
SCIENTIFIC STUDY OF THE GOTHIC-RENAISSANCE ALTARPIECE OF SANTIAGO CHURCH IN ÉCIJA (SPAIN)

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Abstract

This work reports the characterization of inorganic and organic materials used for producing the polychrome of gothic-renaissance altarpiece of 16th century. The study was carried out in the cross sections prepared from small samples. Combined use of optical microscopy, micro-FTIR spectroscopy, SEM-EDX and XRD techniques has proved to be valuable for the characterization of compounds detected within artworks studied. Gypsum and animal glue animal support, casein and egg, lead oxide, gold and bole layers, iron oxides, red lake, cinnabar, white lead, cobalt smalt, azurite, tin-lead compounds were found. Red colours were obtained by a mixture of vermilion (HgS), and red lead (Pb₃O₄). A red lake was also added in some cases. Hematite was used mostly for the obtaining of violet colour, mixed with azurite in some cases or with smalt in other ones. Green colour was obtained with a mixture of azurite and tin-lead yellow with hydrocerussite and calcite. These pigments and the kind of binders were indicative of original materials or at least not recent interventions.

Keywords: micro-FTIR spectroscopy, XRD, polychrome, support, binder

1. Introduction

By identifying pigments, binders and supports, we can reach back through time and develop a deeper understanding of the materials and techniques used by the painting masters [1-4]. The first step in the traditional procedure is the preparation of cross-sections from the samples, and afterwards the application of conventional analytical techniques on, which include optical microscopy, micro-Fourier transform infrared (FTIR) spectroscopy, and energy dispersive X-rays spectroscopy coupled to scanning electron microscopy (SEM-EDX) [5-11].

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The historical, physical and chemical study of a gothic-renaissance altarpiece in the southwest of Spain was carried out in this work. The temple inside is moorish style. It consists of three naves. The main altarpiece was carved in a transitional style between gothic and renaissance style by Alejo Fernandez Aleman in 16th century.

The Gospel Nave, on the left side of the altarpiece contains the paintings attributed to Pedro de Campaña, one of the masters of the Sevillian painting in the 16th century. The decoration of this nave showed higher alteration degree due to environmental contamination. It suffers greater light intensity.

The Epistle Nave, on the right side of the church contains another valuable altarpiece with polychrome sculpture and oil paintings.

Pedro de Campaña (Pieter Kempene) was a Flemish painter who after his beginning in his country moved into Italy. He was working in Bologna and Venice. His staying in Rome in contact with Polidoro da Caravaggio, Perin del Vaga, B. Peruzzi and others disciples of Rafael and other roman manierism artists influenced by Miguel Angel. About 1527 he installed in Seville carrying out important master pieces in Cathedral and Santa Ana and San Isidoro churches influencing definitely the Sevillian painting. He returned to Brussels in 1562 and became director of the tapestry factory [12].

The present investigation showed the successful application of the combined use of the following analytical techniques performed on cross sections of the representative samples: optical microscopy, micro-FTIR spectroscopy, scanning electron microscopy/energy dispersive X-ray analysis (SEM-EDX) and X-Ray diffraction (XRD). Besides a same cross section allowed different analyses so it minimizes greatly the extraction of samples and the subsequent damage to the artwork.

2. Materials and methods

Several samples from different paintings of both naves (Gospel and Epistle) as well as the altarpiece architecture have been studied.

Cross-sections (Figure 1) were prepared and were observed and photographed with an optical microscope Nikon OPTIHOT (x25, x50, x100 and x200). After preparing the cross-sections, a certain amount of powder samples (mg) was used for the XRD. X-ray diffraction patterns (XRD) were collected with a PANalytical X'Pert Pro diffractometer working at 45 kV and 40 mA, using $\text{CuK}\alpha_{1,2}$ radiation and equipped with a X'Celerator detector and a graphite diffracted beam monochromator.

Elemental chemical analyses of the cross sections were obtained using a HITACHI S-4800 scanning electron microscopy (SEM) instrument equipped with a Link ISIS energy dispersive X-ray (EDX) analyser at an accelerating voltage of 20 kV. Samples were coated with gold or carbon film prior to the SEM-EDX analyses.

