

## INTEGRATED ANALYTICAL TECHNIQUES FOR THE CHARACTERIZATION OF PAINTING MATERIALS IN TWO SOUTH AMERICAN POLYCHROME SCULPTURES

TECHNICAL PAPER

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**In this study, we present work on two sculptures produced in the Jesuit Missions in Paraguay in the 18<sup>th</sup> century. A combination of analytical techniques was applied for the characterization of pigments and plasters. First, cross-sections of the samples were examined by optical microscopy and SEM-EDX. Then, application of transmitted FTIR spectroscopy for selecting samples confirmed the presence of gypsum ( $\text{Ca}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ) used as the preparation layer. Copper resinate was identified in one of the sculptures by a combination of FTIR, SEM-EDX and gas chromatography, together with its characteristic colour as observed in the cross-sections of the samples. The red pigments were identified as vermilion, hematite and minium, together with the organic pigment madder lake identified by HPLC-DAD in one of the sculptures. All these chemical results become more significant and relevant when we considered them in light of the results obtained from research on historical documents and old treatises used in the region.**

### 1 Introduction

South American polychrome sculptures produced during the so-called Colonial period (17<sup>th</sup>-18<sup>th</sup> centuries) are part of what has been identified as the process of evangelization done under the Spanish domain. These images installed in churches, convents or small chapels, show the diverse iconographic discourses that was necessary to develop that process: virgins, saints, christs etc. manufactured in workshops by Spanish, indigenous and creoles people, who used diverse materials – wood, stone etc. – to carve and paint the sculptures. The identification of pigments, dyes, resins, clays or gold by chemical analysis is relevant, as those results can be contrasted with past manuscripts and prints (inventories, merchandise lists, manuals, treatises) where those materials are described or mentioned by their uses and meanings in that region.<sup>1-3</sup> In this sense, the inventories left by the Jesuits after their expulsion in 1767 are of great value for this purpose, as they show the presence of many materials – pigments such as Prussian blue, vermilion, minium, carmine, verdigris, among others –

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Figure 1: Saint Gregorius Magnus (SGM) with the sample locations.



Figure 2: Saint Lion the Papst (SLP) with the sample locations.

that were used by them. In this study, we have worked on two polychrome sculptures (Figures 1 and 2) that were produced in the Jesuit Mission of Trinidad in Paraguay during the 18<sup>th</sup> century and are housed in the Museum of Natural Sciences, La Plata, Buenos Aires province, Argentina.

Elemental analysis was carried out using scanning electron microscopy (SEM-EDX), while material structure was studied with Fourier transform infrared spectroscopy (FTIR). Red organic pigments were identified by high performance liquid chromatography with diode array detection (HPLC-DAD). Specific treatises and manuals, such as Pacheco (1649)<sup>4</sup> and Palomino<sup>5</sup> as well as a list of tools and materials inventoried at the missions of Paraguay after the Jesuits were expelled from Spanish territory in 1767<sup>6,7</sup> were also taken into account in order to evaluate the results.

## 2 Experimental

### 2.1 Samples

Microsamples taken from representative areas of the sculptures (Table 1) were analyzed. A small quantity of each sample was mounted in acrylic transparent resin (Subiton, Laboratories S.A., Argentina). Thin and polished cross-sections were prepared from the samples according to traditional techniques and studied with optical and scanning electron microscopy. The rest was used for FTIR, GC and HPLC-DAD analysis.

Sample	Location	Description
SGM1	Carnation (right corner of the mouth)	Orange red
SGM2	Inside upper lip	Red
SGM3	Pluvial lapel	Red
SGM5	Laurel leaf	Olive green
SGM7	Right side of the sculpture	Brown green
SGM8	Hair behind the right ear	Dark brown
SGM12	Red over gold of the hook	Orange red
SLP2	Carnation (nose, left)	Pink orange
SLP3	Carnation (saint head, left lapel)	Brown red
SLP5	Saint dress, left lapel	Olive green

Table 1: Descriptions of the samples and their locations.

### 2.2 Methods

#### 2.2.1 Microscopy

Observation and photography of the samples' surfaces (before embedding) and of their cross-sections were achieved using a Leica MZ6 stereomicroscope equipped with a digital camera.

