










Multi-technical approach for the characterization of polychrome decorative surfaces at Spanish Mission Churches in Nueva Vizcaya (Chihuahua, Mexico)

Karla Muñoz-Alcocer ^{a,b,c}, Laura Fuster-López ^d, Ma. Luisa Vázquez de Ágredos-Pascual ^e, Francesca Caterina Izzo ^f, Marcello Picollo ^g, Giovanni Bartolozzi^g, Jose Humberto Vega ^h, Diana Maldonado Escobar^c, Alejandro Mitrani ⁱ, Miguel Ángel Maynezⁱ, Edgar Casanova-González ^j, Isaac Rangel-Chávezⁱ and Jose Luis Ruvalcaba-Sil ⁱ

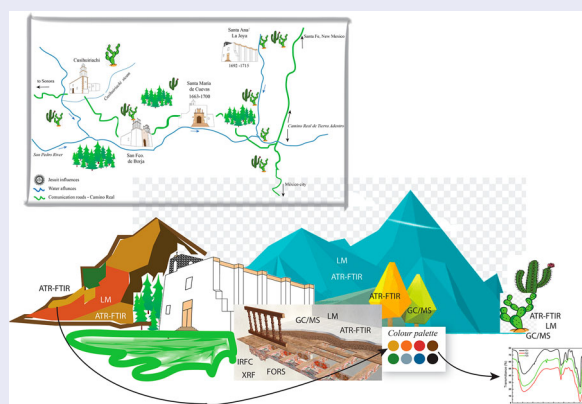
^aMisiones Coloniales de Chihuahua A.C., Chihuahua, Mexico; ^bLaboratorio de Patrimonio Histórico, Chihuahua, Mexico; ^cTecnológico de Monterrey Campus Chihuahua, Chihuahua, Mexico; ^dInstituto Universitario de Restauración del Patrimonio, Universitat Politècnica de València, València, Spain; ^eDpto. Historia del Arte, Universidad de Valencia, València, Spain; ^fScienze e tecnologie per la conservazione dei beni culturali, Ca' Foscari University of Venice, Venezia, Italy; ^gIstituto di Fisica Applicata "Nello Carrara" (IFAC-CNR), Sesto Fiorentino, Italy; ^hFac. de Zootecnia and Ecology, Universidad Autónoma de Chihuahua, Chihuahua, Mexico; ⁱInstituto de Física, Universidad Nacional Autónoma de México, Mexico City, Mexico; ^jCONACYT-Instituto de Física, Universidad Nacional Autónoma de México, Mexico City, Mexico

ABSTRACT

An interdisciplinary and multi-institutional group of science and art conservation specialists has provided new insight into the painting materials used in the polychrome walls and wooden ceilings in four seventeenth century Spanish colonial churches of Nueva Vizcaya (Chihuahua, Mexico). A multi-analytical study of the decorative surfaces was performed in situ using spectroscopic approaches (XRF, FORS), False Colour Infrared Reflectography – IRFC, as well as micro sampling (ATR-FTIR, LM, GC/MS). A survey of natural resources and study (ATR-FTIR, LM) was carried out to elucidate the natural occurrence of a select number of materials in the surrounding areas of the churches. The present paper presents a multi-analytical study and characterization of green, red-orange and black colour pigments and binders selected from the decorative surfaces. The aim of this study is to highlight relationships between local materials and those from the original polychrome ceilings, in order to understand the material and technological influences that converged in the Spanish colonial architecture of northern Mexico.

KEYWORDS

Spanish colonial missions; Chihuahua; tascate; multi-analytical study; Santa Maria de Cuevas; Polychrome wooden ceilings



1. Introduction

In the last five years, a multi-technical research project on the analysis of decorative surfaces of four seventeenth century Spanish Jesuit colonial churches of Nueva Vizcaya (Chihuahua, Mexico) (Marquez 1995, 2008) has been carried out by an interdisciplinary and multi-institutional group of specialists. In addition, a natural resources survey was implemented (Muñoz Alcocer 2018) in order to determine the influences and sources of the original artists materials (Muñoz-

Alcocer et al. 2016). Thus, the study was focused on differentiating those materials that were available locally, due to their natural occurrence in the surrounding areas of the churches, from those that were likely imported through the royal trade that connected Mexico City with the Northern Spanish frontier.

