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Non-destructive in situ examination of a 16th century Spanish panel painting "San Telmo"

ABSTRACT

The panel painting San Telmo by an anonymous 16th century Spanish artist is part of the permanent exhibition at the Fine Arts Museum of Seville, one of the most important Spanish galleries. As part of a larger study on 15th and 16th century Spanish painting, the principal interest of this work was to obtain more information the materials applied in its creation. The research work was carried out in situ in the exhibition room; hence, only non-destructive analytical methods were applied. The painting was first studied with UV light to observe later interventions. After this, a possible preparatory drawing was searched for with IR reflectography (IRR). Finally, a portable X-Ray fluorescence (XRF) equipment was applied for a material analysis. The UV image of the painting clearly revealed later interventions, which helped to select the points for the XRF analysis, to distinguish between original and modern pigments. The XRF analysis showed that the painter's palette was common for the 16th century, and similar to those found in other panels from the same period in the Museum collection, namely: lead white (identified by Pb), yellow and red ochres (Fe), vermilion (Hg), a copper based green pigment (Cu), azurite (Cu), and an organic black, probably bone black (Ca). Several retouches made on the bases of Zn and Ti whites were confirmed. The presence of Ca and Pb in every analysed point shows that there must be a calcium based preparation, probably gypsum, with a lead based priming. Most interestingly, the IR images revealed not only a very precise and decisive artist's brushstroke, observed in the modelling of the subject's head or clothing, but also a change in the shape of the boat that the Saint holds in his left hand (pentimenti).

Keywords: 16th century, panel painting, pigments, preparation, UV, IRR, XRF

1. Introduction

The Fine Arts Museum of Seville, one of the most important Spanish galleries, has a rich collection of paintings and other objects dating from the 14th till the 19th centuries. In the past, the group of artworks that belong to the Spanish painting schools of the 15th and 16th centuries had not been studied in great detail, and thus a collaboration project between the Museum and the Centro Nacional de Aceleradores (CNA-US) in Seville was started some years ago. It is dedicated to the characterization of materials from selected paintings, among which includes the very interesting *San Telmo* panel (Fig. I). It was created in the 16th century by an anonymous Spanish artist and today belongs to the Museum's permanent exhibition. It was restored several years ago; however, no material analysis was performed at that time.

The painting is a deposit of the University of Seville (from 1908) and is originally from a small church in the neighbourhood of San Telmo (Seville), as explained by the inscription on the frame. Although its author is not known, it can be stylistically situated in the Seville painting school of Alejo Fernandez, a well known artist that combined a Hispano-Flemish tradition with a Northern-Italian style into his own artistic expression [1, 2].

San Telmo is painted on a wooden support, made of three vertical panels, joined by three horizontal crossbars, and fixed with round metal nails and forged clamps. During a previous restoration, two wooden stripes on both vertical sides were added. The wood was not analysed, but the vertical panels are thought to be made of walnut and the horizontal ones, pine. On the front side, there is a canvas fixed over the panel. The colour layer is very thin and generally still well preserved, except in the lower part where the painting must have been more exposed to damage (Archives of the Fine Arts Museum, Seville).

2. Objectives and experimental procedure

Although the Museum documentation describes the conservation state of the panel very well, no information on the materials applied was found. This is why the artwork was selected for a non-destructive analysis. The principal objectives were: (a) to get information on the pigments applied, (b) to characterize preparation and priming, (c) to find out preparatory drawings and their possible changes, and (d) to identify later interventions and retouches.

The study of the painting was carried out *in situ* in the exhibition room, and only nondestructive techniques were used: ultraviolet light (UV) to observe later interventions, infrared reflectography (IRR) to reveal possible preparatory drawings, and X-ray Fluorescence (XRF) for material analysis. For UV images that must be obtained in the dark, we used four multi-band split tube handheld UV lamps (254 nm/365 nm) UVGL-55, which were fixed on a stand to illuminate the surface of the entire painting [3, 4]. Images were captured by a Nikon digital camera. For IR reflectography we used a Xenics near

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IR Xeva-XS 512 camera with InGaAs detector, with a resolution of 320 x 256 pixels and a 16 mm F/I.4 Pentax lens. The images are captured with X-Control software. For a precise scanning of a painting surface, the camera is coupled to a platform made by Optimind, which allows a smooth movement in the X and Y directions (Fig. II). This facilitates the obtention of images from the entire painting/artwork. For this purpose, two halogen SDI-800 W light reflectors were also used, which facilitate IR radiation. IRR is an analytical method that captures the reflected IR using a specially designed detector. When an object is illuminated with a halogen light, infrared radiation will not only interact with the surface, but will also penetrate and interact with underlying layers giving in-depth information about the materials used [5, 6]. This is why the preparatory drawings under the painting layers can be observed to reveal important information not only regarding the painting procedure, but also the artist's own hand and therefore, in some cases, the authorship.

