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The Iridescent Painting Palette of Michelino da Besozzo: First Results of Non-Invasive Diagnostic Analyses

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Abstract: This study concerns the characterization of the color palette of Michelino da Besozzo, one of the leading painters and illuminators of the Late Gothic period in Northern Italy. The artist's relationship with the color blue was investigated by considering the recipe for lapis lazuli given by the artist to Giovanni Alcherio in Venice in 1410 and found in the medieval treatise of Jean Lebegue. The paper highlights this important evidence for the study of painting technique in the first half of the 15th century with an analytical and technical study of two paintings: *The Mystic Marriage of Saint Catherine* (Siena, Pinacoteca Nazionale, inv. 171) and *The Madonna of the Rose Garden* (Verona, Museo di Castelvecchio, inv. 173-1B359). These two case studies were approached through analyses carried out with non-invasive and portable techniques such as Energy Dispersive X-ray Fluorescence (ED-XRF) spectroscopy and Fiber Optics Reflectance Spectroscopy (FORS). The results show a color palette based on ultramarine, azurite, verdigris or copper resinate; earths, cinnabar or vermillion; and lead white, yellow and red ochre and lac. These preliminary results made it possible to clarify certain aspects of the artist's style and his painting technique and identify common elements between the two works of art.

Keywords: color palette; painting technique; recipe books; pigments; ultramarine; Michelino da Besozzo; International Gothic style; FORS; ED-XRF

Citation: Delle Foglie, A.; Felici, A.C. The Iridescent Painting Palette of Michelino da Besozzo: First Results of Non-Invasive Diagnostic Analyses. *Heritage* **2024**, *7*, 3013–3033. https://doi.org/10.3390/heritage7060141

Academic Editor: Manuela Vagnini

Received: 29 April 2024
Revised: 25 May 2024
Accepted: 29 May 2024
Published: 4 June 2024

1. Introduction

The non-invasive analyses promoted and carried out as part of the research project *Michelino da Besozzo and the International Gothic style*, [1] have led to the collection of a series of new important information concerning the use of color by Michelino da Besozzo, an excellent painter and illuminator, active in Lombardy and Veneto in about 1388–1450 [2].

Critical studies of the artist's figure have not paid attention, until now, to an examination focused on the painting materials of his corpus of works, such as the use of color and gold, aspects that instead deserve to be explored in the broader context of the study of the artistic techniques of painting and illumination in Europe around 1400. Michelino, like other masters in the late fourteenth and early fifteenth centuries, was a versatile artist capable of expressing his personal aesthetic vision of art in various aspects of artistic production by bringing together the peculiar characteristics of the painter and the illuminator [3], using tools and methods common to both, painting on different media from panel to parchment, and using drawing as a common denominator in the creative process [4].

1.1. Michelino's Recipe for Ultramarine Blue

On Michelino and the use of color, however, the previous critical literature from as early as the mid-19th century [5] reports his recipe for ultramarine blue received and annotated by Giovanni Alcherio, the agent of Milan Cathedral, and transmitted through the

manuscript Latin 6741 (Paris, Bibliothèque nationale de France) [6,7], the treatise compiled by the French humanist Jean Lebègue in 1431 [8]. This text is a collection of technical recipes for the preparation of colors [9] and is, thus, an important resource for understanding workshop practices, as it is direct evidence from various painters and illuminators, collected between 1382 and 1411 by Alcherio, an important figure in the Visconti entourage during the years when the Milan Cathedral was a foyer of international relations [10]. His role and his itinerant travels between Paris and Northern Italy certainly helped to expand these relationships beyond what we can actually assess to date. Manuscript Latin 6741 also includes copies of three older treatises of color by Theophilus, Peter of Saint-Omer and Eraclius [11]. Ines Villela Petit highlighted the importance of the treatise and the ultramarine blue recipe by Michelino da Besozzo. She transcribed the recipe and considered its characteristics in relation to his ability in the art of illumination [12]. Michelino's artworks had previously never been analyzed through diagnostic analyses; this research, thus, allows us to examine his color palette, starting precisely from the study of ultramarine blue and the considerable aesthetic value that this color had in his artistic production.

The recipe collection by Alcherio presents similarities to other coeval examples of color recipe treatises [13], and as for ultramarine by Michelino, the recipe is concise and presents the various states of the color extraction process from the raw material, the powdered lapis lazuli, to the creation of the *impasto* with the addition of various elements (pine rosin, liquid varnish, mastic and olive oil), up to the purification stage. The traditional method of extracting ultramarine blue, "the noble, beautiful, most perfect color", in the same years was accurately described by Cennino Cennini in the sixty-second chapter of the *Libro dell'Arte* [14,15].

It is very important to underline the place where Michelino's lapis lazuli recipe was provided, i.e., Venice. On fol. 39 r of the manuscript Latin 6741, the first three introductory lines for the recipe clearly state the place and date where Alcherio received the recipe from the artist: "The following recipe was obtained in Venice on Tuesday 4 May 1410, from Michelino da Besozzo, the most excellent painter among all the painters in the world" [7].

Venice in those very years was a central place in terms of the trade and purchase of pigments: from Afghanistan, the lapis rock in its natural state transited through the Mediterranean sea and arrived in the center of Europe [16]. Venice represents an important place for Michelino da Besozzo's career, although the evidence of his stay in the city is not documented but is known through the presence of his works. In fact, after his first period of apprenticeship in Pavia, as an illuminator in the scriptorium of Pietro da Pavia during the last decade of the fourteenth century and after working for such prestigious patrons as the Bishop of Novara Giovanni Capogallo and the ducal court of Gian Galeazzo Visconti, the artist stayed in Veneto, probably also on several occasions, in the years 1405 to 1417 [17]. It is possible to hypothesize that the first commission in the region was the frescoes cycle in the church of Santa Corona in Vicenza for the chapel of the nobleman Giovanni Thiene, who is linked to the Visconti court of first Gian Galeazzo and then Filippo Maria Visconti, and later arrived in Venice, as evidenced by the recipe dated to 1410. In the lagoon city, he illuminated the *Epistles of St. Jerome* (London, The British Library, Egerton 3266) for a member of the Venetian Cornaro family, as shown by the heraldic coat of arms. This manuscript cites the year 1414 and offers an important reference point for the artist's Veneto period [18].

1.2. The Expenses "Pro Coloribus"

Another aspect to be considered is the purchase of the painting material by the artists and the business concluded by the commissioners; it is, therefore, interesting to analyze the information that emerges from documentary resources about the purchase of colors for Michelino da Besozzo. In the acquisition of lapis lazuli, the social status of the painter counted, on one hand, whether he was a particularly renowned artist or not, and on the other hand, the economic availability of the patron who in some way "invested" his own money. If we consider the *Liber expensarum operum ab anno 1380 ad annum 1402* (Pavia,

Biblioteca Universitaria, ms. Aldini 509), the document where Michelino is mentioned in 1388 as an active artist in the works of the monastery of the Hermits of St Augustine of San Pietro in Ciel d'Oro in Pavia [19], we note that, since the document quotes the payment records, the purchase of particular pigments is not specified and is only generically cited as expenses "pro coloribus" [20]. On the other hand, among the information instead documented in the registers of the Duomo of Milan, we learn, for example, that on October 31st 1418, the artist worked "ponendi aurum et argentum et azurum ultramarinum" on the sculpted figure of the Virgin Mary in the keystone of the choir [21]. This demonstrates that the artist was employed for the polychrome work on the Cathedral sculptures. Currently, the sculpture, attributed to the hand of Jacopino da Tradate, one of the main creators of the Cathedral's construction site, features the Virgin and Child within the circular frame and is devoid of the original coloring [22]. Concerning the provisioning of ultramarine blue by the artist, we also have documentary evidence in the *Libro mastro*, the document dated to 1427 of the Milanese merchant Vitaliano Borromeo, for whom Michelino and his workshop worked on the frescoes cycle of his palace in Milan [23].