### 2.2.2 Scanning Electron Microscopy (SEM-EDX)

Scanning electron microscopy (SEM) was carried out using a Philips XL 30 ESEM scanning electron microscope. The samples were coated by sputtering with a thin (less than 80 Å) layer of gold.

### 2.2.3 FTIR Spectroscopy

Infrared spectra were obtained by using a Nicolet Magna 550 Fourier transform spectrometer. For each sample 32 scans were recorded in the 4000 to 400  $\text{cm}^{-1}$  spectral range in the transmittance mode with a resolution of 4  $\text{cm}^{-1}$ . Spectral data were collected with OMNIC 7.3 (Thermo Electron Corporation) software. The KBr pressed disc technique (1% sample in KBr) was used. As background the spectrum of the KBr pellet was used.

### 2.2.4 High Performance Liquid Chromatography with Diode Array Detector

Analytical HPLC was carried out on a Gilson 506C HPLC system using a Phenomenex Gemini 5  $\mu\text{m}$  column (25  $\text{cm} \times 4.6 \text{ mm}$  i.d.). Compounds were detected using a 170 photodiode array detector set at 254 nm operated in series with a Unipoint System software recording the absorption spectrum in the range 190-700 nm. Gradient elution was performed using two solvents, A: MeOH and B: 1% (v/v) aqueous orthophosphoric acid. The gradient started with 36% A during 5 min and increased to 90% A within 10 min, followed of 20 min at this condition. Solvents utilized in the HPLC were filtered through a 0.2  $\mu\text{m}$  filter prior to use. The flow rate was 0.8  $\text{mL min}^{-1}$ .

The samples SGM1 and SGM3 and the madder lake standard (Kremer Pigmente, Aichstetten, Germany) were treated with hydrochloric acid (37% HCl, Riedel-de Haen) and methanol (MeOH), Merck) according to the following procedure. The samples were immersed in 400  $\mu\text{L}$  of  $\text{H}_2\text{O}:\text{MeOH}:\text{37\%HCl}$  (1:1:2, v/v) and kept at 100  $^\circ\text{C}$  for 15 min. Then the liquid phases were evaporated (50-60  $^\circ\text{C}$ ) under gentle nitrogen flow. The dry residues were dissolved in MeOH. Finally, the methanolic solutions were filtered through a 0.2  $\mu\text{m}$  inorganic Whatman membrane filter (Schleicher-Schull) and injected into HPLC.

### 2.2.5 Gas Chromatography

Gas chromatography was performed using a Thermo Focus GC chromatograph equipped with a

flame ionization detector and a SPB-20 column (30  $\text{m} \times 0.25 \text{ mm}$  i.d., 0.25  $\mu\text{m}$  film thickness). Temperature programme: 1 min isothermal at 110  $^\circ\text{C}$  and then heated from 110 to 230  $^\circ\text{C}$  at 8  $^\circ\text{C min}^{-1}$ , 230 to 240  $^\circ\text{C}$  at 3  $^\circ\text{C min}^{-1}$ , 240 to 290  $^\circ\text{C}$  at 15  $^\circ\text{C min}^{-1}$  followed by a 6 min hold at 290  $^\circ\text{C}$ .

Sample SGM5 and standard copper resinate (Kremer Pigmente, Aichstetten, Germany) were treated with 1 ml KOH 10% in diluted methanol ( $\text{H}_2\text{O}:\text{MeOH}$  1:1) for 3 h at 60  $^\circ\text{C}$ . Then, the hydroalcoholic solutions were acidified with 10 N HCl and the organic acid compounds were extracted three times with 1 ml of diethyl ether. After solvent evaporation, the residues were derivatised with diazomethane and analyzed by GC.

## 3 Results and Discussion

### 3.1 Preparation Layer

Based on SEM-EDX (Table 2) and FTIR analysis, the preparation layer comprised gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , in both sculptures. The FTIR spectra (Figure 3) were dominated by characteristic asymmetric  $\text{SO}_4^{2-}$  stretching bands at 1140 and 1122  $\text{cm}^{-1}$  together with sharp  $\text{SO}_4^{2-}$  bending bands at 601 and 671  $\text{cm}^{-1}$  and O-H stretching bands at 3406 and 3546  $\text{cm}^{-1}$ .<sup>8</sup> Bands centred at 1689 and 1623  $\text{cm}^{-1}$  typical of water were also observed.