Fourier transformed infrared (FTIR) spectra were recorded by a Nicolet 510 apparatus (Source: Global, Detector: DTGS) in reflection mode, using a

Nic-Plan optical microscope coupled confocally to the spectrometer. For each spectrum, at least 200 scans were accumulated and peak positions were determined using the Nicolet Omnic software, based on a polynomial least squares method.

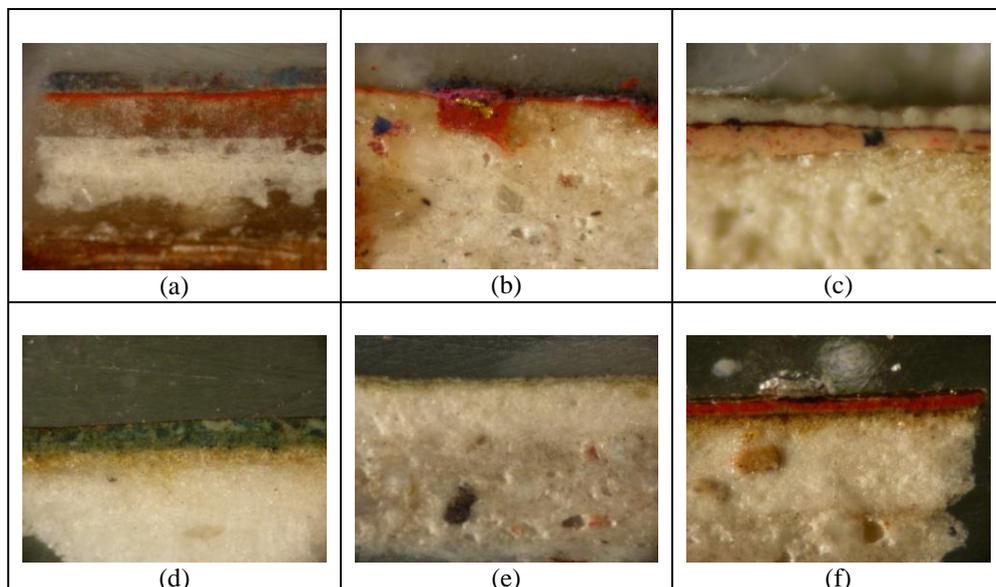


Figure 1. Photomicrographs of cross-sections from different samples coming from: (a-c) the Epistle and (d-f) Gospel naves.

The samples studied are listed below:

- **Nave of Epistle:** *sample 1* - lower side, Virgin mantle (sculptural scene ‘The Calvary’); *sample 2* - upper side, architecture of the altarpiece; *sample 3* - central area Virgin mantle, La Asunción - oil on wood; *sample 4* - dress from the relief “Virgin Asuncion”, lower area; *sample 5* - altarpiece architecture, upper right side.
- **Nave of Gospel, Visitación oil on wood:** *sample 1*- central area Virgin mantle; *sample 2* – sky; *sample 3* - lower side, Santa Ana mantle; *sample 4* - mantle of woman.

3. Results and discussion

3.1. Nave of Epistle

3.1.1. Sample 1 - lower side, Virgin mantle (sculptural scene ‘The Calvary’)

The cross section is represented in Figure 1a. It is noticeable the presence of a thick cementing layer (priming layer) on the wooden support. There are two white layers of preparation and a great amount of organic binder on the top of the second layer. Calcium and sulphur were identified (Figure 2a) in the

chemical analysis of both preparation layers. Gypsum and anhydrite had been characterized by XRD (Figure 3a). It had several polychromy layers: a red layer containing Si, Al, Fe, Ca, K and Mg was shown in Figure 2b what indicated the presence of red bole. A gold leaf (Figure 2d) was found over this layer. A thin white layer had been extended over the gold leaf constituted by Pb (Figure 2c). Finally, a violet layer on the surface was made up by mixing blue and red. Pb and Cu had been reported in the general microanalysis (Figure 2e). It contained blue and red inclusions. Fe was characterized in punctual microanalysis in the red grains (Figure 2f) whereas Cu was identified in the blue ones, Gypsum (calcium sulphate) and anhydrite (dehydrated calcium sulphate) was characterized by the XRD study.

