



THE SAN PIETRO MARTIRE TRIPTYCH BY BEATO ANGELICO: MATERIALS CHARACTERIZATION BY MEANS OF INTEGRATED NON-INVASIVE SPECTROSCOPIC MEASUREMENTS

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Abstract

This work presents some results showing how the integrated use of non-invasive spectroscopic techniques is extremely useful for deepening the knowledge of an artwork. The object under study is the Triptych of San Pietro Martire by Beato Angelico, (152 cm x 172 cm x 10 cm), a panel painting from the San Marco Museum in Florence. The analytical protocol was developed to characterize the materials used by the artist and to clarify some doubts concerning the dating. Fiber optic reflectance spectroscopy (FORS) was useful to obtain information concerning the composition of the artist's palette, composed of pigments commonly used in 15th century Italian easel painting. Of particular interest, is the presence of green areas obtained by a mixture of azurite and lead and tin yellow. These data suggest that the painting could be dated back to the artist's early period, when Beato Angelico was in contact with Lorenzo Monaco, while in his mature works, green parts were commonly painted with green pigments. X-ray fluorescence (XRF) measurements integrated and completed the FORS results, allowing to better characterize most of the pigments. Furthermore, investigations carried out by portable total reflection infrared spectroscopy (TR-FT-IR) provided information about the organic materials used as binders, both in the ground and in the paint layers.

Keywords: *Non-invasive technique; FORS; XRF; portable FT-IR; Pigments and binders characterization*

Introduction

The aim of the present work was to demonstrate the potentialities of the integration of non-invasive spectroscopic techniques, i.e. Fiber optic reflectance spectroscopy (FORS), X-ray fluorescence (XRF) and portable total reflection infrared spectroscopy (TR-FT-IR), in solving cultural heritage issues. These techniques were applied in a multidisciplinary study of a 15th century triptych attributed to Beato Angelico.

The *Triptych of San Pietro Martire* is a panel painted by the Italian early Renaissance master Beato Angelico, it was executed around 1428-1429 and actually housed in San Marco National Museum in Florence.

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The painting is one of Beato Angelico's first documented works. According to some scholars, the painting belongs to the early period of the artist, which is among one of the most complex and critically discussed in the Italian history of art. In the Triptych a strong influence by Gentile da Fabriano, who worked in Florence between 1420 and 1425, is evident [1, 2]. This influence can be seen especially in the decoration of the Holy Virgin's cloth and in the delicate embroidery of the dress of the Child. However, some scholars attribute the work to a later period. Observing the plasticity of the Madonna and the Child, but above all its pyramid of figures, it is clear the influence of Masaccio. Indeed this work could be contemporary of the *Madonna con Bambino e Sant'Anna* painted by Masaccio and Masolino da Panicale between 1424 and 1425. The variety of influences and their simultaneous occurrence in the heterogeneity of the panel, allow to hypothesize the execution in the mid-twenties, anticipating at least three years to the traditional dating [2, 3].

Experimental

Measurements were performed in the *Laboratori di Restauro della Soprintendenza Speciale per il Patrimonio Storico, Artistico ed Etnoantropologico e per il Polo Museale della Città di Firenze*, during the restoration of the artwork.

Portable digital microscope

To document each spot and to observe the surface and the state of conservation of the pictorial surface, a portable digital microscope was used (mod. DG-2A *Scalar*). The instrument provides high quality images with a magnification of 25x to 200x.

X-ray fluorescence (XRF)

XRF spectra were recorded using a portable X-ray fluorescence analyzer, mod. *TRACeR III-SD* (Bruker). The instrument is equipped with an X-ray tube (Rh target), and a Silicon Drift Detector (SDD) with resolution of 190 eV at 10,000 cps. The excitation parameters used during the investigations were: voltage of 40 kV and current of 22 μ A. The acquisition time was 100 s. Under these conditions the portable instrument allows the detection of elements with atomic number higher than aluminum ($Z > 12$).

Total reflection infrared spectroscopy (TR-FT-IR)

Measurements were performed using a Bruker Optics Inc. (mod. FT-IR ALPHA) portable FT-IR spectrometer in total reflection mode. The spectrometer is equipped with a high resolution camera interfaced to a PC in order to ensure, for every measurement, a correlation between the analyzed area and the infrared spectral information obtained. The measured area is 5 mm in diameter and the distance from the surface investigated is of 15 mm. The detector is a DTGS and the IR radiation is emitted by a Globar source with a color temperature of about 1500 K (SiC Globar). The range of acquisition was 7500-375 cm^{-1} with a spectral resolution of 4 cm^{-1} . For the acquisition of the background a dedicated golden plate was used.

