reds and browns	Ultramarine blue Co-blue	Cr-greens Green earth	Bone black Black earth	Zinc white Sangiovanni
Notre-Dame de l'Assomption La Roche (1927–1928)	Cd-yellow Yellow ochre	Fe-based reds and browns	Ultramarine blue Co-blue	Cr-greens Green earth	Bone black Black earth	Sangiovanni
St. Pierre Fribourg (1933)	Naples yellow	Fe-based reds and browns	Ultramarine blue	Cr-greens ^a	Bone black Black earth	Zinc white Lithopone ^a Sangiovanni ^a
Notre-Dame du Valentin Lausanne (1934)	Cd-yellow Yellow ochre	Fe-based reds and browns	Ultramarine blue Co-blue	Cr-greens Green earth	Bone black Black earth	Sangiovanni
Couvent des capucins Sion (1947)	Cd-yellow Yellow ochre	Alizarine lake Vermilion Fe-based reds and browns	Ultramarine blue Co-blue Cerulean blue	Cr-green Green earth	Black earth	Sangiovanni

^aMixed with other pigments.

In some portions of the murals *Trinity* in Semsales and *St. Francis receiving stigmata* in Sion, retouching of small details were made with pigments and binders not identified elsewhere. Historical and archival research reports that Severini returned to these two sites. Therefore, possibly these are retouching made by Severini, but it is not possible to exclude that these are later interventions by somebody else.

Overall, this study enabled the identification of the pigments used by Severini and revealed significant insights into the artist's *modus operandi* in terms of the paint binders and *a fresco* vs *a secco* techniques. Although working in the 20th century, when paint tubes had become available on the market, Severini created his paints mixing pure pigments and applied them *a fresco* or with a lime-based technique, and only rarely with an organic binder. He often mixed pure pigments to achieve specific tones, and this is clearly visible in all the cross-sections examined, while there is no evidence in his notes or from these investigations that he ever used already made paints.

AUTHOR CONTRIBUTIONS

Patrizia Moretti conceived and wrote the draft article, interpreted and compared all the analytical data obtained, performed the noninvasive investigations, and mounted the micro-samples in cross-sections for the invasive investigations; Stefan Zumbühl and Nadim Scherrer performed the laboratory invasive analyses on

the cross-sections and interpreted the results; Francesca Piqué (project coordinator) defined the investigation methodology, collected and documented the microsamples with Patrizia Moretti, and supervised all phases of the research. The manuscript was reviewed and accepted by all authors.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data supporting the findings of this study are available within the article and in the Supplementary Materials. All the raw data is archived in digital form on the server of the University of Applied Sciences and Arts of Southern Switzerland (SUPSI). Raw data can be obtained through the corresponding authors (Patrizia Moretti) upon request.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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