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Non-invasive characterization of Bernardino Luini's color palette: a spectroscopic campaign on the frescos of Santuario della Beata Vergine dei Miracoli in Saronno (Italy)

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***Abstract* – One of the greatest masters of northern Italian art between the 15th and 16th centuries is certainly Bernardino Luini, who was strongly influenced along with other important artists of his period by the painting technique of Leonardo da Vinci. In this paper, we report the results of the analytical campaign conducted on two wall paintings depicting the Marriage of the Virgin and the Adoration of the Christ Child made by Luini in the Santuario della Beata Vergine dei Miracoli in Saronno (Italy) between 1525 and 1529. The multi-analytical approach through X-ray fluorescence (XRF), Fourier transform infrared reflection (R-FTIR) and Raman spectroscopy allowed us to characterize the color palette used in the paintings and thus, through comparison of the results, to provide support for a more certain attribution of the Adoration of the Christ Child.**

I. INTRODUCTION

Bernardino Luini (1481 ca. - 1532) was certainly one of the greatest exponents of northern Italian art and painting at the turn of the 15th and 16th centuries. Over the entire period of his activity, Bernardino was strongly influenced by the work and techniques of Leonardo da Vinci (1452 - 1519), to such an extent that he is considered one of the major exponents of the so-called Leonardeschi, together with other significant artists as Francesco Melzi (1491 - 1570), Gian Giacomo Caprotti (1480 - 1524), Ambrogio De Predis (1455 ca. - 1509), and Giovanni Antonio Boltraffio (1467 - 1516). It is unclear whether he was ever a pupil of Leonardo directly, but he certainly adopted in his art many of the characteristics also expressed by the Master in his painting [1].

This paper presents the methodology and discusses the results of the non-invasive analytical campaign conducted on two frescos painted by Bernardino Luini between 1525 and 1529 in the Santuario della Beata Vergine dei Miracoli in Saronno (Italy). The fresco depicting the Marriage of the Virgin is located inside the church, in the area of the ante presbytery, while the other, portraying the Adoration of the Christ Child and whose attribution to Luini is still debated, is located outside under the portico on the left side [2].

With the aim to characterize the color palette used in the paintings and thus, through comparison of the results, to provide support for a more certain attribution of the Adoration of the Christ Child, a non-invasive multi-analytical campaign was undertaken [3,4]. The on purpose