1.3. Two Case Studies of Panel Paintings

In light of the considerations so far, the study of Michelino da Besozzo's color palette is certainly a field of investigation of great interest. Nancy Turner studied the recipe collection of Giovanni Alcherio in connection with the painting materials used in some illuminated manuscripts from the Paul Getty Museum Collection [24]. The manuscripts analyzed through the techniques used (XRF and UV–visible spectrophotometry) were the Book of Hours by the Boucicaut Master and workshop of the Rohan Master, Ms.22 (86.ML.571) [25], the Book of Hours by the Follower of the Egerton Master, Ms. Ludwig IX 5 (83.ML.101) [26] and *Des cas des nobles hommes et femmes* by the Boucicaut Master and workshop, Ms.63 (96.MR.17) [27]. This study highlighted how in the illuminators' workshops there was a real system of procedural exchange and sharing of techniques that went hand in hand with the use of the same models and mutual stylistic influences. It is evident, therefore, that analyzing the paintings of Michelino da Besozzo with non-invasive techniques and the related study of pigments offers an opportunity to investigate not only the artistic techniques used by the master but also the period of International Gothic in the foyer of artistic relations between Italy and France.

This article examines two particular case studies: *The Mystic Marriage of Saint Catherine* (Siena, Pinacoteca Nazionale) and *The Madonna of the Rose Garden* (Verona, Museo civico di Castelvecchio). In 2012, a first technical study was carried out on the *Mystic Marriage* of Siena with IRR and ED-XRF analyses [28].

The new scientific study of the two works of art presented in this paper has the aim of developing an interdisciplinary research project [1] with a view to close collaboration between the methods and tools of science applied to cultural heritage. A common analysis protocol with the combination of non-invasive and portable techniques such as Energy Dispersive X-ray Fluorescence (ED-XRF) spectroscopy and Fiber Optics Reflectance Spectroscopy (FORS) [29,30] was applied for the characterization of the color palette of Michelino da Besozzo. The works were analyzed under two completely different conditions, The *Mystic Marriage* was analyzed inside a room attached to the Restoration Laboratory in the Pinacoteca di Siena, as shown in Figure 1a, while for the *Madonna of the Rose Garden*, the analyses were carried out on site in the hall of the Museo di Castelvecchio in Verona. We note, in particular, the exposition conditions of the *Madonna of the Rose Garden* in Carlo Scarpa's original setting, with the work mounted on a system of ceiling tie-rods that determine its height from the floor, as shown in Figure 1b.

(**a**) (**b**)

Figure 1. On-Site Energy Dispersive X-ray Fluorescence (ED-XRF) spectroscopy analyses: (**a**) *The Mystic Marriage of Saint Catherine*, Siena, Pinacoteca Nazionale; (**b**) *The Madonna of the Rose Garden*, Verona, Museo di Castelvecchio.

2. Materials and Methods

2.1. The Mystic Marriage of Saint Catherine

The *Mystic Marriage of Saint Catherine of Alexandria with St. John the Baptist and St. Anthony the Abbot* (Siena, Pinacoteca Nazionale, inv.171) is a work painted in tempera and gold on panel (75 × 58 cm), dated between 1400 and 1404 [31,32], and it is shown in Figure 2. It is the only signed work by the artist, so it represents an essential element of comparison for the reconstruction of the corpus of the artist's works. The painting shows extreme elegance in its composition and can be described as a luxury object. The preciousness of the materials used is evident in the gold background and in the pastille reliefs, with the elegant Gothic lettering of the names of the saints and in the master's signature, as well as in the decoration of the crowns and halos. The holes in the upper part of the panel suggest that the work was originally mounted in a frame probably worked in a lobed profile. The painting emphasizes the artist's delicate style with the figure of the Virgin seated on a throne, which is skillfully drawn in its spatial projection with reliefs, as well as punching and the incisions in gold. The Virgin holds the Child, who hands the ring to St. Catherine of Alexandria, in the usual iconography that characterizes the episode. The attribute of the torture wheel is lightly incised in the gold at her feet. On either side are the slender figures of St. John the Baptist and St. Anthony the Abbot, both with their own iconographic attributes. Anthony, dressed in the black robes of the Order of the Antonians of Vienne, is accompanied by a small piglet, while John wears the fleece and holds a scroll. We do not go into critical discussion concerning the history of this work since the focus of this study

is precisely on the elements that emerge from the study of pigments. The main color that characterizes this work is blue, starting with the Virgin Mary's mantle, which has an ornamental border of gold circles and a rather dark green inner lapel of the dress. It may be noted that the alternation of blue and green is used by Michelino da Besozzo in the Virgin of the Coronation of Duke Gian Galeazzo Visconti in the famous manuscript of the *Funeral Eulogy* written by the Augustinian Pietro da Castelletto and illuminated in 1403 (Paris, BnF, Latin 5888) [3,33]. In the manuscript, blue is the color of choice and is distinguished by its particular degree of brilliance and intensity in the Virgin's dress, where the flap of green inner cloth is visible at knee level and between the folds [12]. The same pattern of blue and green is used for the Virgin's dress in the *Book of Hours* ca 1390 (Avignon, Bibliothèque municipale, ms 111) [3,34], in the *Annunciation* on folio 20r, in the *Nativity* on folio 21r, and in the *Adoration of the Magi* on folio 22r. In this case, however, the grisaille technique of execution with watercolor elevations has typical glazing due to the diluted pigment and its effects on the parchment. Michelino still uses the two colors in the dress of St. Augustine in the manuscript of *Enarrationes in Psalmos*, folio 239r (Vatican City, Biblioteca Apostolica Vaticana, Vat. Lat. 451), illuminated in Pavia between 1400 and 1402 [35,36]. The blue-and-green pair is also found in several folios of the *Bodmer Book of Hours* (New York, The Pierpont Morgan Library, MS M.944) [37], ca. 1420, where the quality of execution excels, for example, in the scene of the *Presentation in the Temple* fol. 11 v, the *Visitation* fol. 52 v and the figures of *St. Luke the Evangelist* fol. 75 v and *St. Catherine of Alexandria* fol. 83v. In the panel of the *Mystic Marriage* of Siena, blue returns in the mantle of St. John the Baptist, but it seems fainter than in the Virgin's mantle. Another dominant color is the pink of St. Catherine of Alexandria's mantle, which tends towards purplish in some parts and appears lightened in others, depending on the degree of intensity given to the brushstroke and the light and shadow effects of the folds at the bottom. The mantle has white fur lining and a pseudo-kufic ornamental border that is currently barely visible due to the fall of gold. The saint's underlying robe, on the other hand, is a darker pink tending towards purplish red, while the sleeve has a decorative pattern of small five-petaled flowers in gold. This motif returns, for example, in the *opelanda*, the typical fashionable dress of the time, worn by one of the twelve Virtues accompanying Gian Galeazzo, "Count of Virtues", in the Coronation image illuminated in the *Funeral Eulogy* (BnF, Latin 5888) [33]. It is specifically the Virtue of Charity who holds a lighted torch in her hand. Going further to observe the color palette used by the artist, we note the dark and dense black of the dress of St. Anthony the Abbot, the different shades of brown used for the fleece and hair of St. John the Baptist and a nuanced yellow–orange for the hair of the Virgin Mary, the Christ Child and St. Catherine. Another point of interest is the observation of the flesh tones, particularly those of St. Catherine of Alexandria and the Child, which show, in several parts, a fine graining of white lead dots used to create effects of points of light that are almost meant to suggest the sensitive and natural tenderness of the skin.

