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Spectroscopic and Imaging Analyses on Easel Paintings by Giovanni Santi

Maria Letizia Amadori [1,*], Gianluca Poldi [2], Giulia Germinario [3], Jgor Arduini [1] and Valeria Mengacci [1]

[1] Department of Pure and Applied Sciences, University of Urbino, P.za Rinascimento 6, 61029 Urbino, Italy
[2] Department of Letters, Philosophy and Communication, University of Bergamo, Via Pignolo 76, 24121 Bergamo, Italy
[3] Institute of Heritage Science—CNR, Via per Monteroni, 73100 Lecce, Italy
* Correspondence: maria.amadori@uniurb.it; Tel.: +39-33-9633-8838

Featured Application: The results from this research paper contribute to the knowledge of Renaissance painting materials and techniques allowing the implementation of the central Italy Renaissance painting database.

Abstract: The most important painter from Urbino in the last decades of the 15th century (1439 ab.–1494) was Giovanni Santi, the father of Raphael. The lack of scientific literature about Santi's practice and the possible peculiar role of Urbino in the development of painting techniques in northern Italy suggested in-depth investigations of the entire corpus of his paintings. A well-established sequence of multispectral imaging, spectroscopic and microscopic investigations was performed on 24 wood panel paintings and 2 canvases attributed by most scholars to Giovanni Santi (1439 ab.–1494) to collect a large set of significant data. This systematic research allowed his painting technique to be defined, starting from the type of supports he used and from the features of the underdrawing, which quite frequently included characteristic regular hatching. The pigments used were widely investigated by means of ED-XRF and reflectance spectroscopy (vis-RS); a meaningful multivariate statistical method (PCA and HCA analysis) was also applied to the ED-XRF dataset acquired for representative hues. In particular, the vis-RS technique proved to be a simple and effective diagnostic tool to detect many pigments, including indigo, and to distinguish between two different types of red lakes, avoiding sampling and more complex analyses. Santi used lead white, Fe-Mn-based pigments, vermilion, red lake, natural blue ultramarine, azurite, copper-based green pigments (particularly verdigris), lead-tin yellow, scarcely ever orpiment and, in a few green mixtures, also indigo. Despite the palette being linked to tradition, the master appeared to introduce some peculiarities, such as the addition of glass powder, and mixing pigments both in a traditional way and using them to create chromatic effects unusual for his time. This research confirmed that the systematic use of the integrated non-invasive methods is highly representative, and the results of this wide diagnostic campaign provided a significant dataset which allowed the implementation of a scientific database related to central Italy Renaissance paintings and materials.

Keywords: renaissance painting; IR imaging; vis-RS; ED-XRF analysis; PCA; HCA

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1. Introduction

Urbino was one of the most distinguished centres of the Italian Renaissance, due to the cleverness and culture of its duke, Federico da Montefeltro. His court hosted talented architects, decorators and painters such as Luciano Laurana, Francesco di Giorgio Martini, Donato Bramante, Paolo Uccello, Piero della Francesca and the Flemish Justus of Ghent (usually identified with Joos van Wassenhove), with whom Giovanni Santi was certainly connected [1,2].

In recent years, based on documentary sources, art historians revised the biography and the artistic activity of Giovanni Santi (Colbordolo, ab. 1439–Urbino, 1494) [3]. He was

an eclectic man: poet, painter and brilliant scenographer in Montefeltro's court. In 1484, the year of the death of his father, Sante di Peruzzolo, he joined the fatherly workshop in crafts and fine arts. His participation in the artistic life of Urbino is documented between 1468 and 1471; at that time, he was in charge of following and hosting Piero della Francesca during his stay in Urbino [1]. Several hypotheses were formulated about his acquaintance with Pietro Perugino [4] in whose workshop the young Raphael was trained [5].

Despite many technical studies dedicated to Raphael [6,7] or Perugino [8], only a few scholars have investigated Santi's works [9–11]. The scarcity of scientific literature about Santi's paintings and the peculiar role of Urbino in the development of Renaissance painting in northern Italy required a diagnostic project aimed at obtaining information on his painting materials and executive techniques.

Starting some years before Santi's exhibition held in Urbino between 2018 and 2019 [3], an integrated multi-analytical campaign based on the use of both non-invasive and micro-invasive investigations was carried out to examine his painting materials and technique. The research concerned 24 wood panel paintings and 2 canvas paintings (Table 2), as well as two mural paintings held in the Church of St. Dominic in Cagli [10], covering the larger part of Santi's surviving work and a large period of his activity, from 1470–1475 to 1494, the year of his death.

Table 1. List and description of Giovanni Santi's paintings involved in the diagnostic campaign, with the code given to each work and the related analysis. The dates marked with an asterisk (*) were deduced from inscriptions, documentary sources and references; the others are those generally hypothesized by art historians [3,5].

Painting and Code	Location	Panel Size	Supports Description	Date	Non-Invasive Analyses
Muses (Clio, Melpomene, Erato, Calliope, Euterpe, Polyhymnia, Terpsichore)—MC	Florence, Galleria Corsini	83 × 40 cm	1 board	1470–1480 (or 1480–1490)	Vis, IRR, IRC, Vis-RS, ED-XRF, DM
Dead Christ in the Sarcophagus with the Symbols of Passion—GSCSP	Urbino, Galleria Nazionale delle Marche	25 × 20 cm	1 board	1475–1482	Vis, IRR, IRC, UVF, Vis-RS, ED-XRF, DM
Apostles (St. James, St. Jude Thaddeus, St. John the Evangelist, St Matthew, St. Philippe, St. Paul)—GSST	Urbino, Galleria Nazionale delle Marche	97 × 40 cm	1 board	ante 1480 (1475?)	Vis, IRR, IRC, Vis-RS, ED-XRF, DM
Christ administers the Communion to Saint Peter—CRISP	Urbino, Casa Raffaello	110 × 79 cm	3 vertical boards, poplar	About 1474–1480	Vis, IRR, IRC, ED-XRF, DM
Martyrdom of Saint Sebastian—GSM	Urbino, Casa Raffaello	210 × 166 cm	5 vertical boards, poplar	1487–1488	Vis, IRR, IRC, Vis-RS, ED-XRF, DM
Dead Christ Supported by Two Angels—GSCMA	Urbino, Galleria Nazionale delle Marche	35 × 23.5 cm	1 board	1483–1485	Vis, IRR, IRC, DM
Sacred Conversation—GRAD	Gradara, Rocca di Gradara (Museo Civico)	210 × 164 cm	8 vertical boards	1484 *	Vis, IRR, IRC, Vis-RS, ED-XRF, DM
Sacred Conversation—GSMF	Fano, Museo Civico	221 × 184 cm	7 vertical boards, poplar	1484–1489	Vis, IRR, IRC, Vis-RS, ED-XRF, DM
Annunciation—GSA	Urbino, Galleria Nazionale delle Marche	233 × 162 cm	12 horizontal boards	1485–1490	Vis, IRR, IRC, UVF, Vis-RS, ED-XRF, DM
Dead Christ and the Virgin—GSCM	Urbino, Galleria Nazionale delle Marche	54 × 41 cm	1 board	1482–1490	Vis, IRR, IRC, UVF, Vis-RS, ED-XRF, DM