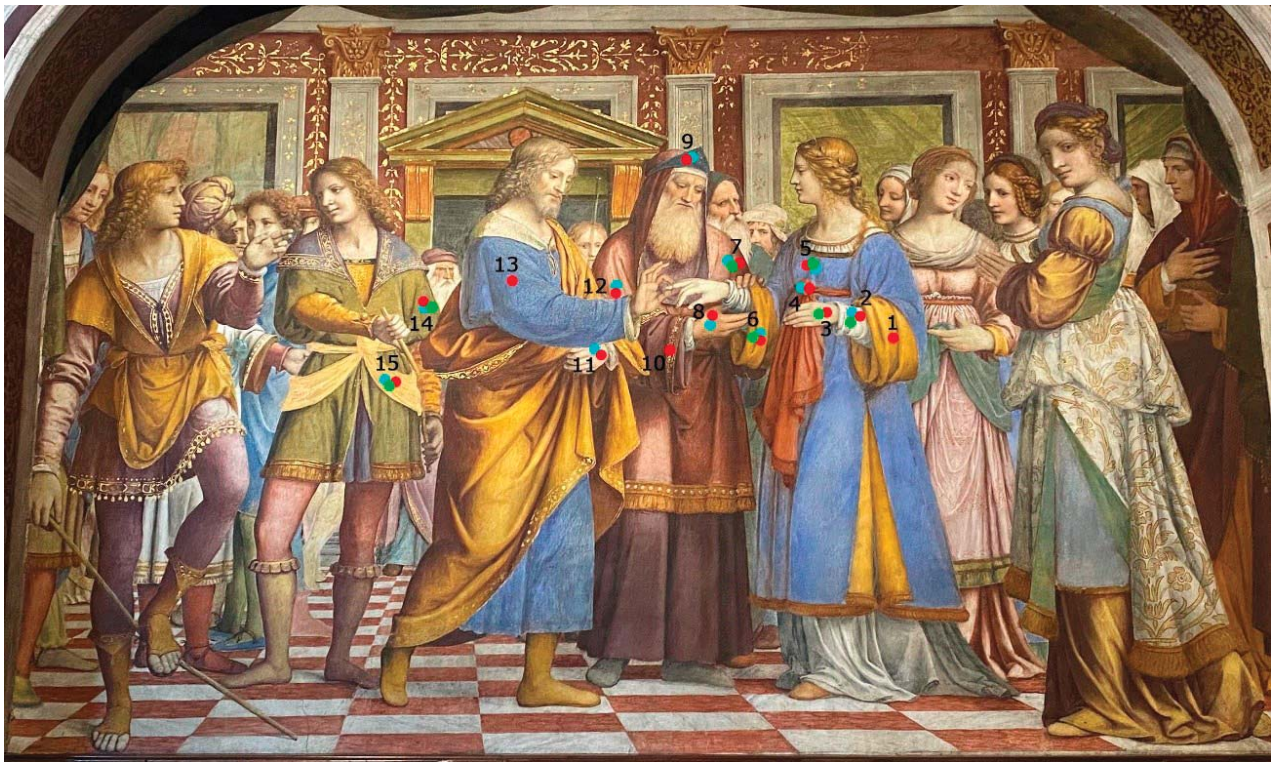

Figure 1. Visible image of the Marriage of the Virgin with the different analytical spots acquired on the fresco with XRF (red), R-FTIR (green), and Raman (light blue) marked.

selected portable spectroscopic equipment included X-ray fluorescence (XRF), Fourier transform reflectance infrared (FTIR) and Raman spectroscopies. The results collected through the three techniques allowed us to gain information about the elemental and molecular composition of the mineral pigments used in the frescos, as well as to identify the degradation phases related to the different preservation states of the two artworks.

II. EXPERIMENTAL

II.A X-Ray Fluorescence (XRF)

Non-invasive and in-situ XRF analyses were performed with a portable XRF spectrometer EIS XRS 38, equipped with a Silicon Drift Detector (SSD) and a low-power X-ray tube (W anode). The analytical spot diameter was 3 mm. The selected working conditions were measuring time 60 s, tube voltage 30 kV, tube current 30 μA, and acquisition channels 2048 [5,6]. Data were acquired and processed using the DPPMCA software.

II.B Reflection FTIR spectroscopy

The two frescoes were investigated by non-invasive FTIR analysis using an Alpha portable spectrometer (Bruker Optics, Germany/USAMA). The spectrometer is equipped with an R-Alpha external reflectance module (optical layout 23°/23°). The compact optical bench consists of a Globar, a permanently aligned RockSolid interferometer (with gold mirrors) and an uncooled DLaTGS detector. It was employed at a working distance of 15 mm, thus analyzing spots of about 5 mm in diameter. Pseudo-absorbance spectra [log(1/R); R = reflectance] were acquired in the range between 7500 and 375 cm^{-1}, with a spectral resolution of 4 cm^{-1}. Spectra from a gold flat mirror were used as background. Reflection infrared spectra were transformed, when necessary, into absorbance spectra by applying the Kramers-Kronig Transformation (KKT) [7]. Data were acquired and processed using OPUS 7.2 software package.

II.C Raman spectroscopy

Raman analyses were carried out by means of a BWTek i-Raman EX portable spectrometer. The instrument is equipped with a fiber optic probe of 85 μm diameter and a Nd-YAG laser source emitting at 1064 nm. All the spectra were obtained as an average of 20 - 40 scans in the spectral range 200 - 2500 cm^{-1}, with a resolution of 4 cm^{-1}. All data were acquired and processed by means of the BWSpec software.

III. RESULTS AND DISCUSSION

III.A The Marriage of the Virgin

On the fresco painted by Luini inside the church, five different colors were identified as significant: white, yellow, red, blue and green (Figure 1). In addition, some

