



Conserving Cultural Heritage

Editors

María J. Mosquera
M.L. Almoraima Gil

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CONSERVING CULTURAL HERITAGE



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Departamento de Química Física, Universidad de Cádiz, Spain



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Analysis of materials during the restoration of *Tota Pulchra*

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ABSTRACT: *Tota Pulchra* (around 1600), a high quality copy of a painting made by an anonymous artist copying probably an Italian painter Giuseppe Cesari, was recently restored due to its bad conservation state. Before and during its intervention, the artwork was analysed in order to get information about materials and painting technique and help at the restoration process. Several invasive and non-invasive techniques for material identification have been used. Extracted samples were studied with OM, SEM-EDX, FTIR and GC-MS. The results revealed the usual palette for the 16th century, linseed oil binder, chalk based preparation and a complex pigment mixture for priming, as well as several later interventions. Under the OM, also organic fibers from the canvas were identified as flax support for the painting.

1 INTRODUCTION

1.1 *Tota Pulchra*

Origin and authorship of this canvas are unknown, but according to its style, it can be situated around 1600. It is probably a copy of a painting made by Giuseppe Cesari (1568–1640), an Italian Mannerist painter, much valued in Rome by the Popes and high society. He developed a personal style characterized by strong colours and chiaro-scuro, and was known as a fresco and as a canvas painter (Röttgen 2002). One of his artworks known as *Inmaculada* was sent to a College of Jesuits in Seville (today at the Royal Academy of Fine Arts of San Fernando in Madrid), where it became very famous and was probably copied several times. One of these copies can be found today at the Royal Academy of Fine Arts of St. Elisabeth of Hungary in Seville. Due to its bad conservation state, it was recently restored by the professionals of the Andalusian Centre for Cultural Heritage (Centro Andaluz de Patrimonio Histórico – IAPH) and during that time, also several material analyses were carried out to support the intervention process.

1.2 *Conservation state*

The conservation state of the painting was very degraded, principally due to a fracture in the lower part of the canvas, but also due to natural processes

of ageing of the materials and to some unfortunate interventions in the past. Therefore, the restoration was principally directed towards the removing and repairing of the existing damages, but also to return to the painting its aesthetic presentation.

2 OBJECTIVES AND EXPERIMENTAL

2.1 *Objectives of the analyses*

To support the intervention, the painting was analysed before and during the process. The objectives of the analyses were to get information on (a) support/canvas, (b) preparation and priming, (c) pigment palette of the artist, (d) binder and varnish used, (e) inner structure of the painting, (f) preparatory drawing and possible *pentimenti*, (g) later interventions, and with all these, (h) the painting technique and artwork's history. The information should allow the restorers to better distinguish original parts from later additions and to carry out supported cleaning of the painting surface, as well as to use the same or similar materials as the original ones.

2.2 *Experimental procedure*

For the analysis of the painting, non-invasive and invasive techniques were selected (Artioli 2010, Volpin & Appolonia 2002). Among the first ones,



Figure 1. Caption of *Tota Pulchra* by Giuseppe Cesari (1600).

the examination with transmitted light and UV fluorescence was applied to see later interventions, then infrared reflectography (IRR) was used to detect possible preparatory drawing and at the end radiography for the inner structure of the painting. As non-invasive technique also X-Ray Fluorescence (XRF) (Fig. 2) was carried out directly *in situ* to identify inorganic materials (preparation, priming, pigments) present in the painting. A tungsten (W) tube was used, always under the same measurement conditions (voltage 34 kV, cathode current 80 mA and time of 200 sec) to compare the spectra obtained (Seccaroni & Moioli 2004).

Besides, three samples of colour layers (Virgin's blue coat and pink tunic, angel's knee) and one of textile fibers from the canvas were extracted. The first three were prepared as cross-sections in a polished methacrylate resin and studied under optical microscope (OM) and scanning electron microscope (SEM) with energy dispersive X-Ray Spectroscopy (EDS) at the IAPH laboratories. Organic fibers were studied under OM. For identification of organic materials, such as binders, varnishes and lakes, Gas Chromatography with Mass Spectroscopy (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR) in transmission and in ATR mode at the Arte-Lab in Madrid.



Figure 2. Caption of in situ XRF analysis. The equipment uses RX30 EIS S.L. X-Ray generator of 30 kV and Amptek SDD detector with energy resolution 140 keV.

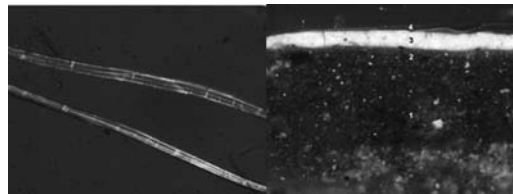


Figure 3. (a) Caption of linseed fibers under OM. (b) Caption of a cross-section under OM (x20). Virgin's pink tunic. Preparation (1), dark underpainting (2), light pink (3) and varnish (4) layers can be distinguished.

