SPECTROPHOTOMETRIC ANALYSIS FOR PIGMENT PALETTE IDENTIFICATION: THE CASE OF “PROFETA STANTE”

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ABSTRACT

A modern restoration intervention on paintings needs a preliminary investigation of constitutive materials. This investigation is important to take the proper choices before the restoration intervention and it is decisive in order to provide significant research topics. Spectrophotometric analyses have been carried out on “Profeta Stante”, a Fifteenth century oil-painted panel, in order to determine artist’s colour palette using an absolutely non-invasive method. In accordance with the principle of selective light absorption, which is the basis of spectrophotometry, the result of this analysis are reflectance spectra, the trend of which is typical of each pigment or dye. Then, the particular behaviour of a painted surface to a source emitting the visible wavelength range gives evidence of its nature and it shows how every single pigment is also characterized by the presence of other colour components that confer to it its own hue. Following the false colour infrared (IR-FC) photography outcomes, thirty measurement points, representative of the different colour present in the painting, have been chosen in order to identify the artist’s palette and also to evaluate reliability and limits of spectrophotometric and colorimetric analysis when used as preliminary investigation for pigments identification. This work as a whole aims at ensuring an exhaustive pigments comprehension by the combination of the non-invasive techniques which the Centro Conservazione e Restauro “La Venaria Reale” makes use of. The undoubted advantage is to limit the quantity of micro-sampling in accordance with the principle of minimum invasiveness. Following the adopted diagnostic protocol, when the spectrophotometric analysis were found to be insufficient for the pigments’ identification, further non-invasive analysis, such as the X-ray fluorescence (XRF), have been used to solve identification problems.

1. Introduction

The Foundation “Centre for Conservation and Restoration (CCR) La Venaria Reale” hosts a graduate course of the University of Turin in Conservation and Restoration of Cultural Heritage, as well as housing a Restoration Laboratory and a Scientific Laboratory for analysis and research on materials of works of art and technology for conservation. In May 2010, the Civic Museum of Ancient Art in Palazzo Madama, in Turin, has kindly put one of its works of art, the panel painting “Profeta stante”, at the CCR’s disposal, to be studied during a graduation research work. In the most recent inventories of Palazzo Madama, this painting dates back to 1450-’60 and, by the point of view of the artistic style and technique, it’s placed in the area of the painter Jean Bapteur. During the documentation phase, however, it was possible to note that the panel shows the marks of a mechanic working, as if it were planed with a mechanized machinery. For this reason the scientific investigation on the constitutive materials of the artefact has been planned, having two purposes: the identification of original and possible superimposed materials verifying the ascribed dating and the study of the conservation condition aiming to address the restoration activities. Then, since every work of art is a unique piece, the scientific investigation has been carried out through the combination of those non-invasive techniques which the Centro Conservazione e Restauro “La

1 Documents can be found in the Fondazione Torino Musei offices. The inventory number is 468/D.
Venaria Reale” makes generally use of: the undoubted advantage of the use of non-invasive analyses is to limit the quantity of micro-sampling in accordance with the principle of minimum invasiveness. Following the false colour infrared (FC-IR) photography outcomes, thirty measurement points, representative of the different colour present in the painting, have been chosen in order to identify the artist’s palette and also to evaluate reliability and limits of spectrophotometric analysis when used as preliminary investigation for pigments identification. When the spectrophotometric analysis was found to be insufficient or not so clear, a further non-invasive analysis, X-ray fluorescence (XRF), has been used to solve attribution questions.

2. The panel painting “Profeta stante”

The wood panel painting “Profeta stante”, a Fifteenth Century dated artwork by the inventories of Palazzo Madama, represents a stood man wearing a blue tunic with a cowl and a green stole. On a background realized with gold leaf applications, a scroll encircles the man who, in the common iconography, corresponds to the figure of the Prophet [1].

The frame of the panel is incomplete and, because of the presence of eight nail holes, this painting is supposed to be a side panel of a polyptych [2].

As mentioned before, the observation of the marks of the panel working, carried out during the elaboration of the research work, has actually risen an issue about the dating of the artwork: in fact, the marks of a mechanic working have been found out in some areas of the panel surface, as it were planed with a mechanized machinery [3]. It’s important to underline that the Encyclopédie by Diderot and D’Alambert doesn’t mention anything about mechanized machinery used for wood and rock cutting: on the contrary, the first notes are documented during the first half of the nineteenth century.

The apparently perfectly conserved green stole of the prophet has represented another interesting aspect of this issue. It is clear that the superficial characteristics of an area of paint could deeply depend on the nature of the pigments [4], but these green and yellowish green areas of paint figuring the stole are particularly smoothed, showing a superficial texture not present in other areas of the painting.

The entire surface of the panel shows an ageing pattern craquelure of different typologies but always characterized by large paint islands, while, in the green areas, only a microcraquelure is well evident (see Fig. 1).

