

Article

A Study on Correggio Wall Paintings: Characterization of Technique and Materials of Abbey Church of S. Giovanni Evangelista in Parma, Italy

Antonella Casoli ^{1,*}, Pier Paolo Lottici ²  and Danilo Bersani ² 

¹ Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parco Area delle Scienze 17/A, 43124 Parma, Italy

² Department of Mathematical, Physical and Computer Sciences, University of Parma, Parco Area delle Scienze 7/A, 43124 Parma, Italy; pierpaolo.lottici@unipr.it (P.P.L.); danilo.bersani@unipr.it (D.B.)

* Correspondence: antonella.casoli@unipr.it

Featured Application: The results derived from this research contribute to the body of knowledge available from 16th century Italian paintings materials, and are considered useful for the conservation and restoration plan of similar paintings.

Abstract: This study deals with the materials of the sub-arch painting of the Del Bono Chapel of the Abbey Church of S. Giovanni Evangelista in Parma, Italy, datable to around 1523. The artist is Antonio Allegri, known as Correggio (1489–1534), who is considered to be one of the greatest painters of the 16th century. Micro-Raman spectroscopy, micro-Fourier transform infrared spectroscopy and gas chromatography coupled with mass spectrometry were used as the main techniques to identify the pigments and binding media. The analysis enabled us to identify the pigments which were characteristic of the epoch. Correggio's palette was composed by mineral pigments—sometimes expensive ones such as lapis lazuli, azurite and cinnabar—together with a wide range of earths, or by synthetic pigments like smalt blue. From the amino acid content determination, it was shown that, in the samples containing lazurite, smalt, hematite, green earth and goethite, the protein fraction was attributable to the presence of a mixture of egg and animal glue, from which the use of the a secco technique could be assumed, with pigments that did not need organic binding media on the wall. For the gilding sample, the study found that Au foil had been applied on a brown background (oil-based missione).

Keywords: wall paintings; Correggio; pigments; organic binders; micro-invasive techniques; Raman spectroscopy; GC-MS



Citation: Casoli, A.; Lottici, P.P.; Bersani, D. A Study on Correggio Wall Paintings: Characterization of Technique and Materials of Abbey Church of S. Giovanni Evangelista in Parma, Italy. *Appl. Sci.* **2022**, *12*, 4810. <https://doi.org/10.3390/app12104810>

Academic Editor: Filomena De Leo

Received: 4 April 2022

Accepted: 7 May 2022

Published: 10 May 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

This investigation originates from the need, despite years of studies, to deepen the understanding of Correggio's painting technique. Correggio was the principal painter of the Parma school of the High Italian Renaissance, and was responsible for some of the most sensuous and vigorous works of the 16th century [1]. Correggio is considered a master of chiaroscuro. His real name was Antonio Allegri, while 'Correggio' comes from his native town—at that time a small independent fief in the Po Valley ruled by the Counts of Correggio—where the artist was born in 1489 and died in 1534. In 1518–1519, Correggio worked in Parma, where he frescoed the Chamber of the Abbess in the monastery of San Paolo, and where, in 1520, he worked on the dome of San Giovanni Evangelista Abbey Church [2–4], together with his shop workers, amongst whom was a young Parmigianino.

To understand the art of Correggio, the authority is the monograph "CORREGGIO" by David Ekserdjian [5], together with the series of "Lecture Allegriane" presented annually by the Fondazione Il Correggio [6].

We have previously published studies on the technique employed by Correggio in the wall paintings of the Cathedral of Parma [7] dome, and on the wall paintings of the dome and of the nave frieze of the Abbey Church of San Giovanni Evangelista, in Parma [8,9].

Here, we describe our analytical study of the Del Bono Chapel mural paintings in the Abbey Church of San Giovanni Evangelista (Figure 1). We focused on the Chapel's sub-arch decoration, attributed to Correggio, which represents the Eternal Father (in the center), the Fall of St. Paul (on the left) and Saints Peter and Andrew (on the right), datable to around 1523.



Figure 1. A view of the wall paintings of the sub-arch of Del Bono Chapel in the Abbey Church of S. Giovanni Evangelista in Parma, Italy, representing the Eternal Father (in the center), the Fall of St. Paul (on the left) and Saints Peter and Andrew (on the right).

The wall paintings were restored in 1960 by Renato Pasqui, who used sodium hydroxide and a vinyl glue, and heavily repainted them, imitating in his own way the style of Correggio. In December 2004, the restorer Marcello Castrichini commenced a new conservation campaign, under the supervision of the Superintendence for Historical, Artistic and Demo-ethno-anthropological Heritage of Parma and Piacenza.

The complex chemical composition of paint layers in wall paintings may be related to many factors: the technique followed by the artist, the effect of the aging and of the environment, and the consequence of past conservation practices. The chemical characterization of materials used in the creation and restoration of a mural painting is extremely useful for surveying historical events and for gaining a better knowledge of the artistic heritage. This study investigates both the original constituent materials, and those converted into an integral part of the work of art itself as a consequence of aging and restorations. Assessing the state of conservation of a painting is key to choosing a conservation strategy based on both prevention and intervention. The conscious choice of analytical techniques for understanding the chemical composition of the painting materials, and studying the degradation processes, is of prime importance.

Before starting the restoration work, a scrupulous study of Correggio's materials and painting technique was required. The aim of this paper was to obtain a description of the inorganic and organic components employed by Correggio: the pigments and the organic binding media. The objective was to explain the painting technique, the state of preservation, the possible additions made during previous restorations, and the current decay processes.

We believe this study to be a significant and essential precondition for the subsequent conservation and restoration of these unique mural paintings.

2. Experimental

2.1. Samples

Before starting the diagnostic study, the wall paintings were investigated by ultraviolet-induced fluorescence imaging technique, which revealed evidence of fluorescent materials, i.e., colorants, varnishes, organic binding media, restoration products [10,11]. This allowed us to choose the sampling points of interest.

A total of 22 micro-fragments of the painting layers, the sizes of which were smaller than 1 mm², were collected from the margins of existing lacunae, in correspondence with superficial cracking. Sampling was performed according to the principle of minimum invasiveness, by gently rubbing the colour from the surface, or by detaching a small piece of the painting, in order to evaluate the pictorial palette and the organic binding media, the painting technique, the state of preservation, the possible decay processes and the possible additions made during earlier restorations (Figure 2, Table 1).

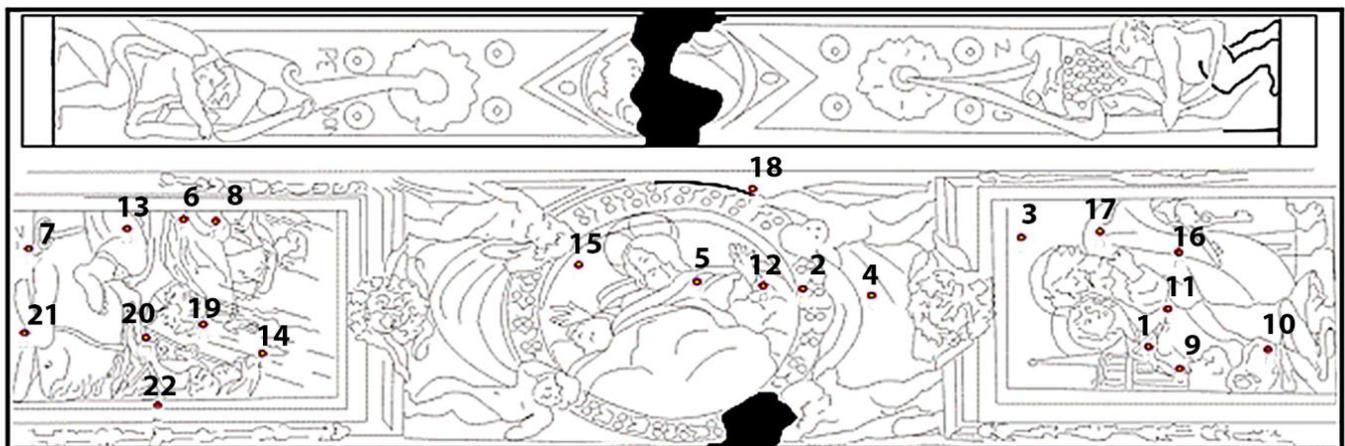


Figure 2. The sub-arch of Del Bono Chapel in the Abbey Church of S. Giovanni Evangelista in Parma: the numbers refer to the micro-sampling points (B1 to B22 samples in Table 1).

