Analytical investigations on polychrome artworks from the wooden ceiling of "ex-Ospedale San Matteo" in Pavia

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Abstract – The ex-Ospedale San Matteo in Pavia, constructed in 1449, featured wooden ceilings adorned with unique angelic decorations. Restoration efforts began in the late 1980s, with some panels completed in 2001. Currently, ten restored panels are on display and the Museum of Archaeology of the University of Pavia is initiating a new conservation project to restore the entire wooden ceiling, starting in 2024. The main aim of this preliminary project was the characterization of the colour palette, as a support for the restoration procedures. Non-invasive analysis using XRF and ER-FTIR spectroscopies revealed a colour palette, including cinnabar, azurite, copper-based greens, white lead, calcite, iron-based reds, yellow ochre, and organic-based black.

I. INTRODUCTION

The construction of the ex-Ospedale San Matteo in Pavia was completed in 1449 with a roof characterized by flat wooden ceilings decorated with hundreds of angels, one different from the other, to give a heavenly and consoling vision to the sick (Fig.1). The construction of a Baroque dome in 1770, about 30 meters high, resulted in the breaking through and loss of the central section of the 15th century wooden ceiling, of which only a few sections remain visible. Given the poor condition of preservation, from the late 1980s, restoration of some sample wooden panels was begun. The project was completed, although only on some bays, in 2001. Currently, 10 panels restored during the 1990s campaign are properly preserved and on public display at the Museum of Archaeology of the University of Pavia. In the wake of the latter project, completed more than twenty years ago, the Museum of Archaeology is starting a new conservation project to make this extraordinary and unique heritage, planning the restoration of the entire wooden ceiling from 2024 [1,2]. The current conditions of degradation of both the wood substrate and the painted layers, due to fires and water infiltrations that occurred over the centuries required strong maintenance and restoration procedures, as well as a preliminary diagnostic campaign that could support the first approach to the artworks.

Under this scenario, an analytical campaign on 4 wooden polychrome panels (Fig. 2) was performed. The main aim of this preliminary project was the non-invasive characterization of the colour palette used in the paintings, as a support for the first restoration procedures. For this purpose, Visible-Ultraviolet-Infrared (Vis-UV-IR)

multispectral imaging, X-ray radiography, optical microscopy, X-ray Fluorescence (XRF) spectroscopy, and External Reflection FTIR (ER-FTIR) spectroscopy were selected.



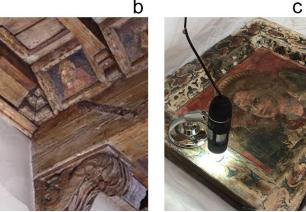


Fig. 1. (a) the wooden ceiling of the ex-Ospedale San Matteo decorated with hundreds of panels, and (b) a detail of the decoration. (c) One of the selected polychrome panels during a preliminary observation through a digital microscope

II. EXPERIMENTAL

A. Photografic investigation

Visible (VIS) and Ultraviolet-induced Fluorescence (UVIF) [2], were acquired using a Nikon D600 full-frame digital camera (Nikon Corporation, Tokyo, Japan) with a 50 mm, f.1.4 Nikkor objective (Nikon Corporation, Tokyo, Japan). Visible illumination was provided by two soft-box LEDs (T = 5400 K), while UV illumination was provided by two CR230B-HP 3W projectors with an emission peak cantered at 365 nm. As for the Infrared Reflectography (IRR) images, a customized Nikon D4 full-frame digital camera with a 50 mm f/1.4 Nikkor objective. The IR radiation was produced by two Philips IR lamps PAR38 175W.

B. Optical microscopy

The magnification of details was performed with an

Olympus SZX10 stereomicroscope (Olympus, Tokyo, Japan) equipped with an Olympus HD DP73 camera. The images were collected through Stream Essentials software.

C. X-Ray radiography

To explore the structural features and their alterations, X-Ray Radiography (RX) [3] was carried out by means of a portable X-Ray Tube Porta 100 HF (4 shots at 50 kV, 50 μ A, 1 s exposure time) produced by Job Corporation (Yokohama, Kanagawa, Japan) and a Fujifilm CR UR-1 photosensitive radiographic plate scanned with CR35NDT Dürr NDT.

D. X-Ray fluorescence (XRF)

Non-invasive XRF analyses were performed with a portable XRF spectrometer EIS XRS 38 [4], 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 μ A, and acquisition channels 2048. Data were acquired and processed using the DPPMCA software.

E. Reflection FTIR spectroscopy (R-FTIR)

The FTIR analyses in reflection mode were performed a non-invasive Alpha portable spectrometer (Bruker Optics, Germany/USAMA) [4]. The spectrometer is equipped with an R-Alpha external reflectance module (optical layout $23^{\circ}/23^{\circ}$). 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 analysing spots of about 5 mm in diameter. Pseudoabsorbance 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). Data were acquired and processed using OPUS 7.2 software package.