Sample	SEM-EDX results
SGM1	S, Ca (Al, Si)
SGM2	S, Ca (Al, Si)
SGM3	S, Ca
SGM5	S, Ca (Cu, Si)
SGM7	S, Ca (Cu, Al, Si)
SGM8	S, Ca (Al, Si)
SGM12	S, Ca (Al, Si)
SLP2	S, Ca (Al, Si, Hg, Pb)
SLP3	S, Ca (Al, Si)
SLP5	S, Ca (Al, Si, K)

Table 2: Results of SEM-EDX analyses on preparation layers. Elements in parentheses are minor or in some cases contaminants or impurities.

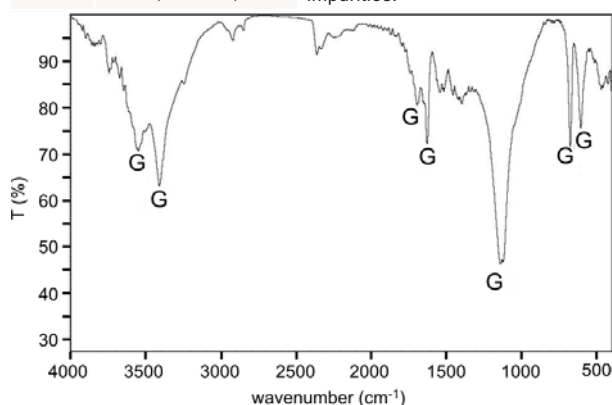


Figure 3: FTIR spectrum in transmission mode of sample SGM2 (G: gypsum).

### 3.2 Pigments

Copper resinate was identified in samples SGM5, SGM7 and SLP5, while three mineral red pigments (vermilion, red lead and red ochre) as well as madder lake were characterized in the samples SGM1, SGM2, SGM3, SLP2 and SLP3. Umber was identified in sample SGM8.

#### 3.2.1 Copper Resinate

Optical examinations of cross-sections of samples SGM5, SGM7 and SLP5 (Figure 4) showed a degraded olive-green colour and the presence of amorphous non-crystalline particles.

SEM-EDX analysis revealed the element copper (Table 3) and this suggested the presence of copper resinate, a compound of cardenillo (verdigris) and a vegetable resin, similar to those obtained from some conifers or copal trees used as incense by Native Americans. It is composed mainly of copper salts of resinic acids.<sup>9</sup> The FTIR spectra of samples SGM5 and SLP5 (Figure 5) showed a broad absorption band at 1720-1600  $\text{cm}^{-1}$  attributable to copper resinate (1710 and 1610-1600  $\text{cm}^{-1}$ ) and superimposed to gypsum peaks (1683 and 1625  $\text{cm}^{-1}$ ) of the preparation layer. Both samples showed characteristic  $\nu\text{C-H}$  stretching of oil at 2919 and 2850  $\text{cm}^{-1}$ .

Analysis by GC of an additional sample of SGM5 and comparison with a standard of copper resinate showed the presence of palmitic and stearic acids together with diterpenoid acids confirming the presence of this pigment in both sculptures (Figure 6).

Copper resinate was commercialized in Europe in liquid form, as a powder (dissolved in linseed oil to make a varnish) and also in grain form. The 1767 inventories of the Mission of Saint John show the presence of painters that used cardenillo (verdigris) within their colours.<sup>6,7</sup> It is worth mentioning that Spaniards used the green cardenillo varnish for coating or making a *velature* on some blue pigments as indigo and azurite or applied directly on the primer layer, as in SGM and SLP samples, a procedure that produces an intense green. We have identified the use of copper resinate in a collection of paintings from the highlands of Peru in the Andean region during the colonial period (1610-1780).<sup>3</sup>

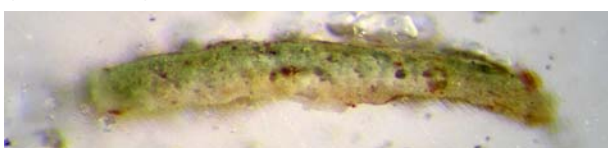


Figure 4: Cross-section of sample SLP5.

