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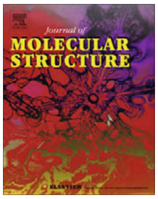

Comparison between micro-Raman and micro-FTIR spectroscopy techniques for the characterization of pigments from Southern Spain Cultural Heritage

M.L. Franquelo [a,*], A. Duran [a,b], L.K. Herrera [a], M.C. Jimenez de Haro [a], J.L. Perez-Rodriguez [a]

[a] *Materials Science Institute of Seville (CSIC-Seville University), c/Americo Vespucio, 49, 41092 Sevilla, Spain*
[b] *Centre de Recherche et de restauration des musées de France–CNRS UMR 171, Palais du Louvre, Porte des Lions, 14 Quai François Mitterrand, 75001 Paris, France*

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ABSTRACT

An extensive overview of the complementary use of micro-FTIR and micro-Raman spectroscopy in the Cultural Heritage studies is described in this work.

The samples have been prepared using the cross-section technique. This technique allows the examination of a large portion of a single paint layer in its original condition. A variety of pigments from samples belonging principally to the Cultural Heritage of Southern Spain were characterized by micro-Raman spectroscopy using visible excitation sources and micro-FTIR spectroscopy. The pigments studied comprise blue (azurite, ultramarine blue, Prussian blue), red (vermilion, haematite, red ochre, red lead, etc.), ochre and yellow (goethite, orpiment, realgar, etc.), green (malachite, copper resinate), and white (calcite, gypsum, white lead, titanium white, barite, lithopone) pigments, among others. An orientation is given for their appropriate and unequivocal characterization. Characterization by micro-FTIR and micro-Raman presents difficulties with some pigments. In these cases, analysis by EDX solves most of these doubts. The combined use of both spectroscopic techniques, together with SEM–EDX microanalysis, provides one of the most useful methods in the characterization (and possible dating) of materials used in Cultural Heritage.

1. Introduction

Pigment identification on substrates such as canvas, polychromed sculptures, wall paintings, and ceramics is very important for understanding the history of a work of art and the resolution of problems related to conservation, restoration, dating and author attribution. Many techniques have been used for pigment identification, including micro-Raman analysis, micro-Fourier-transformed infrared (FTIR) analysis and energy dispersive X-ray (EDX) analysis, which are some of the most suitable ones for this purpose.

The characterization of the materials and pigments from artworks requires samples with all the layers, from the varnish to the support (fiber, wood, wall, leather or metal). If a sample contains all the layers, it will provide wide information about the way in which the painting was carried out with no need of interpolating the information from different fragmented samples.

The preparation of cross-sections, or stratigraphies, constitutes a critical step in the understanding of the physical nature of the pictorial surface, defining where the original painting ends and the re-painting starts, visualizing the degradation, and even revealing the techniques of different artists. Indeed, it constitutes one of the most usual techniques in the work of the museum scientist. The information available is determined by the quality of the sample and the suitable process of preparation of the cross-section [1–3].

Normally, the first technique that is applied to the prepared cross-section is optical microscopy, which provides information about the morphology of the grains of pigment (homogeneity, size, form), the state of aggregation and the optical characteristics [4,5]. Subsequently, the same cross-section is appropriate for other techniques of analysis, such as micro-FTIR, micro-Raman spectroscopy and microanalysis by energy dispersive X-rays coupled to scanning electron microscopy (SEM–EDX). Analysis performed in this way with a cross-section grants the possibility of identifying pigments, supports and binders, and it involves the removal of just one sample and thus significantly reduces the damage to the artwork.

The application of spectroscopic analyses has a long history, which begins in the fifties. In 1966, the work by Olin [6] was continued in a series of articles on the identification of pigments and analysis of binders, varnishes and natural dyes on works of art using IR spectroscopy [7,8]. The introduction of Fourier-transformed spectrometers provided a new vision in the utility of the

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* Corresponding author. Address: Materials Science Institute of Seville (CSIC-Seville University), c/Americo Vespucio, 49, 41092 Sevilla, Spain. Tel.: +34 954 489532; fax: +34 954 460665.
E-mail address: maria.luisa@icmse.csic.es (M.L. Franquelo).

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technique [9–13]. Frequently, the procedure for obtaining the IR spectra was based on grinding a small proportion of the sample and homogenizing it into a KBr pellet. All these analyses, performed by transmission FTIR spectroscopy, are completely destructive to the samples. Complementary and more detailed results can be achieved by microscopy coupled with FTIR spectroscopy to analyze the specimens of the cross-section layer by layer, in an area of few microns, in reflectance mode. This is micro-FTIR [11,12].

Micro-Raman spectroscopy, like micro-FTIR spectroscopy, can be used for the identification of constituent materials of Cultural Heritage as far as they provide information about characteristic vibrational levels [14–20]. Nevertheless, not all transitions between vibrational molecular levels are allowed. Some transitions can appear only in the infrared spectrum, some only in the Raman one, and some in both of them at coincidental frequencies; others cannot be observed in either of the spectra. The IR- or Raman-allowed or forbidden transitions are determined by the selection rules.