Fiber optic reflectance spectroscopy (FORS)

FORS measurements in the 350–2200 nm range were performed using two single-beam Zeiss spectroanalyzers, model MC601 (190–1015 nm range) and model MC611 NIR 2.2WR (910–2200 nm range), housed together in a compact and portable *chassis* for *in situ* analyses. The data acquisition step was 0.8 nm/pixel for the 1024-element silicon photodiode array detector (MCS601), and 6.0 nm/pixel for the 256-element InGaAs diode array detector (MCS611 NIR 2.2 WR). The radiation between 320 nm and 2700 nm, which was provided by a voltage-stabilized 20 W halogen lamp (mod. CLH600), was carried to the surface by means of a quartz optical fiber bundle that also transported back the reflected radiation to the detectors. The

geometry of the probe-head was $8^{\circ}/8^{\circ}$. Calibration was performed by means of a 99% Spectralon[®] diffuse reflectance standard. Each spectrum acquired was the result of the average of three acquisitions. All spectra were elaborated using Aspect Plus[®] software from Zeiss. Spectra were compared with reference ones available in the IFAC-CNR database [4].

Results and discussion

Measurements were performed using all the described techniques, on 217 spots to recreate the entire palette used by the artist. The figure 1 shows the studied painting.



Fig. 1. The Triptych of San Pietro Martire, Beato Angelico, 1428-1429 (152 cm x 172 cm x 10 cm).

Ground layer

Concerning the identification of the materials used in the ground layer, the FORS data acquired, indicate that the support was prepared with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which has a reflectance spectrum with characteristic features in the NIR region (fig. 2). In fact, gypsum shows a typical absorption band, due to the first overtone of the O-H stretching of the water, is around 1430-1550 nm and is divided into three sub-bands centered around 1450, 1490 and 1535 nm, plus other water combination bands at higher wavelengths (approximately 1200, 1750 and 1945 nm) [5].

The spectral characteristics of gypsum were less evident in the gilded areas because the gold foil acted as shielding layer for the FORS signal. The XRF elemental analyses showed a peculiar presence of high counts of lead all over the painting, even on black areas. These data led to sustain the presence of a second ground layer, or *imprimitura*, made with lead white ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) [6, 7]. This pigment was used also in the white areas, as confirmed observing the presence of carbonates bands related to lead white in the IR spectra ($1405, 681 \text{ cm}^{-1}$) [8].

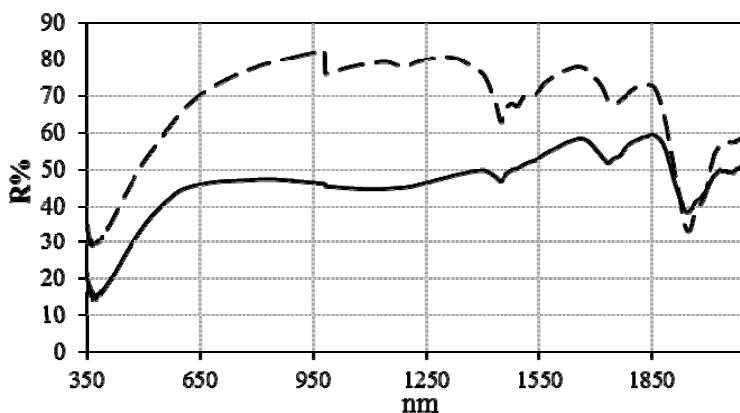


Fig. 2. FORS spectra of two areas from the painting showing gypsum's spectral features (1430-1550nm, 1200nm, 1750nm, 1945nm).

Black colored areas

By means of the spectroscopic techniques here presented, is not possible to identify the black pigment used, just to suggest the use of an organic black pigment [7, 9, 10].