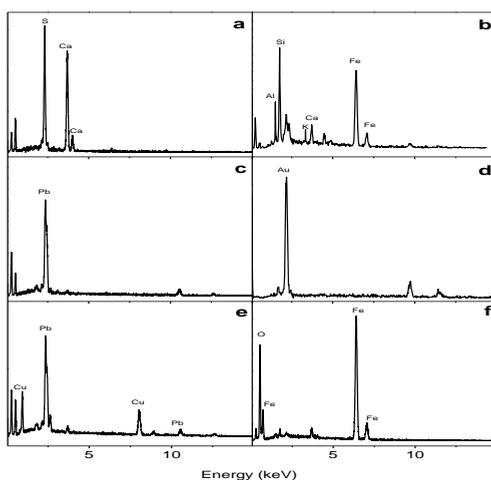


Figure2. EDX microanalysis of sample 1 (a-f).

The characterization of the oxoanions and organic functional groups were performed by means of the micro-FTIR spectroscopy. Absorptions of sulphate group (SO_4^{2-}) at 1158 cm^{-1} and silicate ($\nu\text{ Si-O}$) at 1067 cm^{-1} appeared in the inner preparation layer. Absorptions due to SO_4^{2-} group was identified in the upper preparation layer. Micro-FTIR spectrum of the upper layers allowed the characterization of carbonate absorption attributed to copper basic carbonate, azurite (1428.44 cm^{-1}); this band corresponds to a ν_3 stretching vibrations of the CO_3^{2-} ion and its position varies greatly depending on the cation. With regards to the binders, proteic bands were mostly identified in the lower layers: absorptions at 1434 of C-H bending, 1581 of NH_2 of amide II, 1630 of bending of NH_2 of amide II and 1643 cm^{-1} of stretching vibrations of carbonyl C=O of amide group. Bands at 1730 of C=O ester type bonding probably of tryglicerides and 1238 cm^{-1} corresponding to triglycerides esters together with absorptions due to SO_4^{2-} group (main absorption at 1160 cm^{-1}) appeared in the upper side of the preparation layer and the interface with the polychromy layers. So the first

imprimation layer on the support was prepared with a proteic binder probably due to animal glue (Figure 4a) but oily and proteic compounds were found in the upper layers so it could be attributed to whole egg used as glue or maybe casein which contains a certain amount of triglycerides. Nevertheless, the presence of Ca and P in some analysis near the surface were indicative of the $\text{Ca}_3(\text{PO}_4)_2$ which organizes casein micelles.

Micro-FTIR spectrum of the upper layers allowed the characterization of carbonate absorption attributed to copper basic carbonate, that was, azurite ($1428,44 \text{ cm}^{-1}$); this band corresponds to a ν_3 stretching vibrations of the CO_3^{2-} ion and its position varies greatly depending on the cation.

3.1.2. Sample 2 - upper side, architecture of the altarpiece

A zone with four layers was found. The two preparation layers were made up of a mixture of gypsum, dolomite and quartz (Ca, S, and lower proportion of Mg and Si in the microanalysis) and glued with protein, probably animal glue. There was also a red bole and a gold leaf. Si, Mg, Fe, Al and Ca were reported in the red layer. Gold was applied over the red bole layer. Gypsum, dolomite (calcium and magnesium carbonate) and quartz were characterized by XRD study.

3.1.3. Sample 3 - central area, Virgin mantle, La Asunción - oil on wood

A preparation extended in two layers of calcium sulphate was also found. This sample showed two polychromy layers: a white layer containing Pb and a red one with Hg and S (Figure 5a). In some punctual analyses on the red layer a high amount of aluminum was detected by SEM-EDX (Figure 5b) suggesting the presence of a red lack in this paint. Lack pigment was manufactured by precipitating natural organic dyestuffs obtained from insects and plants sources with an inert inorganic host matrix. Aluminum hydroxide had been the substrate used for organic lack [13]. Chlorine attributed to an alteration product was also found.