Table 1. The collected samples (B1 to B22), their color and their description. Under each sample the list of pigments (P) and other substances detected by Raman spectroscopy is reported. For the samples analysed by means of GC/MS, the binders found are indicated.

B1 Blue



robe of St. Andrew

P: lazurite, smalt, green earth (probably celadonite), lead white, lead tin yellow type I, massicot, cinnabar, calcite, magnesite, gypsum, anatase.
Binders: egg, animal glue.

B2 Gilding



central garland around the Christ

P: romarchite, cuprite, calcite, gypsum, anatase.
Binders: egg, animal glue, linseed oil

B3 Blue



Heaven over St. Peter and St. Andrew

P: smalt, calcite, massicot

Table 1. Cont.

<p>B4 Blue</p> 	<p>B5 Blue</p> 	<p>B6 Blue</p> 
<p>drape between the angels P: smalt, carbon, calcite, gypsum.</p>	<p>robe of the Christ on central round P: smalt, cinnabar, calcite.</p>	<p>robe of St. Paul P: lazurite, smalt, cinnabar, calcite.</p>
<p>B7 Green</p> 	<p>B8 light green</p> 	<p>B9 Green</p> 
<p>meadow under the horse P: green earth, goethite, hematite, cinnabar, calcite, carbon black. Binders: egg, animal glue.</p>	<p>near the mantle of St. Paul P: green earth, lazurite, hematite, cinnabar, calcite.</p>	<p>shoulder of St. Andrew P: malachite, lazurite, goethite, lead tin yellow type I, cinnabar, indigo.</p>
<p>B10 Bright Green</p> 	<p>B11 Red</p> 	<p>B12 Red</p> 
<p>the dress of St. Andrew P: green earth, unidentified blue organic dye, cinnabar (traces), calcite, gypsum, hematite, anatase.</p>	<p>drape on the robe of St. Andrew P: cinnabar, calcite.</p>	<p>mantle of the Christ P: cinnabar, hematite, calcite, gypsum.</p>
<p>B13 Red</p> 	<p>B14 Yellow</p> 	<p>B15 Yellow</p> 
<p>the trousers of St. Paul P: hematite, cinnabar (traces), calcite.</p>	<p>rays of light on St. Paul P: hematite, goethite, calcite.</p>	<p>around the Christ P: goethite, cinnabar (traces), calcite.</p>
<p>B16 Dark Yellow</p> 	<p>B17 Light Yellow</p> 	<p>B18 Purple</p> 
<p>mantle of St. Peter P: cinnabar, hematite, calcite.</p>	<p>mantle of St. Peter P: goethite, massicot, hematite, calcite, gypsum, anatase.</p>	<p>garland around Christ P: goethite, cerussite, calcite.</p>

Table 1. Cont.

B19 Light Yellow	B20 Yellow	B21 Black
		
over the hair of St. Paul P: goethite, cerussite, calcite. Binders: egg, animal glue.	under the hand of the soldier P: cerussite, cinnabar, anatase, calcite, carbon black. Binders: egg, animal glue.	shadow of the paw of the horse P: carbon black, goethite.
B22 Brown		
		
band of the scene with St. Paul P: carbon black, goethite, calcite.		

Firstly, to describe the pigments, all the raw samples were investigated by Raman micro-spectroscopy. Subsequently, chemical analyses were carried out on samples B1, B2, B7, B19 and B20 by FTIR spectroscopy and GC-MS for the description of the organic binders. Materials due to previous restorations and possible degradation were also examined in the samples.

2.2. Instruments and Methods

2.2.1. Optical Microscopy

The raw samples were observed by means of an Optika SZR-2 optical stereo-microscope, with zoom objective up to $3.5\times$ and eye-pieces up to $20\times$, allowing a total maximum magnification of $70\times$. The samples were illuminated by a fiber-optics system with halogen lamp. Observations at higher magnifications were made using the Olympus BX40 microscope integrated into the micro-Raman apparatus, using objectives up to $100\times$).

2.2.2. Scanning Electron Microscopy Coupled with Energy-Dispersive X-ray Spectroscopy (SEM-EDS)

SEM-EDS studies were carried out using a Jeol 6400 high-vacuum scanning electron microscope coupled with Energy-Dispersive X-ray (EDS) detector by Oxford Instruments (15 kV, 0.28 nA, ~ 1 mm beam diameter, 60 s counting time). The EDS analysis system enabled compositional analysis. Elemental data were obtained by means of INCA-Energy software. The samples were sputter-coated with graphite to avoid charging effects prior to the SEM-EDS examination.

2.2.3. Micro-Raman Spectroscopy

Non-polarized Raman spectra were recorded using a He-Ne laser operating at 632.8 nm as excitation (nominal 15 mW maximum output) in a nearly backscattering geometry with a Horiba LabRam micro-spectrometer (300 mm focal length spectrograph) equipped with an integrated Olympus BX40 microscope. The spectral resolution was about 2 cm^{-1} . The Rayleigh radiation was blocked by a notch filter, and the backscattered Raman light was dispersed by an 1800 grooves/mm holographic grating on a Peltier-cooled CCD, made by an array of 1024/256 pixels. The entrance slit width was fixed at $100\text{ }\mu\text{m}$. The laser power

was adjusted by means of a series of density filters, to avoid any damage to the samples, or uncontrolled thermal effects. The average power on the sample was always less than 3 mW. Spectra were collected using 100× or ultra-long working distance-50× microscope objectives. Typical exposures were 10–60 s, repeated 3–5 times. The system was frequently calibrated using a 520.6 cm⁻¹ Raman band of silicon or by means of reference emission lines of Ar or Cd vapour light sources. The data analysis was done by LabSpec built-in software. Raman spectra were collected in selected spots on the surface of the samples to analyse the composition of the different layers of painting [12].

2.2.4. Micro-Fourier Transform Infrared Spectroscopy (FTIR)

Micro-FTIR spectra were taken in attenuated total reflectance (ATR) mode, using a ThermoNicolet “Continuum” Nexus line micro-spectrophotometer, equipped with a mercury-cadmium-telluride (MCT) detector. A micro-slide-on ATR silicon crystal directly connected to the objective has been employed. Infrared spectra were recorded in the 4000–650 cm⁻¹ range, resolution 4 cm⁻¹ and 120 scans. All spectra were collected on micro-samples and are presented in transmittance units after baseline correction [13].

2.2.5. Gas Chromatography—Mass Spectrometry (GC-MS)

A Focus GC (Thermo Scientific, Waltham, MA, USA), coupled to a DSQ II (Thermo Scientific) with single quadrupole and split-splitless injector, was used. The mass spectrometer was operated in the EI positive mode (70 eV). The carrier gas was used in the constant flow mode (He, purity 99.995%) at 20 mL/min. The separation of the components was done by means of a fused-silica capillary column (RXI-5, Restek) with a 0.25 μm (30 m × 0.25 mm × 0.25 μm) methyl-silicone (5% phenyl) film, and the injector was used in splitless mode.