Finally, the blue tunic of the prophet has been investigated with particular attention, following the interesting outcomes of the false colour infrared (FC-IR) photography.

Fig. 1. Conservation condition of the green areas. Visible light photograph.
3. Materials and Method

Pigment investigation has been performed beginning from a careful examination of the false colour infrared (FC-IR) photography outcomes. Actually, various imaging techniques that are sensitive to a portion of the infrared spectrum have important application in the field of the artistic diagnostic and conservation, representing a preliminary tool for pigment investigation [5].

The FC-IR photographs of the painting panel “Profeta stante” have been taken by an Art Innovation CCD camera in two different ranges of wavelengths (500-950 nm and 500-1100 nm) with the following characteristics:

- CCD monochromatic sensor with progressive image scanning.
- Pixel: 1600 x 1200,
- Signal transfer with standard interface IEEE 1394 “Firewire”,
- Lens: wide-angle lens with C assembling of 23 mm F/1.4 and lens with zoom with C assembling of 18-108 mm F/2.5,
- Diffused lighting with two halogen lamps of 75 W and 3200 °K colour temperature.

Afterwards, spectrophotometric analysis have been carried out by a CM-700D Konica Minolta spectrophotometer. In accordance with the principle of selective light absorption, the result of this analysis are reflectance spectra, the trend of which is typical of each pigment or dye. The particular behaviour of a painted surface to a source emitting the visible wavelength range gives evidence of its nature and shows how every single pigment is also characterized by the presence of other colour components that confer to it its own hue [6, 7, 8].

The CM-700D Konica Minolta spectrophotometer collects reflectance spectra with the following characteristics:

- Wavelength range: 400 nm to 700 nm
- Wavelength pitch: 10 nm
- Geometry: d/8 (diffused illumination, 8-degree viewing angle), SCI+SCE (specular component included and excluded)
- Light source: pulsed xenon lamp (with UV cut filter)
- Measurement/illumination area: ⊙ 8 mm

All the spectra are normalized to both their maximum and their minimum reflectance value in order to better compare the curves.

XRF (X-Ray Fluorescence) analyses have been carried out with μ-EDXRF Bruker ARTAX 200 collecting spectra at 30KeV, 1300 µA with a live time of 60 s using He as fluxing gas to be able to better detect elements with low atomic weight.³

4. Results and discussion

The present paper shows the results of the diagnostic analysis performed on “Profeta stante” with the non-invasive techniques only just described and concerning the two principle areas of paint that appeared the most interesting ones.

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² The shots have been made in darkness condition. The samples are placed horizontally on the table. The camera has been placed above it and diffused lighting realized with two halogen lamps symmetrically put at a 45° edge at a distance of 90 cm. The monochromatic sensor of the FC-IR camera has been set calibrating the 20% of the light for any RGB channel on a grey paper. The calibration of the IR 950-1100 nm has been performed on a grey paper too, keeping a reflectance index of 80% of the infrared.
³ The instrument works in the energy range from 0 to 50 KeV at a maximum of current of 1500 µA. Detector has an energy resolution lower than 150 eV (FWHM) for Kα of Mn (5,9 keV).
4.1 Blue areas of paint: the tunic

As mentioned before, a remarkable aspect of the painting interested the blue areas of paint representing the tunic. These areas had a blue and in places a red false-colour: in particular, the red ones are visible in the right part of the stole near the neck of the Profeta (Fig. 2). So the presence of two different false-colours let suppose that the artist used two different pigments at least to realize the tunic. According to the literature, various pigments such as Cobalt Blue, Smalt, Indigo and Lapis usually have a red false-colour [9, 10].

In order to solve this investigative question, spectrophometric analysis was applied selecting three significant measurement points on the red false-colour areas and as many points on the blue false-colour ones.

The black curve in figure 3 represents the reflectance spectrum of a red false-colour area. Actually, the interpretation of the results wasn’t so easy, showing the limits of the spectrophometric technique when used to investigate colour mixtures.

The graph shows the measured spectrum compared with the ones of two standards of pure powder pigments, Azurite (light blue curve) and Indigo (dark blue curve). Even comparing the reflectance spectrum of an area under investigation with the spectra of single powder pigments, it is possible to see that the trend of the measured point’s spectrum is similar to the Azurite’s one along the short wavelengths of the visible spectrum; its tail in the long-wavelength end, on the contrary, has a trend that is similar to the Indigo’s one.

Finally, the as possible presence of a Lead White pigment in the mixture could explain the shift to 510 nm of the main reflectance pick [11].

Actually, the comparison of the measured curve with an available database of reflectance spectra of pictorial materials [12] has allowed to suppose that both Azurite and Indigo have been used to paint the tunic of the prophet and also that Indigo has been probably used as preparation layer under the Azurite layer. Generally, in fact, a thin film of Indigo on an Azurite layer doesn’t show a red colour in FC-IR because of the high infrared absorption of the Azurite underneath.