Table 2. *Cont.*

Painting and Code	Location	Panel Size	Supports Description	Date	Non-Invasive Analyses
Visitation—GSV	Fano, Santa Maria Nuova Church	217 × 197 cm	6 vertical boards	1488–1490	Vis, IRR, IRC, IRCF, Vis-RS
Sacred Conversation—GSMFF	Frontino, Montefiorentino Convent	326 × 283 cm (with frame)	12 vertical boards	1489 *	Vis, IRR, IRC, Vis-RS, ED-XRF, DM
Sacred Conversation (*Buffi* altarpiece)—GSPB	Urbino, Galleria Nazionale delle Marche	330 × 221 cm	13 horizontal boards	1489 *	Vis, IRR, IRC, UVF, Vis-RS, ED-XRF, DM
Holy Martyr—GSSR	Urbino, Galleria Nazionale delle Marche	48 × 37 cm	1 board	1490–1494	Vis, IRR, IRC, UVF, Vis-RS, ED-XRF, DM
Saint Roch—SR	Urbino, Casa Raffaello	243 × 147 cm	2 vertical pieces of herringbone canvas	1490–1494	Vis, IRR, IRC, UVF, vis-RS, ED-XRF, DM
Tobias and the Archangel Raphael—GSS	Urbino, Casa Raffaello	245 × 158 cm	2 vertical pieces of herringbone canvas	1490–1494	Vis, IRR, IRC, UVF, vis-RS, ED-XRF, DM

This paper presents the results of in situ investigations, including photographic, reflectographic, spectrometric, spectroscopic and microscopic methods, focused on easel wood and canvas paintings, as they represent a quite homogeneous group from a technical point of view. In addition, a multivariate data treatment (PCA and HCA analysis) was applied to a large set of ED-XRF data acquired for the different hues investigated to verify whether the chemometric approach, scarcely ever used for paintings, can be useful to obtain more information on the painter's palette.

2. Materials and Methods

2.1. Imaging Techniques

Multispectral imaging was performed in the visible (diffused and raking light photography) and IR range (infrared reflectography, IRR; false colour infrared, named IRFC or IRC), in order to obtain information about conservation, underdrawing or changes, and also to have preliminary data on the distribution of some pigments.

IRR and IRFC analyses were carried out with a 20 Mpx Samsung digital camera (operating in the IR range 0.85–1 μm) and in some selected cases an IR remote scanning device operating in a broader IR range, the Osiris camera by Opus Instruments (InGaAs detector, spectral range 1–1.7 μm), was also used to achieve greater transparency from some painting layers. For visible light, a 16 Mpx Nikon digital camera was also employed.

2.2. Digital Micrographs (DM)

In situ preliminary observations were carried out with a Dino-Lite Universal USB digital microscope (interface USB 2.0, sensor CMOS 5 Megapixels, equipped with a polarizer, anti-reflection and IR cut-filter > 650 nm), directly connected to a PC. Images were acquired at 50× and 220× magnifications.

2.3. Reflectance Spectrometry (Vis-RS)

Diffuse reflectance spectrometry, mainly operating in the visible range (vis-RS), useful to identify some pigments of the external layers, was performed using a handheld spectrophotometer Minolta CM-2600d equipped with an inner integrating sphere (spectral range 360–740 nm, 10 nm acquisition step, d/8 geometry, UV included, 3 mm diameter spot, measurement time 1 s, specular component included and excluded). Many measurements were performed on each colour. A personal database and literature data were used to compare spectra which were processed with Microsoft Excel and Spectra Magic software.

2.4. Energy-Dispersive X-ray Fluorescence (ED-XRF)

X-ray fluorescence analysis was carried out using an Oxford Instrument X-Met 8000 energy dispersive handheld spectrometer (X-Flash SDD detector, 6 mm diameter spot, Rh target X-ray tube operating both at 8 kV, 50 μA and 40 kV, 8 μA). The measurement time was 60 s: 44 s at 8 kV, to better detect lighter elements, and 16 s at 40 kV, for heavier ones (including Sn, Sb and Ba K-lines). The data were processed using the Artax Bruker software. The ED-XRF analysis was mainly carried out on the same points selected for vis-RS investigations for a total of 340 measurement points.

2.5. Chemometric Analysis

Multivariate statistical analysis (PCA: principal component analysis and HCA: hierarchical cluster analysis) was used to obtain a description of the system by looking for a hidden pattern by data reduction based on correlations among single elements, leading to a reduced number of variables that characterize a certain group of data. We were also interested as to whether and how it could be useful to treat a large number of ED-XRF spectra with PCA and HCA, relying on the power of the statistical approach based on the availability of a large dataset of samples from the same author.

PCA and HCA elaborations on ED-XRF count per second (cps) values and the resulting graphs reported in the text (scatter plots and dendrogram) were obtained using the statistical packages of Originlab v8.0 (Northampton, MA, USA).

3. Results

The analytical campaign provided wide documentation of Santi's easel paintings covering a period of about 20 years. Table 2 refers to the current location of the artworks and the respective acronyms of the measurement points regarding vis-RS, ED-XRF and DM. All the investigations indicated in Tables S1–S7 that were carried out on the same points are described. The ED-XRF results are listed in Table S8a–f, grouped by colour. The main features concerning materials and technique are synthetically reported and discussed with the associated tables and selected images. More information is available in the supporting material (Figures S1–S10).

3.1. Supports and Preparatory Layers

Most of the examined panels were painted on wood planks arranged vertically or horizontally as appropriate and reinforced with large butterfly keys on the recto, made evident by expansions and contractions or raking light observations [10]. Following 15th-century tradition, Santi's large altarpieces are substantially rectangular, or with an arched top such as the *Annunciation* [12] and the *Buffi* altarpiece (Figure 1a,b). Generally, plank thickness ranges between 2 and 3 cm. Medium-sized and small panels consist of one or a maximum of two thin planks, usually of good quality, without the batten system, such as the six *Muses* panels of the Corsini collection attributed to Santi (Figure 1c). Uniform size and format distinguish six panels depicting the *Apostles*. The support of the small-sized devotional panel of *Holy Martyr* is made of a single plank.

The original textile support of *Saint Roch* (Figure 1d) and *Tobias and the Archangel Raphael* consists of two pieces of herringbone canvas sewn vertically [11].

Focusing on the ground layer, ED-XRF analysis carried out on the lacunas of the painting layers detected Ca and S related to calcium sulphate.

Figure 1. (**a**) *Annunciation*; (**b**) *Buffi* altarpiece; (**c**) Clio, *Corsini Muses*; (**d**) *Saint Roch*.

3.2. Underdrawing

IR reflectography, with the use of two complementary IR bands, allowed the preservation state of the painting film to be clarified and both underdrawing and changes (also called pentimenti) to be visualized. As it is known, broadband IR (1–1.7 μm range) allowed better transparency of areas painted with thicker layers or with some pigments such as copper-based ones or vermilion [13,14].

As IR reflectography images showed, Santi typically outlined figures, architectural elements or other objects with grey-black lines that appear to be executed with a thin brush soaked with a liquid carbon-based ink (Figure 2a). The incisions that are sometimes read in IR in some rectilinear and curved elements indicate the use of rulers and compasses. The brush contour drawing in various works, especially the older ones such as the *Apostles*, shows enlargements—due to unequal pressure of the brush—and undulations in the presence of some folds, according to a characteristic method of the painter. In many paintings, especially belonging to the painter's maturity, a hatched underdrawing can also be seen by IR imaging, particularly in the dress figures, under the shadows (Figure 2b) [10]. The inclination of the hatching is mainly from top right to bottom left, as typical of right-handers, but not fixed even within the same work: its direction varies to follow the volume and the shape of the different parts of the object, suggesting that the author was a versatile

draftsman. The hatching is sometimes elaborate and accurate; in other cases, it is quicker and less pronounced. The hatching was generally used to indicate the shades and shadows to be followed by paint, to have a preliminary idea of the effect of the lights and shadows and the volumes of the figures before applying the colour.

