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Spectroscopic investigation of a '*Virgin of Sorrows*' canvas painting: A multi-method approach

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Abstract

The investigation of unmatched ancient objects is an attentive and arduous activity to conservation scientists. An important aspect of art analysis is the question on sampling and avoiding damage on the artefact during the study. A possible way to maximize the information that is extracted from the historical object is using several sensitive micro-analytical techniques on the same micro samples. As an illustration of this multi-method approach, in this work, a canvas painting '*Virgin of Sorrows*' was studied and its materials were analysed in order to roughly date and to authenticate this object of art. Proton induced X-ray emission (PIXE), neutron activation analysis (NAA), optical microscopy, scanning electron microscopy (SEM), micro-Raman spectroscopy (MRS) and Fourier transform infrared spectroscopy (FT-IR) were used, obtaining successful results. These methods allowed identifying the different inorganic pigments (iron oxide, carbon black, white lead, Prussian blue) as well as indigo. Optical microscopy and SEM revealed the layered structure of the samples, while FT-IR enabled to determine the nature of the varnish used (shellac). By using these complementary techniques, it was possible to identify the materials in the painting, which are indicative for the period of manufacturing the artwork.

Keywords: Art analysis; Pigments; Oil paintings; Falsification; Proton induced X-ray emission (PIXE); Scanning electron microscopy (SEM); Micro-Raman spectroscopy (MRS); Neutron activation analysis (NAA); Fourier transform infrared spectroscopy (FT-IR)

1. Introduction

Since ancient times, men have collected a large amount of religious art objects. Art production has propitiated a rise and speculation in art prices and together with this, transgressions occur such as theft, falsification and illegal art trade. Mexico is not an exception and thus, it is not surprising to find falsifications of paintings from national artists like, among others, *José María Velasco* (1840–1912), *Frida Khalo* (1907–1954), *Diego Rivera* (1886–1957) and *José Clemente Orozco* (1883–1949). Colonial paintings and religious motifs have been falsified or copied as well [1].

This work handles on the examination of forgeries in Mexican oil paintings. In Mexico, little historical information is available on the techniques and materials that were used by Mexican artists during the Colonial period (1535–1810 A.D.). Here, the first effort in the country is presented to perform this kind of study, using as much as possible both historical and technical data. An oil painting, representing the '*Virgin of Sorrows*' was studied in this work. It was acquired by a private collector as 'an ancient painting', without documentation on its provenance, artist signature or elaboration date. The aim of this study was to date and authenticate

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the work. Traditionally, these investigations include image description, investigation of the underdrawing, iconographic analysis, examination of the general condition of conservation and a study of the canvas structure. In this case, all these examinations were performed by a team of art-historians and conservation specialists, who found that the painting was elaborated during the last half of the 18th Century, or the first third of the 19th Century (i.e. between ca. 1750 and 1830). In this type of devotion paintings, the Virgin is depicted with either one or seven swords into her hart, which represents her at the cross, suffering for Christ's sacrifice. The worship of the '*Virgin of Sorrows*' appeared in New Spain since the 16th Century and became popular during the 17th and 18th Century, staying popular during almost the whole 19th Century.

In order to be able to identify forgeries as such, several valuable tools are at the investigator's disposal. Obviously, the study of art history and of the cultural heritage helps to solve falsification crimes [2]. Traditionally, dating and the determination of the provenance and the authenticity of artworks have mainly been carried out by art-historians and restorers. In the case of canvas paintings, they focus their interest on aspects such as technique, style, colors, iconography, type of canvas, tensions in the canvas and the state of conservation of the object of art. Most of their investigations are done by the naked eye and by microscopic analysis. Together with the information that is obtained by these methods, consistent evidence of the art materials obtained by means of analytical investigations may help answering specific questions of the art-historians and specialists [3]. In Mexico, during the last years, there is a growing interest for the scientific analysis of antique objects of art. However, an important drawback for the wide application of spectroscopic methods of investigation of antiquities is the fear that the precious artefact might be damaged during analysis. There are discussions going on whether or not it is allowed to sample the artefact for analysis. In any case, if sampling is required or not, the scientist always has to balance the possible risks of damage against the profits that are obtained from the investigation. For each examination, although it is impossible to express this in a numeric format, the risk-of-damage/information ratio should be considered and optimized as much as possible. One way to rise this ratio is done by increasing the amount of information that is obtained from the micro-samples. This is what makes a multi-method approach so favourable.

Today, several methods of experimental physics and analytical chemistry are applied to the identification of pigments in paintings, painted artefacts and antiquities, among them, neutron activation analysis (NAA)[4,5], X-ray diffraction (XRD) [6,7] and X-ray fluorescence (XRF) [8,9]. Analysis by proton induced X-ray emission (PIXE) [10,11], low vacuum-scanning electron microscopy (LV-SEM) [6,7] and micro-Raman spectroscopy (MRS) [8,9,12,13] have been applied for the analysis of paintings. Pigments [4–6,12], binding media and varnishes [13,14] were identified with different aims: to reconstruct the palette of a particular artist or to obtain historical information on the relationship between populations, trade and migration of cultural groups. Other reasons are to understand the mineralogical background, to provide knowledge on technological evolution, the study of degradation processes of pigments and binding media to help in the preservation and restoration of the objects and to check the authenticity or provenance [1,2,6,8,9,11]. All these studies are based on the analysis of artists' materials, pictorial techniques, manufacture process, etc. During history, painting techniques were conditioned by the size, quality, shape, availability and commercialisation of the painting materials [15–17].

2. Experimental

2.1. Samples

Some investigations could be performed directly on the painting. The areas that have been examined are marked in Fig. 1. In order to be able to perform other investigations as well, sampling of the painting was necessary.

For reasons of comparison, as far as possible, the same positions were sampled, taking advantage of painting's fissures; if not similar shaded areas were chosen (Fig. 1). Samples were labelled Blue-1, Blue-2, Red-3, Red-M4, White-5 and Black-6. They were obtained from the painting by carefully scraping minute portions of the surface from the six col-

Fig. 1. Sampling positions on the '*Virgin of Sorrows*' painting. Samples are labelled: (1) Blue-1, medium blue; (2) Blue-2, light blue; (3) Red-3, left hand; (4) Red-M4, left wrist; (5) White-5, veil; and (6) Black-6, bottom of tunic right side.