This method enabled us to obtain two chromatograms for each sample: the first one from fatty acid derivatives, the second one from amino acid derivatives [14,15].

3. Results and Discussion

Before the diagnostic study, the mural paintings were explored by ultraviolet-induced fluorescence imaging technique, which reveals fluorescent materials, i.e., colorants, varnishes, organic binding media and restoration products. This enabled us to choose sampling points of interest. For example, we report in Figure 3 the B20 sample picking point (under the hand of the soldier) in a zone with characteristic organic fluorescence.



Figure 3. The sampling point for the B20 sample, in normal (red spot in the insert) and in UV light (red circle, main image).

The pigments and the organic binding media detected in the collected samples are summarized in Table 1, and described in the following Sections 3.1 and 3.2.

3.1. Pigments

3.1.1. Blue

In B1, B3, B4, B5 and B6 blue samples, the analysis under the optical microscope shows the presence of intense-blue-colored fragments of a glassy appearance, embedded in a white matrix typical of smalt (or ‘smaltino’) obtained from potassium and aluminum-rich silica glass, containing cobalt. This blue pigment has no characteristic Raman signature, because the glassy matrix produces only weak, broad Raman bands, and the cobalt ions have no Raman characteristic features. However, a typical broad fluorescence signal, with a maximum of nearly 690 nm (apparent Raman shift $\sim 1300\text{ cm}^{-1}$, when exciting at 632.8 nm) is present in all the Raman spectra, giving an indirect confirmation of the presence of smalt [7,16].

A more direct confirmation was obtained by the SEM-EDS analysis of some of the blue grains [17]. The SEM images, obtained by backscattered electrons, provided evidence of conchoidal fracture and the presence of Co, As, K, Si, Al, Fe, proving the widespread occurrence of blue smalt in the blue samples examined. In particular, the fragment B3, taken from the sky above the Saints Peter and Andrew, confirmed the use of smalt to obtain the blue of the sky. Figure 4 shows an SEM image of sample B3, obtained by backscattered electrons, and the corresponding elemental mapping, evidencing the chemical elements Co, Al, K, Si, Na, Fe.

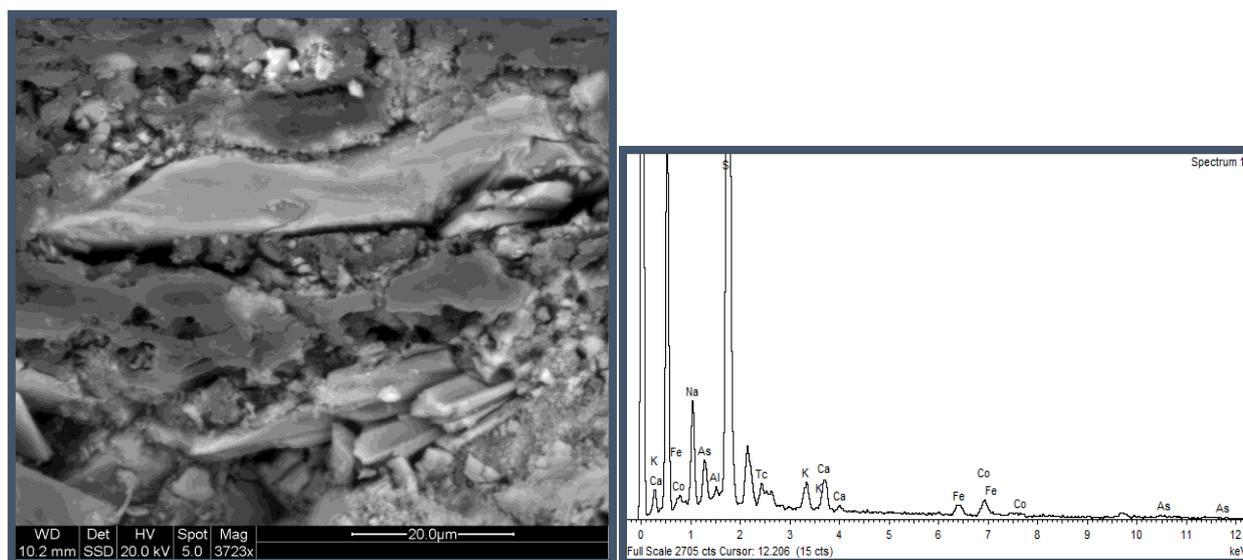


Figure 4. Scanning electron microscopy (BSE) image, taken from sample B3 (left), and the elemental spectrum by EDS (right) across this area.

Under optical microscope observation, blue sample B1, taken from the robe of St. Andrew, showing grains of different colors, interestingly, indicating that the hue was obtained by different pigments. The Raman analysis also detected blue grains with the signature of lazurite $[(\text{Na,Ca})_8(\text{AlSiO}_4)_6\text{SO}_4\text{S,Cl}]_2$, the main component of lapis lazuli (Figure 5). Red grains presented the strong Raman spectrum of mercury sulphide HgS (cinnabar). Yellow grains were composed by the synthetic pigment lead tin yellow type I (Pb_2SnO_4) and massicot (PbO). Green grains were due to a green earth. The white matrix was calcium carbonate (CaCO_3), mainly belonging to the plaster, with a minor presence of magnesite MgCO_3 (probably accidental) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The latter could be found in the plaster, but is often due to sulphation process, as discussed in the following. In the B5 and

B6 samples, the blue color was obtained using a combination of smalt and lazurite with minor cinnabar.

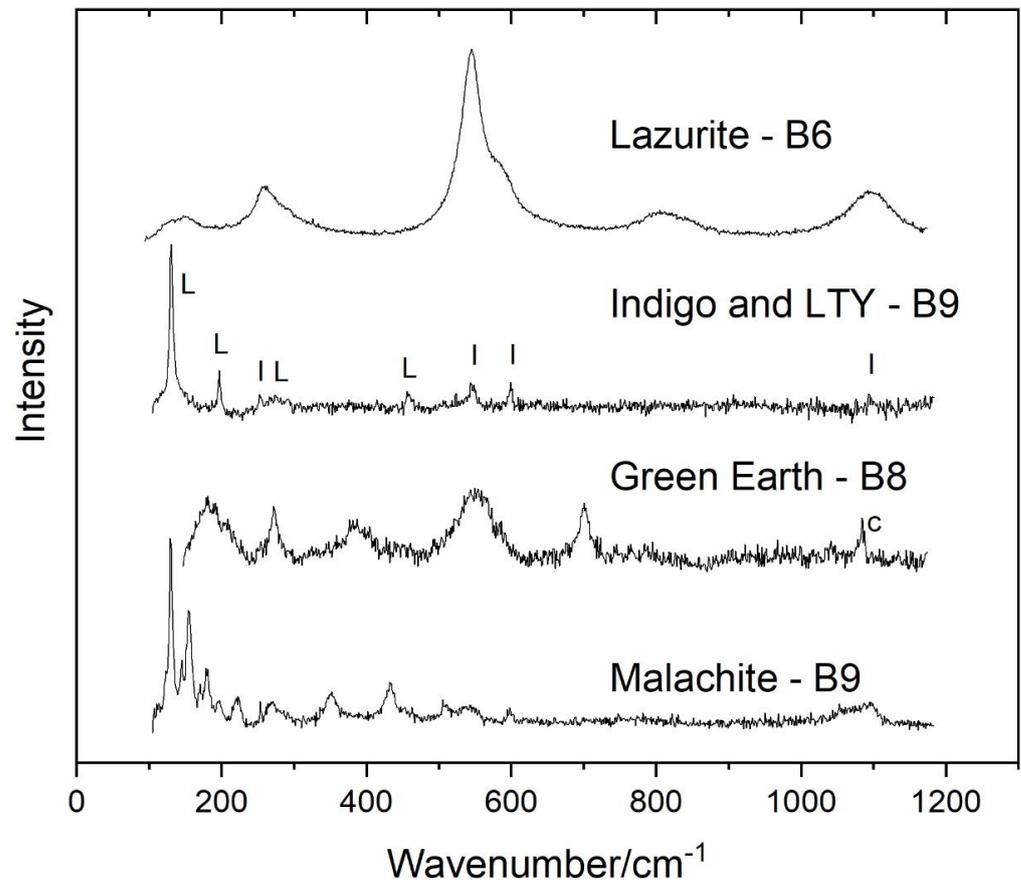


Figure 5. Raman spectra of blue and green pigments. L = Lead tin yellow type I (LTY), I = Indigo, C = Calcite.