Figure 2. Michelino da Besozzo, *The Mystic Marriage of Saint Catherine*, Siena, Pinacoteca Nazionale, with permission from Ministero della cultura. Foto Archivio Musei Nazionali di Siena.

2.2. The Madonna of the Rose Garden

The Madonna of the Rose Garden (Verona, Museo di Castelvecchio, inv. 173-1B359) is a work painted in tempera and gold on panel transferred to canvas (130 × 95 cm) dated around 1415–1420 [38,39], as shown in Figure 3. The critical history of the work is particularly complex in that its attribution to Michelino da Besozzo is still debated by scholars, alternating with that of Stefano di Giovanni, also known as Stefano da Verona [40]. Andrea De Marchi recently reaffirmed the attribution to Michelino with a date in the third decade of the 15th century [41]. The painting came from the women's monastery of San Domenico dell'Acquatraversa in Verona and was already very damaged when it arrived in the propriety of the Municipality of Verona. A series of restoration interventions are documented, starting from a report in 1857, but damage and repainting over time have altered the original condition of the painting, making a coherent reading difficult. In fact, because of this poor state of preservation, the decision was made in 1950 to transport it on canvas [42]. The composition of the work refers to the iconographic subject of the Garden of Paradise, with the rose garden full of small birds and the Madonna of Humility seated on a large cushion while holding the divine Child. In the lower part, almost at the entrance of the garden, guarded by two peacocks is the figure of St. Catherine of Alexandria, recognizable by the two symbols of martyrdom: the wheel and the sword that are placed on the ground. Thanks to some X-ray images kept in the Archive of the Civic Museums of Verona [43], it is possible to note the large area of damage that affected the figure of Saint Catherine of Alexandria and the angel delivering the palm in her hand. In fact, the figure of the saint in the X-ray appears in a different posture, with her arm adhered to her body and her hand weaving the garland of flowers, so the saint's hand and much of her forearm are completely repainted, as are some areas of her robe. The painting is brightened by the presence of many minute angels who animate the scene and are arranged in different

groups and attitudes, ranging from those reading a book to those adoring the Virgin Mary and those playing with water gushing from the fountain. The work has a gold background visible at the top, where several silhouettes in the form of fluttering angels are painted and incised in gold. Gold is evident in the pastille reliefs of the crown of St. Catherine, in the haloes with the rays of the Virgin and Child, in the fountain and in the handle of the sword. The space of the enclosed garden is depicted on an ochre-colored background, and the vision is extended deep into the labyrinth of the rose bower. The dominant colors of the panel are a very dark blue for the Virgin's mantle, bordered by a pattern of concentric circles similar to that of the Virgin of the *Mystic Marriage* of Siena. The mantle also shows a very flattened drapery and very dense brush strokes, unusual for the artist's style, which instead proceeds with successive layers of color and transparent effects through overlapping glazes. The blue returns in a lighter, brighter hue in several parts of the painting, as in the splendid angels. The angels are painted following a precise alternation of blue–red–white colors, except for the one angel who wears a particularly bright yellow robe. A deep blue is also present in the necks of the two peacocks. Another color to pay attention to is the red used for the Virgin's robe and the mantle of St. Catherine of Alexandria. This red is lightened in some parts but seems very similar in hue to that used by Michelino da Besozzo in another panel painting referring to the master's later period: *The Marriage of the Virgin*, ca. 1430 (New York, Metropolitan Museum) [44,45]. Indeed, the red of the cloak of St. Joseph, who is handing the ring to the Virgin, seems very similar to that of St. Catherine in the *Madonna of the Rose Garden* and has the same ornamental pseudo-kufic border in the lower part.

Figure 3. Michelino da Besozzo (attr.), *The Madonna of the Rose Garden*, Verona, Musei Civici, Museo di Castelvecchio, Archivio fotografico (foto Gardaphoto, Salò).

2.3. Analytical Techniques

2.3.1. Energy Dispersive X-ray Fluorescence Spectroscopy (ED-XRF)

The spectrometer consists of an X-ray tube (Amptek Mini-X, Amptek Inc., Bedford, UK) with an anode target of rhodium and a beryllium window with a thickness of 127 μm, and it was powered by an accelerating potential difference of 38 kV and a tube current of 80 μA. The detector is a Peltier-cooled silicon drift with an amplifier and integrated multichannel analyzer (Amptek 123-SDD, Amptek, Bedford, MA, USA), providing for any detected X-ray photon a current pulse with an amplitude proportional to the energy of the photon. The detector has a surface area of 25 mm^2, a thickness of 500 μm and a beryllium window thickness of 12.5 μm.

The energy resolution, defined as the full-width half-maximum (FWHM) of the manganese Kα line at 5.9 keV, is 140 eV. The detection limit of the instrument ranges from 10^2 to 10^3 ppm [46].

The distance of the sample from the sensitive area of the detector was 3.5 cm and that from the generator anode was 3 cm. The measured area was about 14 mm^2. The preset acquisition time was 300 s.

The spectra were analyzed with Pymca 5.5.5 [47] to calculate the net area of the elements' characteristic peaks. The areas were then normalized to the live time to obtain the photon rate.

2.3.2. Fiber Optics Reflectance Spectroscopy (FORS)

Fiber Optics Reflectance Spectroscopy was performed with an AvaSpec spectrophotometer (Avantes, Apeldoorn, The Netherlands) equipped with a CCD linear sensor (2048 pixels) and a diffraction grating with 300 lines/mm, blazed at 500 nm, which covers a spectral range from 300 to 1100 nm with a spectral resolution of 0.8 nm. The illuminator was a halogen lamp (HL-2000 FHSA, Avantes). The measurement geometry was 2 × 45°:0° through a bifurcated fiber (diameter of 600 μm) for the illumination, with a 200 μm diameter fiber (NA 0.22 ± 0.02) for the reflected light. The sampled area's diameter was 1 mm. The system uses the Avantes software AvaSoft-COL 8.3.1.0. The reflectance spectra were collected from 380 to 1000 nm. In some cases, the reflectance spectra were converted in apparent absorbance through the following equation: A = log (1/R). Smoothing with the Savitzky–Golay procedure with a 2nd-degree polynomial order and 55-point window was applied to all spectra.

3. Results and Discussion

This section presents the results of the characterization of the palette of the *Mystic Marriage of Saint Catherine* and the *Madonna of the Rose Garden* paintings, performed by means of ED-XRF spectroscopy and FORS.

In Figures 4 and 5, the analyzed areas are shown. Due to the fixed position of the *Madonna of the Rose Garden* and its dimensions, it was not possible to analyze with ED-XRF the upper part of the painting.

The results of the ED-XRF analyses are reported in Tables S1 and S2 of the Supplementary Materials.

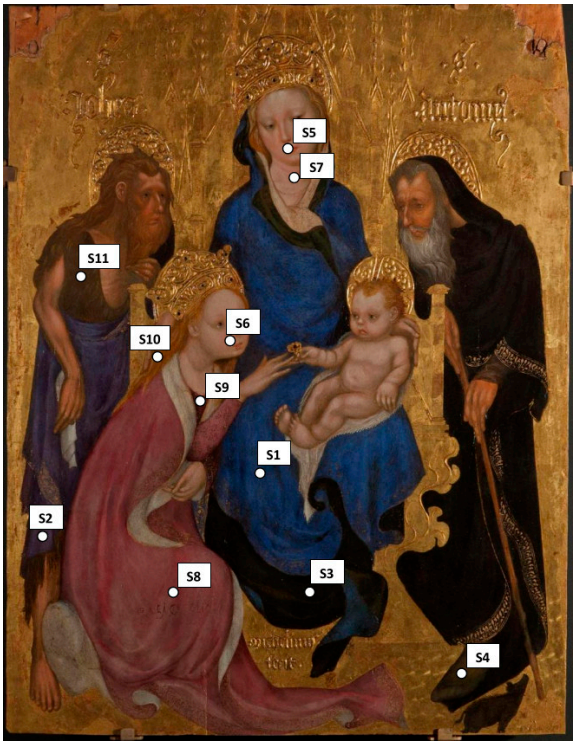


Figure 4. The analyzed areas of *The Mystic Marriage of Saint Catherine* painting.

