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IMAGING, SPECTROSCOPIC AND SAMPLE ANALYSIS OF A 16TH CENTURY CANVAS PAINTING REPRESENTING THE HOLY TRINITY WITH SAINTS

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Abstract

This contribution focuses the attention on the documentation and diagnostic campaign on a 16th century canvas painting representing The Holy Trinity with the Saints Lawrence and Famiano, performed on the occasion of the restoration work carried out in the Laboratory of the master degree course in Conservation and Restoration of Cultural Heritage at University of Tuscia. The diagnostic investigation started with the documentation and non-invasive analysis through multispectral imaging and X-ray fluorescence spectroscopy respectively. After this first non-invasive step, micro-samples were taken for laboratory analysis through micro-stratigraphic inspection of cross-sections and morphological observation of canvas fibres. The results of the analysis, useful for the restoration work, highlighted the presence of a wide variety of pigments such as smalt blue, azurite, vermilion, lead white, lead and tin yellow, red and yellow ochre. Moreover, the ultraviolet fluorescence image showed the presence of an intense red fluorescence on the God garment, suggesting the use of an organic dye that was characterized through surface enhanced Raman spectroscopy. The most interesting result, revealed by infrared reflectography, was the reading of an inscription which allowed to redefine the dating of the painting with respect to that established by the stylistic and documentary analysis alone.

Keywords: canvas painting, The Holy Trinity, multispectral imaging, XRF, micro-stratigraphy

1. Introduction

The painting, object of the present paper, is located in the church of Saint Lawrence in the little town of Gallese (Viterbo district) and represents The Holy Trinity between Saint Lawrence and Saint Famiano [1; 2; https://artbonus.gov.it/2410-dipinto-la-trinit%C3%A0-e-i-santi-lorenzo-e-famiano.html, accessed on 17.08.2021]. The painting measures 250x170 cm (Figure 1). According to stylistic and iconographic details it has been dated back to the beginning of the 17th century. However the reading of the artwork was very difficult due to its bad

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state of preservation and to the various interventions made over time. The painting, in fact, had a devotional value for the faithful of the church and it was re-painted and restored more times, as usually occurred for devotional artworks.

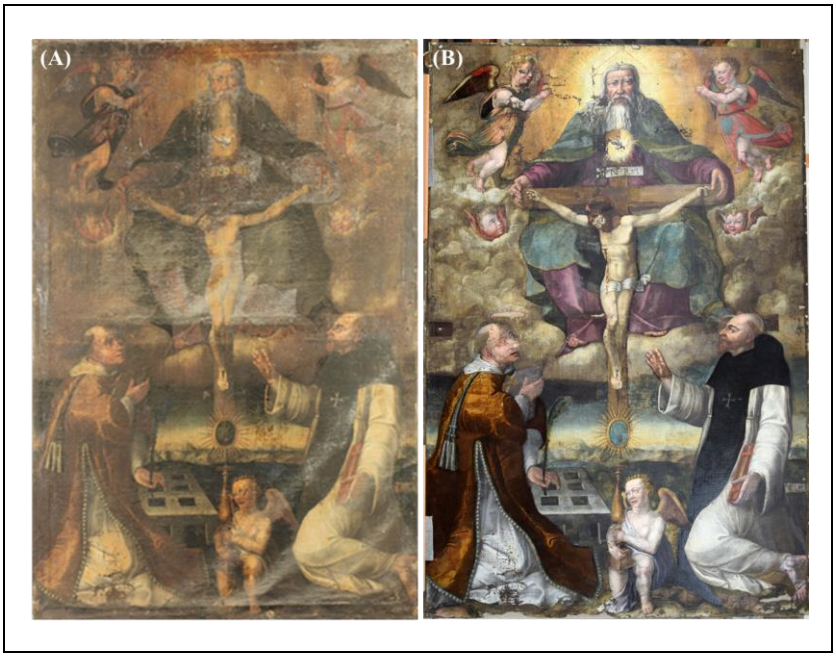

Figure 1. The painting representing The Holy Trinity with the Saints Lawrence and Famiano: (A) before and (B) after the partial cleaning of the surface superimposed.