3.1.2. Red and Purple

In the Del Bono Chapel, Correggio used a combination of hematite ($\alpha\text{-Fe}_2\text{O}_3$, the chromophore phase of red ochre) and cinnabar (HgS) to create the red colors, as in samples B12 and B13 (Figure 6). The presence of iron and mercury has been confirmed by means of EDS analysis, which is evidence that the two pigments are mostly not mixed together, cinnabar being applied over a thick layer of hematite. In one sample only (B11), cinnabar was found alone.

It is worth noting that cinnabar has been found in 13 out of 22 samples, regardless of their dominant color. Even taking into account its easy detectability, due to the very strong Raman signal, cinnabar appears to be one of the main pigments used by Correggio to modify the hue.

In sample B18, taken from the garland around the Christ of the central round, hematite $\alpha\text{-Fe}_2\text{O}_3$ was found to be the basis of the purple colour, together with tin oxide SnO .

3.1.3. Yellow and Brown

The palette of yellow, yellow-orange and brown colours in the Correggio wall paintings is strongly characterized by the use of yellow ochre, whose chromophore phase is the iron hydroxide goethite $\alpha\text{-FeOOH}$ (Figure 6). Goethite was found in all yellow and brown samples (B14, B15, B17, B19 and B22), often mixed with red ochre (hematite). The only exception is the dark yellow sample (B15) where only hematite was found. Cinnabar was also observed, in very small amounts, in different yellow samples. Lead oxide (PbO ,

massicot) was identified in just one yellow sample (B17), together with yellow and red ochres. In brown sample B22, carbon black was used to darken the colour.

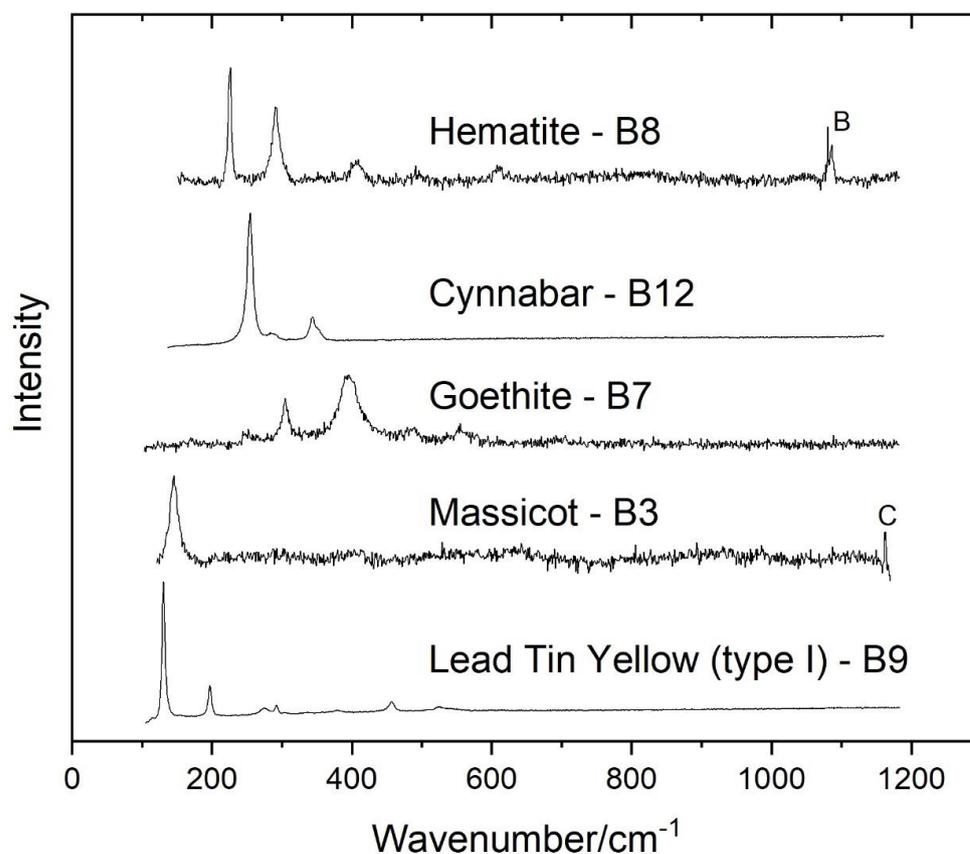


Figure 6. Raman spectra of red and yellow pigments. B = White lead, C = Calcite.

3.1.4. Green

Despite the availability of expensive pigments, for the large majority of the green parts of the wall paintings, cheap green earths were used, probably due to their chemical stability allowing for their use a fresco. More specifically, the position of the Raman bands (174, 202, 279, 393, 544 and 701 cm^{-1}) seems to suggest the use of iron-containing phyllosilicate celadonite $\text{K}(\text{Mg}, \text{Fe}^{2+})(\text{Fe}^{3+}, \text{Al})[\text{Si}_4\text{O}_{10}](\text{OH})_2$ (Figure 5) [18].

Copper basic carbonate malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$) was revealed only in sample B9. Malachite is not compatible with the fresco technique: it should be applied a secco and the presence of an organic binder is expected. To obtain the particular green hues in all the green samples, a large number of different yellow, red and blue pigments had been added. For example, in the B9 sample, together with malachite, also identified were lazurite, goethite, cinnabar, lead tin yellow type I and the organic blue dye indigo ($\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$). A second organic blue dye, still unidentified, whose Raman spectrum is slightly different from the indigo one, was detected in sample B10.

The lead tin yellow type I (Pb_2SnO_4) pigment, unusual for the paintings of this church [19], was not used by Correggio in the yellow parts, but we found it in a blue (B1) and in a green (B9) sample; it was probably intended to be mixed with blue pigments to obtain particular green hues.

3.1.5. White

The main white 'pigment' found is calcium carbonate (CaCO_3); this is expected in fresco paintings, because calcite is the main component of the plaster. But it is also intentionally used as white pigment ('bianco di san Giovanni') in most of the white parts of the painting or to lighten other colors. However, in a blue sample (B1) and in a couple

of yellow samples (B19 and B20), basic lead carbonate hydrocerussite $(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2$ (white lead or biacca) and lead carbonate cerussite PbCO_3 were identified (Figure 7).