Blue and green colored areas

Due to the lack of any characteristic signals, the XRF study, carried out on blue areas, excluded the presence of copper or cobalt based blue pigments. However, FORS spectra easily allowed to identify the pigment used as lapis lazuli ($3\text{Na}_2\text{O}\cdot 3\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2\cdot 2\text{NaS}$) characterized by a maximum reflectance band centered at 460 nm and a strong absorption band centered around 600 nm, owing to a charge transfer electronic transition [4, 5]. Just in few blue areas, by means of XRF elemental analysis, copper signals, related to the presence of azurite ($2\text{CuCO}_3\cdot \text{Cu}(\text{OH})_2$), were observed. This identification was confirmed by means of FORS spectra in which this pigment exhibits a maximum reflectance band at about 454 nm, an intense absorption band centered at about 900 nm and a strong and characteristic absorption band in the region of the NIR (approximately 1500 nm) all referred to the copper(II) *d-d* transition [5]. Figure 3a, b show the FORS and XRF spectra obtained from the green mantle of the Child.

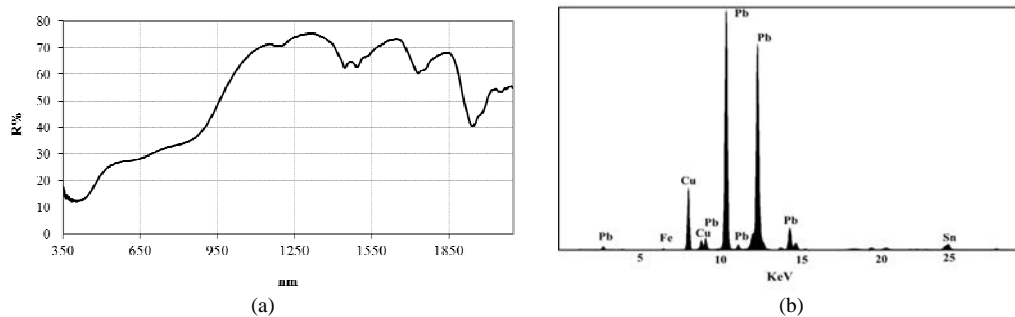


Fig. 3. Spectra of the Child's mantle: (a) FORS and (b) XRF

Spectral features, related to the presence of azurite in mixture with a yellow pigment, were detectable in FORS spectrum [4, 5]. As well, observing the high magnification images reported in figure 4, blue grains were clearly visible in the green-yellowish matrix.

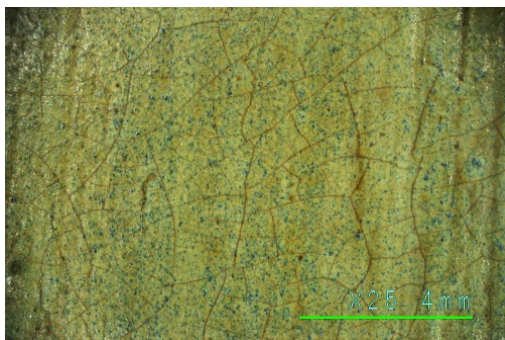


Fig. 4. High magnification image of an area of the Child's mantle (25X).

The XRF analysis confirmed the use of a mixture. The spectrum (fig. 3b) showed high counts of copper, lead and tin which suggested the use of a composite green made with azurite and lead and tin yellow (Pb_2SnO_4) [11, 12]. According to the scholar palette's reconstruction, the use of composite green is related to the beginning of the artistic activity of Beato Angelico, while the use of pure green copper-based pigments is documented in his maturity; this information could support the scholar's thesis classifying this Triptych as belonging to the early period of the artist.

Red and pink colored areas

XRF spectra performed on the red areas showed a high amount of mercury indicating the use of cinnabar (HgS) [11, 12]. About the complexion the most prominent peaks in all XRF spectra registered were due to Pb and Hg. This seemed to imply the use of a mixture of lead white and cinnabar.

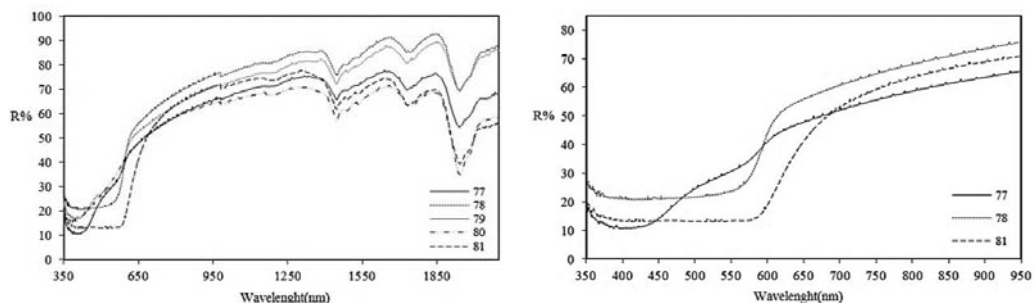


Fig. 5. FORS spectra comparison of five areas on the dress of the Child (350-2200 nm) and the detail of three areas (350-950 nm).