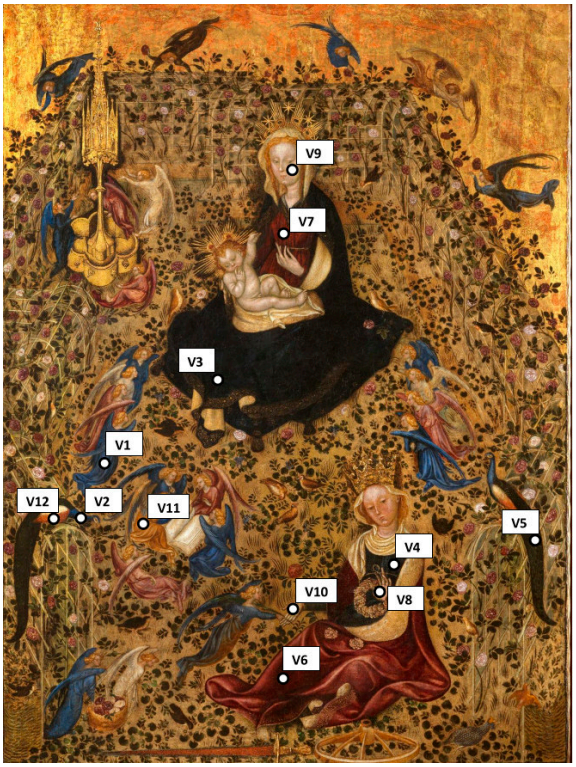
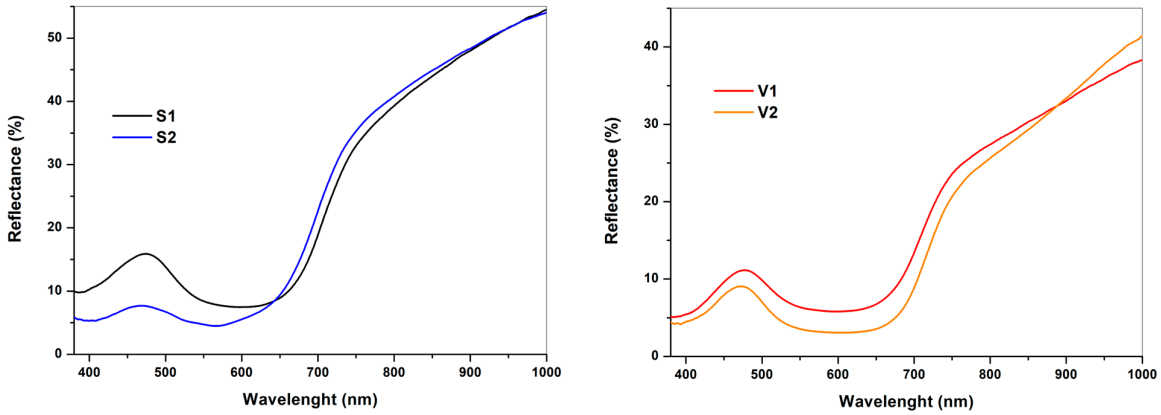


Figure 5. The analyzed areas of *The Madonna of the Rose Garden* painting.

3.1. Blue Pigments

In Figure 6a, the FORS spectra acquired on the *Mystic Marriage of Saint Catherine* painting in the areas corresponding to the Virgin Mary's and St. John the Baptist's mantels are shown (S1 and S2). Both spectra show a maximum of reflectance at ca. 475 nm and an increase in its values in the infrared region. This spectral behavior is characteristic of the ultramarine pigment [48]. The spectrum acquired on St. John the Baptist's mantle (S2) slightly differs from the other one: the reflectance values in the blue region are lower, corresponding to a darker color, while a small increase between 550 nm and 650 nm is observed.

The FORS spectra of two blue areas of the *Madonna of the Rose Garden*, the vest of an angel (V1) and the neck of one of the peacocks (V2), are reported in Figure 6b. Also, in this case, the characteristic features of the spectra allow us to identify the main pigment present in the pictorial layer as ultramarine.



(**a**) (**b**)

Figure 6. Fiber Optics Reflectance Spectroscopy (FORS) spectra measured in the following areas: (**a**) the areas S1 (black curve) and S2 (blue curve) of the *Mystic Marriage of Saint Catherine* painting; (**b**) the areas V1 (red curve) and V2 (orange curve) of the *Madonna of the Rose Garden* painting. The FORS spectra are characteristic of ultramarine pigment.

Natural ultramarine is obtained by grinding and purifying lapis lazuli, a stone composed of lazurite ($Na_7Ca(Al_6Si_6O_{24})(SO_4)(S_3)^{-}\cdot H_2O$) [49], which gives the blue hue to the pigment, and other minerals whose nature and relative amounts depend on the deposits from which the lapis lazuli stone has been extracted. Although the pigment, during its preparation, is subjected to purification processes, some impurities remain, and the detection of their presence allows us to distinguish natural ultramarine from its synthetic form. In the past, X-ray fluorescence spectroscopy has proved to be an effective tool for lapis lazuli provenance studies [50].

The ED-XRF analyses on the blue areas of the *Mystic Marriage of Saint Catherine* painting (Table S1) show the presence of aluminum (Al), silicon (Si), sulfur (S) and calcium (Ca). These elements are compatible with the chemical composition of lazurite. Nevertheless, it is possible that calcium and sulfur are also contained in a gypsum-based preparatory layer, as suggested by the presence of strontium (Sr). In fact, strontium is one of the elements constituting celestine ($SrSO_4$), a mineral usually associated with gypsum. Calcium can be also related to calcite ($CaCO_3$) or diopside ($CaMgSi_2O_6$), minerals commonly associated with lazurite in lapis lazuli stone [51]. The ED-XRF analyses have also detected the presence of iron (Fe) and potassium (K). Iron can be ascribed to pyrite (FeS_2), another mineral often associated with lazurite [51]. The presence of potassium can be due to minerals such as phlogopite, nepheline and afghanite [51,52] or to KOH contained in ash lye used during the extraction process. In the area corresponding to St. John the Baptist's mantel,

the amount of iron is higher than in the Virgin's mantle, and mercury (Hg) and gold (Au) have also been detected. The presence of iron and mercury is due to the fact that the mantle has been painted on Saint John the Baptist's leg, the flesh tone of which has probably been realized using an earth and/or an ochre mixed with a small amount of cinnabar or vermillion, (HgS). Instead, the presence of gold in the ED-XRF spectrum indicates that Saint John the Baptist's figure has been painted on the gold background.