This paper presents the analysis of the materials used to produce the polychrome surfaces of four Spanish Colonial Churches located at Santa Maria de Cuevas (SMC), Cusihiuriachi (CUSI), San Francisco de

CONTACT Karla Muñoz-Alcocer  karla@misionescoloniales.org

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Borja (SJB), and Santa Ana (ANA). In addition, the paper describes the analysis of the natural materials collected in the localities of the four churches. This analysis was carried out in order to determine the role if any, local materials played in producing paints that could have been used in the decoration of these interiors (Figure 1). For this purpose, the characterization of dyes and pigments of the decorative surfaces was carried out *in situ* by X-ray fluorescence and fibre optic reflectance spectroscopy together with laboratory techniques that required micro samples, such as infrared spectroscopy, light microscopy, and Gas Chromatography integrated Mass spectroscopy. False colour infrared imaging technique was also used to document and study the investigated surfaces. The collected local natural materials (plants, extracts, rocks, clay and river water) around the four sites were used to reproduce representative mock-ups following ancient painting techniques. The first results on these mock-ups showed the significant influence of water from the nearby Rio San Pedro. A well correlated match was found between the spectra from samples taken from the decorative surfaces and those from mock-ups that were prepared with local water (Muñoz-Alcocer, et al. 2017b).

The previous analytical results have also revealed the use of iron oxide based pigments, which were well known by the local Indian community. Indigo, cochineal, malachite and red lead (minium) -which had not been previously documented in Chihuahua's Tarahumara Indians' palette (González 1972; Pennington 1963) – were also found (Muñoz Alcocer 2018). The presence of *Indigofera Suffruticosa* had already been registered by local botanists at the deeper levels of the Sierra Tarahumara Canyons, located an eight-hour distance from the studied area (Lebgue Keleng 2001). A cactus (*Opuntia*) with a manifest of cochineal was found at one of the church towns as well. Considering that indigo and carmine dyes had a great economic and symbolic value in pre-Hispanic times, and that therefore both colours were exchanged by the trade routes of ancient Mesoamerica as described in historical writings (e.g. Matricula de Tributos, ca.1522-30; Berdan & de Durand 1980; Sahagún 1577; Sarabia Viejo 2004), it could be possible that such dyes and pigments were produced locally and traded. The characterization of indigo (Gettens 1962; Gettens et al. 1946; Vázquez de Ágredos Pascual et al. 2014; Doménech et al. 2014) and cochineal (Dahlgren de Jordan 1954) in these decorative ceilings had been documented