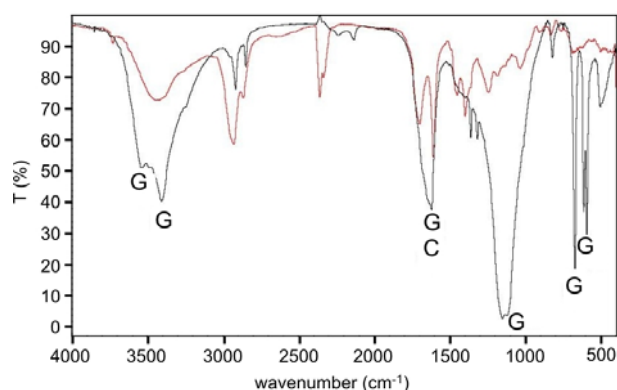


Figure 5: FTIR spectrum in transmission mode of sample SLP5 (G: gypsum, C: copper resinate) (black line) and standard copper resinate (violet line).

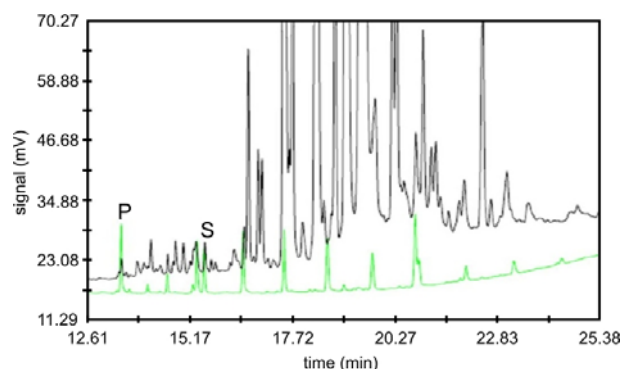


Figure 6: GC chromatograms of sample SGM5 (green line) and a standard of copper resinate (black line). P: palmitic acid, S: stearic acid

Sample	Analytical results	Pigment
SGM1	SEM: Pb (88%), Red grain: Al (26%), Si (39%), Pb (8%), K (1%), Ca (1%), Ti (1%); Fe (4%); HPLC-DAD: alizarin + purpurin	Madder lake + white lead
SGM2	SEM: Hg (58%), S (17%), Pb (25%)	Vermilion + red lead
SGM3	SEM: 1. Red layer: Al (13%), Si (55%), S (14%), K (6%), Ca (7%), Fe (5%); 2. Red layer: Al (22%), Si (36%), S (6%), Hg (24%), K (2%), Ca (4%), Fe (6%); HPLC-DAD: alizarin	Vermilion + madder lake
SGM5	SEM: Cu (4%), S (41%), Ca (48%), Si (5%), Al (1%), Fe (1%); GC: resin	Copper resinate
SGM7	SEM: Cu (3%), S (43%), Ca (52%), Si (2%); GC: resin	Copper resinate
SGM8	SEM: Al (8%), Si (35%), K (2%), Ca (2%), Mn (8%), Fe (45%)	Umber
SGM12	SEM: 1. Red layer: Mg (3%), Al (27%), K (8%), Si (51%), Ti (1%), Fe (10%); 2. Red layer: Mg (3%), Al (24%), S (11%), Si (37%), K (5%), Fe (10%); Ca (13%)	Ocher
SLP2	SEM: Al (1%), Hg (5%), Si (2%), Pb (92%)	Vermilion + Red lead
SLP3	SEM: Pb (99%), Ca (1%)	Red lead
SLP5	SEM: Cu (53%), Si (23%), Al (14%), Ca (3%), K (3%), Fe (4%)	Copper resinate

Table 3: Results of SEM-EDX analyses of the pigment layers.

#### 3.2.2 Vermilion and Red Lead

Vermilion ( $\text{HgS}$ ) is a vivid red colour resulting from the roasted mixture of mercury and sulfide. The natural mineral form is called cinnabar.<sup>10</sup> This pig-



Figure 7: cross-section of sample SGM2.