The material analysis of San Telmo was carried out with X-Ray Fluorescence, an analytical technique that identifies chemical elements (and not molecular composition) with atomic numbers higher than 14 (Z>14). Therefore, it serves for the characterization of inorganic materials rather then organic ones. Also, materials with the same characteristic chemical element can not be distinguished (for example, copper based green pigments). Nevertheless, it is a very useful technique for a preliminary material analysis of Cultural Heritage, especially where no samples can be taken from the artwork [3, 7, 8]. Our XRF equipment is a portable device that consists of an EIS X-Ray generator RX38 and silicon drift detector (SDD) of 140 eV energy resolution (Fig. III). An Al filter of 1 mm thickness was coupled to the X-Ray tube exit to suppress the W L peaks of the anode that overlaps with the Cu K peaks, which is important in the identification of several pigments. On the spectra Zr K α and K β peaks from a collimator of the detector can appear, but these do not interfere with the results. The diameter of the radiated spot was 3 mm. The painting was measured under the same fixed conditions: 80 µA cathode current, 30 kV applied high voltage and 300 s preset live time. The fixed conditions allowed the direct comparison of the results at different analysed points in a semi-quantitative analysis. All colours and tonalities were analysed, and therefore 33 points were selected across the painting surface. The pigments were identified according to the characteristic energy (keV) of the X-ray peaks in each obtained spectrum, which correspond to specific chemical elements.

3. Results

3.1. UV light

Under the UV light several retouches were observed, seen as dark areas on the surface (Fig. IV). Newer materials do not give off the UV fluorescence as the old ones do, so they are easy to detect under the UV light [3, 4]. Those are mostly found along the exterior borders and at the junction of the three wooden panels. Through time, those materials dried and slightly moved, which is why the painting layers were also damaged along the junctions. There are also many smaller areas over the entire surface that had to be restored. The UV images also served also as a support for a better selection of the points analysed by XRF, in order to distinguish between the original and modern pigments.

3.2. IR reflectography

The results obtained with IRR fulfilled our expectations; they revealed a complete preparatory drawing made by the artist. It was probably carried out with black carbon, which has a very good absorption under IR radiation. We can appreciate the artist's decisive brushstroke in the elaboration of the principal figure, the shades of the clothing (Fig. V) and the formulation of the smaller elements in the composition, such as the architecture in the background or the boat in San Telmo's left hand. An interesting discovery was observed in the shape of the boat: it was originally bigger than in the final execution (Fig. VI). Some changes can be seen also on the Saint's head – in the shape of his mouth and of his hair, as well as in the position of his left hand. Besides his precise drawing, therefore, also *pentimenti* were discovered, which reveal to us the artist's painting procedure and changes to the composition.

3.3. X-ray Fluorescence

The painting was analysed at 33 points of different colours, tonalities, shades and highlights, in order to get information on the pigments applied. The results showed that the principal chemical elements in all analysed points are Ca, Fe, Cu, Hg and Pb, while Ti, Zn and Au can only be found only in specific ones. The presence of those elements proportional to the area of their characteristic peaks (values of their count numbers/cps) varies depending on the pigment applied and its relative quantity at the radiated point.

3.3.1. Preparation and priming

In all analysed points the presence of Ca, Hg and Pb can be observed. The peak areas vary, depending on the colour analysed. However, their constant presence shows that they must form part of the entire painting surface. The Ca peak area is generally low, so it must come from deeper layers, probably from the preparation. This was confirmed on the gilded areas, where there are no colour layers between the preparation and the bole with gold, therefore the Ca signal is stronger and easier to detect. In these spectra (Fig. 1), the area of Ca peaks increases several times and so confirms the existence of a calcium based preparation. It could be made of calcite (calcium carbonate, $CaCO_3$) or gypsum (calcium sulphate, $CaSO_4$). Keeping in mind that it is a Spanish artwork where gypsum was a common panel preparation, the second identification is more probable [9, 10, 11].

On the other hand, the presence of Hg and Pb in all of the analysed areas identifies the existence of a priming layer made of a lead based pigment (probably lead white) and vermilion. Vermilion is not a common pigment for priming, so the results were unexpected. However, its use can be confirmed also by the naked eye: in some cases, a reddish layer can be observed under the upper painting layer.