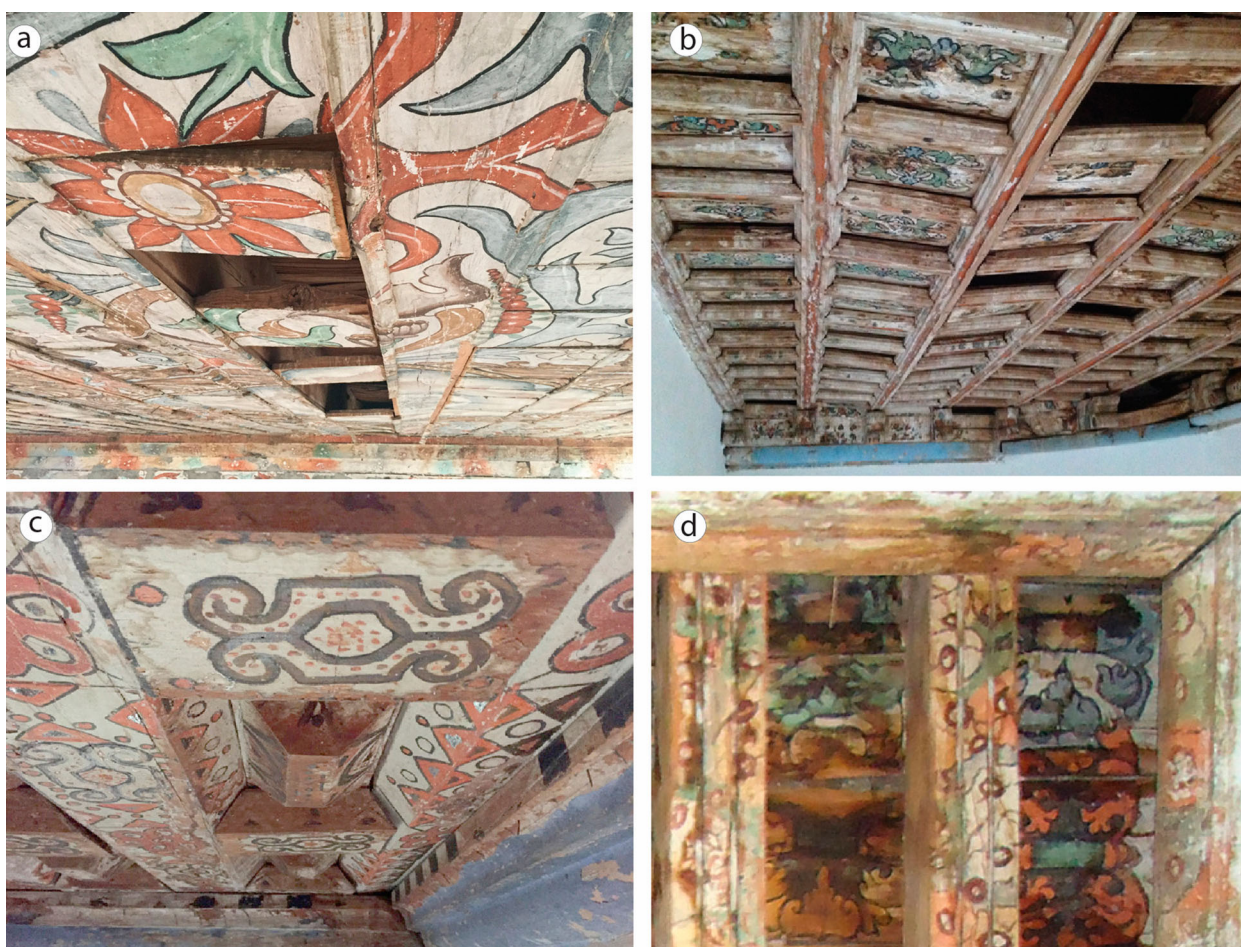


Figure 1. Detail of the polychrome wooden ceilings from Santa Maria de Cuevas (a); Cusihiuriachi (b); San Francisco de Borja (c) and Santa Ana de la Joya (d). K. Muñoz Alcocer, 2015.