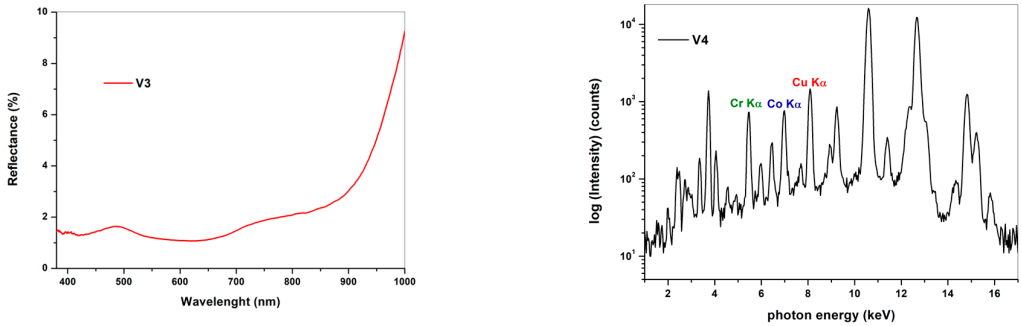
The results of the ED-XRF analyses performed in the blue areas of the *Madonna of the Rose Garden* painting, corresponding to the vest of an angel (V1) and the neck of one of the peacocks (V2), do not clearly support the attribution of the blue hue to the use of ultramarine. Due to the bad conservation state of the painting, the pictorial layer is very thin, and consequently, the amount of material analyzed is very low. With these experimental conditions, it is very difficult to detect light elements, and for this reason, it is not possible to establish if aluminum, which is one of the elements characterizing the ultramarine pigment, is present in the analyzed areas. Nevertheless, the FORS spectra acquired in these areas and the detection of elements compatible with the impurities and minerals present in lapis lazuli stone still allow us to hypothesize the use of ultramarine.

In the *Madonna of the Rose Garden* painting, other blue areas, darker than the previous ones, are present. In particular, they correspond to the Virgin Mary's mantel and St. Catherine's vest, as well as the cushion on which the Virgin is seated.

The ED-XRF analysis performed on the Virgin Mary's mantle area (V3) shows the presence of copper (Cu) (Table S2), and this element can be associated with the use of azurite ($Cu_3(CO_3)_2(OH)_2$). The presence of azurite is also confirmed through the detection of elements present in minerals commonly associated with it [53]: arsenic (As) is present in olivenite ($Cu_2(AsO_4)(OH)$), zinc (Zn) in smithsonite ($ZnCO_3$) and barium (Ba) in baryte ($BaSO_4$). Bismuth (Bi) was not detected, and this excludes the presence of mixite, which has been identified in the azurite used by Giotto [54] and some illuminated manuscripts [55,56]. A not-negligible amount of iron is also detected, indicating the probable use of an earth pigment in addiction to azurite [57].

As an example, in Figure 7a, the FORS spectrum acquired in the area of the Virgin Mary's mantel (V3) is shown. The spectrum is compatible with the presence of azurite; nevertheless, a slight increase in the reflectivity values in the infrared region leads us to hypothesize the presence of ultramarine probably superimposed to azurite [56,57]. Unfortunately, ED-XRF analyses cannot support this hypothesis since, as previously told, the conservation state of the *Madonna of the Rose Garden* made very difficult the detection of aluminum and silicon.

In the analyzed area of Saint Catherine's mantle (V4), the ED-XRF analysis detected not only the presence of copper but also cobalt (Co) and chromium (Cr) (Figure 7b and Table S2), pointing out that this area underwent a modern repainting intervention.



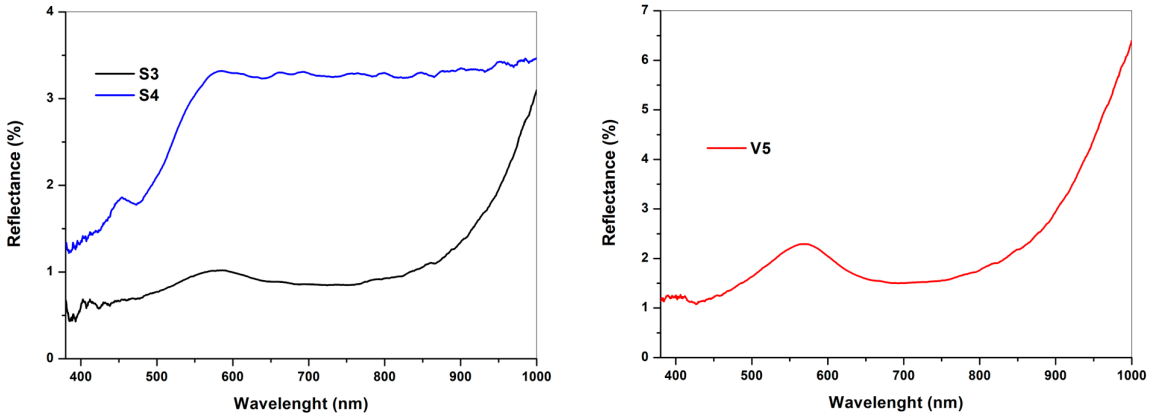
(**a**) (**b**)

Figure 7. (**a**) Fiber Optics Reflectance Spectroscopy (FORS) spectrum measured in the area V3 of the *Madonna of the Rose Garden* painting. The spectral features suggest the presence of ultramarine superimposed to azurite. (**b**) A detail of the ED-XRF spectrum measured in area V4 of the *Madonna*

of the Rose Garden painting. The peaks relative to the K_α lines of copper (Cu), cobalt (Co) and chromium (Cr) are indicated.

3.2. Green Pigments

The ED-XRF analysis of the area corresponding to the inner lapel of the Virgin Mary's mantle (S3) in the *Mystic Marriage of Saint Catherine* shows the presence of a copper-containing pigment (Table S1). The color of the mantel is so dark that, to the naked eye, it is not easy to establish if it has a blue or green hue, but the FORS analysis helped us to answer this question. Although the FORS spectrum is similar to the one of a black pigment, showing very low values of reflectance, it still maintains the spectral features of a green pigment (Figure 8a, black curve). Probably, it deals with verdigris or copper resinate, despite a shift in the reflectance maximum (ca. 580 nm) towards higher wavelengths with respect to the one of the two pigments [48,57]. In addition to copper, the ED-XRF analysis reveals the presence of tin (Sn) (Table S1). This element can be ascribed to a yellow pigment, probably lead–tin yellow (Pb_2SnO_4 or $Pb(Sn,Si)O_3$), added to the green one or used alone in a glazing layer. The combined use of verdigris, or copper resinate, together with lead–tin yellow has been attested in illuminated manuscripts [57,58] and the Polittico dell'Intercessione painted by Gentile da Fabriano [59].



(**a**) (**b**)

Figure 8. Fiber Optics Reflectance Spectroscopy (FORS) spectra measured in the following: (**a**) areas S3 (black curve) and S4 (blue curve) of the *Mystic Marriage of Saint Catherine* painting; (**b**) area V5 (red curve) of the *Madonna of the Rose Garden* painting. The FORS spectra measured in areas S3 and V5 show the spectral features characteristic of verdigris or copper resinate, while the one measured in area S4 allows us to identify green earth pigment.

A not-negligible amount of iron, together with other elements such as aluminum, silicon, potassium, chromium and manganese (Mn), is also detected by ED-XRF (Table S1), suggesting the presence of an earth and/or ochre pigment. The complex composition of the pictorial layer, revealed by ED-XRF analysis, may justify the shift in the reflectivity maximum observed in the FORS spectrum.

The dark green peacock tail (V5) in the *Madonna of the Rose Garden* shows a FORS spectrum similar to the one measured on the Virgin Mary's mantle in the *Mystic Marriage of Saint Catherine* (S4) (Figure 8b): the reflectivity presents low values, and its spectral features are similar to the ones of verdigris or copper resinate. Also, in this case, the reflectivity maximum (ca. 570 nm) is shifted towards higher wavelengths. The ED-XRF analysis confirms the presence of a copper-based pigment (Table S2) together with a small amount of iron, probably contained in an earth or ochre pigment.