III. RESULTS AND DISCUSSION

Preliminary observations carried out on the 4 wooden panels selected for the study revealed the presence of a rather classic and similar colour palette for all the four, consisting mainly of red, blue, green, white and black for the frames and of red, yellow, blue, brown, flesh pink tone, white and black for the backgrounds and figures of the angels. As for the structural features of the wooden support, the observation of the X-rays radiographies collected panels did not reveal the presence of any woodworm galleries or other structural damage. However, it was possible to highlight the nails used to attach the different parts of the wooden boards to each other (Fig. 3). The analytical study using XRF and R-FTIR focused on



Fig. 2. The four polychrome panels. For each panel the visible (left) and UV (right) images are shown. The panels 1, 2, 3, 4 are shown respectively from (a) to (d).

identifying the pigments used in these areas. Here, the multi-analytical results are presented as the final interpretation of the identified pigments. As for the frames, the red of the floral decorations appears to be cinnabar, while the blue and green areas were painted with copperbased pigments: azurite, copper green (resinate and/or malachite) sometimes lightened with white lead [5-7]. The widespread presence of calcium, sometimes associated with sulphur, and traces of celestine (strontium sulphate) point to the use of chalk together with calcite, probably attributable to the past bleaching and covering of the surfaces with chalk [8]. The white decorations are characterised by the presence of chalk [9], celestine in traces and a possible residue of some proteinaceous material [10]; the black ones do not show characteristic marker peaks of a mineral pigment and, therefore, were probably made with an organic-based material [11].

As for the figures of the angels, the flesh tones were made

in all the panels by mixing white lead and small amounts of cinnabar, hematite or red earth to obtain a pinkish colour, while azurite was used for the wings, altered and blackened in several areas due to the alkaline environment produced by the subsequent bleaching of the panels with chalk [9,12]. The red areas of the clothes were painted with cinnabar, while the blue parts with azurite and the white parts with white lead. Interestingly, white lead was not used in the white decorations of the frames. The yellow paintings were made using iron-based pigments like ochres together with, in some areas, cinnabar and probably organic black, in order to obtain more orange or brown colours [11,13,14]. Small amounts of white lead are also sometimes found in the yellows, although the presence of lead yellow cannot be excluded. Two different pigments were used for the background: cinnabar in panels 1, 2, 3, while azurite, altered and blackened, in panel 4 (Fig. 2d). The presence of protein glue and chalk, detected in the

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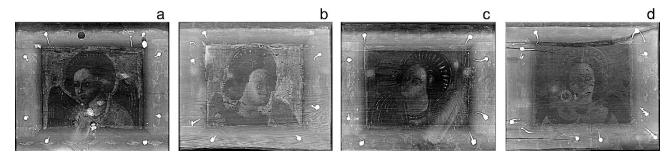


Fig. 3. RX radiographies of the four panels. The panels 1, 2, 3, 4 are shown respectively from (a) to (d).

areas where there is no longer any drafting and the wood is exposed, could confirm the hypothesis that the wooden boards were prepared with chalk and protein glue [15,16].

Table 1. Summary of the identified pigments and wooden preparation.

Area	Color	Pigment	Ref
Frame	Red	Cinnabar	5,6,11
	Blue	Azurite	5,6
	Green	Cu-based green	6,7
	White	Chalk	6,8,9
	Black	Organic black	6,11
Faces	Flesh tones	White lead, cinnabar, red earth	5,6,11, 12,13
Wings	Blue	Azurite	5,6
Clothes	Red	Cinnabar	5,6,11
	Blue	Azurite	5,6
	White	White lead	5,6,13
Hairs and decorations	Yellow, brown	Yellow ochre, cinnabar, white lead, organic black	5,6,11, 12
Background	Red	Cinnabar	5,6,11
	Blue	Azurite	5,6
Wooden preparation	-	Chalk, protein glue	10,14

IV. CONCLUSIONS

The multi-analytical non-invasive investigation through XRF and R-FTIR of the palette used to make the panels under investigation revealed an almost complete homogeneity in the selection of pigments for the four different wooden panels and their frames, decorated with floral decorations. The identified palette, summarized in Table 1, is rather simple and includes cinnabar, azurite, Cu-based greens, white lead, calcite, Fe-based reds, yellow ochre and organic-based black.

For a more accurate analysis of the materials and to better study the different stratigraphies, some already acquired and embedded samples will be analysed using SEM-EDX and FTIR-ATR. Upon completion of the analyses, the wooden panels will be restored at the Piccolo Chiostro Conservation and Restoration Centre in Pavia and exhibited at the Archaeological Museum of the University of Pavia.