Fig. 1. XRF spectrum of gilded nimbus confirming the presence of gold (Au) on a bol (Fe) layer. High Ca peaks reveal the existence of calcium based preparation (probably gypsum)

3.3.2. Pigments

On the bases of the elemental analysis, the inorganic pigments on the painter's palette were identified. The artist used pigments that were common for the 16th century [8, 10–16]. The white pigment was lead white ((PbCO₃)₂·Pb(OH)₂), characterized by Pb, used for white draperies and to lighten up darker pigments. Together with vermilion (Hg) was the principal pigment for flesh colour, where ochres (Fe) and copper based green pigment (Cu) were also used to obtain a desired tonality. The areas of characteristic peaks in the spectra obtained from flesh tones vary depending on if the tonality is lighter or darker. In lighter ones, Pb peaks are higher, while in darker ones, Fe, Cu and Hg peaks are stronger (Fig. 2). Vermilion (HgS) was one of two red pigments selected by the painter and identified with Hg. Apart from the flesh tones, it was also applied in the clothing of small figures (maybe sailors or merchants) on the boat and in the background, as well as in the priming as explained above. The other inorganic red pigment was red ochre (Fe₂O₂) characterized by Fe peaks. It was mostly used in a mixture with other pigments, especially in flesh tones or for darker areas. In addition, yellow ochre (Fe(OH)), the only inorganic yellow pigment on the artist's palette, was mostly mixed with others; however, direct analysis of yellow confirmed its use (Fe peaks). Copper was found in several analysed points of blue and green. In blue areas the pigment is without a doubt azurite $(2CuCO \cdot Cu(OH)_{2})$, while the identification of the green pigment is more complicated. There are several green pigments based on Cu, which is the only chemical element detected by XRF. This is the reason why it is not possible to make their precise identification with this technique. Nevertheless, in the 16th century there were mostly three Cu based green pigments in use, malachite (CuCO₃·Cu(OH)₂), verdigris (Cu(CH₃COO)₂·2H₂O) and copper resinate (Cu(C₁₉H₂₉COO)₂), which according



Fig. 2. Comparison of two XRF spectra obtained from flesh tones on the Saint's cheek (straight line) and hand (dot line). The colour is made of lead white (Pb), vermilion (Hg), ochre's (Fe) and a copper based green pigment (Cu). Peak intensities vary depending on a darker or lighter tonality, observed especially with Fe peaks (ochre)

to recent investigations is not a pigment but a product formed from a reaction between the varnish and verdigris [17]. The cover strength of malachite in the oil technique is not very strong and its green colour not very intense; this is why the most probable pigment in this painting is verdigris. The black pigment used for the final contours and for shades, as well as for the darkening of other pigments, is probably bone black. It is characterized by Ca that appears on the spectra of dark and black areas. However, for its certain identification C and P peaks should also be confirmed, but those two chemical elements are too light (Z>14) to be detected by XRF. San Telmo's nimbus was also analysed and high Au peaks on the spectra confirm the presence of genuine gold. It was applied in thin leaves over a layer of red bole, identified by Fe (Fig. VI).

3.3.3. Later interventions

XRF analysis carried out on several points selected on the bases of UV images confirmed the presence of modern pigments applied for retouches. The presence of Zn and Ti show the use of zinc (zinc oxide, ZnO) and titanium whites (titanium dioxide, TiO_2), the first one entered the artistic market at the end of the 19th and the second in the beginning of the 20th century [10, 11, 15, 16]. They were mixed together with other traditional ones, especially ochres (Fig. 3).



Fig. 3. XRF spectrum of an area of later intervention. Zn and Ti peaks confirm the application of modern pigments Ti and Zn whites

4. Conclusions

The panel painting San Telmo, part of the permanent exhibition in the Fine Arts Museum of Seville, was analysed with non-destructive techniques: UV, IRR and XRF. Later retouches, preparatory drawings and *pentimenti* were discovered, and most of the painting materials were identified on the basis of their characteristic chemical elements. We were able to confirm the application of a calcium based preparation, which is most probably gypsum, and a priming layer made of a lead based pigment potentially and vermilion. The pigments on the painter's palette are common for the 16th century. It was possible to identify only inorganic pigments; however, the painter must have also used organic colorants, mostly red lakes. These cannot be confirmed by XRF due to their characteristic chemical elements with Z>14. The artist usually mixed two or more pigments to obtain a specific colour. The highlights were modelled by adding more lead white, while shades were obtained with ochres and/or bone black. The comparison of these results with our database, obtained during the research project between the Museum and CNA-US, shows the similarity in the selection of pigments, to that used by other Spanish artists of the time. Also the application of genuine gold on top of the bole was a common procedure also found on other Museum panels analysed so far. A complete study of this panel represents important additional information for a better understanding of Spanish painting schools of the 15th and 16th centuries.

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