(a) **(b)**

Figure 2. IR reflectography: (**a**) the *Muses*, Clio, detail of the dress with outline underdrawing; (**b**) *Buffi* altarpiece, Baptist's mantle, detail with parallel hatching underdrawing.

A few changes were detected, and not particularly significant, as in the architecture of the building of the Annunciation or the shift back of Tobias' leg in *Tobias and the Archangel Raphael*. In the *Visitation* of Fano, the handmaid's foot in the background was drawn naked, before being covered by the pinkish shoe based on a red lake and white lead.

3.3. Pigments and Dyes

3.3.1. Blue and Violet Hues

Vis-RS analysis allowed the first reliable characterization of the pigments used in the blue and violet areas; depending on the hues, azurite ($Cu_3(CO_3)_2(OH)_2$) or natural ultramarine ($Na_7Ca(Al_6Si_6O_{24})(SO_4)(S_3) \cdot H_2O$) was mixed with variable amounts of lead white ($(PbCO_3)_2 \cdot Pb(OH)_2$) to increase the opacity of the colour [15].

The precious natural ultramarine, derived from lapis lazuli stone, can be easily detected by vis-RS because of the typical absorbance band of lazurite around 590–600 nm (Figure 3a, solid lines) and the strong increase of reflectance in the red-NIR spectrum [16]. This blue pigment cannot be unambiguously and directly revealed by ED-XRF due to the low sensitivity of the instrument to the light elements typical of the lazurite mineral (Al, Na, Si).

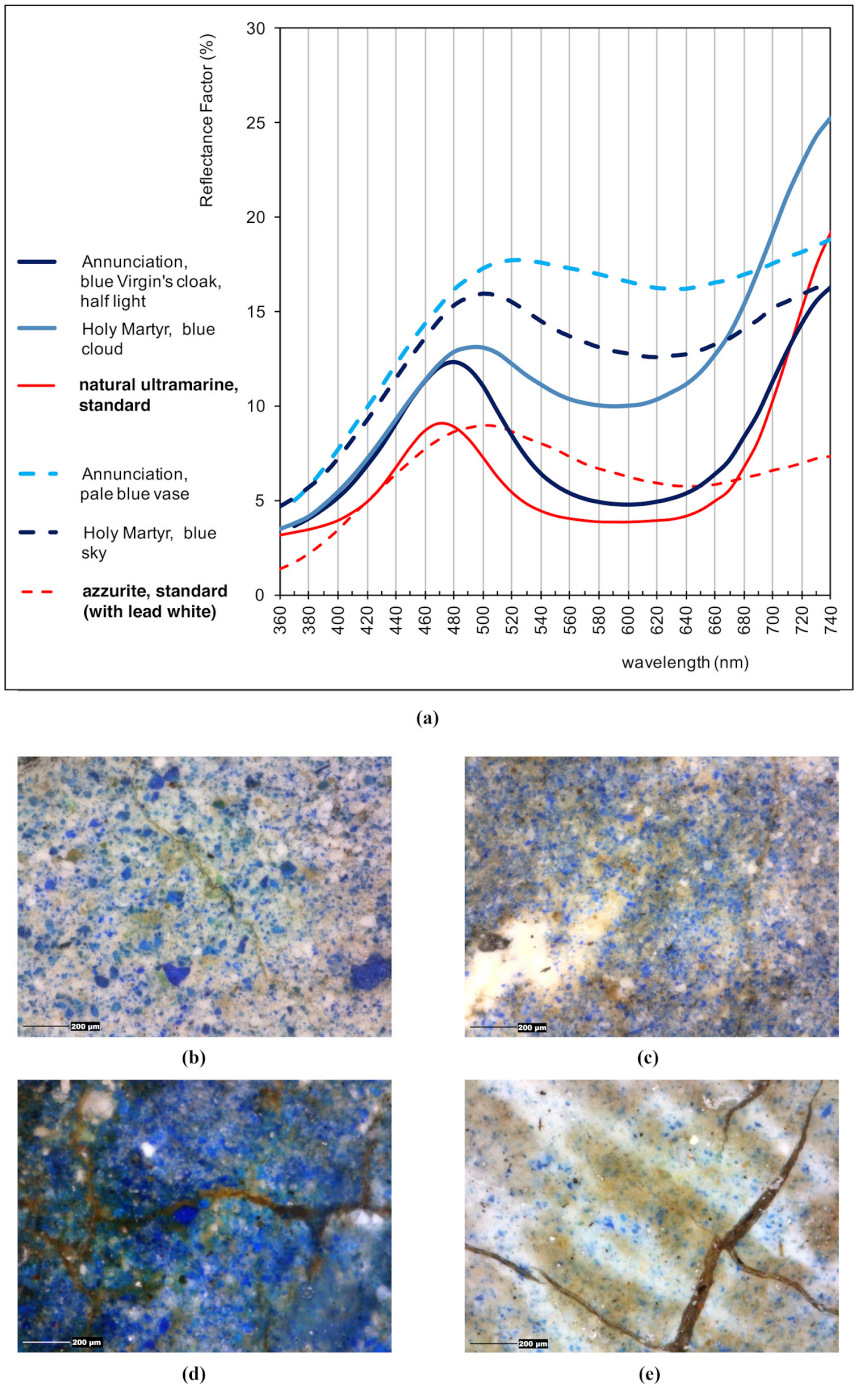


Figure 3. (**a**) Vis-RS spectra of the blue hues of the *Annunciation* and *Holy Martyr*: comparison between natural ultramarine (solid lines) and azurite (dashed lines). The reference spectra measured on standards (pigments bound in siccative oil) are displayed in red. Digital micrographs (220×): *Holy Martyr*: (**b**) blue sky, azurite, (**c**) blue cloud, natural ultramarine; *Annunciation*: (**d**) Virgin's cloak, natural ultramarine, (**e**) pale blue vase, azurite.

Natural ultramarine is the prevalent blue found in *Sacred Conversation* of Montefiorentino (GSMFF 1, 4, 29, 34, 36) (Figure S1a,b; Table S1), *Apostles* (GSST 1, 17, 18, 34), *Muses* (MC 1, 11, 17–18, 23–24), *Christ administers the Communion to Saint Peter* (CRISP 2) and *Tobias and the Archangel Raphael* (GSS 29–32).

Azurite was detected because of the typical vis-RS absorbance band around 630–640 nm (Figure 3a, dashed lines). This blue pigment is the one found in the *Sacred Conversation* of Gradara (GRAD 1, 11–13) and Fano (GSMF 1, GSMF 10, GSMF 25), and *the Martyrdom*

of Saint Sebastian (GSM 5, 10), (Table S1). In the *Buffi* altarpiece (GSPB 12–13, 23, 27), the blue areas are painted with azurite (Figure S1c,d) except for the Child's band (GSPB 11bis), made of ultramarine blue (Table S1).