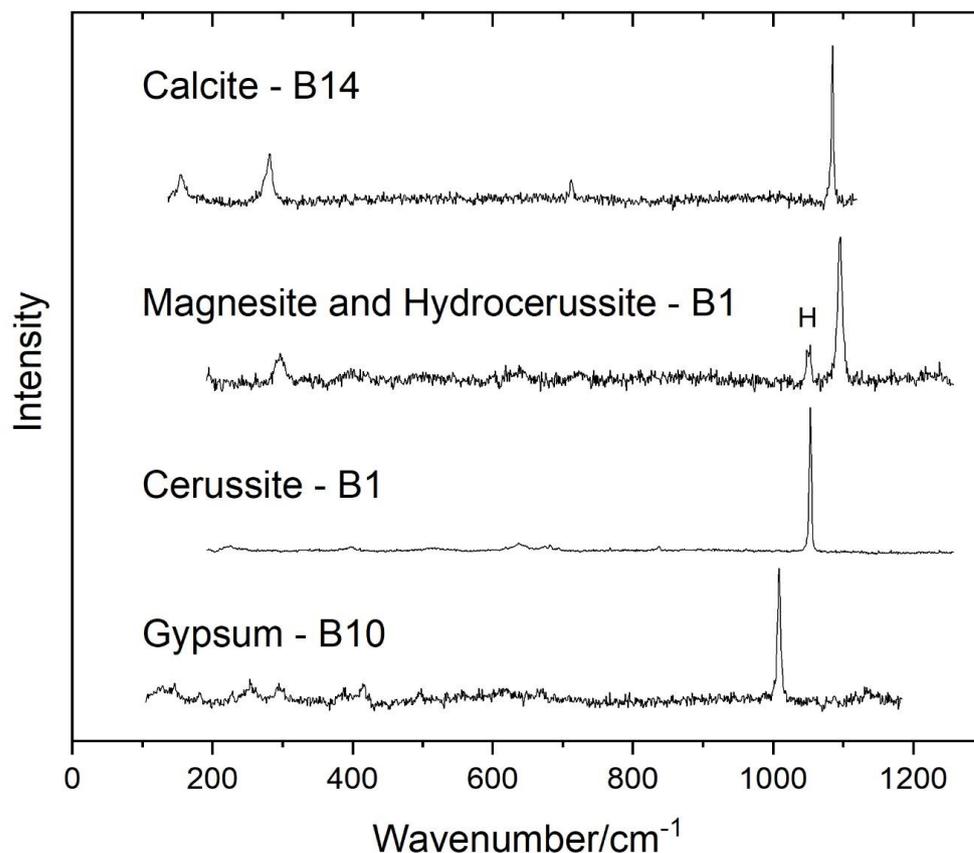


Figure 7. Raman spectra of white pigments. H = hydrocerussite.

3.1.6. Black

Throughout the wall painting, the pigment used to obtain the black color and to darken the other colors, is carbon black, detected by its typical Raman spectrum showing two broad and intense bands at 1320 and 1570 cm^{-1} (not shown). The dark sample B21, taken from the shadow of the paw of St. Paul's horse, contains black carbon together with goethite, and should be considered a dark brown.

3.1.7. Gilding

The gilding sample B2, taken from the central garland around the Christ, consists of a bright thin layer with a golden aspect over a thick matrix. Raman analysis identified tin oxide SnO (romarchite) and copper oxide cuprite Cu_2O (Figure 8). The hypothesis is that Au foil had been applied on a brown background where the Au foil was applied on the oil-based missione [20].

3.2. Organic Binding Media

The study, which aimed to identify the organic binders, began by analyzing the blue (B1), yellow (B19 and B20), gilding area (B2) and green (B7) collected samples, by means of FTIR spectroscopy. Typical bands of proteinaceous material—i.e., the characteristic CH stretching (2924 and 2954 cm^{-1}), C=O stretching of amide I (1643 cm^{-1}) and N-H bending of amide II (1539 cm^{-1})—were detected. Based on these results, GC-MS was used to identify the lipidic and proteinaceous materials.

Only the gilding sample B2 gave both lipidic and proteinaceous content. The analysis of the lipidic fraction, performed by GC-MS, revealed azelaic acid (CC9), palmitic acid (C16:0) and stearic acid (C18:0) as the main fatty acids (Figure 9).

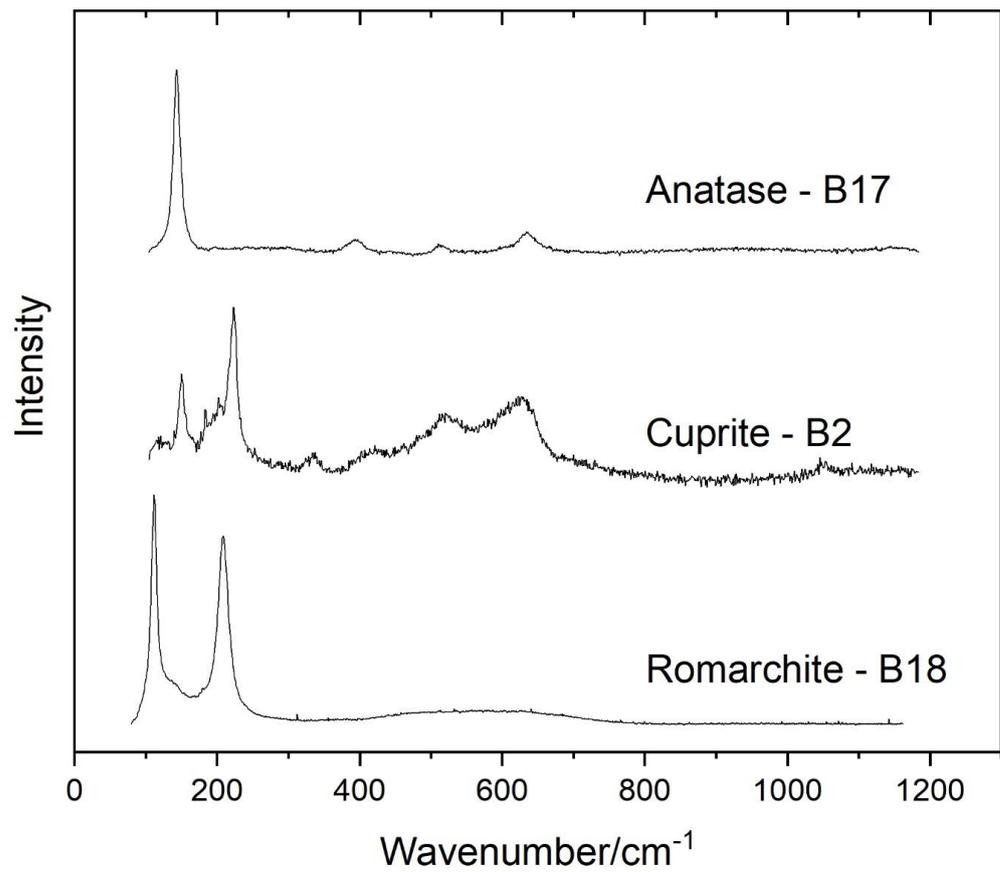


Figure 8. Raman spectra of different oxides found in the gilding material, and used for restorations.