Famiano is the patron saint of Gallese and his body rests in a church named after him and located just outside the city walls [2]. Originally from Cologne, Quuardus (this was the original name of the saint) was a Cistercian monk and dedicated his life to pilgrimages (Rome, Santiago di Compostela, Holy Land) and the hermit life. After a long stay in Spain, in 1150, during the journey back to his homeland, he reached Gallese where he died on 8 August of the same year. The fame of the miracles attributed to him and attested by tradition, it prompted the people to change the name of Quuardus in the easier Famiano and the cult materialized in the construction of the church, built in the thirteenth century on the burial place of the saint [1, 3].

The preliminary inspection of the painting, made by restores and student of the Conservation and Restoration course, revealed the presence of various lacerations and deformations of the canvas. Moreover, the surface was completely altered in colour due to the browning of the varnish and of the superimposed protective applied in past interventions.

The restoration work was absolutely necessary for re-establishing the correct visibility of the painting and for repairing the lacerations of the canvas.

The restoration was supported by a diagnostic campaign aimed at: identifying the pigments, the canvas fibre typology and the stratigraphy. To reach this goal, multispectral imaging technique, spectroscopic analysis and micro-sample investigation were performed. In the choice of the diagnostic techniques, also for educational purposes, a well-established strategy was followed which starts from multispectral investigations for imaging and point spectroscopy, both non-invasive, and then selects few samples to be exploited for laboratory investigations in order to define the important aspects for the restoration and future conservation of the work [4-6].

2. Experimental

Ultraviolet fluorescence (UVF) photography was performed by using a Nikon D5300 digital camera equipped with 18/105 mm multifocal zoom lens. For UV lighting, two 365 nm filtered sources, operating at 3000 mW, were used. On the camera optics Kodak Wratten 2B filters (light yellow) and 85B (amber filter) were mounted, in order to eliminate the reflections of the UV and to attenuate the dominant blue typical of ultraviolet shots.

Infrared reflectrography (IRR) was focused on the right side of the painting in correspondence of an inscription no more visible, in order to make if clear. IR photography was performed using a modified digital camera Samsung Model NX3300 supplied by Madatec (MI-Italy). The camera was equipped with a zoom lens Pentax-A 50 mm at a maximum aperture of 2. In front of the camera lens, a filter was placed, cutting IR radiation at 950 nm. Two DigiX IR lamps were used for irradiating the painting.

X-ray fluorescence spectroscopy was performed by the portable equipment Surface Monitor (Assing™). The measuring conditions were the following: Ag tube operating at 40 kV and 76 μA beam current; scan time 60 s; distance 94 mm.

After the non-invasive investigation, sampling of micro-chips of painting materials was carried out. The preliminary imaging and XRF punctual analysis allowed for limiting the number of samples to 3 micro-chips of material from the painting (two from the front and one from the back side), following the approach of minimal sampling for religious artworks knowledge [7]. The micro-fragments were used for micro-stratigraphic analysis and morphological study of the canvas fibres. In particular, observation and photography of the sample cross-sections and fibres embedded in Canada Balsam were performed by a Zeiss Axioskop polarising optical microscope equipped with a Zeiss AxioCam digital camera. Cross-sections were studied also under UV radiation using a Mercury Vapour lamp directly connected to the microscope in order to observe fluorescence of the materials.

3. Results and discussion

Ultraviolet fluorescence photography (UVF), performed after the partial removal of the surface layer, revealed the presence of probable organic pigments characterised by intense and brilliant red fluorescence, visible in the garment of God the Father (Figure 2).

Figure 2. UVF image of the painting representing The Holy Trinity with the Saints Lawrence and Famiano, after the partial removal of the surface browned layer.

Some abraded areas are also visible in different zones of the surface, particularly evident in the left side, in correspondence of the face of Saint Lawrence: these zones are characterised by a light blue fluorescence probably due to the glue of the ground layer and to the canvas [8].

UVF analysis was very useful to address the analysis for pigments and dyes characterization, and also for the subsequent restoration steps, i.e. further cleaning and final retouching [9]. In fact, it was decided to take a sample from

the red garment of God the Father to analyse the stratigraphy and, above all, to characterize the typology of organic dye.