According to vis-RS and ED-XRF analyses (Table S1), azurite was mixed with lead white to obtain the sky of the *Holy Martyr* (GSSR 22) (Figure 3a,b). Probably, the blue shade of clouds (GSSR 20–21; Figure 3a,c) and the sea (GSSR 106) was, conversely, obtained by overlapping natural ultramarine on the azurite layer. In the Virgin's mantle of the *Annunciation* (GSA 7–8) and in the sky shading (GSA32 bis-33bis), ultramarine was identified in the upper layer by vis-RS, while Cu was detected by ED-XRF (Figure 3a,d), indicating a double layering too [17]. The data support the hypothesis that the same technique was used in the sky shading and the mountains of *Saint Roch* (SR 1–2, 4). Natural ultramarine was detected in the far mountains (GSA 27) and God's globe (GSA 34bis), while azurite was identified in the peculiar blue hue of the vase (GSA 31; Figure 3e; Table S1).

The natural ultramarine pigment was mixed or overpainted with a coccid-derived red lake (such as kermes or some European cochineal), sometimes brightened with lead white, to create violet hues (Table S2). This is the case of the shoes (MC 5) and the robe of the *Muses* (MC 34); the shadow of the mantle (GSST 2) and the book of the *Apostles* (GSST 35); and several figures' clothes of the *Sacred Conversation* of Montefiorentino and the angel of the *Annunciation* (Figure S2a–c). In *Tobias and the Archangel Raphael*, the red lake was sometimes mixed with ultramarine blue (GSS 11) and sometimes with azurite (GSS 5). The occurrence of Mn, detected by ED-XRF in the red lake-rich areas, could suggest the use of powdered glass [18,19].

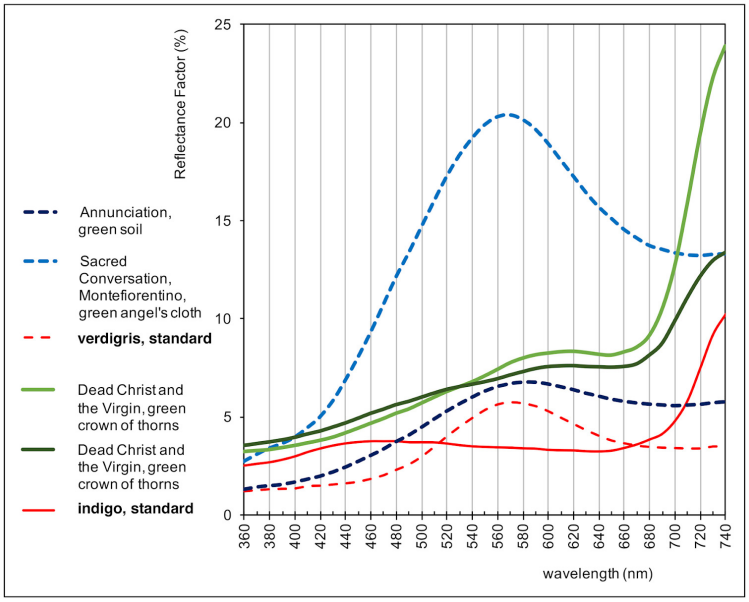
In the violet dress of the praying woman of the *Buffi* altarpiece (GSPB 17–18), natural ultramarine with the red lake was applied on a Cu-based layer (Figure S2d–f; Table S2). The same mixture was also used in the *Holy Martyr* to glaze the robe in the shaded areas (GSSR 109). Azurite and the coccid-derived red lake were used in the dresses of *Sacred Conversation* of Gradara (GRAD 23) and *Martyrdom of Saint Sebastian* (GSM 7, 12). In the latter panel, the same combination was used in the loincloth and in the *Dead Christ in the Sarcophagus with the Symbols of the Passion* (GSCSP 8). Indigo and the coccid-derived red lake [20] were identified in the *Dead Christ and the Virgin* (GSCM 40–41).

3.3.2. Green Hues

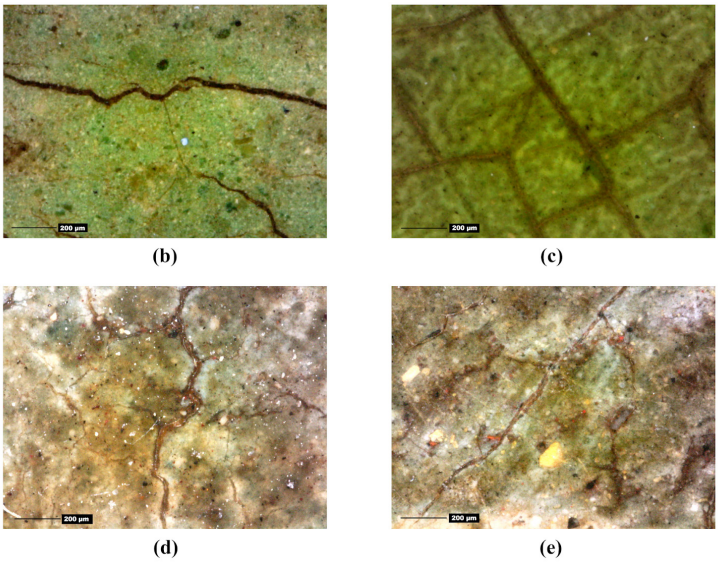
In the green the vis-RS analysis allowed the wide use of copper acetate or verdigris ($Cu(C_2H_3O_2)_2$-$2Cu(OH)_2$) to be identified due to the absorbance band around 720 nm shown in some spectra (Table S3). ED-XRF detected the presence of Cu-based pigments mixed with Pb-Sn yellow (Pb_2SnO_4 or $PbSnO_3$) such as in the *Muses* (MC 8, 37, 38; Table S3), *Christ administers the Communion to Saint Peter* (CRISP 3), *Martyrdom of Saint Sebastian* (GSM 3–4), *Saint Roch* (SR 9) and *Tobias and the Archangel Raphael* (GSS 1, 4). Sometimes Fe-based pigments were also detected (Table S3) such as in the Apostles (GST 29, 41), the *Buffi* altarpiece (GSPB 15, 24), and the *Sacred Conversation* of both Gradara (GRAD 6, 22) and Montefiorentino (GSMFF 19, 37, 51; Figure S3a,b).

In the green soil of the *Annunciation*, Santi used pure verdigris (GSA 10; Figure 4a, lower dashed curve, and Figure 4b). The Cu-acetate was usually mixed with Pb-Sn yellow (GSA 2, 19, 71; Table S3), adding a few azurite particles in the far hill (GSA 28).

According to the digital microscopy, in the green crown of thorns of the *Dead Christ in the Sarcophagus with the Symbols of the Passion* (GSCSP 1), green particles probably related to malachite ($Cu_2(CO_3)(OH)_2$ were observed, mixed with As-based yellow pigment (probably orpiment: As_2S_3) and Fe-based pigments (Figure S3c,d; Table S3). As an exception, in the small-sized panel of *Dead Christ and the Virgin* (GSCM 1), the green tone of the crown of thorns is a mixture of blue and yellow pigments (Figure S3e,f). Vis-RS analysis revealed the use of indigo (Figure 4a,d,e), with its typical 650–660 nm abs. band [21], combined with As-based pigment (probably orpiment) and Fe-based pigments, detected by ED-XRF.



(a)



(b) (c)

(d) (e)

Figure 4. (**a**) Vis-RS spectra of green hues: comparison between verdigris (dashed lines) and a mixture of indigo with As-containing yellow (solid lines). The reference spectra measured on standards (pigments bound in siccative oil) are displayed in red. Digital micrographs (220×): (**b**) *Annunciation*, green soil; (**c**) *Sacred Conversation of* Montefiorentino, green angel's cloth; (**d**,**e**) *Dead Christ and the Virgin*, green crown of thorns.