In the XRD diagram reflections of gypsum, bassanite (hemihydrated calcium sulphate) cerussite (lead carbonate) and hydrocerussite (basic lead carbonate) were identified.

In the micro-FTIR spectrum recorded of both layers together, white and red ones, absorptions due to carbonate, oily and proteic compounds were identified: 1431 and 1405 cm^{-1} (s) and 842 cm^{-1} (m) (mixture of carbonates), 1726 (ester bonding C=O), 1657 (C=C of fatty acids or C-O amide I), 1549 (NH_2 group of amide II), 2939 and 2859 cm^{-1} (stretching C-H).

3.1.4. Sample 4 - lower area, dress from the relief 'Virgin Asuncion' (Figure 1b)

A red bole and a gold leaf were found above the double layer of preparation. The red bole contained Si, Al, Ca, Fe, Pb and K attributed to bole. A

higher proportion of Ca was detected in this case. It is probably a micaceous mineral mixed with red lead too. There was a violet layer on the surface. Its general microanalysis presented mainly Pb with a certain proportion of Si and Ca. The violet colour was obtained as a mixture of red and blue pigments. A mixture of red and blue grains was observed by optical microscopy. The red grains were composed by hematite (iron oxide), whereas in the blue ones Si, K, As, Co and Fe was identified (Figure 5c) attributed to cobalt smalt.

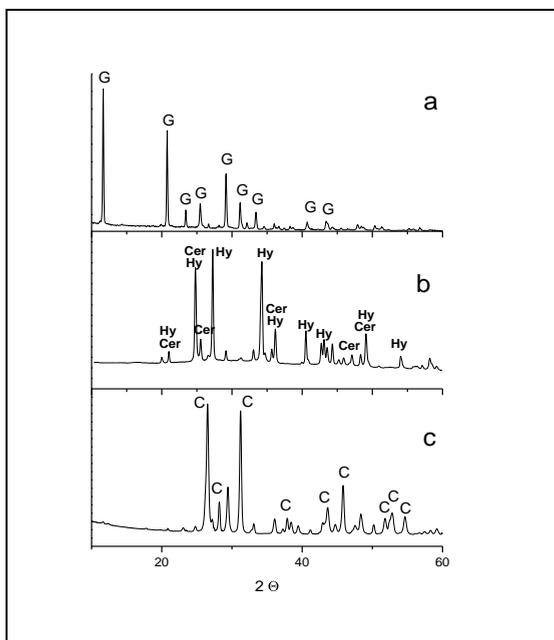


Figure 3. (a) XRD diagram of sample 1 and (b, c) sample 5.

The micro-FTIR study allowed the characterization of proteic compound in the preparation layer and both proteic and oily compounds in the upper layers. The micro-FTIR spectrum of the red bole is shown in Figure 4b where are reported the absorptions due to stretching Si-O of silicates at 1010 and 1040 cm^{-1} , the oily and proteic compounds at 1733 cm^{-1} (ester type bonding), 1656 cm^{-1} (C-O group of amide I), 1545 and 1465 cm^{-1} (NH_2 group of amide II), 1238 and 1055 cm^{-1} (triglycerides esters), 2924 and 2860 cm^{-1} (stretching of C-H group).

3.1.5. Sample 5 - upper right side, altarpiece architecture (Figure 1c)

Over the preparation layers composed of calcium sulphate were found two white polychromy layers with red inclusions. In the general microanalysis of the white polychrome layers, Pb was identified and the red grains contained Hg and S attributed to cinnabar. The white colour was composed by a mixture of cerussite (lead carbonate) and hydrocerussite (basic lead carbonate) as the results of XRD indicated (Figure 3b). The presence of cinnabar was also confirmed by XRD (Figure 3c).