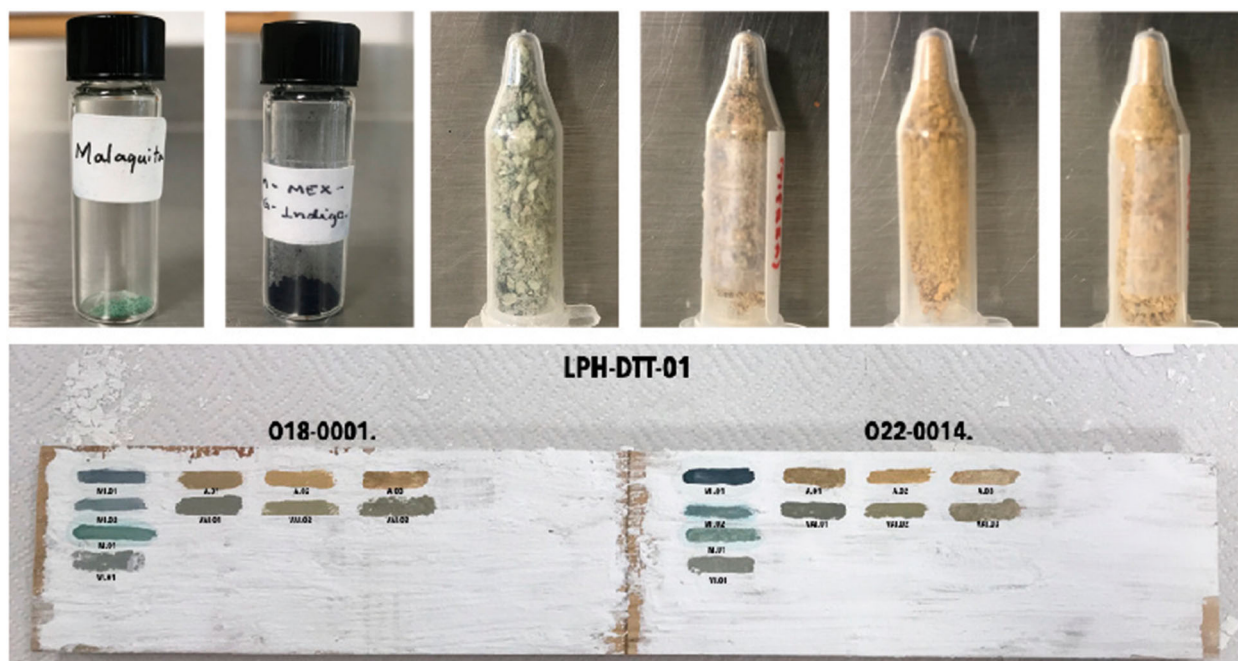


Figure 2. Characterization of the green colours from Santa María de Cuevas and Cusihiuriachi ceilings. View of the materials used and the mock-ups prepared with their identification number.

mock-ups were divided into two sections as a function of the water used (Table 2).

2.3. Analytical methods

2.3.1. Non-invasive

False Colour Infrared (FCIR). Photographs under Infrared (IR) and visible radiation (VIS) were registered in order to create a False Colour image (FCIR). This is done by overlapping both pictures, and a new colour scale is produced. In this case, a Sony Handycam camera HDR-PJ760 with an IR Filter 760 nm was used. In addition, Lowe Totta lamps of 750W with halogen bulbs of 3200K were used for illumination. The FCIR is generated by merging the RG

channels with the infrared image. FCIR is obtained when the B channel is given to the imaged G channel, the G channel to the imaged R channel, and the R channel to the acquired IR image. The final result of the new RGB image is a False Colour image (Warda et al. 2011). FCIR photographs were observed using an Apple MacBook OS X El Capitan with a screen calibrated in RGB Adobe (1998). Grey dot gain 20% and spot gain 20%.

X-Ray fluorescence (XRF). Spectra were acquired with a Tracer-III SD (Bruker) handheld spectrometer. Acquisition conditions were 40 kV, 11 μ A for 30 s per region. All spectra were processed with the software Spectra Artax v.7.4.6.1 (Bruker) in order to measure the X-ray intensities.

Table 2. Pigments and ground experimental chart.

Water source	Wood	Ground	Code	Malachite (g)	Indigo (g)	Green earth (g)	Yellow earth (g)	water (gotas)	Vinegar (gotas)			
San Pedro river water PH-DTT-01 022-0014	Pine wood	CaSO ₄ + H ₂ O SMC + Tascate resin-gum	MI.01	0.02	0.01	–	–	4	2			
			MI.02	0.01	0.001	–	–	2	1			
			M	0.035	–	–	–	3	2			
			VI	–	0.005	0.308	–	8	4			
			AA	–	–	–	0.305	5	3			
			AB	–	–	–	0.305	5	3			
			AC	–	–	–	0.306	5	3			
			VAL.A	–	0.01	0.2	0.2	6	4			
			VAL.B	–	0.01	0.2	0.2	6	4			
			VAL.C	–	0.01	0.2	0.2	6	4			
			Cusihiuriachi steam water LPH-DTT-01 018-0001		CaSO ₄ + H ₂ O CUSI + Tascate resin-gum	MI.01	0.02	0.01	–	–	4	2
						MI.02	0.01	0.001	–	–	2	1
M	0.035	–				–	–	3	2			
VI	–	0.005				0.308	–	8	4			
AA	–	–				–	0.305	5	3			
AB	–	–				–	0.305	5	3			
AC	–	–				–	0.306	5	3			
VAL.A	–	0.01				0.2	0.2	6	4			
VAL.B	–	0.01				0.2	0.2	6	4			
VAL.C	–	0.01				0.2	0.2	6	4			

Fibre Optics Reflectance Spectroscopy (FORS). In situ FORS analysis was performed using a portable Field-Spect-4 spectroanalyser by ASD Inc., equipped with optical fibre bundles. Spectra were acquired in the 300–2500 nm range with 10 nm spectral resolution. The probe-head covers a 1 cm² area and is equipped with a halogen lamp. All spectra were recorded in reflectance and then saved in both reflectance and apparent absorbance (Log [1/R]) modes, with a 0.2 seg. integration time. A certified reflectance standard provided by ASD Inc (AS-02035-000CSTM-SRM-990-362) was used for calibration. FORS spectra were compared with spectral databases and reference samples for the identification of pigments and other materials.