3.3.3. Yellow and Brown Hues, Gold

In almost all the paintings, ED-XRF and vis-RS analyses carried out in yellow areas (GSMF 4, 6, 36, 31–32; GSS 2; GRAD 2–3; MC 6; GSMFF 11, 47) detected Pb and Sn related to lead-tin yellow and Fe-based pigments (Figure S4a,b; Table S4). Brown hues containing Fe indicate the presence of yellow/brown ochre or earth, testified by the 450 nm Fe^{3+} band in vis-RS [22]. In the brownish areas and shadows, Cu-based green pigments were added to darken the yellow hues as can be seen in *Saint Roch* (SR 12) and the *Buffi* altarpiece (GSPB 25). Sometimes, Pb-Sn yellow and Fe-based pigments were applied on a Cu-based layer (GRAD 4). Vermilion was used for conveying a warm tone to the brownish hues in *Saint Roch* (SR 6, 8), *Muses* (MC 14), *Holy Martyr* (GSSR 25), *Sacred Conversation* of Montefiorentino (GSMFF 40, 13), Apostles (GSST 4, 24) and the *Buffi* altarpiece (GSPB 7).

Concerning the gilding decorations (Table S4), Santi used gold for a few details only in Saint John the Evangelist (GSST 27; Figure S4c,d) while lead-tin yellow was used to depict embroidered hems and other decorations in *Sacred Conversation* of Fano (GSMF 6, 31–32, 36; Figure S4e,f), *Sacred Conversation* of Gradara (GRAD 2, 4) and *Muses* (MC 14, 36).

In the *Annunciation*, the decorated motif on the edge of the Virgin's cloak is based on orpiment, such as its lining (GSA 8bis, 34).

3.3.4. Grey and Black Hues

As it is known, ED-XRF is not useful for identifying organic black pigments due to the low Z number of their characteristic chemical elements. However, trace amounts of some inorganic elements such as Ca, S and K can be related to carbon black [23,24]. These elements were found in most of the grey and black areas, such as in *Annunciation* (GSA 36), *Muses* (MC 35) and *Sacred Conversation* of Montefiorentino, but only future micro-invasive analyses should confirm this. Conversely, bone/ivory black can be hypothesised for the P occurrence, such as in many of the grey and black hues of the Montefiorentino altarpiece.

As expected, vis-RS was not able to distinguish between carbon black and phosphorous-based black, but it allowed us to detect some blue pigments added, such as natural ultramarine and azurite. The first precious blue pigment was added to obtain the grey hues of the armours in the *Sacred Conversation* of Montefiorentino (GSMFF 44–46, 50). Azurite was identified in the grey hue of the capital of the *Annunciation* (GSA 32, Table S5). Equally, Cu-based pigment was revealed by ED-XRF in the black shadows of the armour of Count Oliva (GSMFF 78), in the black hues of Saint George's armour and chain mail (GSMFF 73–76; Figure S5a–c), in Saint Anthony Abbot's mantle (GSMFF 77), in the praying man's black dress (GSPB 22) of the *Buffi* altarpiece, in the black angel's collar of the *Annunciation* panel (GSA 36), in the black dresses and architecture of the *Buffi* altarpiece, in Melpomene's black horn (MC 35), in the dark grey of the architecture of the Saint Philippe panel (GSST 16) and in some black areas of *Sacred Conversation* of Fano (GSMF 34–35). Azurite was observed by DM in the small-sized devotional panels of *Dead Christ in the Sarcophagus with the Symbols of the Passion* (GSCP 17) and *Dead Christ and the Virgin* (GSCM 32–33; Figure S5d,e) (Table S5). In the architectural wooden frame of the Montefiorentino altarpiece, As-based pigments and bone black ($Ca_5(OH)(PO_4)_3$)) were detected in the greyish false marble decoration (GSMFF 52–55). Lead white and Fe-based pigments were used to modify the hues as well as a small amount of vermilion (HgS) found in Melpomene's black horn (MC 35; Table S5).

3.3.5. Red, Pinkish Hues and Flesh Tones

In the *Sacred Conversation* of Fano (Figure S6; Table S6), a madder-type lake [20], extracted from the roots of Rubia sp., was also detected due to the bands at 510 and 550 nm, highlighted because of the contribution of purpurin [25,26]. In this altarpiece, the madder-type lake and the Child's drapery were used for a few details (GSMF 51). A coccid-derived red lake (carmine-type) was detected in many paintings (Figure S6; Table S6) because of 520–530 and 570 nm absorption bands [27,28]. The colours of Saint Roch's robe (GSMF 13), St. Helen's mantle (Figure S8a–c; GSMF 17) and the carnation flower held by the Christ Child (GSMF 22) were obtained with a coccid-derived lake (Figure 3a) [10]. In the Virgin's red dress (GSMF 19) and in the drape of honour behind her (GSMF 23), spectra with intermediate characteristics can be observed, and a mixture of the two red lakes can be hypothesized.

Mn was detected by ED-XRF in the *Tobias and the Archangel Raphael* (GSS 8), in the *Sacred Conversation* of Fano (GSMF 23) and Montefiorentino (GSMFF 16, 23–26, 32–33, 65, 68), and in the *Martyrdom of Saint Sebastian* (GSM 1, 6). Its presence could be related to powdered glass [18,19], probably added to the red lake to improve the drying of oil paint [29], or perhaps to reach a different consistency and fluidity of the paint, or to obtain a diverse effect of the layer brightness. Red lake glazing depicted with meticulous hatching occurs in the shades of many of Santi's paintings such as in the Angel's mantle of the *Annunciation* and in the Baptist's mantle of the *Buffi* altarpiece (Figure S7a–c).

Vermilion was used in bright red hues such as in St. Paul (GSST 4). Sometimes it was applied as an underpainting of red lakes, such as in *Saint Roch* (SR 5) and Clio (MC 20, 25–26) panels, or mixed with them.

As-based pigments, such as orpiment and realgar (As_4S_4), occur in the deeper orange shades mixed with vermilion or overpainted on it (Table S6) such as in the *Sacred Conversation* of Fano (GSMF 3) and Montefiorentino (GSMFF 18, 22, 49, 65), in *Annunciation* (GSA 12–13), Erato (MC 43), the *Buffi* altarpiece (GSPB 11, 20) and Saint Roch (SR 5).