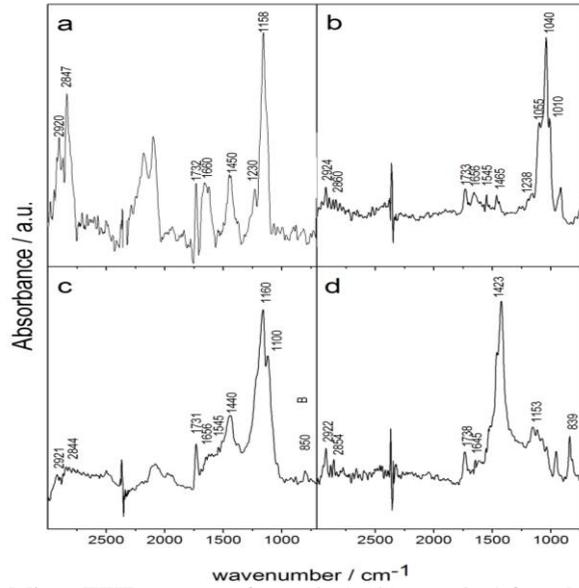


Figure 4. (a) Micro-FTIR spectra of sample 1, (b) sample 4 from Nave of Epistle, (c) sample 1 and (d) sample 6 from Nave of Gospel.

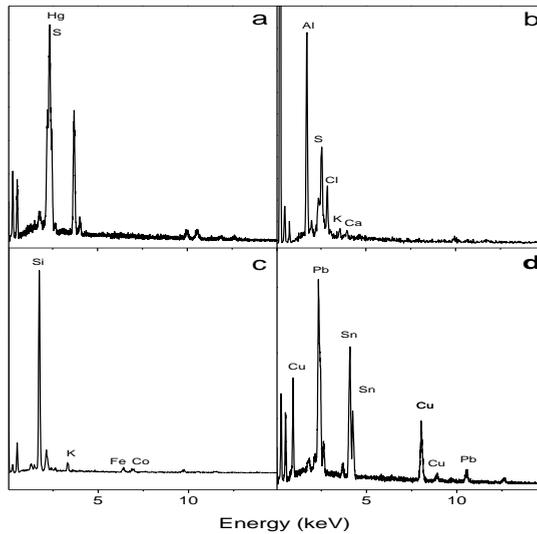


Figure 5. (a, b) EDX analysis of samples 3 and (c) 4 from Nave of Epistle and (d) sample 4 from Nave of Gospel.

3.2. Nave of Gospel - Visitación oil on wood

The preparation was also extended in two layers in this artwork and was made of gypsum and proteic compound.

3.2.1. Sample 1 - Central area, Virgin mantle (Figure 1d)

There was a double priming layer composed by a mixture of calcium sulfate and carbonate. The first one also presented Si and Al in its composition (possible aluminium silicate). Characteristic absorptions of calcium sulfate (stretching ν S=O at 1116.73 cm^{-1}), calcium carbonate (ν C=O at 1440 (s) and 850 (m) cm^{-1}) and proteic compound (1656.25 , 1546.41 and 1450 cm^{-1}) were reported by micro-FTIR spectroscopy as well as ν Si-O of silicates (as shoulders at about 1090 cm^{-1}) (Figure 4c).

There was a great amount of yellowish binding medium spread on top of the priming layer whose micro-FTIR spectrum could indicate the possibility of casein or animal glue (ν C-O amide I at about 1656 cm^{-1} , -NH₂ group of amide II at 1548 and bending δ C-H at 1456 cm^{-1}). The greenish blue stratum of polychrome contained Pb and Cu. By means of micro-FTIR characteristic bands of carbonate attributed to copper carbonate were identified (1420 cm^{-1}). A certain proportion of oily compound was probably present in this layer.

By means of XRD study, gypsum, bassanite, hydrocerussite, cerussite and azurite (basic copper carbonate) were characterized.

3.2.2. Sample 2 - Sky (Figure 1e)

The first priming layer contained Ca, S and Si in lower proportion. A thin yellow layer with greenish blue grains inside containing Pb, Ca, S and Cu was found. It was also observed a thin layer of resinous compound (varnish) darkened probably due to the formation of the insoluble black lead sulphide, PbS. The blue colour was obtained using a mixture of hydrocerussite and azurite.