However, for the pinkish dress of the Child, significant differences were founded between the spectra obtained for the yellow areas and for the adjacent red ones. In figure 5 the FORS spectra of five areas, highlighted in figure 6, are compared.

Different spectral features were visible, particularly in the 350-700 nm range indicating the presence of cinnabar, lead white, a yellow pigment and maybe minium (Pb_3O_4) for the orange shadows. The comparison between the FORS results with those obtained using XRF, indicated that the artist used a mixture of cinnabar and lead white to paint the dress and lead and tin yellow to create a more yellowish hue, while the pink areas should have been plausibly

painted with a mixture made with lead white, minium and an organic red dye (not univocally identifiable by means of these techniques).

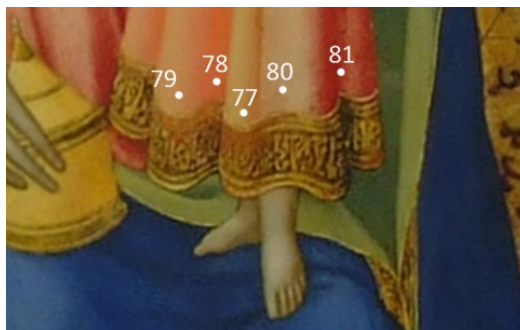


Fig. 6. Detail of the Child's dress with the measurement spots

Organic materials

The application of TR-FTIR, useful for the detection of both organic and inorganic materials, could help in the identification of the used binder [7]. The painting layers seem to be executed with egg-based medium, whose characteristic absorption peaks fall around at 4330 cm^{-1} and 4260 cm^{-1} [13, 14]. The presence of a varnish on the surface made difficult the analysis of the spectra recorded, mainly in the region of the mid-infrared ($4000\text{--}400\text{ cm}^{-1}$). In fact, the characteristic absorption bands of the binder were partially or totally overlapped by those belonging to a terpenic resin, as dammar [13, 14]. For this reason it was not possible, with this technique, to make a positive identification of the binding media used by the artist; to obtain a correct and complete characterization, a sample should be required.

As an example, in figure 7 is shown the spectrum acquired on a white area.

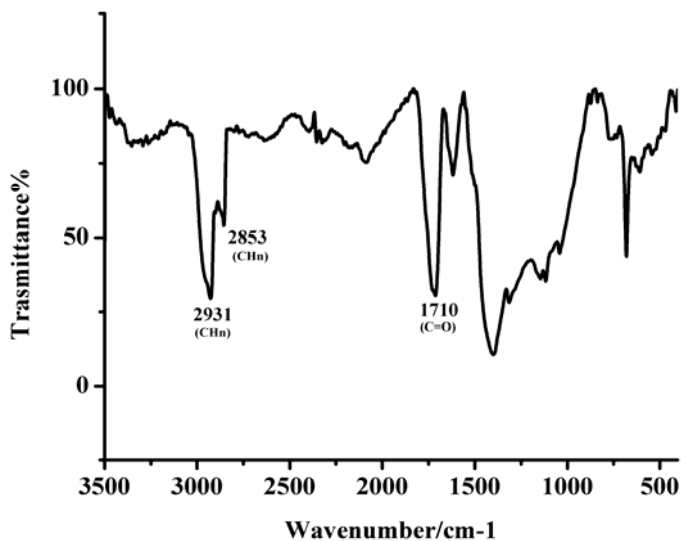


Fig.7. TR-FT-IR, KK transformation, showing peaks of CH_n groups stretching ($2931, 2853\text{ cm}^{-1}$) and C=O stretching (1710 cm^{-1})