Infrared reflectography (IRR) analysis was particularly relevant because it allowed for reading the inscription on the right side of the painting, near the left hand of Saint Famiano with the date (A.D. 159? die 17 April, see Figure 3) [10, 11]. The last number of the year is not certain, but this result is very important because it anticipates the date of realization of the artwork (at the end of 16th century) if compared to that traditionally established by the art historians (beginning of the 17th century).

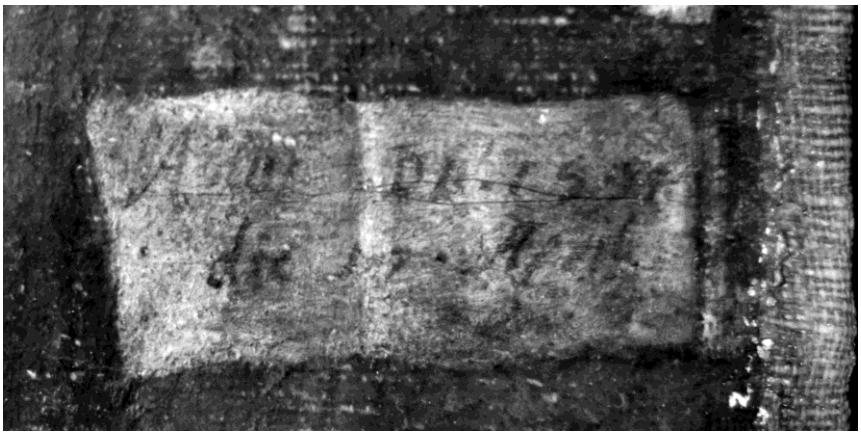

Figure 3. IRR image of the inscription, near the left hand of Saint Famiano.

After the multispectral imaging, X-ray fluorescence punctual analysis was focused in fifteen selected spots in order to define the pigment palette used by the painter (Figure 4). The XRF points of analysis were chosen in accordance with the teacher restores and with the students of the master course in Conservation and restoration of cultural heritage. XRF analysis allowed for detecting the chemical elements (with atomic number more than 16) in the fifteen examined points with the relative amount expressed in cps (counts per second) [12, 13].

The overall results are shown in the Table 1. Lead (Pb) is detected in all measured points, suggesting its presence in the ground layer and/or in the priming. When exhibiting higher counts, Pb can be associated to lead-based pigments such as lead white that can be supposed used for lightening the colours, such as in points X2, X4, X5, X8 and X10. In the point X8, Pb is associated to tin (Sn) indicating the presence of lead/tin based yellow (the so called *Giallorino*) [14, 15].

Sn has been detected also in points X12 and X14, again in correspondence of yellow areas, confirming the use of a led/tin based pigment. Traces of Sn are detected also in point X9 where high counts of zinc are found. Point X9 is located in correspondence of a dark zone close to the little dove on the breast of

God the Father. It can be supposed the presence of an oxidized zinc lamina or the application of zinc white pigment, now darkened. The eventual presence of zinc white indicates a re-painting being this pigment used starting from the 19th century. This finding has been considered interesting and it was decided to take a sample from this area.