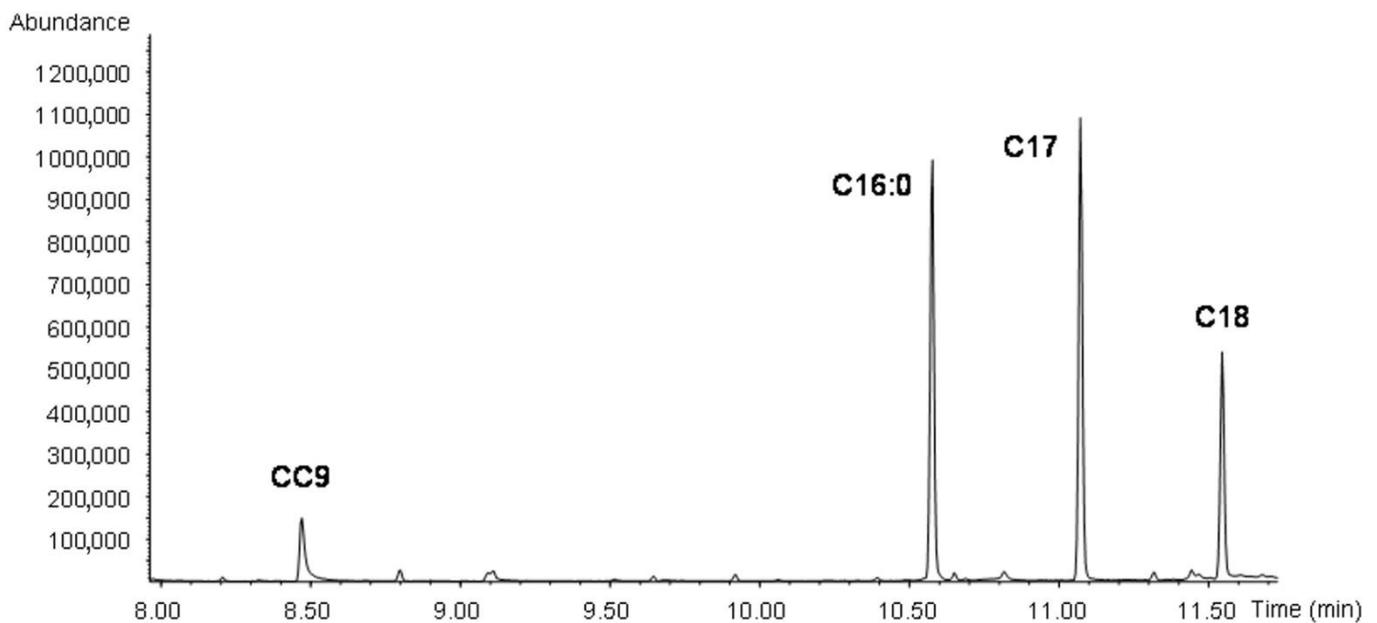


Figure 9. GC-MS chromatogram of the lipidic fraction of the B2 sample (gilding sample with fragments of gold taken from the central garland around the Christ). CC9 = azelaic acid, C16:0 = palmitic acid, C17: tetracosane (internal standard), C18:0 = stearic acid.

The presence of azelaic acid, and the absence of polyunsaturated fatty acids, are characteristic of an oxidized lipidic medium, being dicarboxylic acids the oxidation products of polyunsaturated acyl chains during the aging processes [21,22].

The value of the azelaic/palmitic acid ratio indicated the presence of drying oils in the sample.

The palmitic/stearic acid (P/S) ratio is stable over time, and can give information about the type of drying oil used by the artist, i.e., linseed, walnut or poppy seed oils [23,24]. Values of P/S in the ranges 1.4–2.1, 2.4–2.9 and 2.9–4.1 were obtained indicating linseed oil, walnut oil and poppy seed oil, respectively [10]. The P/S value 1.4 observed for the gilding B2 sample, suggested the presence of linseed oil. Our hypothesis is that Au foil had been applied on a brown background where the Au foil is applied on the oil-based missione [17]. In the ‘a missione’ technique, drying oils (typically linseed oil), were used to glue the metal foils [24]. The oil gilding technique appears to have been described by Cennino Cennini, and widely used in painting between the 14th and 15th centuries [25].

Chromatograms of samples B1, B2, B7, B19 and B20 show the amino acids features. Figure 10 shows the chromatographic profile of B7 sample.

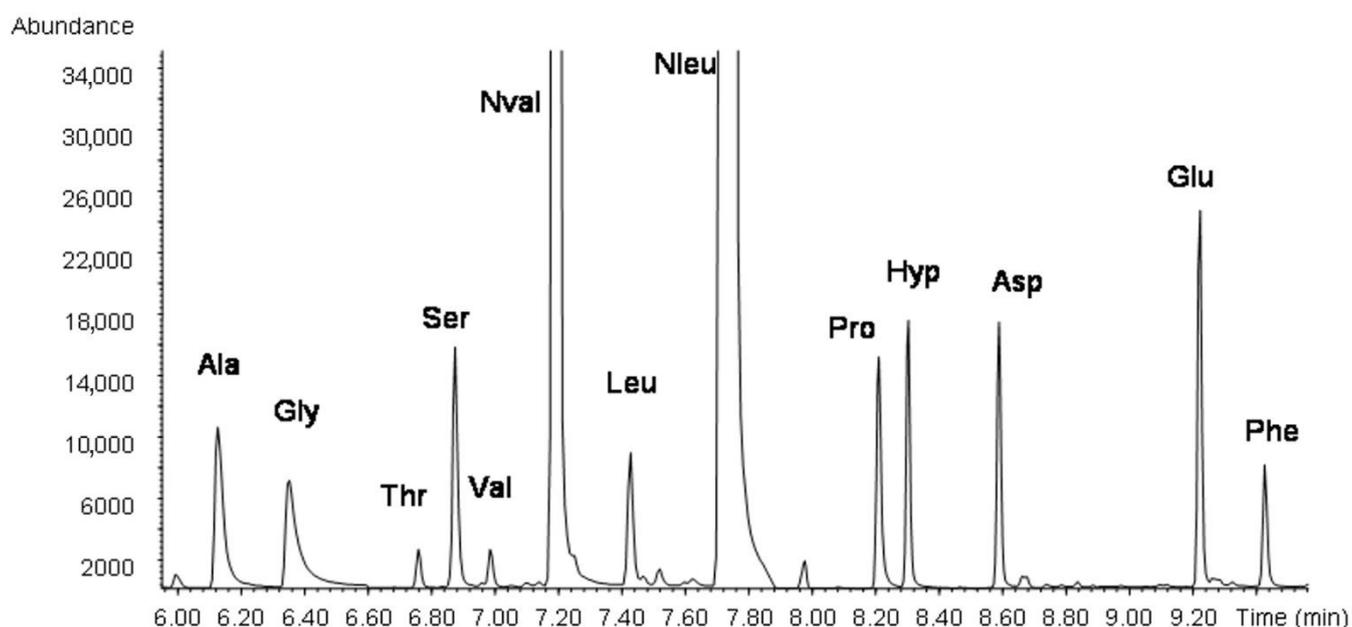


Figure 10. GC-MS chromatogram of the proteinaceous fraction of B7 sample (green sample taken from the meadow under the horse of St. Paul). Ala = alanine, Gly = glicine, Thr = threonine, Ser = serine, Val = valine, Nval = norvaline (internal standard), Leu = leucine, Nleu = norleucine (internal standard), Pro = proline, Hyp = hydroxyproline, Asp = aspartic acid, Glu = glutamic acid, Phe = phenylalanine.

To identify the binding media, the percentage content of amino acids in each sample was compared to those from a dataset of 43 reference samples of egg (whole, egg white, egg yolk), casein and animal glue, belonging to the reference collection of the Opificio delle Pietre Dure in Florence, Italy [26]. Principal component analysis (PCA) was done on the correlation matrix of the relative percentage contents of eight amino acids (aspartic acid, glutamic acid, proline, hydroxyproline, phenylalanine, alanine, glycine and leucine) [27,28].

The PCA score plot is described in Figure 11: it locates all the samples in a new cluster suggesting a combination of egg and animal glue binders in all the samples.

The presence of the same mixture of binders in samples B1, B7, B19 and B20, where Raman analysis evidenced lazurite, smalt, hematite, green earth and goethite, allowed us to hypothesize the use of the a secco technique also with pigments that did not require the employment of organic media.