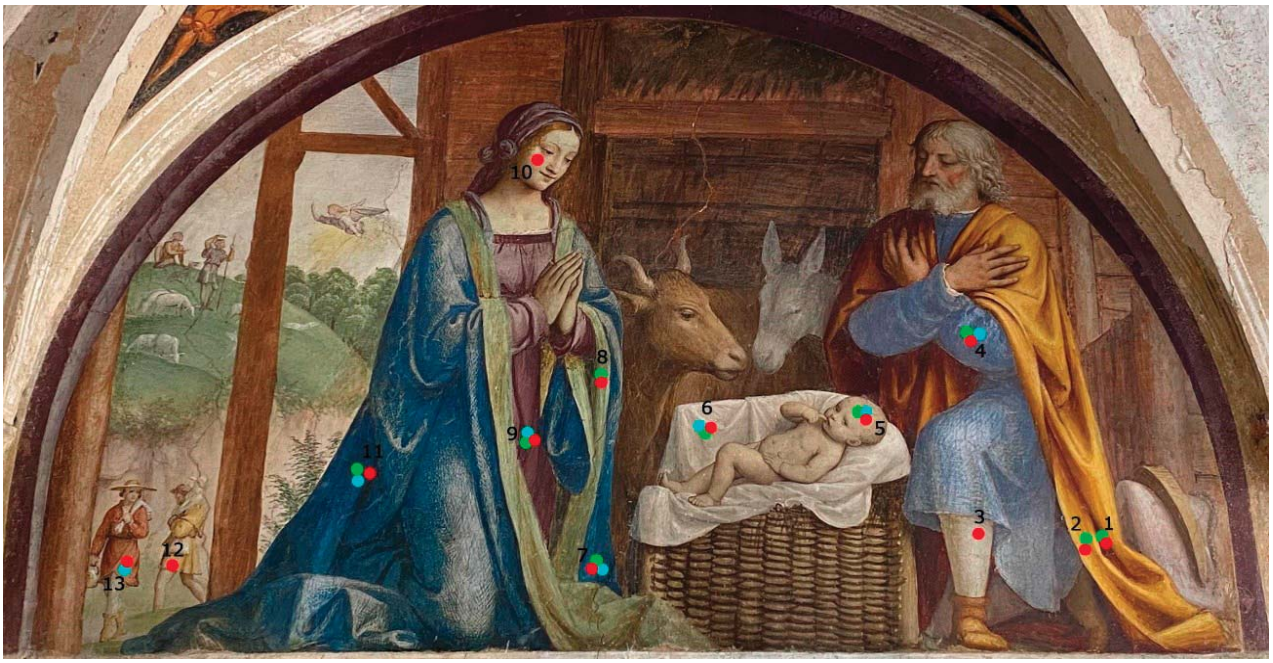

Figure 2. Visible image of the Adoration of the Christ Child with the different analytical spots acquired on the fresco with XRF (red), R-FTIR (green), and Raman (light blue) marked.

golden decorations were analyzed. The results obtained on this wall painting are summarized in Table 1.

XRF investigations carried out on white areas in correspondence with the mantle sleeve of the Virgin revealed the predominant signal of calcium (Ca), generally ascribed to calcium carbonate [8]. This result is also supported by R-FTIR and Raman analyses, which showed the characteristics absorption band of calcite respectively around 1420 and 870 cm^{-1} for R-FTIR [9] and 1085, 711, and 282 cm^{-1} for Raman [10]. The presence of high counts of Iron (Fe) in the skin tones suggested the addition of red or umber earth, probably red ochre, to obtain the tone desired by Luini. As for the red and yellow areas, the high XRF signals of Fe suggested the presence of earth pigments [8], as also confirmed by Raman bands of red ochre at 222, 290 and 404 cm^{-1} [11]. Different XRF signals were instead identified in correspondence with the yellow belt of the figure to the right. In particular, the presence of lead (Pb) and antimony (Sb) led us to assume the presence of a lead-antimony yellow, possibly Naples Yellow [8] mixed with the yellow ochre. The blue shade of the mantle of Mary was identified by R-FTIR as the lapis lazuli pigment thanks to the characteristic bands at 1010 and 970 cm^{-1} [12]. This hypothesis can only be supported by the significant increase in counts of sulphur (S) highlighted in the same area by XRF. As for the blue of the mantle of Joseph, the XRF analysis highlighted the presence of cobalt (Co), arsenic (As), nickel (Ni), and Fe, all related to smalt [8], as well as low counts of copper (Cu), attributed to azurite [8]. In addition, another blue area was investigated: the crown of the priest and the shawl of the young man next to Joseph. The XRF analysis revealed the presence of Cu, attributed to azurite, possibly dry-applied during re-paintings to cover the original decoration. As for the green pigments of the dress of the young man on the left, only the XRF analysis provided useful results: the signals related to Fe and Ca suggest the presence of a mixture of green earth pigment with calcium carbonate [8].

Finally, the golden decorations on the sleeve of the priest in the middle were probably realized through the application of sheets of gold leaf posed on an iron-rich adhesive substrate, the so-called bole [13]. In fact, the XRF analysis showed high counts of Fe, together with Au. Traces of Hg, Pb, and Cu were also detected.

Table 1. List of spots selected on The Marriage of the Virgin with the related attributions

Spot No.	Color	Attribution
1	Yellow	Yellow ochre
2	White	Calcium carbonate
3	Skin	Red ochre, Calcium carbonate
4	Red	Red ochre
5	Blue	Lapis lazuli
6	Yellow	Yellow ochre
7	Red	Red earth
8	Light brown	Red earth, calcium carbonate
9	Blue	Smalt, azurite
10	Gold	Gold leaf on *bolo*

11	Skin	Red ochre, Calcium carbonate
12	Light red	Red ochre, calcium carbonate
13	Blue	Azurite
14	Green	Green earth, calcium carbonate
15	Yellow	Yellow ochre, Naples Yellow