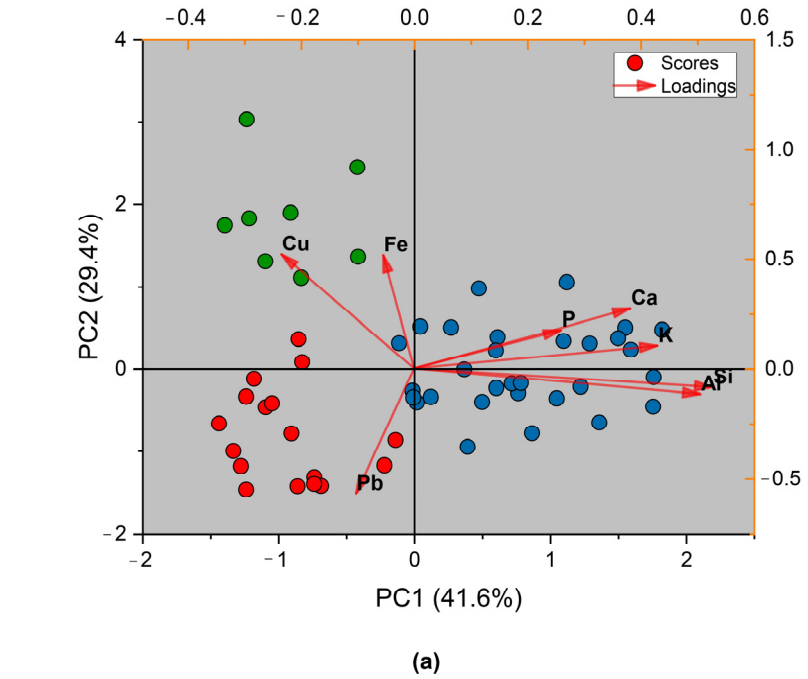
Vis-RS and ED-XRF analyses carried out on the flesh hues of females and the Child (Table S7) identified lead white and small amounts of vermilion (GSSR 19; GRAD 4; GSMFF 27) mixed with ochre (GRAD 5, GSCM 28), depending on the desired hue. Sometimes green Cu-based pigments (GSST 8; GSMFF 29–31; GSPB 8, 10, 31) and bone black were added.

In the little devotional panel of the *Dead Christ in the Sarcophagus with the Symbols of Passion* (GSCSP 7), the flesh tone was depicted using lead white, green Fe-based pigment very finely ground, applied on a green earth-based layer, perhaps to allow a bruised appearance (Figure S8a,b). As usual, male flesh tones are typically darker than females' (Figure S8c,d) or children's ones, with higher contents of Fe-based pigments and charcoal black, the latter seen in DM (Figure S8e,f). Shadows were obtained with thin glazes containing brown pigments (probably earth) and black particles.

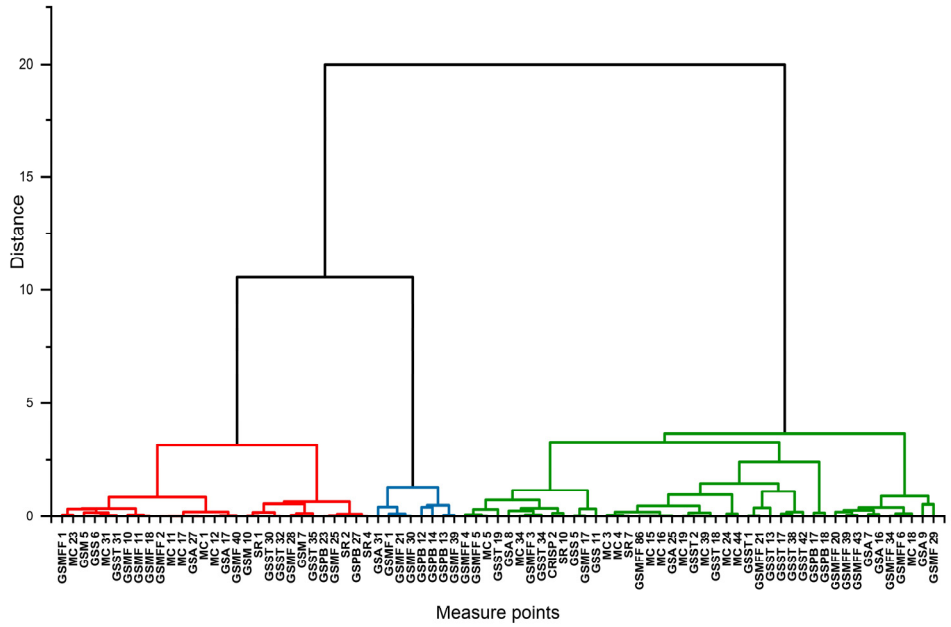
3.4. Multivariate Statistical Analysis

Multivariate statistical analysis was applied to the ED-XRF data to identify additional latent information from the elemental composition. This is made possible, in particular, when the number of spectra, about 340, is such that overall reasoning can be useful to support the interpretation of the statistical results. The measurement areas were preliminarily grouped by autoptic observation according to their hue and then submitted to multivariate data treatment; only the data related to the blue and red hues was further considered, whereas the remaining data connected to the other hues did not bring any useful or interesting information to discuss. HCA classification results were incorporated on PCA plots by using the same colour codes for the dots for better reading.

Regarding blue areas (56 ED-XRF spectra), HCA clearly defines similarities within two main blocks (Figure 5b, red and green branches on the top against the blue branch on the downside) that in the PCA biplot are in correspondence with the measurement points characterized by the predominance or the absence of Cu (Figure 5a, negative PC1 and positive PC2), i.e., paint layers based on azurite or, conversely, ultramarine as previously identified by vis-RS. In addition, HCA splits the Cu-rich areas into two subgroups (red and green branches in Figure 5b) that PCA identifies as depending on the presence or the absence of Pb (Figure 5a, positive/negative PC2), which typically refers to sky or clouds. On the contrary, the group of data on the blue branch of HCA corresponds to measurement points with positive PC1, identifying blue hues related to the use of ultramarine blue as confirmed by vis-RS. A minor contribution of Cu on ultramarine areas can be assessed by PCA for those points in the region of positive PC1 and PC2, but that HCA cannot clearly identify; probably they are related to the use of both ultramarine and azurite (mixed or layered) as previously identified by vis-RS. In addition, it is worth noting how differentially the two blue pigments are used among the analysed artworks: most of the data acquired on *Apostles* (GSST), *Sacred Conversation* of Montefiorentino (GSMFF) and the *Muses* (MC) are aggregated on the positive PC1 quadrant (Figure S9a–c), i.e., there is a prevalence of use of the precious ultramarine pigment; whereas the data regarding the *Sacred Conversation* of Fano (GSMF) are aggregated on negative PC1 (Figure S9d) with both blue clothes details and pale sky areas made with azurite. *Annunciation* (GSA) and the *Buffi* altarpiece (GSPB) are equally spread both on positive and negative PC2 (Figure S9e,f), indicating two blue pigments used to obtain the desired blue hues depending on the subject (i.e., azurite for the dress of the Virgin—GSPB 12, 14—against ultramarine for the dress of the praying woman GSPB 17–18).



(a)

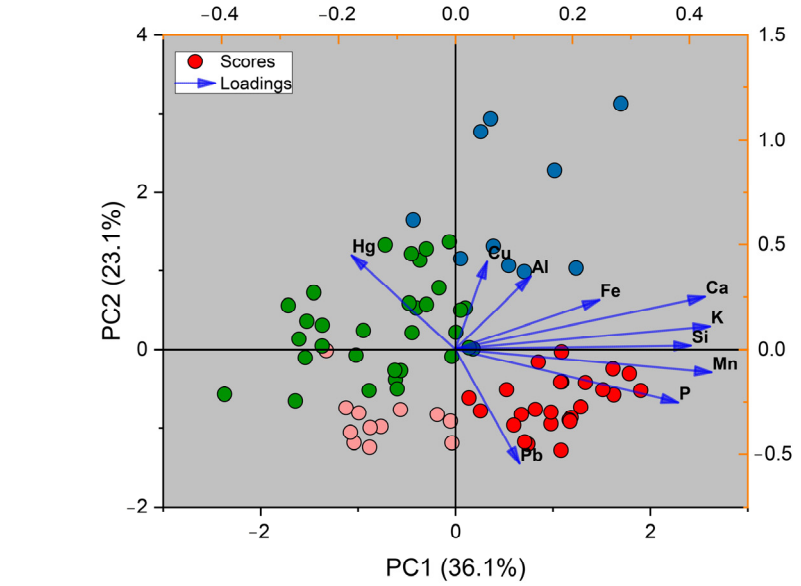


(b)