An iron-based green has been found in Saint Antony's shoe (S4) in the *Mystic Marriage of Saint Catherine* (Table S1). The presence of other elements, such as aluminum,

silicon and potassium, is compatible with the use of green earth ($K[(Al, Fe^{III}), (Fe^{II}, Mg)](AlSi_3, Si_4) O_{10}(OH)_2$) [60]. The possible use of a green earth pigment is also supported by the presence of small quantities of chromium, an element sometimes contained in this pigment [61]. The FORS spectrum (Figure 8a, blue curve) shows low values of reflectance and the principal characteristic feature of the green earth spectrum, that is, the maximum of reflectance, located, in our spectrum, at ca. 580 nm [60,62,63]. The characteristic shoulder at ca. 485 nm [56,60,63] is hardly visible, while the absorption maximum at 760 nm [48] is absent. In addition, a small peak at ca. 455 nm is visible. A spectral feature at this energy can be found in the FORS spectra of the raw Sienna earth [64,65], as it is possible that this pigment has been used to realize the underlying brown layer (Figure 9). The analyzed area also contains cinnabar, or vermillion, as attested by the presence of mercury, detected by ED-XRF (Table S1). Also, this pigment has probably been used in the underlying layer. The complexity of the pictorial stratification can justify the differences in the FORS spectrum measured in this area with respect to the one measured on a purer green earth pigment.

Figure 9. Detail of *The Mystic Marriage of Saint Catherine* painting: Saint Antony's shoe.

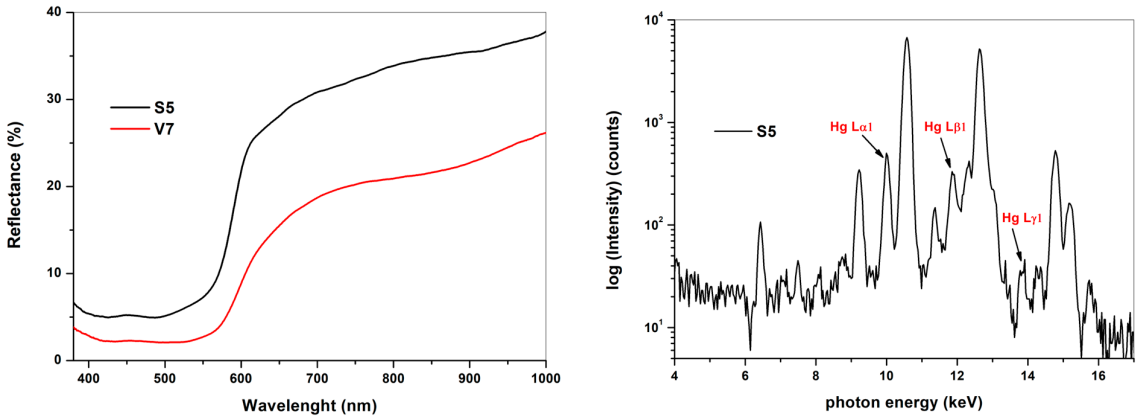
3.3. Red Pigments

In the *Mystic Marriage of Saint Catherine*, the red areas are limited to the mouths. The ED-XRF analysis performed in the area of the Virgin's mouth (S5) reveals the presence of mercury, associated with cinnabar or vermillion (Figure 10b and Table S1). In Figure 10a (black curve), the FORS spectrum acquired in the same area (S5) is shown. The sigmoidal shape of the cinnabar, or vermillion, spectrum is observed. The inflection point, located at ca. 590 nm, is slightly shifted towards lower wavelengths with respect to pure cinnabar or vermillion [48,66]. Due to this shift and the presence of a relative minimum of the reflectance at about 450 nm, the use of an organic pigment, not detected by ED-XRF, together with cinnabar, or vermillion, cannot be excluded.

Also, present in the Saint Catherine's mantel area (V6) in the *Madonna of the Rose Garden* is cinnabar or vermillion, as attested by the detection of mercury during the ED-XRF analysis (Table S2). Nevertheless, in addition to this element, huge quantities of barium, strontium and zinc have been detected, suggesting that this area has been subject to strong restoration interventions or repainting.

Cinnabar, or vermillion, has probably been used also in the Virgin's vest (V7), as revealed by the FORS spectrum measured in this area (Figure 10a, red curve). In fact, the sigmoidal shape of the spectrum, together with the position of the inflection point at ca. 600 nm, is compatible with the presence of one of these pigments. Nevertheless, the presence in the spectrum of an absorption feature at ca. 850 nm suggests that cinnabar (or vermillion) has probably been mixed with an iron-based pigment [48]. Unfortunately, due to the location of this area in the upper part of the painting, it was not possible to perform

an ED-XRF analysis, which would either confirm or refute the presence of mercury and iron.



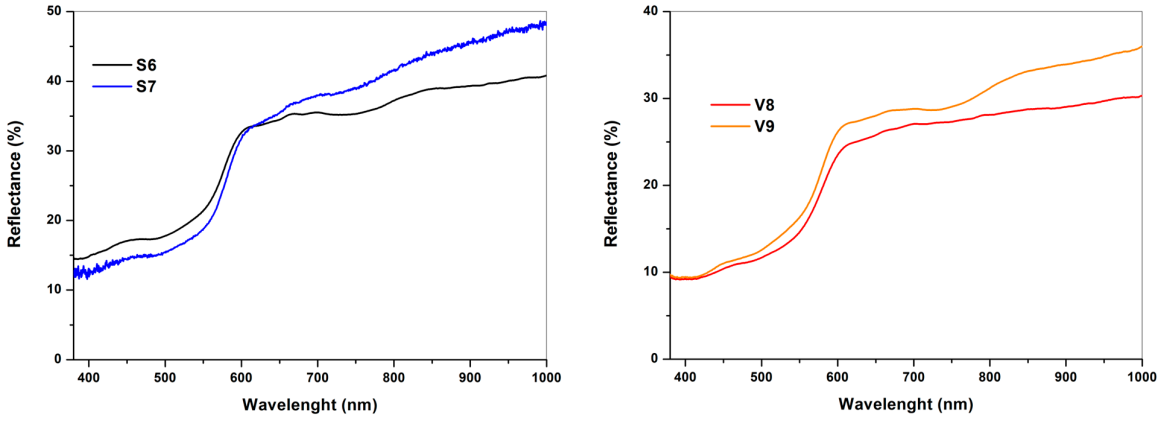
(**a**) (**b**)

Figure 10. (**a**) Fiber Optics Reflectance Spectroscopy (FORS) spectra measured in area S5 (black curve) of the *Mystic Marriage of Saint Catherine* painting and area V7 (red curve) of the *Madonna of the Rose Garden* painting. The FORS spectra suggest the presence of cinnabar or vermillion, probably used together with an organic pigment, in area S5, and an iron-based pigment in area V7. (**b**) A detail of the ED-XRF spectrum measured in area S5 of the *Mystic Marriage of Saint Catherine* painting. The peaks relative to the $L_{\alpha 1}$, $L_{\beta 1}$ and $L_{\gamma 1}$ lines of mercury (Hg) are indicated.

3.4. Flesh Tones

All the flesh tones in the two paintings (S6, S7, V8 and V9) are characterized by the presence of mercury, contained in cinnabar or vermillion, and a huge amount of lead (Pb), associated with *biacca* ($2PbCO_3.Pb(OH)_2$) (Tables S1 and S2). In all the areas analyzed, iron is also present (Tables S1 and S2), suggesting the use of earth or ochre pigments.