3 RESULTS

3.1 *Painting support*

Support for the painting is composed of canvas, and preparation. The analysis by OM of textile fibers from the canvas showed characteristic image of linseed fibers (Fig. 3a), which allows identification of flax support. This was covered with a thin layer of preparation, made of chalk, identified with XRF and SEM-EDS. It seems that there are not two separate layers of preparation and priming, but that they are combined; chalk is mixed, with other pigments, applied to give to the surface a common darker tone which facilitates later colour modelling and makes painting quicker (Fig. 3b). Material analyses identified earths (Fe), traces of lead white (Pb), vermilion (Hg), lead-tin yellow (Pb, Sn) and azurite (Cu). The presence of azurite in priming surprises due to its elevated cost, but under OM blue particles can be identified. Also, some pyrite and titanium oxide (rutile) nodules are observed.

3.2 *Pigments and binders*

Most of the pigments were identified with non-destructive XRF technique and also confirmed with SEM-EDS or FTIR. In some cases, the last two

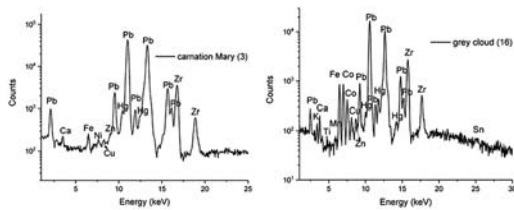


Figure 4. (a) Caption of XRF spectrum showing carnation of the Virgin Mary, made of lead white (Pb), vermilion (Hg), red or/and yellow ochres (Fe) and a Cu based green pigment. (b) Capture of XRF spectrum of a gray cloud in the background. Blue smalt (K, Co, Ni, As), lead white (Pb), red ochre (Fe), vermilion (Hg) and umber (Mn, Fe) are identified.

techniques cleared the doubts in identification by XRF, which can be limited due to several factors (Seccaroni & Moiola 2004). With XRF different colours and tonalities were selected, in order to get the whole palette and also to find out how the shades and highlights were carried out. The pigments used are general for the time between the 16th and the 17th centuries (Eastaugh 2008, West Fitzhugh 2012): lead white (identified by Pb peaks), which was used also in carnations (Fig. 4a) and for highlights; for yellow colour, the painter used mostly yellow ochre (Fe), while lead-tin yellow (Pb, Sn) was used for highlights or to reproduce gold (stars, Virgin's aureole). There were three substances used for red colour: red ochre (Fe) and vermilion (Hg) identified by XRF and EDS, but also red lake, identified by FTIR.

As for blue colour, the artist chose two pigments: expensive azurite (Cu) for more important areas like Virgin's or angel's vestments or for shades on white cloths. Also, violet colour was obtained mixing azurite with vermilion, red ochre and lead white. On the other hand, much cheaper blue smalt (K, Co, Ni, As) was applied in wider areas of background, as sky, clouds (Fig. 4b) or the sea. This pigment also suffered non-reversible chemical changes, has darkened and lost its blue hue (Eastaugh et al. 2008, West Fitzhugh et al. 2012). As green pigment, a copper based one was used, which cannot be identified precisely due to characteristic Cu chemical element, identical for several green pigments. Having in mind the time of the artwork, it could be verdigris or copper resinate. For shades and darker hues, umber (Mn, Fe) and bone black (Ca) were added. For identifying organic materials, GC-MS was the best solution; it allowed to precisely characterize the binder used by Cesari as linseed oil and therefore to confirm the painting technique as oil one.

3.3 Preparatory drawing and inner structure

Unfortunately, no preparatory drawing was discovered by IRR, however it helped revealing some later interventions not observed under the UV light, as well for general location of Fe and Pb based pigments. On the other hand, radiography showed that the canvas is composed of 4 vertical stripes and also showed some deeper later interventions, together with the



Figure 5. (a) Caption of a detail under UV light, (b) capture of radiography detail. Retouches, the line between two canvas strips and canvas structure can be observed.

identification of the areas painted with Pb or Hg based pigments.

3.4 Later interventions

They were discovered combining transversal and UV light (Fig. 5a), IRR, radiography (Fig. 5b) and XRF elemental analysis. In the retouched areas, the presence of modern pigments from the end of 19th and beginning of the 20th centuries were discovered, such as titanium (Ti) and zinc (Zn) whites, and rarely (Cd) cadmium yellow.

4 CONCLUSIONS

Material analysis of *Tota Pulchra* identified pigment palette common for the 16th century, linseed oil as the binder and a complex mixture of pigments for the preparation layer on linen canvas. The artwork was accordingly relined, surface consolidated and cleaned, lacunas were plastered and chromatically reintegrated, following the analytical results. The restored painting has returned to its collection.

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