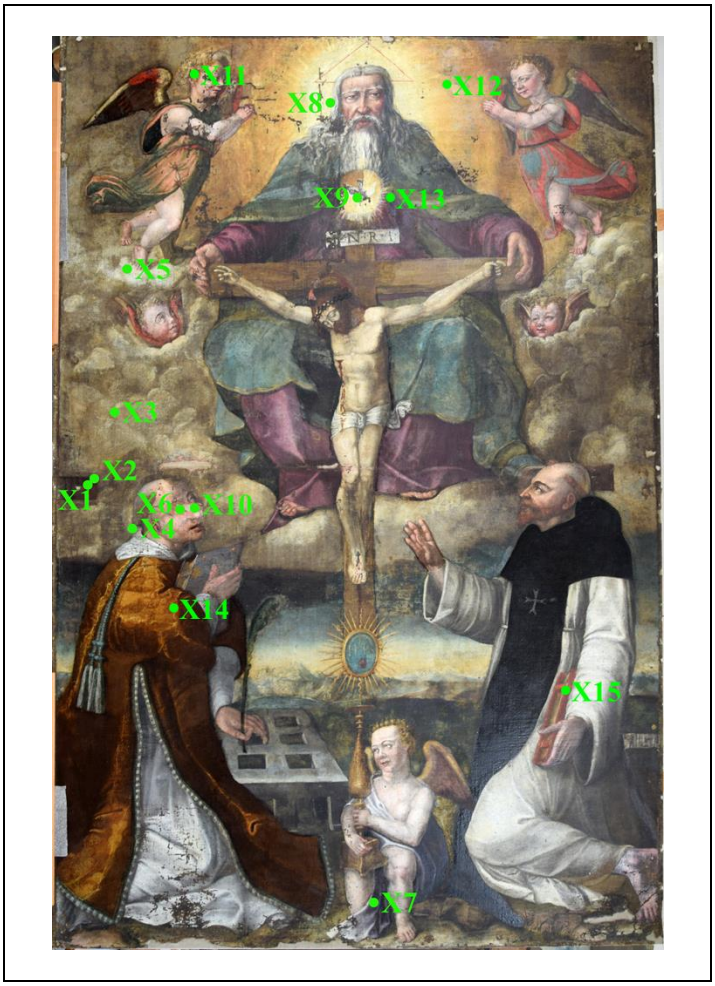

Figure 4. Image of the painting representing The Holy Trinity with the Saints Lawrence and Famiano, with the points of XRF analysis.

Iron (Fe) and calcium (Ca) are present in almost all the examined points suggesting their association to the ground layer. Higher counts of Fe have been measured in points X1, X2 and X3 probably due to the use of iron-based pigments, such as ochre. The presence of potassium in X1 and X3 confirms the use of ochre, natural pigments based on iron oxides and hydroxides associated to K-silicates [16].

Table 1. Results of XRF analysis on the painting. The values in the table are the counts per seconds (cps) detected by the XRF spectrometer. Tr is referred to traces of the detected chemical element.

Point	Chemical elements								
	K	**Ca**	**Fe**	**Co**	**Cu**	**Zn**	**Sn**	**Hg**	**Pb**
X1	136	287	778	240					5803
X2		239	559	180					6339
X3	87	295	722						4885
X4		174	294	tr	2347				6255
X5		50	203	109					6795
X6		228	225						562
X7		185	265		1991				3125
X8							97		7061
X9		115	297			3652	tr		4601
X10			295						6730
X11		79	89					142	3008
X12			71				60		1990
X13		231	259		4746				1367
X14		99	244		178		59		2392
X15		185	270					492	584

Cobalt (Co) was detected in the points X1, X2, X5 and X4 (traces) indicating the presence of smalt probably mixed with lead white to obtain a light blue colour.

Copper is detected in four examined points: two blue areas corresponding to the mantle of God the Father (point X13) and of the angel at the base of the cross (X7) and two other zones, one on the yellow mantle of Saint Lawrence in correspondence of a re-painted area (X14), and finally in the clouds near the head of Saint Lawrence (X4). In the first two points a copper-based pigment, presumably azurite (a basic copper carbonate) may be supposed for obtaining the blue colour of the mantle. In the other two points (X4 and X14) the presence of copper can be associated to the same pigment, i.e. azurite, used for the sky probably applied before painting the figure of Saint Lawrence and the clouds. It seems that the sky was realised with two different blue pigments: smalt, in the upper part, and azurite in the lower part.

Vermilion or cinnabar (HgS, artificial or natural) has been used for the book (point X15) and for the flesh hue of the angel (point X11), but not for the face of Saint Lawrence (points X6 and X10) that is in correspondence of a re-painting, according to the restorers evaluation. The difference in the materials of the flesh colour in Saint Lawrence constitutes a further confirmation of a re-painting area.

To deepen some questions remained unsolved after the non-invasive analysis on the painting, three samples were taken: P1 from the red garment of God the Father, P2 from the blackened zone on the dove (in correspondence of point X9) and P3 from the back and constituted by some fibres from the canvas, in order to characterize the typology of textile.

Cross-section of sample P1 is shown in the Figure 5.