The absorption bands at 4330 cm^{-1} and 4250 cm^{-1} , related to combinations of the fundamental stretching and bending vibrations of the CH_2 groups, suggested the use of egg as binder. Even the absorption bands at 5145 cm^{-1} , 5675 cm^{-1} and 5790 cm^{-1} could be related to the presence of an egg-based binder [13, 14]. However, the peaks at 2931 cm^{-1} and 2853 cm^{-1} , associated to the stretching vibrations of CH_n groups ($n = 1,2,3$), are characteristic of both egg and dammar [13, 14]. Also the peak at 1710 cm^{-1} due to a $\text{C}=\text{O}$ stretching cannot be related with confidence to the binder or to the resin. The bands characteristic of a proteinaceous material in the range $1650 - 1350\text{ cm}^{-1}$ were not detected. For this reason it was not possible to give a sure identification of the binder used by Beato Angelico.

Conclusions

The diagnostic campaign here presented, proved how the integration of different non-invasive analytical techniques and the mutual comparison of the data obtained could be a powerful tool for the examination of paintings, giving an almost complete characterization of the constituent materials of an artifact avoiding any sampling. *In situ* XRF and FORS spectra were acquired and provided strong evidence about the pigments used. Molecular information obtained from TR-FTIR corroborated and, in some cases, completed the pigments identification and suggested the use of egg as binders. Surface examination using a portable optical microscope is a simple technique which, when combined with other analytical methods, can help to document spot measurements and to characterize the state of conservation of the artwork.

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References

- [1] M. Scudieri, **Bagliori Dorati – Il Gotico Internazionale a Firenze 1375-1440**, Giunti, Firenze, 2012, pp. 164-166.
- [2] M. Scudieri, S. Giacomelli, **Fra Giovanni Angelico. Pittore miniatore o miniatore pittore?**, Giunti, Firenze, 2007, pp. 120-126.
- [3] G. Cornini, **Beato Angelico**, Art e Dossier, 155, Giunti, Firenze, 2000, pp. 5-20.
- [4] * * *, Fiber Optics Reflectance Spectra (FORS) of pictorial materials in the 270-800 nm range; database dell'Istituto di Fisica Applicata Nello Carrara (IFAC-CNR), <http://fors.ifac.cnr.it>;
- [5] M. Bacci, *UV-Vis-NIR, FT-IR and FORS spectroscopies. Modern Analytical Methods in Art and Archaeology*, **Chemical Analysis Series**, 155, John Wiley and Sons Inc., 2000, pp. 321-362.
- [6] A. Aldrovandi, M. Picollo, **Metodi di documentazione e indagini non invasive sui dipinti**, Il Prato, Firenze, 2007.

- [7] M. Galeotti, R. Mazzeo, D. Pinna, **Scientific examination for the investigation of paintings. A handbook for Conservator-Restorers**, Centro Di, Firenze 2000.
- [8] * * *, Database IRUG ed. 2007, INP00120, <http://www.irug.org/resources/irug-spectral-database>;
- [9] V. Bevilacqua, L. Borgioli, G.I. Adrover, **I pigmenti nell'arte dalla preistoria alla rivoluzione industriale**, Il Prato, Firenze, 2010.
- [10] S. Volpin, L. Appolonia, **Le analisi di laboratorio applicate ai beni artistici policromi**, Il Prato, Firenze, 1999.
- [11] C. Seccaroni, P. Moioli, **Fluorescenza X – Prontuario per l'analisi XRF portatile applicata a superfici policrome**, Nardini, Firenze, 2004.
- [12] R. Cesaro, G.E. Gigante, A. Castellano, J.S. Iwancky, *Portable System for Energy Dispersive X-Ray Fluorescence Analysis*, **Encyclopedia of analytical Chemistry**, (Editor: R.A. Meyers), John Wiley & Sons, New York, 2000, pp. 13327-13338.
- [13] M. Vagnini, C. Miliani, L. Cartechini, P. Rocchi, B. G. Brunetti, A. Sgamellotti, *FT-NIR Spectroscopy for non-invasive identification of natural polymers and resins in easel paintings*, **Analytical and Bioanalytical Chemistry**, **395**, 2009, pp. 2107-2118.
- [14] C. Miliani, F. Rosi, A. Daveri, B.G. Brunetti, *Reflection infrared spectroscopy for the non-invasive in situ study of artists' pigments*, **Applied Physics A**, **106**, 2012, pp. 295-307.

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