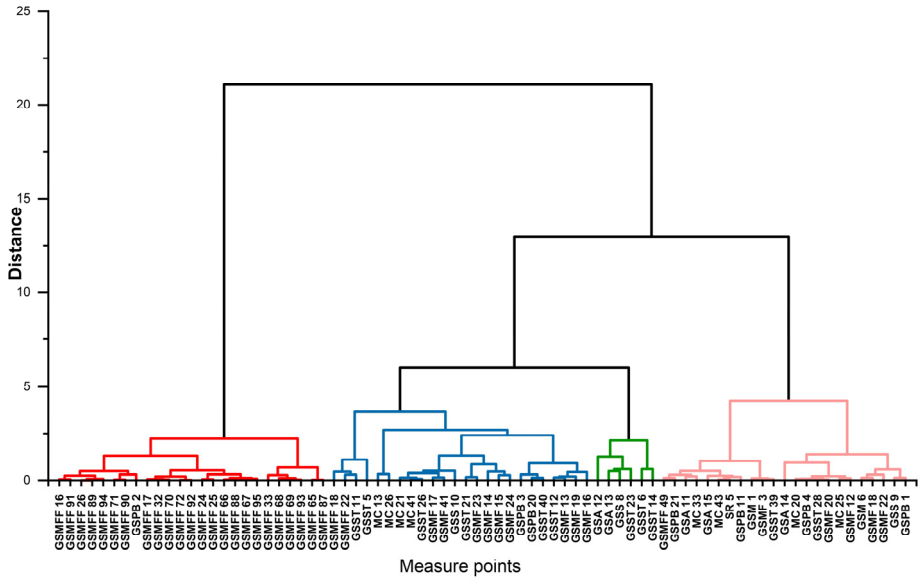
Figure 5. Blue hues: (**a**) loading and score plots of PCA; (**b**) clusterization by ward method on count per second (cps) of the main elements found in the areas evaluating squared Euclidean distance.

Comparable information is obtained with the red hues: Figure 6a reports score and loading plots for 78 red points aggregated in four groups also visible in the HCA where two main blocks are highlighted (Figure 6b). The more numerous HCA branch is subdivided into three subgroups (labelled blue, green and pink in Figure 6b) emphasizing the use of Hg-based pigment (upper-left quadrant with negative PC1 and positive PC2 in Figure 6a) against the use of the red lake (confirming by Vis-RS), characterized by the presence of some elements that are possibly related to the dyestuff preparation technique (Al, P, Ca, positive PC1, red dots, red HCA branch). Moreover, the vermilion-rich areas split up into the more pure red brilliant hues (green dots in Figure 6a) against the purple-red hues or

shadow areas in which Cu pigments (blue dots, blue HCA branch in Figure 6b) were also used or the paler Pb-reach hues (pink dots, pink HCA branch in Figure 6b). The occurrence of Fe, Mn and Si in the red lake areas is probably related to the use of powdered glass (SGMF 17; GSS 8; GSMFF 16; GSPB 1; GSA 12–13) [18].



(a)



(b)

Figure 6. Red hues: (**a**) loading and score plots of PCA; (**b**) clusterization by ward method on count per second (cps) of the main elements found in the areas evaluating squared Euclidean distance.

Moreover, the distribution of scores and loading plots (Figure S10) suggests the use of red dyestuff and Hg-based pigment in different ways and concentrations in all the paintings and highlights the prevalence of the red lake only in the *Sacred Conversation* of Montefiorentino (GSMFF).

4. Discussion

The wooden supports of Santi's paintings are built according to the central Italian tradition. Conversely, the yarn of Santi's investigated canvases (painted in 1490–1494), with a herringbone structure, appears to be completely uncommon for a painting of the time because it spread starting from the following century. It is possible that Santi sought to experiment with this type of canvas to take advantage of some surface texture effects or to verify its greater stability and resistance than the conventional yarn used in *Saint Jerome* many years before (1475–1478), kept in the Vatican Museums [11].

IR reflectographic images allowed a characteristic hatched underdrawing to be highlighted while the few changes indicate that the painter carefully studied the compositions before painting. The use of hatched underdrawing for shading is quite rare in the 15th century in central Italy, particularly in Tuscany and Umbria, perhaps less in the Marches, while it is well documented in the Ferrara area (Cosmè Tura, Ercole de' Roberti, etc.) and in the Veneto area, in the workshops of Jacopo and above all Giovanni Bellini [30] and Giambono [31], but also in the young Mantegna [32], a painter particularly praised by Santi in his manuscript so-called "Cronaca rimata" [33].

Regarding pigments, the results achieved by the multi-analytical approach confirmed that Santi's painting palette is coherent with Renaissance practice [34] and it is composed of natural ultramarine, azurite, indigo (detected only in two cases and quite rare in the late 15th century), Cu-based pigments, lead white, lead-tin yellow, As-based pigment, Fe-based pigments, vermilion, red carmine-type lake and madder lake.

The painter used natural ultramarine in blue hues such as in the *Sacred Conversation* of Montefiorentino, the *Muses*, the *Apostles* and *Christ administers the Communion to Saint Peter*. At least some of them were commissioned by high-end clients and the choice of a precious blue pigment can be related to the client's willingness to spend. Instead, the less expensive azurite is the prevalent pigment found in *Sacred Conversation* of Gradara, *Martyrdom of Saint Sebastian* and the *Buffi* altarpiece.

According to the results, the clothes were usually painted using natural ultramarine while azurite was employed for the sky. Otherwise, the two pigments were mixed or sometimes a glaze of natural ultramarine was overlapped on an azurite layer, such as in the *Holy Martyr* and Annunciation. The blue ultramarine was also mixed with a coccid-derived red lake to obtain violet hues found in the *Sacred Conversation* of Montefiorentino or overlapped on the azurite paint such as in the *Buffi* altarpiece. Santi employed green Cu-based pigments, particularly verdigris, mixed with Pb-Sn yellow to obtain different hues.

Only in the *Dead Christ and the Virgin* was the green tone of the crown obtained by mixing indigo with As-based pigment (probably orpiment) and ochre. The mixture of indigo and orpiment, quite rare in the late 15th century, is mentioned by Cennino Cennini in his treatise on painting, written in the late 14th–early 15th century [35].

The yellow hues and some embroidered hems were obtained generally using Pb-Sn yellow; orpiment and gold were found respectively in the *Annunciation* and in the *Apostles*.

The artist frequently used lead white, pure—for highlights and subtle brush finishes—or mixed with black to obtain grey tones. Some blue pigments were detected in grey and black hues, such as the blue ultramarine in the armours of Count Oliva and Saint George (*Sacred Conversation* of Montefiorentino) or azurite both in the architecture and the black dress of the *Buffi* altarpiece. Probably, the precious blue pigments were used to obtain a particular grey: the use of ultramarine ashes is in fact attested in the greyish-blue hue of the horses' harness of the Jacopo di Cione *Crucifixion* (about 1360–1370) [36]. In the case of black hues, Cu-based pigments were also added to increase siccative properties [19,37].