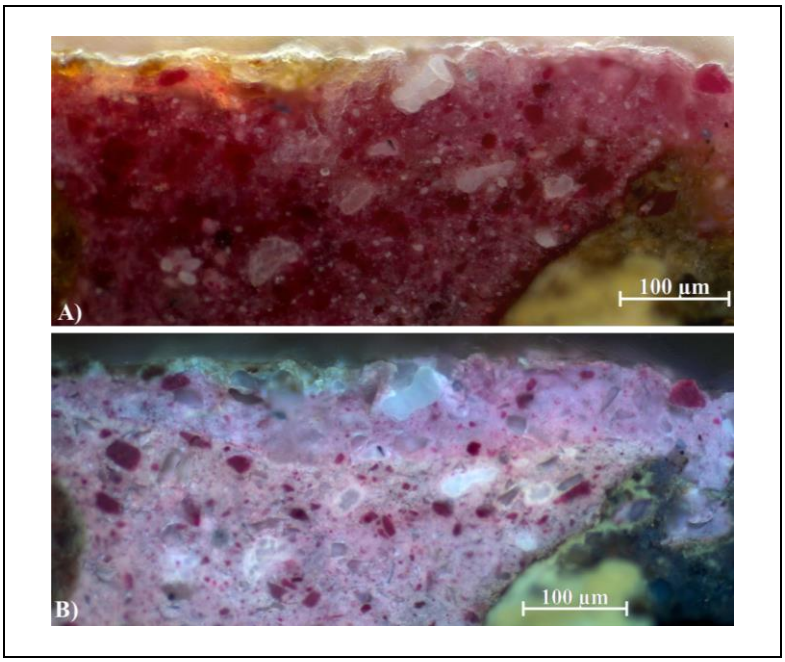

Figure 5. Cross-section of sample P1 under optical microscope: A) reflected light, B) ultraviolet fluorescence. Magnification 200X.

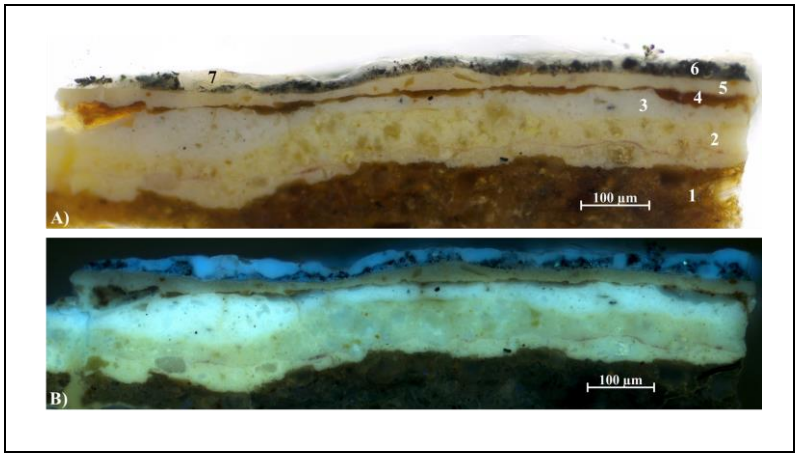

Figure 6. Cross-section of sample P2 under optical microscope: A) reflected light with the numbers indicating the layers, B) ultraviolet fluorescence. Magnification 100X.

The thick painting layer is made of red and white particles. The red grains are characteristic of organic dyes and are fluorescent under UV radiation. The morphology and the colour of these particles suggest the presence of cochineal as red organic dye [17]. This hypothesis was confirmed by surface enhanced Raman spectroscopy (SERS) [18-20], performed on the micro-sample in the

Laboratory of the Physics Department at Sapienza University of Rome, that gave the spectrum of cochineal red [21]. Considering the wide extension of the area of the garment of God the Father, the exclusive use of a great amount of cochineal indicates the preciousness of the painting and above all the religious value for the faithful. Sample P2 was also examined through cross-section and SERS in order to understand the technique and, above all, the presence of Zn, as revealed by XRF spectroscopy. Cross-section of sample P2 is shown in the Figure 6.