The B2 sample, being a gilding, shows the use of linseed oil, and of egg and animal glue.

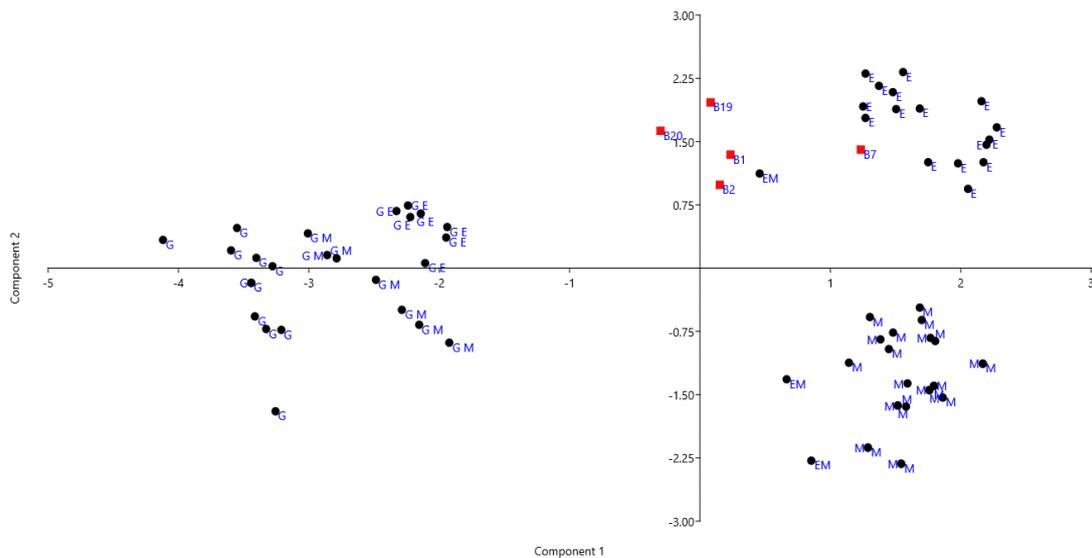


Figure 11. PCA score plot of wall painting samples and reference materials (painted models simulating ancient polychromies, containing G: animal glue; GE: animal glue and egg, GM: animal glue and milk, M: milk; E: egg; EM: egg and milk).

3.3. Restoration and Degradation Materials

To identify materials that were due to previous restorations, FTIR spectra were made on the samples. In particular, the FTIR spectrum of the superficial part of the B1 sample (the blue sample taken from the robe of St. Andrew) is reported in Figure 12. The spectrum shows gypsum (calcium sulfate bi-hydrate) ($3522, 3403, 1685, 1619, 1112, 670 \text{ cm}^{-1}$) and calcite (calcium carbonate) ($1418, 874 \text{ cm}^{-1}$).

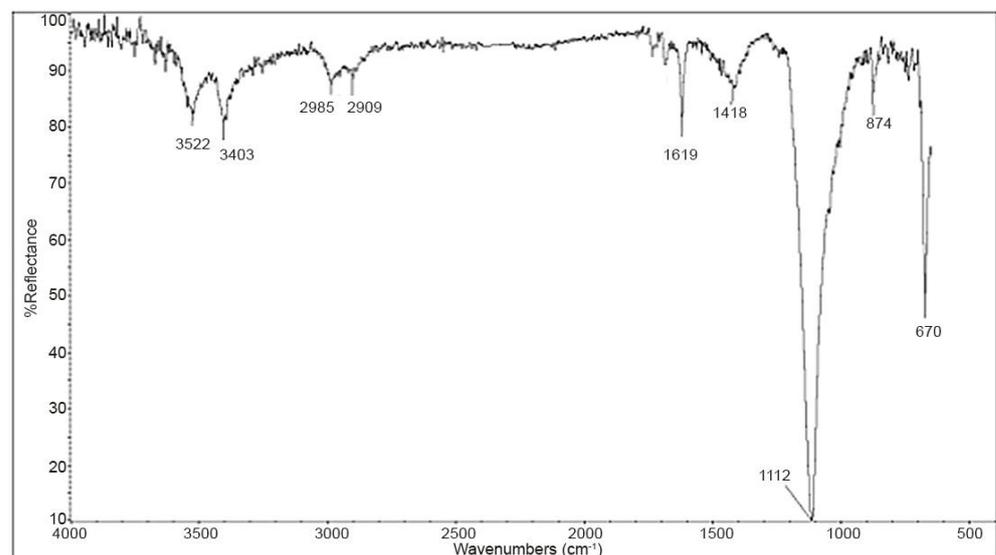


Figure 12. FTIR spectrum of the superficial part of sample B1 (blue sample taken from the robe of St. Andrew).

We note, in addition, the features of an organic substance at $2985, 2899 \text{ cm}^{-1}$ (C-H stretching) and at 1732 cm^{-1} (C=O stretching), suggesting the presence of acrylic resins, like Paraloid™, which could be due to previous restorations. This synthetic compound seems to have been used mostly on green and blue zones.

In many samples, anatase, TiO_2 , has been identified by Raman spectroscopy (Figure 6). The synthetic pigment, titanium white TiO_2 , was introduced in recent times, around 1920, and this could indicate recent restorations. Raman spectroscopy is however very sensitive

to anatase mineral, which can be present in traces in many natural compounds as impurity. Nevertheless, here its presence appeared too abundant to be considered accidental.

The small amount of gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ detected on the surface of different samples by the bands at 1132 cm^{-1} , 1007 cm^{-1} and 414 cm^{-1} , seems to exclude its intentional use as pigment. It could be considered as a degradation product, due to the reaction of calcium carbonate with sulphuric acid, formed by the oxidation of SO_2 and SO_3 , which are easy to find in urban areas.

4. Conclusions

This study was carried out to learn about the technique and the materials used by Correggio for the painting of the under-arch of the Del Bono Chapel in the Abbey Church of S. Giovanni Evangelista in Parma.

It was carried out mostly by means of FTIR and Raman spectroscopies and GC/MS. This combination of techniques enabled the characterization of pigments and binding media, shedding new light on the wonderful technique of Correggio. The palette is very rich, with a widespread use of precious pigments, such as lapis lazuli and cinnabar, not only to obtain pure colors, but also to create different hues.

Cheaper pigments such as green earths and red and yellow ochres, were also used, very often mixed in a large number of components, to obtain the desired chromatic effect.

We wanted also to understand if we were dealing with entirely fresco wall paintings, or if there were areas made a secco, and if these areas were due to the presence of pigments that require the use of organic binders for their application, such as azurite and malachite. From the amino acid content determination through GC/MS it was shown that, for all samples examined, the proteinaceous fraction was attributable to the presence of a combination of egg and animal glue, present as binding media in the samples containing lazurite, smalt, hematite, green earth and goethite. This allowed us to assume the use of the a secco technique also with pigments that do not necessitate the use of organic media on a wall.

For the gilding sample B2, we concluded that Au foil had been applied on a brown background where the Au foil is applied on the oil-based missione.

There was also evidence of products that were a consequence of degradation (gypsum). In many samples, anatase, TiO_2 , was identified by Raman spectroscopy. This synthetic pigment, introduced around 1920, could indicate recent restorations, as well as the identification of the acrylic resins, like Paraloid™, a durable and non-yellowing polymer used for consolidating wall paintings.