Additionally, UV–Vis–NIR (350–2200 nm) FORS data were also acquired on a panel piece of the polychrome nave ceiling of Santa Maria de Cuevas at IFAC-CNR, Sesto Fiorentino, Florence, Italy. Two Zeiss spectra analysers (models MCS 601 UV/VIS and MCS 611 NIR 2.2 WR, respectively) were used. The radiation between 320 and 2700 nm, which was provided by a voltage-stabilized 20w halogen lamp (module Model CLH600), was conveyed to the sample by means of a quartz optical fibre bundle that also transported the reflected radiation to the detectors. A 8°/8° probe-head, which can investigate an approximately 2-mm diameter spot was used. A 99% Spectralon® diffuse reflectance standard was used to calibrate the system.

2.3.2. Micro- Invasive analytical studies

Optical light microscopy (LM). Samples were observed in detail using a Stereomicroscope Olympus SZX16 with a 1XPF Palapo lens. Photos were taken with a Nikon Camedia C-5050 camera in automatic mode at 300 dpi.

Cross-sections were prepared in an epoxy resin (Epo-Tek 301-1), the two components (resin and sensitizer) were mixed and cured at an ambient temperature (23°C) for 24 h. Each sample was encapsulated with the sample code on a label. Samples were studied and photographed with an Olympus BX51 optical microscope equipped with transmitted and reflected light with bright field, dark field and polarized light. In addition, a selected number of samples were also photographed with a DINolite microscope in visible (VIS) and ultraviolet (UV) light in order to identify where organic components may be located.

2.3.2.1. Infrared spectroscopy in Attenuated Total Reflectance mode (ATR-FTIR). A Bruker Alpha-P ATR-FTIR spectrophotometer equipped with a Platinum ATR sampling module (diamond crystal) was used to collect spectra in the 4000–400 cm⁻¹ range. The spectra were examined with Quick Compare OPUS software. ATR-FTIR spectra obtained were

compared to the spectral library of traditional and natural resources materials (cochineal, azurite, malachite, lead, natural earths, etc.) created at Laboratorio de Patrimonio Histórico (LPH). The unlimited access to the equipment and software made infrared spectroscopy the predominant analytical technique. The interpretation of results was based on ATR-FTIR spectra and their correspondence with the other analytical studies results. The abbreviations used to describe the intensity of absorption bands are the following: (s) strong; (m) medium; (w) weak; (br) broad; (sh) sharp; (d) deformation and (p) present. In some cases, a combination of these abbreviations is used (e.g. "ms" for medium strong).

Gas chromatography–mass spectrometry (GC-MS) analysis were carried out to identify the organic binding media present in the paint and ground layers. For this purpose, two different procedures developed by Conservation Science research group at Ca' Foscari University (Venice) were used. For lipidic, waxy and resinous materials, the samples were transesterified using (trifluoromethylphenyl) trimethylammonium hydroxide, an overnight reaction as described in (Fuster Lopez et al. 2016; Izzo 2011; Izzo et al. 2014a; Izzo et al. 2014b). GC-MS analysis were performed using an Agilent 6890N GC instrument with a capillary HP-5 column, 30 m, 0.25 mm, 0.5 µm interfaced with an 5973 Network MS. The temperature programme was set from 80 °C to 300 °C with a ramp of 10°C/min, held at 300°C for 2 min. The MS was run in Full Scan mode (m/z 40–600), 1.9 scans/s. Quantitative GC-MS analysis was performed using nonadecanoic acid as internal standard. For proteinaceous and polysaccharidic materials, amino acids and carbohydrates were analysed as N,O-acetyl methyl esters after hydrolysis with trifluoroacetic acid and derivatisation (Henk Van Keulen of the Cultural Agency of the Netherlands and then implemented by Francesca C. Izzo at Ca' Foscari University of Venice). GC-MS analysis were performed using an Agilent 6890N GC instrument with a capillary Carbowax Column, 30 m, 0.20 mm, 0.5µm interfaced with an 5973 Network MS. The temperature programme was set from 80 to 250°C, with a ramp of 20°C/min until 210, then 2°C/min until 250°C. The MS was run in Full Scan mode (m/z 40–500). Mannitol and Norleucine were used as internal standards.

