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# A new approach to the determination of the synthetic or natural origin of red pigments through spectroscopic analysis

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ABSTRACT

This work suggests a way of differentiation between the natural or synthetic origin of inorganic materials that were historically used in the Cultural Heritage field. An exhaustive review of different reported procedures of synthesis of pigments was conducted, as well as a review of the accompanying minerals in case of natural pigments. The natural or synthetic origin of the pigments studied in this work was performed through the characterization of the accompanying minerals, in the case of the natural pigments, or the trace elements that are present as part of synthesis by-products or washing/purifying reagents and/or reactants that have only been partly removed in the final steps of these processes. This work characterized red pigments due to their wide variety, complexity and possibility of use in different mixtures. The following pigments were studied: cinnabar-vermilion, red lead and iron pigments. Also mixtures of these pigments between them and with red lake were also studied. Natural cinnabar was accompanied by silicon oxide (opal, chalcedony or quartz), calcite, clay minerals and, sometimes, pyrite. K together with S indicated a synthetic pigment (vermilion) obtained through the wet method. Nevertheless, K has not been found in layers containing only vermilion in our samples. The presence of Sn in some cases indicated vermilion that came from the dry process. K from the synthesis always appeared in the red lead pigment. The red natural ochre was confirmed by presence of clay minerals and iron. It should be said that Ca and S, and sometimes Al and K, were usually found in Mars red pigment. The presence of Al and Ca allowed the identification of carmine lake.



## 1. Introduction

The characterization of the different materials used in artwork is a well-established matter in the scientific studies in the Cultural Heritage field. The identification of the pigments on such substrates as canvas, polychrome sculptures, wall paintings, and ceramics is undoubtedly important in understanding the history of a work of art, as well as in the resolution of problems related to conservation, restoration, dating and author attribution. Several techniques are especially suitable for pigment identification, including micro-Raman, micro-Fourier-transformed infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and X-Ray fluorescence (XRF) [1–6]. Analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS) is another powerful tool for analysing complex matrices [7]. This technique results in the determination of organic materials because it can identify specific pyrolytic profiles and molecular markers [8,9].

However, the assignation of the natural or artificial (synthetic) character of pigments has been one of the most difficult questions that have been discussed in the scientific studies in the Cultural Heritage field. The optical microscopy using both transmitted and reflected light has been applied to distinguish morphology (i.e. azurite and malaquite) and also to characterize impurities [10,11].

For a proper characterization of the constituent materials and a determination of its natural or synthetic character, samples that contain all the layers, from the varnish to the support (fiber, wood, wall, leather or metal) are required. The analysis of chemical elements in low concentrations will provide hints for the determination of both the different synthesis procedures and the determination of the accompanying minerals that are present in low proportion in the natural materials. Therefore, the preparation of cross-sections containing all the layers of the artworks, allows for a better understanding of the physical nature of the pictorial surface, and it can define where the original painting starts and ends, helping in the visualisation of the degradation, and even revealing the techniques of the different artists [4].

The optical characteristics should provide some clues pointing towards the nature of the pigments, but some difficulties occur, especially in the case of the red strata studied in this work. Red colours are often obtained through mixtures, and the overlapping of different pigments

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and dyes renders the observation difficult and requiring complementary techniques. The integrated information will be of help in the discrimination of the synthetic or natural origin of the materials.

For this purpose, we have reviewed the different methods of synthesis of red pigments throughout history, and we have tried to identify the possible reagents that were added in excess to the process of synthesis and/or the possible by-products that were not completely removed after the purification and washing process. To accomplish this, we searched for different trace elements in the microanalysis that was conducted with SEM-EDX. In other cases, some of the accompanying minor minerals have indicated the natural origin. This was achieved, in some cases, through micro-Raman spectroscopy.

The aim of this work was the discrimination of the natural or synthetic origin of pigments and pigments mixtures. Different methods of characterization were described, and a hypothesis based upon the characterization of certain key elements in low proportion in the chemical composition of the samples was suggested. Samples belonging to different artworks from the Cultural Heritage of Southern Spain were studied.

The colours studied in this work were red and ochre pigments containing cinnabar/vermilion, iron oxides, red lead and red lake.

## 2. Experimental

### 2.1. Materials

Samples were taken from different representative artworks from the Southern Spain Cultural Heritage. Several masterpieces from the Spanish Gothic and Andalusia Baroque periods were studied; artworks and samples taken are included in Table 1.

Cross sections of small samples taken from the different studied artefacts were prepared following the previously described methodology [12].