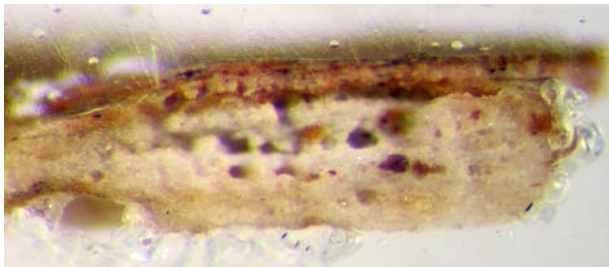


Figure 8: Cross-section of sample SLP3.

ment was recognized microscopically by its colour (Figure 7) and identified by SEM-EDX analysis on cross-sections of samples SGM2, SGM3 and SLP2.

In the sample SGM2 the presence of lead suggested that vermilion had been mixed with lead white or red lead. The FTIR spectrum of SGM2 (Figure 3) showed no characteristic peaks for lead white, a basic lead carbonate ( $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ). Therefore, the presence of lead in this sample could be attributed to minium or Saturn red, a burnt lead oxide ( $\text{Pb}_3\text{O}_4$ ).<sup>11</sup> The same mixture of red pigments has been identified in sample SLP2 on the basis of SEM-EDX analysis and FTIR spectroscopy. Mixed with linseed oil, red lead was used as a drier or an adulterant in other reds, notably vermilion.<sup>11</sup> The mixture of red lead and vermilion has already been identified in a painting from Mateo Pizarro and in another from Marcos Zapata.<sup>3</sup> These two painters were active between the last decade of the 17<sup>th</sup> century and the second half of the 18<sup>th</sup> century in the Puna de Atacama (northwest of Argentina, southwest of Bolivia and northeast of Chile) and in Cuzco, respectively. As for our sculptures, it's worth seeing that the use of this mixture corresponds with the advises offered by Pacheco, when talking about carnation's techniques, specially mouths.<sup>4</sup>

Sample SLP3 belonging to a carnation of a saint's head carved on the left lapel showed a brown red-dish pigment layer in its cross-section (Figure 8). SEM-EDX analysis revealed a peak for lead and a minor peak for calcium, suggesting the use of red lead, a pigment highly recommended for carnations.<sup>1</sup>

### 3.2.3 Red Lake

The cross-section of sample SGM1 taken from the carnation of the right corner of the mouth (Figure

9) showed a paint layer of orange-red colour because of the presence of red particles. Analysis by SEM-EDX of this layer revealed a strong intensity for lead while red grains showed high x-ray intensities for aluminium, silicium and lead with minor peaks for potassium, calcium, titanium and iron, which suggested a mixture of an organic lake and a lead pigment.

The FTIR spectrum of sample SGM1 (Figure 10) depicts characteristic peaks for gypsum at 1140-1220, 676 and 600  $\text{cm}^{-1}$  together with an intense absorption band at 1405  $\text{cm}^{-1}$ , characteristic of  $\text{CO}_3^{2-}$  stretching, attributable to white lead.<sup>12</sup>

In order to identify the presence of an organic lake, an unmounted sample SGM1 was hydrolyzed and analyzed by HPLC-DAD. Two compounds (peaks 1 and 2) were detected at 254 nm (Figure 11). Comparing with chromatograms of cochineal, madder, brazilwood and lac dye standards, alizarin (peak 1) and purpurin (peak 2) could be identified. Alizarin is the main colouring matter of madder which comes from the roots of *Rubia tinctorum* while purpurin is the partial decarboxylation product of the glycoside pseudopurpurin. Although in fresh madder roots no purpurin can be detected, its large proportion in commercial madder is formed during the manufacturing process and storage.<sup>13</sup> In South America several species of *Galium* were used for dyeing, while others belonging to the genus *Relbunium*, include some of the oldest and most important sources of vegetable red dyes of pre-Columbian civilizations. A general characteristic of all the species of *Relbunium* used for dyeing in South America is the absence of alizarin among the red anthraquinone colourants present in the roots.<sup>14-16</sup>

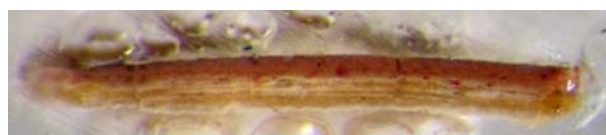


Figure 9: Cross-section of sample SGM1.