3. Results

3.1. Ground layer

Natural occurring deposits of gypsum and calcite are present in the region of study. In San Francisco de Borja, a clay kiln oven traditionally used to burn calcite was found. In Santa Maria de Cuevas, the deposit of gypsum is a little farther from the mission than that

of calcite. Clay ovens to burn calcite, as well as those traditionally used to heat clay vessels and to bake bread, are found associated with the patios of the houses built under Spanish colonial influences.

Gypsum is present in the ground layer in Santa Maria's nave ceiling, at Cusihuirachi, and at San Francisco de Borja. Anhydrite and hemihydrate sulfate (Hunt et al. 1950, 427), are also present in some spectra. In Santa Maria, some weak bands ($875, 711 \text{ cm}^{-1}$) of calcium carbonate (CaCO_3) were detected as well in some spectra from the ground layer. Calcium carbonate (1429s, 872sh, 712psh) was used as the main ground component at the narthex ceiling of Santa Maria. In addition, absorption bands related to anhydrite (670msh, 614p, 593msh) and hemihydrate sulphate (3600p, 3440p, 1151ms, 1120sh, 1690p, 667def, 466p) and dihydrate (3544m, 3407m, 3250br, 1109, 490p, 414psh) were also detected in the narthex ceiling of Santa Maria de Cuevas.

The use of calcium carbonate as the ground layer at the narthex ceiling in Santa Maria could have been for aesthetic impact. In fact, a ground layer whiter than gypsum was needed to contrast the white-grey grisaille used to decorate the painted panels and to create a perspective effect. (Muñoz Alcocer 2018, 263). Another, reason could be related to painting technique and the type of wood that was chosen; however, further studies need to be done in order to attribute the use of calcium carbonate as a ground layer due to these two factors.

In Santa Ana de la Joya, only calcium carbonate was detected. It is uncertain why calcite was chosen by the painter, and could simply be that these materials were more readily available. However, gypsum was present in Santa Ana and was used in the preparation of

some pigments. Clearly, the use of this material for artistic purposes was known, and that its substitution by calcium carbonate at the underlying levels was an intentional choice- as found in a red-orange sample taken from the bearing beam of the choir in Santa Ana. Here, it is most likely that the red and yellow ochre were mixed with gypsum to create the orange colour instead of having gypsum applied for the ground layer. Also traces of gypsum were detected in blue areas (Hunt et al., 1950, 427). In this case, the blue colour was obtained by mixing an unidentified dye with gypsum (3408br, 1622m, 672sh, 610sh, 592sh) to produce the desired hue. These findings were supported by XRF and FORS data (Figure 3).

ATR-FTIR spectra from samples taken from the mock-ups prepared with calcium sulphate and hemihydrate mixed with tascate resin-gum were compared with those from the ground layer of the case studies. A significant correlation was obtained with Santa Maria de Cuevas (94%) and Cusihuirachi (90%), but lower with San Francisco de Borja (65%). Also of significance is that the ground layer prepared with hemihydrate sulphate and tascate resin-gum, produced grey lines similar to those observed at the ground layer of Santa Maria de Cuevas, but not at the ground layers of the other case studies (CUSI,SFB,ANA) (Figure 4).

3.2. Painted layers: pigments and dyes

3.2.1. Green

The visual comparison between the VIS image and FCIR allows the identification of some hue changes in the green colour. In comparison to other colours, green is the colour that changes the most. This