In this case, the stratigraphic pattern is more complex than that found in sample P1. In fact, seven layers can be distinguished under the optical microscope:

1) brown ground layer used for preparing the canvas;
2) priming of the painting, exhibiting a yellowish fluorescence under UV radiation (this layer contains yellow particles that have been characterized by Raman analysis as lead-tin yellow type I, Pb_2SnO_4);
3) original white layer probably made of lead white used for realizing the dove and the surrounding area;
4) original strongly browned varnish layer;
5) another ground layer with a pale yellow fluorescence, applied to perform the re-painting (this layer contains lead-white as revealed by Raman spectroscopy);
6) an altered blackened layer that is the one containing zinc. The appearance of this layer leads back to the use of a lamina.
7) the second varnish applied on the re-painting and characterised by light blue fluorescence that could be associated to protein-based glue.

The investigation of the two cross-sections, combined with the UVF photography and XRF spectroscopy, supplied valuable information about the technique and the materials, absolutely fundamental for the restoration work and for a better knowledge of the painting.

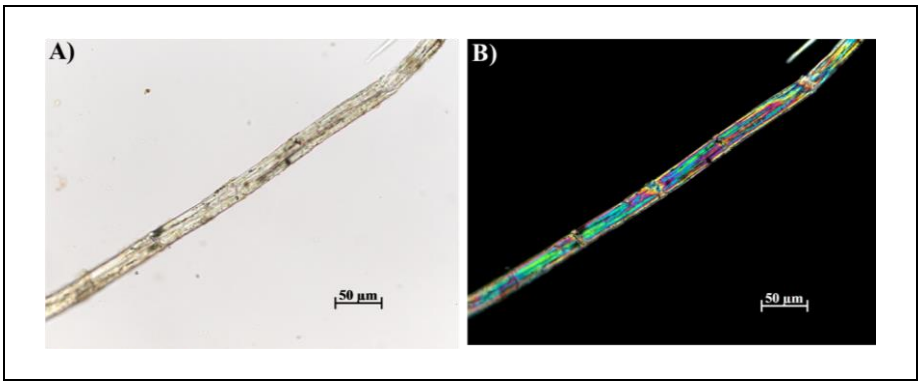

Figure 7. Single fibre from the canvas, under transmitted light: A) parallel polars, B) crossed polars. Magnification 200X.

First of all, the exclusive use of an organic dye to paint the garment of God the Father suggests the preciousness of the artwork for the faithful. In addition, the use of lead-tin yellow type I further confirms the relevance of the painting being this pigment quite expensive due to the modality of production [15, 22]. This pigment was widely used in the Renaissance, starting from the end of the first quarter of the 15th century until the end of 17th century [15, 23].

The clear identification of a superimposed layer in correspondence of the dove on the chest of God the Father, helped the restorers to guide the cleaning of the surface and the subsequent steps of the work.

The last sample is referred to the fibres of the canvas, taken from the back of the painting. The Figure 7 shows the microscope images of the fibre sample that exhibits the typical characteristics of flax: regular fibres with cross hatchings, and a fine lumen visible at the centre [24, 25].

4. Conclusions

The diagnostic investigation of an artwork revealed fundamental for supporting the restoration intervention, supplying information on constituent materials, hidden details, superimposed layers, and so on. In the case of the canvas painting representing The Holy Trinity with the Saints Lawrence and Famiano, the diagnostic analysis, focused on specific problems arising at the beginning and during the restoration activities, allowed for characterizing the painting pigments in the areas of interest, the fibres of the support belonging to flax, the re-painted zones and the reading of an inscription that dates back the artwork to the end of the 16th century, instead of the beginning of the 17th, as art historian supposed.

The extensive use of cochineal for painting the garment of God the Father has been considered a relevant issue to better understand the history of the artwork. In fact, the exclusive presence of great amount of this dye confirms the importance of the painting for the faithful and so the choice of applying a relative expensive colour instead of a cheaper material, such for example ochre.

The analysis revealed the use of two blue pigments: smalt for the sky in the upper part of the painting and azurite in the lower part and in the garment of God the Father and of the angel.

Lead-tin yellow type I was also found in the yellow priming of the painting in in some yellow areas.

The extensive use of lead-based pigments seems to corroborate the presence of siccative oil as binder. In fact, the painting has been considered as oil on canvas and no further analysis was considered necessary for confirming the binder, also in accordance with the approach of minimal sampling and minimal diagnostics that should be focused on the relevant issues to support the restoration, conservation and knowledge of cultural heritage.

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