The micro-FTIR study allowed the characterization of sulfates and proteic compounds in both layers of preparation. The following crystalline phases had been identified by XRD: gypsum, bassanite, anhydrite, hydrocerussite and quartz.

3.2.3. Sample 3 - lower side, Santa Ana mantle (Figure 1f)

The polychrome presented a greenish yellow layer containing Pb, Ca and Cu. In some punctual analysis Sn was also identified. Green colour was obtained with a mixture of azurite and tin-lead yellow with hydrocerussite and calcite. There was also a thin white layer containing Pb and Ca. A red upper layer contained S, Hg and Pb: a dark thin layer on the surface contained Ca and Pb and a certain amount of P, Si, Al, Cl and K.

By means of micro-FTIR spectroscopy characteristic bands of sulphate and carbonate were identified in both strata of preparation. Nevertheless, carbonates are present in higher proportion in the lower priming layer. In the red layer the absence of absorptions due to carbonates indicated that Pb was present in this layer as minium, that is, red lead (Pb₃O₄). Thus, the red colour is obtained

as a mixture of cinnabar and red lead. Gypsum, bassanite, anhydrite, hydrocerussite, cerussite and quartz are characterized by XRD.

The layer on surface was also darkened due to the formation of PbS. The thin white layer was a glaze spread to nuance the lower green colour.

3.2.4. Sample 4 - mantle of woman

There was a thin white layer containing Pb above the double preparation layer. In the microanalysis by SEM-EDX performed on a blue layer on top of this stratum, Pb and Cu were mainly reported as well as Si, Ca, Al and K. There was a yellowish white glaze on top of this layer with Pb and Sn (Figure 5d), So, blue colour was made up with a mixture of azurite and aluminium silicates glued with eggs. On top of this layer a thin yellowish white obtained with lead-tin yellow and lead and calcium carbonates gave the final shade.

The micro-FTIR study performed on the blue layer allowed the characterization of carbonates attributed to azurite 1423 cm^{-1} (s) and 839 cm^{-1} (m). A mixture of proteic and oily compound was also found, as well as in the layers on surface as shown in Figure 4d.

4. Conclusions

The information provided by this study helped to a better description of the execution technique and corroborated a certain hypothesis about the author. Besides, the acknowledge of the materials used in the artwork manufacture will help to future interventions.

Complete characterization of the polychrome has been carried out by techniques such as scanning electron microscopy-energy dispersive, micro-FTIR spectroscopy and X-ray diffraction in the cross-sections prepared with small samples taken in the gothic-renaissance altarpiece of Santiago Church in Ecija (Spain). The study of the cross-sections has facilitated the characterization of all layers and the pigments from the support to the most external layer.

The study of both naves in the headboard altarpiece (Epistle and Gospel) has yielded valuable data with regards to the materials and execution technique. The thick stratum of preparation extended in two layers of gypsum with a proteic binder was a procedure by Pedro de Campaña (1503-1508) a Flemish painter in the Spanish Renaissance. Nevertheless, the presence of Ca and P in some analysis near the surface were indicative of the $\text{Ca}_3(\text{PO}_4)_2$ which organizes casein micelles.

With regards to the polychromy, red, blue, violet and greenish blue are the most abundant pigments. Red boles as preparation layers of gold leaves were found. All golden layers are made of gold.

Red colours were obtained by a mixture of vermilion (HgS), and red lead (Pb_3O_4). The red lead could have been mixed with the vermilion in order to reduce the price of the pigment and to facilitate the drying of the oil paints. A red lake was also added in some cases. Hematite was used mostly for the

obtaining of violet colour: mixed with azurite in some cases or with smalt in other zones.

Green colour was obtained with a mixture of azurite and tin-lead yellow with hydrocerussite and calcite. These pigments and the kind of binders suggested original materials or at least not recent interventions.

With regards to the degradation products, the black PbS on surface in layers containing Hg, S and Pb pigments deserves a special mention.

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