III.B Adoration of the Christ Child

The second fresco painted by Luini was located under the porch on the left side of the church. A color palette similar to that of the fresco described above was identified. However, the most relevant colors seemed to be white, yellow, red, blue and green (Figure 2). The results of the multi-analytical campaign are summarized in Table 2. R-FTIR and Raman spectroscopies characterized in almost the entirety of the respective datasets the presence of gypsum, identified through R-FTIR by the presence of the typical bands around 1130, 675, and 600 cm^{-1} [14] and by the strong Raman band at 1009 cm^{-1} [15]. The widespread presence of gypsum was ascribed to the transformation of calcium carbonate in calcium sulphate due to the polluting SO2 and oxygen [16], typically found on outdoor frescoes and, therefore, is to be considered a degradation product rather than an actual pigment.

As for the color palette, the white areas analyzed through XRF revealed the presence of high counts of Ca, attributable to calcium carbonate used as a pigment [8]. In the skin tones of the Virgin on the left, a significant increase in counts related to Fe suggested the presence of earth pigments, possibly red or brown earth or red ochre. In the same areas, Raman spectroscopy measurements could only recognise calcite bands at 1086 and 286 cm^{-1}, and the very strong band of gypsum at 1009 cm^{-1} [15] because of the great fluorescence background that characterized all the spectra obtained on this fresco. The yellow pigments used in the mantle of Joseph also seemed to be compatible with those found in the Marriage of the Virgin: the dark yellow is mainly composed of ochre, as suggested by the high counts of Fe revealed through XRF [8]. Moving to light yellow areas is clearly visible a decrease in intensity of Fe signal and a strong increase in counts of the Pb and Sb signals, attributed to Naples yellow [8]. In addition, high counts of Fe related to ochre were also revealed in correspondence with the yellow dress of the figure in the lower left-hand part of the fresco. The analyses of the few red areas revealed the presence of red ochre pigments, except for the red dress of the young man in the lower left-hand part. The presence of Pb, even if identified in traces by XRF, suggested the use of lead-based red pigment as minium mixed with the ochre [8]. As for the blue, two different areas were identified and analyzed: the mantles of Joseph and Mary. The XRF results obtained on Joseph's mantle revealed the presence Co, Fe, Ni, and As, all attributable to the presence of smalt blue [8]. The XRF signal of Cu, even if low in counts, could also suggests the presence of azurite. A different situation was revealed on Mary's mantle: the high predominant XRF signal of Cu, together with the R-FTIR bands centered at 4380, 4244, 2560, 2500, 1430 cm^{-1} were linked to the presence of a large amount of azurite [12,14]. In addition, an amount of smalt blue was revealed through the characteristic XRF signals. It is still unclear whether azurite was dry-layered over the fresco-painted surface or previously mixed with smalt and then applied. As for the green part of Mary's mantle, the high XRF counts of Fe suggest the presence of green earth, as for the other fresco.

Table 2. List of spots selected on the Adoration of the Christ Child with the related attributions

Spot No.	Color	Attribution
1	Dark yellow	Yellow ochre
2	Yellow	Yellow ochre, Naples yellow
3	White	Calcium carbonate
4	Blue	Smalt, azurite
5	Skin	Earth pigments, calcium carbonate
6	White	Calcium carbonate
7	Blue	Azurite, smalt
8	Green	Green earth
9	Red	Red earth
10	Skin	Earth pigments, calcium carbonate
11	Blue	Azurite, smalt
12	Yellow	Yellow ochre
13	Red	Minium, red ochre

IV. CONCLUSIONS

In the present work, two different frescoes painted by Bernardino Luini in Saronno (Italy) between 1525 and 1529 were analysed by means three different spectroscopic techniques, namely XRF, R-FTIR, and Raman. The analytical campaign provided decisive information on the color palette, making it possible to compare the pigments used in the two wall paintings. All the pigments identified are historically consistent with the period of production, even if partially different from the palette highlighted in previous research on several Luini's easel paintings [17]. On both the frescoes, Luini selected calcium carbonate as white, yellow ochre and Naples yellow, red ochre and/or umber earth, and Fe-based green. Some differences were highlighted in the blue pigments, mainly used in the mantles of Joseph and Mary. In fact, if Joseph's mantle was painted with smalt in both the artworks, the mantles

of Mary revealed the presence of two different pigments: lapis lazuli in the Marriage of the Virgin inside the church and azurite, with some trace of smalt, in the Adoration of the Christ Child placed outside. These differences might be due to the different placement, and consequently different preservation, of the two wall paintings. Further colorimetric and hyperspectral analyses will be performed to deepen the knowledge of Luini's color palette and the distribution of pigments, as well as to better identify the restoration areas.

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