In molecules with low symmetry, most of the vibrational modes appear in both the IR and Raman spectra, but, normally, with very different intensities, because the polarizability change for a vibration (which is a required selection rule for Raman scattering) differs from the dipolar moment change (a required selection rule for IR absorption) for the vibration [21,22]. Thus, the vibrational information obtainable by Raman and IR spectroscopy is not identical, but complementary [23].

EDX analysis has also been widely used to characterize the elemental chemical composition of cross-sections [24–27].

The purpose of this work is to characterize the different layers in cross-sections of samples belonging to different artworks from the Cultural Heritage of Southern Spain using two complementary techniques, micro-infrared and micro-Raman spectroscopy. The use of EDX analysis is also discussed.

2. Experimental

2.1. Materials

Samples were taken from different representative artworks from Southern Spain Cultural Heritage. Wall painting samples from Pompeii were also studied.

2.1.1. Polychromed sculptures

Our Lady Santa Ana is a triplex polychromed sculpture of Santa Ana, the Virgin Maria and the Child, dating from the Spanish Gothic period, XIVth century, which has suffered subsequent restorations. Saint Pascual Bailon, Saint Francis of Assisi and the Virgin Maria, well known as "Cieguecita," are all sculptures made by Martinez Montañes from Andalusian Barroque, XVIIth century.

2.1.2. Canvas

These pieces include Virgin and the Child painted by Murillo, from the Fine Art Museum, Sevilla, XVIIth century; a portrait collection of Carmelitas Saints, from Descalzos Church, Ecija, Sevilla, XVIIIth century; and paintings by Mohedano from Carmen Church in Antequera, XVIIIth century.

We also investigated wall paintings from the House of the Golden Bracelet in Pompeii (2nd century B.C.), Cartuja Monastery, XVI and XVIIth centuries, and El Salvador Church, XIXth century, both of them in Sevilla.

Other pieces in the Alhambra of Granada.

Cross-sections were made up following the methods of Khandekar [1], Wachowiak [28] and Durán [29].

2.2. Methods

First, the cross-sections were studied using a stereomicroscope (Nikon HOPTIHOT) with objectives ×25, ×50, ×100 and ×200, and equipped for microphotography (Nikon 4500 digital camera). The stratigraphic sequence of different cross-sections was identified.

The FTIR absorbance measurement was performed in a range of wavenumbers between 700 and 3000 cm^{-1}, using 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 is coupled confocally to the spectrometer, which allows us to perform micro-FTIR on each layer of the sample. The detector is cooled by means of a liquid nitrogen trap.

A dispersive integrated Raman system, the Horiba Jobin–Yvon Labram Infinity, was employed to probe the Raman scattering. The optical microscope is coupled confocally to an 800 mm focal length spectrograph equipped with two switchable gratings. Two external visible diode lasers (solid state source) are available: one is at 514.5 nm and the other at 752.5 nm. It has a CCD detector, and the resolution is of 1800 lines/mm; the time of acquisition was 100 s in almost all the cases, and the size of the analyzed zone approximately 5 μm.

The reflected and Rayleigh scattered photons, which represent the main source of interference, are removed by a holographic notch filter specific to the laser energy. Almost all the measurements shown in this work have been scanned at a 50x magnification. The number of scans oscillates between 10 and 50, and the exposure time for every scan is of 1–2 s.

Elemental chemical analyses were obtained using a scanning electron microscope Jeol JSM5400 equipped with an X-ray dispersive energy analyzer.

3. Results

Conventional optical microscopy was used for preliminary examinations and to locate regions of interest in all the cross-sections studied in this wok. A selection of cross-sectional microphotographs is shown in Fig. 1.

Concerning characterization of the inorganic pigments, a classification based on their colors is made in this work. In this work we will try the analysis from different perspectives.

3.1. Blue pigments

3.1.1. Azurite

Azurite, a basic copper carbonate with the formula $2\text{CuCO}_3\cdot\text{Cu(OH)}_2$, is a naturally occurring mineral extensively used as an artistic pigment, especially throughout the Middle Ages and the Renaissance [30,31].

As a preliminary investigation, an elemental analysis may be performed by EDX to identify the metallic cations in different carbonates present in the studied samples: copper in azurite, calcium in calcite, and lead in white lead. Copper has been detected in many of the blue layers of the cross-sections studied in this work. However, the determination of copper does not confirm the presence of azurite, because several blue pigments have copper in their chemical composition, and it is necessary to use other experimental techniques to confirm the presence of this pigment.

For the reflectance micro-FTIR spectra of the carbonate based pigments under study, it was found that in the spectral region extending from 1600 to 1400 cm^{-1}, which contains the ν_3 stretching vibrations of the CO_3^{2-} ion [11], the experimentally observed bands showed great variability both in position and relative intensity in our samples, although it is not usually very