Author Contributions: Conceptualization, A.C. and P.P.L.; methodology, A.C. and D.B.; software, D.B.; validation A.C. and P.P.L., formal analysis A.C., P.P.L. and D.B.; investigation, A.C., D.B.; resources, A.C. and P.P.L.; data curation, A.C., D.B.; writing—original draft preparation, A.C.; writing—review and editing, A.C., P.P.L. and D.B.; visualization, A.C., P.P.L. and D.B.; supervision, P.P.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Toscano, G.M. *Nuovi Studi sul Correggio*; Libreria Aurea Parma: Parma, Italy, 1974.
2. Ghidiglia Quintavalle, A. *Gli affreschi del Correggio in San Giovanni Evangelista*; Silvana Editoriale d'Arte: Milano, Italy, 1962.
3. Ghidiglia Quintavalle, A. *La cupola del Correggio in San Giovanni a Parma*; Sansoni: Firenze, Italy, 1962.
4. Mendogni, P. *Il Correggio a Parma*; Ugo Guanda Editore: Parma, Italy, 1989.
5. Ekserdjian, D. *Correggio*; Yale University Press: New Haven, CT, USA, 1997.
6. Available online: <https://www.fondazioneilcorreggio.it> (accessed on 15 February 2022).
7. Bersani, B.; Berzioli, M.; Caglio, S.; Casoli, A.; Lottici, P.P.; Medeghini, L.; Poldi, G.; Zannini, P. An integrated multi-analytical approach to the study of the dome wall paintings by Correggio in Parma Cathedral. *Microchem. J.* **2014**, *114*, 80–88. [[CrossRef](#)]

8. Bonazzi, A.; Bonomi, R.; Casoli, A.; Mangia, A.; Sgarabotto, P. Indagini chimiche e mineralogiche dei dipinti murali del Correggio. In *Un Miracol d'arte Senza Esempio. La cupola del Correggio in S. Giovanni Evangelista a Parma*; Tipolitografia Benedettina Editrice: Parma, Italy, 1990; pp. 83–84.
9. Antonioli, G.; Bersani, D.; Lottici, P.P.; Campani, E.; Casoli, A. Indagini Scientifiche. In *Correggio, Parmigianino, Anselmi nella Chiesa di San Giovanni Evangelista a Parma*; Sgarbi, V., Ed.; Skira: Lausanne, Switzerland, 2008; pp. 265–274.
10. Mairinger, F. UV-, IR- and X-ray Imaging. *Compr. Anal. Chem.* **2004**, *42*, 15–71. [[CrossRef](#)]
11. Verri, G.; Clementi, C.; Comelli, D.; Cather, S.; Piqué, F. Correction of Ultraviolet-Induced Fluorescence Spectra for the Examination of Polychromy. *Appl. Spectrosc.* **2008**, *62*, 1295–1302. [[CrossRef](#)] [[PubMed](#)]
12. Bersani, D.; Lottici, P.P.; Casoli, A. Micro-Raman and GC-MS of Frescoes. In *Raman Spectroscopy in Archaeology and Art History*; Edwards, H.G.M., Chalmers, J.M., Eds.; Royal Society of Chemistry, Analytical Spectroscopy Monographs: London, UK, 2005; pp. 130–141.
13. La Russa, M.F.; Ruffolo, S.A.; Barone, G.; Crisci, G.M.; Mazzoleni, P.; Pezzino, A. The Use of FTIR and Micro-FTIR Spectroscopy: An Example of Application to Cultural Heritage. *Int. J. Spectrosc.* **2009**, *2009*, 893528. [[CrossRef](#)]
14. Casoli, A.; Santoro, S. Organic materials in the wall paintings in Pompei: A case study of Insula del Centenario. *Chem. Cent. J.* **2012**, *6*, 107. [[CrossRef](#)] [[PubMed](#)]
15. Bonaduce, I.; Ribechini, E.; Modugno, F.; Colombini, M.P. Analytical Approaches Based on Gas Chromatography Mass Spectrometry (GC/MS) to Study Organic Materials in Artworks and Archaeological Objects. *Top. Curr. Chem.* **2016**, *374–376*. [[CrossRef](#)] [[PubMed](#)]
16. Mortari, C.; Nobre Pais, A.; Esteves, L.; Gago da Câmara, A.; Carvalho, M.L.; Manso, M. Raman and X-ray fluorescence glaze characterisation of Maria Keil's decorative tile panels. *J. Raman Spectrosc.* **2020**, *52*, 60–70. [[CrossRef](#)]
17. Mühlethaler, B.; Thissenj, J. Smalt. *Stud. Conserv.* **1969**, *14*, 47–61. [[CrossRef](#)]
18. Ospitali, F.; Bersani, D.; Di Lonardo, G.; Lottici, P.P. 'Green earths': Vibrational and elemental characterization of glauconites, celadonites and historical pigments. *J. Raman Spectrosc.* **2008**, *39*, 1066–1073. [[CrossRef](#)]
19. Bersani, D.; Antonioli, G.; Lottici, P.P.; Casoli, A. Raman micro spectrometric investigation of wall paintings in S. Giovanni Evangelista Abbey in Parma: A comparison between two artists of the 16th century. *Spectrochim. Acta Part A* **2003**, *59*, 2409–2417. [[CrossRef](#)]
20. Sandu, I.C.A.; Afonso, L.U.; Murta, E.; De Sa, M.H. Gilding Techniques in Religious Art Between East and West, 14th–18th Centuries. *Int. J. Conserv. Sci.* **2010**, *1*, 47–62.
21. Colombini, M.P.; Modugno, F.; Fuoco, R.; Tognazzi, A. A GC-MS study on the deterioration of lipidic paint binders. *Microchem. J.* **2002**, *73*, 175–185. [[CrossRef](#)]
22. Mills, J.S.; White, R. Analyses of paint media. *Natl. Gallery Tech. Bull.* **1980**, *4*, 65–67.
23. Casoli, A.; Cauzzi, D.; Palla, G. The study of binding media in polychrome works of art: The drying oils. *OPD Restauro* **1999**, *11*, 111–121.
24. Sandu, I.; Anca, C.; de Sà, M.H.; Pereirac, M.C. Ancient 'gilded' art objects from European cultural heritage: A review on different scales of characterization. *Surf. Interface Anal.* **2011**, *43*, 1134–1151. [[CrossRef](#)]
25. Cennini, C. *The Book of the Art of Cennino Cennini: A Contemporary Practical Treatise on Quattrocento Painting*; Taylor & Francis Ltd.: London, UK, 2018.
26. Lanterna, G.; Mairani, A.; Matteini, M.; Rizzi, M.; Vigato, P.A. Characterisation of Decay Markers on Pictorial Models Simulating Ancient Polychromies: Target 2.2.2 of the Special Project on Cultural Heritage—CNR—Italy. In *Proceedings of the 2nd International Congress on Science and Technology for the Safeguard of Cultural Heritage in the Mediterranean Basin, Paris, France, 5–9 July 1999*; Guarino, A., Ed.; Elsevier: Paris, France, 2000; pp. 487–489.
27. Casoli, A.; Alberici, L.; Cauzzi, D.; Palla, G. Study of models simulating ancient polychromies. In *Proceedings of the 2nd International Congress on Science and Technology for the Safeguard of Cultural Heritage in the Mediterranean Basin*; Guarino, A., Ed.; Elsevier: Amsterdam, The Netherlands, 2000; pp. 591–593.
28. Casoli, A.; Montanari, A.; Palla, G. Painted models simulating ancient polychromies: A statistical analysis of chemical results. In *Proceedings of the 3rd International Congress on Science and Technology for the Safeguard of Cultural Heritage in the Mediterranean Basin, Alcalá De Henares, Spain*; Elsevier: Paris, France, 2001; pp. 839–845.