REFERENCES

- [1] A.L. Magrassi Matricardi, "Angeli. Le tavolette del soffitto dell'antico Ospedale San Matteo di Pavia", 1st edition, SAGEP Editori Srl, Genova, Italia, 2022.
- [2] R. Gorini, "L'ospedale di San Matteo. Origine e storia della fabbrica", in Storia di Pavia, 3rd edition, Milano, Itala, 1996.
- [3] G. Fiocco, S. Gonzalez, C. Invernizzi, T. Rovetta, M. Albano, P. Dondi, M. Licchelli, F. Antonacci, M. Malagodi, "Compositional and Morphological Comparison among Three Coeval Violins Made by Giuseppe Guarneri 'del Gesù' in 1734," Coatings, 2021, 11, 884.
- [4] G. Fiocco, M. Albano, C.Merlo, T. Rovetta, C. Lee, F. Volpi, A. Bergomi, C.A. Pini, C.A. Lombardi, C. Mariani, V. Comite, M. Malagodi, P. Fermo, V. Guglielmi, "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)" Proc. of 2022 IMEKO TC-4 International Conference on Metrology for Archaeology and Cultural Heritage, 2022.
- [5] C. Miliani, F. Rosi, et al., "Reflection infrared spectroscopy for the non-invasive in situ study of artists' pigments", Appl. Phys. A, 2012, vol. 106, pp. 295–307.
- [6] N. Bevilacqua, L. Borgioli, I. Adrover Gracia, "I pigmenti nell'arte: dalla preistoria alla rivoluzione industriale", Il Prato Publishing House, Saonara (PD), Italy, 2010.
- [7] L. Bonizzoni, S. Bruni, M. Gargano, V. Guglielmi, C. Zaffino, A. Pezzotta, A. Pilato, T. Auricchio, L. Delvaux, N. Ludwig. "Use of integrated non-invasive

analyses for pigment characterization and indirect dating of old restorations on one Egyptian coffin of the XXI dynasty" Microchem. J., 2018, vol. 138, pp.122–131

- [8] P. Fermo, M. Colella, M. Malagodi, G. Fiocco, M. Albano, S. Marchioron, V. Guglielmi, V. Comite, "Study of a surface coating present on a Renaissance Piety from the Museum of Ancient Art (Castello Sforzesco, Milan)" Environ. Sci. Pollut. Res., 2021, vol. 29, pp. 29498–29509.
- [9] M. Gargano, L. Bonizzoni, M. Grifoni, J. Melada, V. Guglielmi, S. Bruni, N. Ludwig. "Multi-analytical investigation of panel, pigments and varnish of The Martyirdom of St. Catherine by Gaudenzio Ferrari (16th century)" J. Cult. Heritage 2020, vol. 46, pp. 289–297
- [10] M.R. Derrick, D. Stulik, J.M. Landry, "Infrared Spectroscopy in Conservation Science. Scientific Tools for Conservation", The Getty Conservation Institute, Los Angeles, USA, 1999.
- [11] V. Guglielmi, M. Andreoli, V. Comite, A. Baroni, P. Fermo. "The combined use of SEM-EDX, Raman, ATR-FTIR and visible reflectance techniques for the characterisation of Roman wall painting pigments from Monte d'Oro area (Rome): An insight into red, yellow and pink shades". Environ. Sci. Pollut. Res. 2022, vol. 29, pp. 29419–29437.

- [12] V. Comite, M. Colella, M. Malagodi, G. Fiocco, M. Albano, S. Marchioron, P. Fermo, "Towards the study of alteration patinas on the marble surface of a Renaissance sculptural group from the Museum of Ancient Art (Castello Sforzesco, Milan)", 2020 IMEKO TC-4 International Conference on Metrology for Archaeology and Cultural Heritage, 2020, pp. 467-471.
- [13] V. Guglielmi, C.A. Lombardi, G. Fiocco, V. Comite, A. Bergomi, M. Borelli, M. Azzarone, M. Malagodi, M. Colella, P. Fermo, "Multi-Analytical Investigation on a Renaissance Polychrome Earthenware Attributed to Giovanni Antonio Amadeo" Appl. Sci., 2023, 13, 3924.
- [14] F. Volpi, M. Vagnini, R. Vivani, M. Malagodi, G. Fiocco, "Non-invasive identification of red and yellow oxide and sulfide pigments in wall-paintings with portable ER-FTIR spectroscopy" J. Cult. Heriage 2023, vol. 63, pp. 158-168.
- [15] F. Volpi. G. Fiocco, T. Rovetta, et al., "New Insights on the Stradivari "Coristo" Mandolin: A Combined Non-Invasive Spectroscopic Approach", Appl Sci., Vol.11, 2021, pp. 1-11.
- [16] C. Invernizzi, T. Rovetta, M. Licchelli, M. Malagodi, "Mid and Near-Infrared Reflection Spectral Database of Natural Organic Materials in the Cultural Heritage Field", Int. J. Anal. Chem., 2018, pp. 1-16.