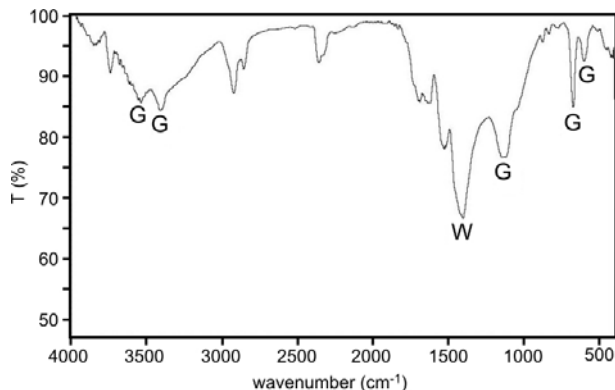


Figure 10: FTIR spectrum in transmission mode of sample SGM1 (G: gypsum, W: lead white).

The strong peak of aluminium in the SEM-EDX of SGM1 together with the identification of a mixture of alizarin and purpurin by HPLC-DAD confirm the presence of madder lake as the red organic grains mixed with lead white for the carnation. Nevertheless, it cannot be ruled out the presence of minium contributing to the orange red colour of the pigment layer. Regarding this mixture, once again Pacheco tells the importance of using lead white and minium as dryers and a Florentine lake for the carnations.<sup>4</sup> This madder lake was probably imported from Spain, as there were good producers, along with Flemish and Italian ones. It is interesting to note that, within the materials described in the Jesuit inventories, an Italian lake is mentioned.<sup>6,7</sup>

The cross-section of SGM3 (Figure 12) showed that for the painting of the pluvial lapel two red paint layers were applied. As for sample SGM1, the presence of an intense peak for aluminium in the SEM-EDX analysis of the upper red layer pointed to an organic lake. The pigment of the inner bright red layer can be attributed to vermilion due to a strong mercury peak by SEM-EDX. HPLC-DAD analysis of SGM2 indicated the presence of alizarin, confirming the application of a madder lake on the vermilion layer.

Although red lakes have been used in colonial South American art, only carmine, the red lake obtained from cochineal, has been identified in paintings from the Andean region.<sup>3</sup> Madder roots have been used for textile dyeing since early times but its use in paintings is rarely documented. As colour-makers obtained dyes from cloths, it may

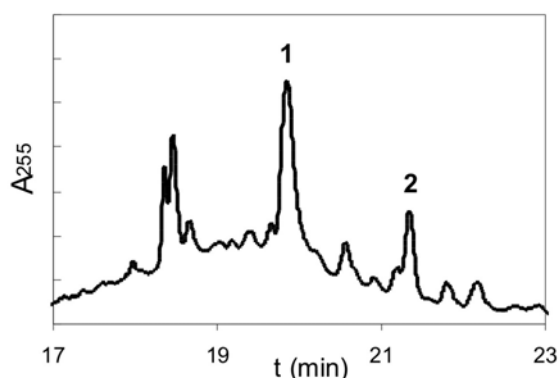


Figure 11: HPLC chromatogram of hydrolyzed sample SGM1 at 254 nm.

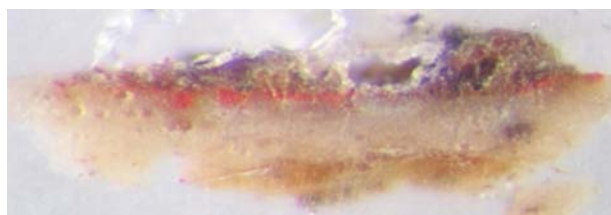


Figure 12: Cross-section of sample SGM3.

be likely that madder dye was employed in the manufacture of red lakes much more often than written evidence would suggest. Madder as a colour name came into use in the early 19<sup>th</sup> century, so it is probable that in the treatises and documents it was simply called lake.<sup>17</sup> As for South America, Father Bernabé Cobo registered the presence of the Chapi-chapi from the Andes, an Andean plant identified as *Relbunium hipocarpium*, which the indigenous people used to dye red wool.<sup>14-16</sup>