In the *Mystic Marriage of Saint Catherine* (S6 and S7), the detection of the same elements present in Saint Anthony's shoe, aluminum, silicon, potassium and, except for the Virgin's neck, chromium, suggests that the same green earth was used. Since lead and mercury highly absorb the characteristic photons emitted by elements with low atomic numbers, we can suppose that some green earth is present in the top layer. This hypothesis seems to be confirmed by the FORS spectra, which are completely different from those of a cinnabar (or vermillion) and *biacca* mixture [67]. As an example, in Figure 11a (black curve), the FORS spectrum acquired on an area of Saint Catherine's face is reported (S6). The spectrum shows the characteristic features of a green earth such as, for example, an absorption at ca. 750 nm. Nevertheless, we cannot exclude the further presence of a green earth in the background.



(**a**) (**b**)

Figure 11. Fiber Optics Reflectance Spectroscopy (FORS) spectra measured in the following areas: (**a**) areas S6 (black curve) and S7 (blue curve) of the *Mystic Marriage of Saint Catherine* painting; (**b**) areas V8 (red curve) and V9 (orange curve) of the *Madonna of the Rose Garden* painting. The FORS spectra measured in S6 and V9 areas suggest the presence of green earth, while the ones measured in areas S7 and V8 suggest the presence of umber earth.

The FORS spectrum acquired in the area of the Virgin's neck (S7) (Figure 11a, blue curve) is different from the ones measured in the other flesh tone areas: the absorption at 750 nm is not visible, and, in the infrared region, the spectrum shows a slightly increasing trend. Another iron-based pigment seems to be used, probably burnt umber earth, as suggested by the presence of manganese, detected by ED-XRF (Table S1), and by the FORS spectrum [68]. Similar FORS spectrum has been measured in the area corresponding to Saint Catherine's left hand (V8) in the *Madonna of the Rose Garden* painting (Figure 11b, red curve). Also, in this case, we can hypothesize that a burnt umber earth has been used, as suggested not only by the FORS spectrum but also by the presence of manganese, detected by ED-XRF (Table S2).

FORS spectra showing spectral features of a green earth have been, instead, measured in the flesh tone areas of the Virgin and the Child. As an example, in Figure 11b (orange curve), the FORS spectrum acquired on an area of Virgin's face is reported (V9). Unfortunately, we do not have information on the elemental composition of this area since, due to its location in the upper part of the painting, it was not possible to perform the ED-XRF analyses.

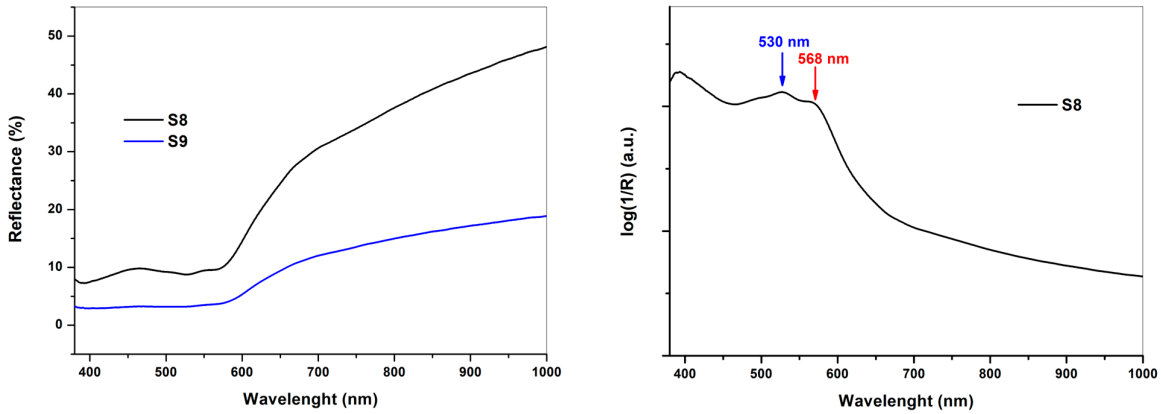
The ED-XRF analyses (Table S2) highlighted a difference in the composition of the pictorial layers corresponding to Saint Catherine's hands. As already told, the main elements found in the left hand (V8) are mercury and lead, while in the right one (V10), these two elements are absent, and the main elements present are barium and titanium (Ti), probably associated with modern barium and titanium whites.

3.5. Pink Pigments

In Figure 12a (black curve), the FORS spectrum of an area of the *Mystic Marriage of Saint Catherine* corresponding to the Saint Catherine's mantle is shown (S8). The spectral behavior of the reflectance suggests the presence of a lake. In order to identify the origin of this lake, i.e., vegetal or animal, the apparent absorbance has been calculated. As shown in Figure 12b, the apparent absorbance presents two relative maxima located at 530 nm and 568 nm, respectively. The position of these two maxima lead us to exclude the use of a vegetal lake, such as, for example, madder, whose apparent absorption maxima are located at lower wavelengths (510–510 nm, 540–545 nm) [48]. Our data, instead, agree with the presence of an animal-derived lake, such as kermes or lac [48]. Although, with FORS analysis, it is not easy to distinguish among the different lakes with an animal origin, it is

worth noting the good agreement of our data with the ones reported in the literature for lac [69,70]. Lac, also known as Indian lake, is derived from insects belonging to the Coccoidea superfamily and the Kerriidae family, such as the Kerria lacca.

In Figure 12a (blue curve), the FORS spectrum acquired on the Saint Catherine's vest is shown (S9). In the spectral region above 580 nm, the reflectance behavior is the same as that measured in the previous area, while in the low-wavelength region, the two absorption structures are hardly visible. The ED-XRF analysis (Table S1) shows that in this area (S9), there is a small amount of mercury. We can, thus, suppose that the lake used in the mantle and the vest is the same, and that for this last one, some cinnabar, or vermillion, has been added to obtain a red hue. The presence of cinnabar, a pigment highly absorbing in the spectral region below 600 nm, can justify the differences between the two FORS spectra observed in this region. Traces of mercury are also detected in an area of Saint Catherine's mantle that appears more brilliant, and, also in this case, the absorption features at low wavelengths are less pronounced.



(**a**) (**b**)

Figure 12. (**a**) Fiber Optics Reflectance Spectroscopy (FORS) spectra measured in areas S8 (black curve) and S9 (blue curve) of the *Mystic Marriage of Saint Catherine* painting; (**b**) apparent absorbance calculated for the spectrum S8. The positions of the two maxima in the apparent absorbance spectrum allow us to identify Indian lake.

In all the analyzed areas (S8 and S9), lead has been detected (Table S1), and it is possible to suppose that the lake has been mixed with *biacca*.

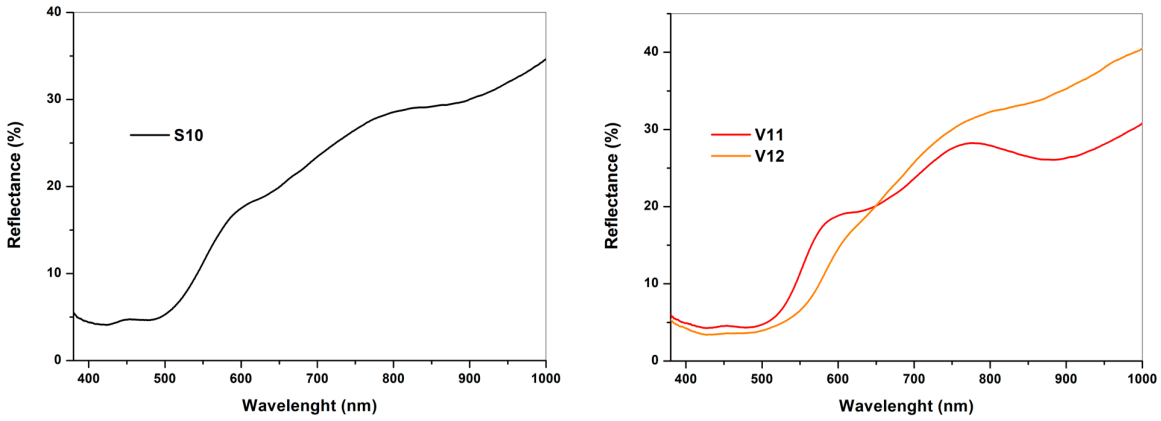
The traces of gold, detected by ED-XRF in Saint Catherine's vest (S9) (Table S1), can be ascribed to the use of this metal for the realization of the ornament present in this area.