In the other areas of the tunic that had only a red false-colour, Azurite could have undergone a loss of material in consequence of the aging and deterioration effects.

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4 The reflectance spectra of Azurite and Indigo come from a database concerning artistic pigments and materials which has been realized by the CCR’ Scientific Laboratory by using the spectrophotometer CM-700d Konica Minolta.
Table 1 shows the results of the XRF investigations made on the same points analysed with the spectrophotometer. The peaks of Ca, Si, Fe, Sr, K can be attributed to the preparation under the painting layers, while the signals of Pb and Cu are related to the pigments. The blue areas having a blue false-colour show more intense peaks of Cu and Pb. All elements are well-matching with the hypothesis on the substrates made after the preliminary spectrophotometric analysis.

Table 1. Results of XRF analyses.

<table>
<thead>
<tr>
<th></th>
<th>Cu (Kα)</th>
<th>Fe (Kα)</th>
<th>Pb (Lα)</th>
<th>Ca (Kα)</th>
<th>K (Kα)</th>
<th>Sr (Kα)</th>
<th>Si (Kα)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 blue (FC red)</td>
<td>157</td>
<td>15</td>
<td>165</td>
<td>118</td>
<td>5</td>
<td>18</td>
<td>5</td>
</tr>
<tr>
<td>3 blue (FC blue)</td>
<td>373</td>
<td>20</td>
<td>239</td>
<td>101</td>
<td>8</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>15 green (FC blue)</td>
<td>1361</td>
<td>18</td>
<td>95</td>
<td>127</td>
<td>12</td>
<td>11</td>
<td>6</td>
</tr>
</tbody>
</table>

4.2 Green areas of paint: the stole

As described in paragraph 2, the green stole of the prophet showed very particular and interesting characteristics because of its superficial texture and of its apparent good conservation condition. The constitutive pigments had been investigated as usual following the FC-IR photography outcomes. As figure 2 shows, the stole had a blue false colour, that could be ascribed to different pigments such as Malachite, Copper Resinate or Copper Acetate.

In this case, from the XRF analyses’ results (table 1) it was possible to reveal the presence of Copper, Lead and Calcium, unfortunately not solving the investigative question (both Malachite and Resinate or Acetate contain Copper).

Subsequently, the spectrophotometric investigative technique turned out to be solving: the reflectance spectra relative to five measurement areas selected on the stole have been collected and compared with standard samples of different green pigments. Because of the proved presence of Copper, a mixture of one yellow pigment with Azurite also has been supposed but, as figure 4 shows, the most reliable interpretation was that the stole had been realized with Copper Resinate.

5 In literature, Azurite has a dark blue false-colour too [9].

6 The reflectance spectrum of Copper Resinate comes from a database concerning artistic pigments and materials which has been realized by the CCR’ Scientific Laboratory by using the spectrophotometer CM-700d Konica Minolta.
In order to evidence this supposition, the graph illustrates one of the reflectance spectra (black curve) compared with the one of a Copper Resinate standard sample (green curve): as it’s easy to see the two reflectance picks have been both recorded at 560 nm and the curves’ trends result very similar. Even the possibility that it could be Copper Acetate has been easily excluded since the Acetate curve showed a reflectance pick at shorter wavelengths.

5. Conclusions

According to the principle of the minimum invasiveness the scientific examination of the wood panel painting “Profeta stante” has been carried out using only non-invasive and non-destructive techniques. The question was to highlight the presence of materials dated after the attribution age. The painting, in fact, was dated back to the Fifteenth Century by the inventories of Palazzo Madama but the panel presented the marks of a mechanized planing ascribed to later periods. The diverse aspect of the surface showing craquelure patterns of different typologies allowed us to hypothesize the presence of recent materials taken back to previous restoration interventions. As well known, indeed, the identification of a modern pigment could allow to reveal fakes or recent interventions, although the finding of ancient pigments only, on the other hand, cannot assure the originality of the artwork. During the entire investigation the spectrophotometric analyses have been carried out following the false-colour infrared outcomes and in combination with the X-ray fluorescence analysis. The spectrophotometric technique has turned out to be successful for pigment investigation, although the interpretation of results needs the availability of databases of pigment reflectance spectra of masstones, depeptones and mixtures to solve some attribution questions. In the case of “Profeta stante”, no modern pigment has been identified. Concerning to the selected hues on this painting, the results have shown that Copper Resinate has been used to realize the green areas of paint, Indigo and Azurite to realize the blue ones. The question of dating is loose end, but anyway the combination of the applied techniques has permitted a good identification of the palette, without sampling.

Acknowledgments

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References

[12] [http://fors.ifac.cnr.it/main.php](http://fors.ifac.cnr.it/main.php)