### 3.2.4 Red Ocher

Optical examinations of cross-section of SGM12 (Figure 13) showed two red pigment layers (1 and 2). SEM-EDX analysis of both red layers revealed strong peaks for aluminium, silicon and iron, which suggested the presence of a red earth. The FTIR spectrum of sample SGM12 (Figure 14) showed characteristic peaks for red ochre together with absorption bands for gypsum at 3409, 1635, 1151-1222, 675 and 602  $\text{cm}^{-1}$ . The red pigment is coloured by hematite (absorption bands at 537 and 469  $\text{cm}^{-1}$ ) but the spectrum also showed the asymmetric Si-O-Si stretching (1100-1000  $\text{cm}^{-1}$ ) due to accessory silicate minerals and the characteristic absorption band due to Si-O stretching (915  $\text{cm}^{-1}$ ) of kaolin.<sup>8,18</sup> The identification of accessory minerals in the FTIR spectrum is indicative of a natural earth and not a synthetic iron oxide.

Earths were widely used as pigments for colouring wooden and ceramic artefacts, rock art, tomb decorations, polychrome sculptures and for paintings

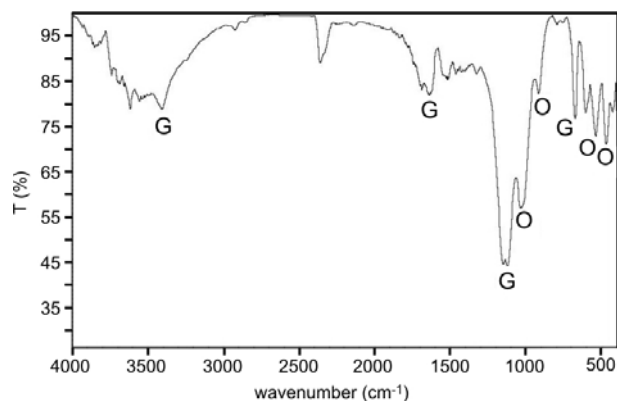


Figure 14: FTIR spectrum in transmission mode of sample SGM12 (G: gypsum, O: red ochre).

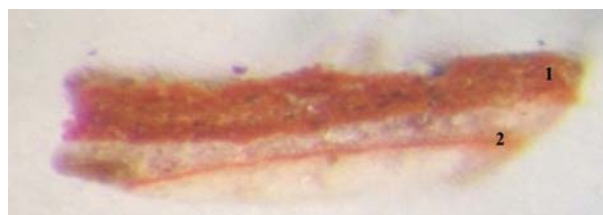


Figure 13: Cross-sections of sample SGM12.

on canvas. On the other hand, earth pigments have been important components in coloured grounds for paintings.<sup>18</sup> Mixtures of hematite with vermilion, red lead and organic red lake have been found in the colonial Andean palette.<sup>3</sup>

### 3.2.5 Umber

The cross-section of sample SGM8 (Figure 15) showed a very thin dark brown pigment layer on a gypsum preparation layer. Analysis by SEM-EDX revealed strong peaks for iron and silicium together with minor peaks for manganese, aluminium, potassium and calcium, indicative of a natural iron oxide pigment, presumably umber.<sup>18</sup> This pigment has been described in documentary sources as being very suitable for shadow or for shading other colours and has been recommended as a good and useful colour for painting in seventeenth-century treatises and eighteenth-century works.<sup>4,17</sup>

## 4 Conclusions

The identified pigments, except madder lake, were very much used in colonial sculpture to prepare

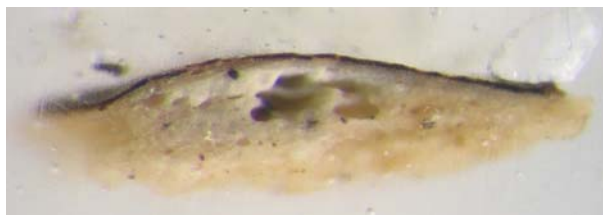


Figure 15: Cross-sections of sample SGM8.

bases, carnations or just to give colour to the different parts of the images. The Spanish manuals as Pacheco's and Palomino's gave wise advises for that purpose. On the other hand, our historical research in archives shows that all these materials were well known in the Jesuit missions, due to the notice we have from the inventories after their expulsion and from Father Sánchez Labrador, who in the 18<sup>th</sup> century wrote many recipes mentioning them. As for our own record, this is the first time we identify madder lake in our Colonial sculpture corpus.

## 5 Acknowledgements

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