### 2.2. Methods

#### 2.2.1. Optical microscopy

The cross-sections were examined using optical microscopy (Nikon HOPTIHOT) with objectives of ×25, ×50 and ×100, and the microscope was equipped for microphotography (Nikon 4500 digital camera). Different analytical techniques were employed to study the sequence of the layers.

#### 2.2.2. SEM–EDX

The cross-sections were examined in a HITACHI S-4800 scanning electron microscope (SEM). Elemental chemical analyses of the cross-sections were performed using a Link ISIS energy dispersive X-ray (EDX) analyser coupled with the SEM at an accelerating voltage of 20 kV.

#### 2.2.3. μ-Raman spectroscopy

The integrated dispersive Horiba Jobin–Yvon Labram Infinity System was employed to record the Raman spectra. Two external visible diode lasers (solid state source) were utilised: one at 532 nm and the other at 784 nm. The instrument possessed a CCD detector, and a grating of 600 groves/mm. An optical microscope is confocally coupled to the Raman spectrometer. The size of the analyzed zones depends on the microscopy magnification. With ×100, the spot size was 1.06 μm, and the spatial resolution was 0.53 μm. Almost all of the measurements were scanned at a ×50 magnification. Each Raman spectrum was recorded for 10 min with a spectral resolution of 2 $cm^{-1}$.

#### 2.2.4. μ-FTIR spectroscopy

The FTIR absorbance measurement was conducted in the range of wavenumbers between 700 and 3000 $cm^{-1}$ with a Nicolet 510 apparatus (Source: Globar, Detector: DTGS). This technique was employed to determine the inorganic anions and organic functional groups present in the compounds. The Nic-Plan optical microscope was coupled confocally to the spectrometer, which created the ability to perform micro-FTIR on each layer of the sample. The detector was cooled by means of a liquid nitrogen trap. The measures were performed in the cross-sections by reflection.

#### 2.2.5. Py-GC/MS analytical procedure

The pyrolysis was performed in two steps: a) desorption at 350 °C and b) pyrolysis at 500 °C. The pyrolysis method utilised was the Double-Shot method. A micro-furnace (model 2020, Frontier Laboratories Ltd) connected to a GC/MS Agilent 6890 system with a silica capillary column (HP 5MS, 30 m × 0.25 m × 0.25 μm I.D.) and a mass selective detector (Agilent 5973) was used. The databases used to interpret the chromatograms were the Wiley5 and the NIST2007 Mass Spectral Libraries.

## 3. Results and discussion

Conventional optical microscopy was utilised for the preliminary examinations and to locate regions of interest in all of the cross-sections

**Table 1**
Works of Arts and studied samples.

| Works of art | Located | Works of art type | Studied samples |
|---|---|---|---|
| Our Lady Saint Ana.<br>Anonimous. 14th century.<br>Several polychrome layers have been found due to restoration | Saint Ana Chapel. Dos Hermanas (Seville) | Polychrome sculpture | SA-1 (original polychrome), SA-2 (layer over SA-1), SA-3, SA-4, SA-5 (original polychrome), SA-6 (layer over SA-5), SA-7 (original polychrome), SA-8 (layer over SA-7), SA-9, SA-10, SA-16, SA-18 |
| Virgen de los Reyes. Anonymous. 14th century | Cathedral of Seville | Polychrome sculpture | VR-1, VR-4, VR-5 (original polychrome) |
| The Assumption of the Virgin. Mohedano. 17th century | Carmen Church. Antequera (Málaga) | Canvas | ASUN-7 |
| Saint Eliseo. Mohedano. 17th century | Carmen Church. Antequera (Málaga | Canvas | SE-4 |
| Christ tied to the column. Anonymous. | Descalzos Convent. Antequera Museum | Canvas | XCCA-1 |
| Annunciation.<br>Pedro de Campaña. 16th century | Santiago Church. (Ecija, Seville) | Altarpiece | ANUN-7 |
| Altarpiece | Santiago Church. (Ecija, Seville) | Altarpiece | S-3 |
| Saint Rosalia of Palermo | Carmen Church. Antequera (Málaga) | Canvas | SRP-1 |
| The simbolic trees | Carmen Church. Antequera (Málaga) | Canvas | ARSB-O |
| Scenes of the life of Saint Alberto. 17th centrury | | | |
| Ordination | Carmen Church. Antequera (Málaga) | Canvas | OR-1, OR-2, OR-3, OR-4, OR-5 |
| Funeral | Carmen Church. Antequera (Málaga) | Canvas | FUN-1, FUN-2, FUN-4, FUN-5 (original polychrome), FUN-8 |
| Ecstasy | Carmen Church. Antequera (Málaga) | Canvas | EXT-6, EXT-7, EXT-8 |