Vermilion, red lakes or Fe-based pigments were used with lead white in red shades and flesh hues. An archaic mixture, typical of Medieval practice and unusual for the Renaissance, composed of lead white and green Fe-based pigment overlapped to a green earth-based layer, was used in the flesh tone of the *Dead Christ in the sarcophagus with the Symbols of Passion*.

A European coccid-derived red lake (carmine-type I) was mostly detected in Santi's paintings while a madder lake occurs only in *Sacred Conversation* of Fano. Despite the madder lake being less expensive than the coccid-derived red lake (carmine-type) [38], it was quite uncommon in Italian painting at this time becoming more employed after 1500, while it was already used in Netherlandish paintings [39]. According to Flemish tradition, Santi applied meticulous hatching red lake glazing to achieve the effect of lights and shades [40].

The presence of colourless powdered glass containing Mn, previously attested in red and green hues of the *Tobias and Archangel Raphael* and *Saint Roch* canvas paintings [11], was confirmed with this study on Santi's panel paintings. The addition of colourless glass powder in oil paintings (15th and 16th centuries), to reduce the drying time or perhaps to give more body to the pigment layer, seems to be a more diffused practice than once known [19,26,29,41–43]. The earlier use of this technique is attested in north European paintings to the 1430s in Netherlands and Germany [29]. The glass powder was detected both in the *Music* [19], attributed to Justus of Ghent (1470s), and the *Comunione degli Apostoli* [44] painted by the Flemish painter in Urbino (1472–1474).

The use of colourless powdered glass is attested also in Perugino and Raphael [19], probably transmitted by the Flemish master or by Santi himself, who well knew Perugino. Therefore, Santi seems to be the first Italian painter who experimented with powdered glass and it is probable that he learned this practice during the stay of Justus of Ghent in Urbino.

5. Conclusions

The huge non-invasive diagnostic campaign carried out on 26 of Giovanni Santi's easel paintings belonging to different periods allowed us to obtain a great deal of information which converged into a database related to central Italy Renaissance painting materials and techniques.

The IR reflectography observation allowed us to distinguish a distinctive style attributable to a single artist, presumably Santi himself: fluid, modulated and continuous in contour lines, and close and regular in the hatching, with proper characteristics. The hatched underdrawing is a peculiarity uncommon at that time in central Italy. Overall, it is hard to define whether some collaborator or pupil of Santi's workshop had a part in the underdrawing, at least copying it from cartoons.

According to the results, Santi employed a wide number of pigments: lead white, natural ultramarine blue, azurite, lead-tin yellow, Fe-based pigments, copper-based green pigments including verdigris, bone black, vermilion, coccid-derived red lakes and, in one painting, also madder lake. He used very rarely indigo, orpiment and probably malachite.

The importance of reflectance spectroscopy, supported by both ED-XRF results and multivariate data treatment of the ED-XRF spectra, to identify many pigments is confirmed in this work. In particular, the vis-RS technique proved to be a simple and effective diagnostic tool in detecting indigo in mixtures and distinguishing between two different types of red lakes, avoiding sampling and complex chromatographic or micro-Raman analyses.

The use of powdered glass, especially in red lakes, was hypothesized thanks to ED-XRF analysis and subsequently verified by micro-samples (the results of which will be presented in a forthcoming paper) in various of Santi's panel paintings, and was previously attested in two canvas paintings.

The results of this research indicated that Santi's painting activity was still based on the Italian tradition, for both the underdrawing and the painting materials, but with some interesting specificities that are typical of this painter, some of which fall within the ambit of experimentation, including herringbone-type canvas.

Apart from the innovative introduction of powdered glass in his painting technique, probably due to the observation of the Flemish painter Justus of Ghent, Santi generally used the pigments in a quite traditional way but sometimes experimented with different chromatic effects and mixtures uncommon for that period.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app13063581/s1. Figure S1: (a) *Sacred Conversation*, Montefiorentino, pale blue sky, detail (b) digital microscope micrograph (220×) (c) *Buffi* altarpiece, pale blue sky, detail (d) digital microscope micrograph (220×). Figure S2: Annunciation altarpiece: (a) Angel's arrow (b) detail (c) digital microscope micrograph (220×) of the area marked in the previous Figure S2a. Buffi altarpiece: (d) praying woman violet dress (e) detail; (f) digital microscope micrograph (220×) of the area marked in the previous Figure S2d. Figure S3: Sacred Conversation, Montefiorentino: (a) Count Oliva, detail (b) digital microscope micrograph (220×) of the area marked in the previous figure. Dead Christ in the sarcophagus with the Symbols of Passion: (c) detail (d) digital microscope micrograph (220×) of the area marked in the previous figure. Dead Christ and the Virgin: (e) Christ's crown of thorn, detail (f) digital microscope micrograph of the thorn (220×). Figure S4: Sacred Conversation, Montefiorentino: (a) angel's dress, detail (b) digital microscope micrograph (220×) of the area marked in the previous figure. The Apostles: St. John the Evangelist's robe edge decoration (c) detail (d) digital microscope micrograph (220×) of the area marked in the previous figure. Sacred Conversation, Fano: (a) St. Helen's detail and (b) her robe damask decoration. Figure S5: Sacred Conversation, Montefiorentino: (a) St. George's chain mail (b) detail (c) digital microscope micrograph (220×) of the area marked in the previous Figure S5a. Dead Christ and the Virgin: (d) detail (e) digital microscope micrograph of the black background (220×). Figure S6: Vis-RS spectra of red hues due to red lakes in the Sacred Conversation of Fano: (a, dashed line) coccid-derived lakes vs. (b, solid line) madder-type lake, and (c, black dotted line) a possible mixture of both. Figure S7: Buffi altarpiece: (a) detail of the Baptist's mantle (b) a detail with red lake-based hatching (c) digital microscope micrograph (220×) of the area marked in the previous Figure S7b. Figure S8: Flesh tones. Dead Christ in the Sarcophagus with the Symbols of Passion: (a) detail (b) digital microscope micrograph (220×) of the area marked in the previous figure. Holy Martyr: (c) detail (d) digital microscope micrograph (220×) of the area marked in the previous figure. Sacred Conversation, Montefiorentino: (e) detail with St. Francis (f) digital microscope micrograph (220×) of the area marked in the previous figure. Figure S9: PCA score and loading plots for blue hues labelled as indicated: (a) Apostles: GSST (b) Sacred Conversation of Montefiorentino: GSMFF (c) Corsini Muses: MC (d) Sacred Conversation of Fano: GSMF (f) Annunciation: GSA (e) Buffi altarpiece: GSPB. Figure S10: PCA score and loading plots for red hues labelled as indicated: (a) Apostles: GSST (b) Sacred Conversation of Montefiorentino: GSMFF (c) Corsini Muses: MC (d) Sacred Conversation of Fano: GSMF (e) Annunciation: GSA (f) Buffi altarpiece: GSPB. Table S1: Results of non-invasive analyses carried out on representative blue hues. Table S2: Results of non-invasive analyses carried out on representative purple/violet hues. Table S3: Results of non-invasive analyses carried out on representative green hues. Table S4: Results of non-invasive analyses carried out on representative yellow, brown hues and gildings. Table S5: Results of non-invasive analyses carried out on representative black and grey hues. Table S6: Results of non-invasive analyses carried out on representative red and pinkish hues. Table S7: Results of non-invasive analyses carried out on representative flesh hues. Table S8: ED-XRF data.

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