Small quantities of iron and the elements characterizing an earth or an ochre pigment have been detected in all the analyzed areas.

3.6. Yellow, Orange and Brown Pigments

The ED-XRF analysis performed on an area of the *Mystic Marriage of Saint Catherine* corresponding to Saint Catherine's hair (S10) suggests that an iron-based pigment, probably a yellow ochre, has been used together with *biacca* and a small amount of cinnabar, or vermillion. In fact, iron has been detected together with lead and mercury (Table S1). Yellow ochre is mainly composed of goethite, an iron oxyhydroxide (α-$Fe^{3+}O(OH)$) [71], and its reflectance spectrum is characterized by an inflection point at ca. 545 nm and two absorption bands at 640 nm and 900 nm [48]. In the FORS spectrum measured in the area of Saint Catherine's hair (S10) (Figure 13a), the inflection point is located at ca. 545 nm, in agreement with the ones of the yellow ochre, while the two absorption maxima are not clearly visible, as in the spectrum of the pure pigment in egg medium [72]. This difference

in the reflectance spectrum with respect to the reference spectra can be due to the presence of *biacca* and cinnabar (vermillion).



(**a**) (**b**)

Figure 13. Fiber Optics Reflectance Spectroscopy (FORS) spectra measured in the following areas: (**a**) area S10 of the *Mystic Marriage of Saint Catherine* painting; (**b**) areas V11 (red curve) and V12 (orange curve) of the *Madonna of the Rose Garden* painting. The FORS spectra acquired in areas S10 and V11 suggest the presence of yellow ochre, while in area V12, a mixture of red and yellow ochre is probably present.

To realize the brown hue (S11), a mixture of an iron-based pigment and cinnabar, or vermillion, has been used, as revealed through the ED-XRF analyses that detected the presence of iron and mercury (Table S1).

Ochre pigments have also been used in the *Madonna of the Rose Garden* painting. In Figure 13b (red curve), the FORS spectrum acquired on an area of the yellow vest of an angel is shown (V11). The inflection point position at ca. 545 nm, together with an absorption band with a maximum at ca. 640 nm, indicates the presence of a yellow ochre. However, the maximum of the absorption band in the infrared region, which is located at 880 nm, is slightly shifted towards the one of a red ochre [48,73]. Probably, a mixture of the two pigments was used. Red ochre is mainly composed of hematite, an iron oxide (Fe_2O_3), [71], so the ED-XRF analysis did not allow us to distinguish between the two ochres.

A mixture of yellow and red ochres has probably been used to realize the orange part of the peacock's wing (V12). In this case, red ochre prevails, as indicated by the inflection point position at ca. 580 nm (Figure 13b, orange curve) [48]. In addition to iron, barium has been detected by ED-XRF (Table S2) (V12). Barium white, due to restoration interventions, is probably present in this area.

4. Conclusions

The scientific investigation of Michelino da Besozzo's color palette has led to the gathering of new information on the painting technique of an artist who was among the most relevant in the International Gothic period in Italy between the late 14th and early 15th centuries. Michelino's special attention to pictorial materials is evident, not only from the high visual quality of his works but also for the transmission of his recipe for ultramarine blue [6,12]. The study of artist's color palette in the two cases of panel paintings, presented for the first time in this paper, added depth to the results of the non-invasive analyses, highlighting the use of precious pigments such as ultramarine blue. The ED-XRF and FORS spectra, in fact, attested to the presence of lapis lazuli in his only signed work: the *Mystic Marriage of Saint Catherine* (Siena, Pinacoteca Nazionale) [31,32].

Less homogeneous and more complex results emerged instead during the study of the blue pigments of the *Madonna of the Rose Garden* (Verona, Musei civici di

Castelvecchio), a work that has undergone several restorations and also has a debated attributive history [38–41]. In the Virgin's mantle, in fact, the material substance of the pictorial layer prevails, with a dark blue mottled appearance with some areas of light blue, in which the undulating movement of the drapery can be seen, which, instead, is completely absent in the current state of the painting. In this case, the FORS spectra show the characteristics of azurite with a small change in the infrared that could be due to the presence of lapis. Interestingly, analysis of the blue of the robe of one of the angels of the *Madonna of the Rose Garden* confirms the use of lapis lazuli. This finding also raises the question of a 'hierarchy' of colors, as the use of the most precious pigment such as lapis lazuli was generally reserved for the Virgin's mantle. The analysis of the flesh tones of both works has revealed some data that allow us to speculate on the painting technique of the artist, who may have spread on the background as a base a tint made from a mixture of white lead and cinnabar red, as well as using a green earth as shading. The ED-XRF and FORS spectra in the *Mystic Marriage* indeed show the characteristics of green earth, while on the neck of the Virgin, a shadow earth may have been added. The presence of green earth is confirmed in some flesh tones of the *Madonna of the Rose Garden*, as in the body of the Child. FORS has also identified that the mantle lapel of the Virgin of the *Mystic Marriage*, although appearing very dark to the naked eye, has the characteristics of a verdigris or copper resinate, with the addition of a yellow of lead and tin [59]. The results of the non-invasive analysis confirmed the area of damage to St. Catherine of Alexandria in the *Madonna of the Rose Garden*, which was already attested in X-ray images and restoration reports, particularly in a portion of the dress and the completely repainted hands of St. Catherine. On the yellow, orange and brown pigments, the use of ochres was highlighted, and on the characterization of the predominantly cinnabar and vermilion reds, an interesting finding emerged that led to the identification of the presence of lac in the brilliant pink dress of St. Catherine in the *Mystic Marriage* of Siena [69,70].

The publication of the first results of the non-invasive analyses, with the combination of ED-XRF and FORS techniques on the two paintings, encourages further in-depth study via a multi-analytical approach and offers the possibility of conducting new studies not only on the painting technique of Michelino da Besozzo but also the perspective of his workshop practices, as well as allowing comparison with other masters of his time, such as Gentile da Fabriano [74].

Supplementary Materials: The following supporting information can be downloaded via this link: https://www.mdpi.com/article/10.3390/heritage7060141/s1, Supplementary Material ED-XRF data. Table S1: Photon rate (cps) relative to the elements detected by Energy Dispersive X-ray Fluorescence (ED-XRF) spectroscopy in The Mystic Marriage of Saint Catherine painting. Table S2: Photon rate (cps) relative to the elements detected by Energy Dispersive X-ray Fluorescence (ED-XRF) spectroscopy in The Madonna of the Rose Garden painting.

Author Contributions: Conceptualization, A.D.F. and A.C.F.; methodology, A.D.F. and A.C.F.; formal analyses, A.C.F.; data curation, A.D.F. and A.C.F., writing—original draft preparation, A.D.F. and A.C.F.; writing—review and editing, A.D.F. and A.C.F.; funding acquisition, A.D.F. All authors have read and agreed to the published version of the manuscript.

Funding: This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement N° 101034324.

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

Acknowledgments: We would like to thank the Pinacoteca Nazionale di Siena and the Museo di Castelvecchio di Verona, involved in this research effort for their permission to carry out non-invasive analyses.

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

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