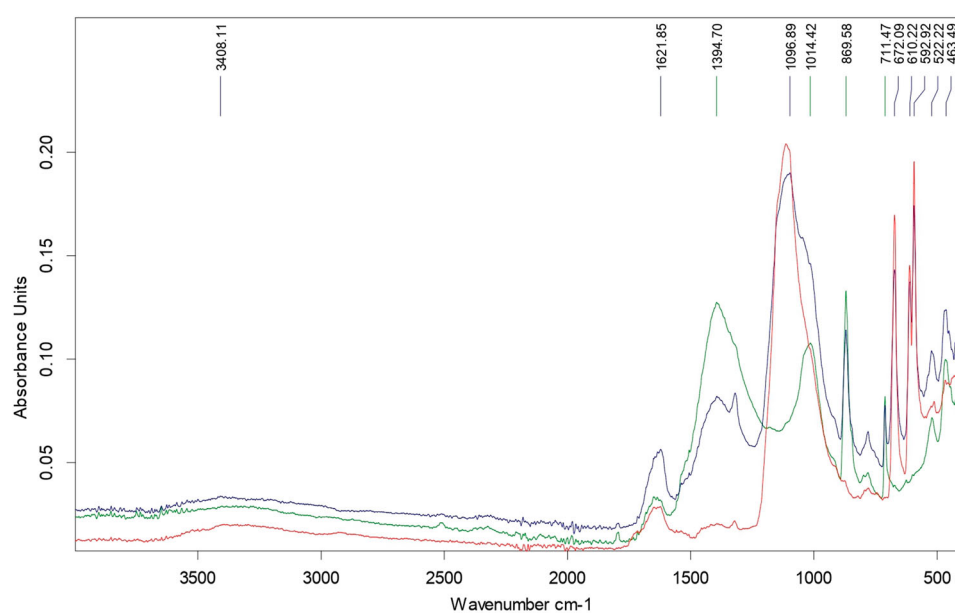


Figure 3. ATR-FTIR spectra from the blue (B.T.02) (blue line) and red-orange (VM.01) (red line) and ground layer (B.T.04) (green line) from Santa Ana de la Joya narthex and baptistery ceiling. Differences can be observed with the calcium carbonate ground layer absorption bands (peaks on blue) and those from the blue and orange samples spectra, where calcium sulphate absorption band are present (K. Muñoz Alcocer, 2019).



Figure 4. Santa Maria de Cuevas nave ceiling panel (a) compared with the mock-ups prepared. The ground layer prepared with hemihydrate sulphate and tascate resin-gum presents the same grey strips as the ceiling panel (c) which are not present at the ground layer prepared sulphate and gypsum without tascate resin-gum (b). K. Muñoz-Alcocer, 2018.

variability is possibly related to the pure condition and aging of the paint layer, and also to the colour preparation. Different green hues can be seen at Santa

Maria de Cuevas (green-yellow and bluish green), Cusihuiachi (dark green and bluish-yellow green), and Santa Ana (Dark & light green). These chromatic hues can be better distinguished in the FCIR (Figure 5). For example, in Santa Maria green-yellow leaf motifs appear blue and greenish blue in FCIR. The leaves that in VIS light have a bluish green hue, are reproduced in FCIR as a bright blue with some tendency to red-purple. FCIR studies gave some hints on the possible composition of the green areas, which could have been painted with malachite ($\text{Cu}_2\text{CO}_3 \cdot (\text{OH})_2$). This pigment, indeed, appears with a bluish hue (Bevilaqua, Borgioli, and Gracia 2010, 241; Moon, Schilling, and Thirkettle 1992, 49), whereas, earth green pigments are rendered with a black or dark blue tint (Bevilaqua, Borgioli, and Gracia 2010, 259; Moon, Schilling, and Thirkettle 1992, 49).

The physical condition of the painted surfaces can affect the final FCIR images and their interpretations. For example, the faded green areas at the polychrome ceiling of Cusihuiachi, appeared in FCIR with a light blue hue suggesting the presence of a copper based green pigment. Also of note are areas that have



Figure 5. VIS and FCIR images details from the case studies ceilings: Santa Maria de Cuevas (a); Cusihuiachi (b); San Francisco de Borja (c) and Santa Ana de la Joya (d). Isaac Rangel-Chávez, Instituto de Física, UNAM, 2016.

been exposed to water damage. In these cases, the greenish details became darker resulting in a darkish pale blue in IR-FC, which should mean that a green earth pigment could have been used. In contrast, the dark green leaves that decorate the semi vertical panels that border the ceiling appear as dark blue to almost black with a reddish tone in IRFC. These variances between the central panels and the side panels suggest that two different pigments made of different materials could have been used.

The same variations were also observed in the case of ANA. Small green crystals encrusted between small yellowish-green particles were seen over LM. The sample taken from a water damaged area shows the green compacted particles fading into a dirty white to brownish colour tone. In the case of SMC, a large white-transparent particle with visible fibre structure was observed on the surface of one of the green samples from the nave ceiling. These particles are well identified and associated with those seen in natural malachite under the microscope (Bevilaqua, Borgioli, and Gracia 2010, 117). Similar small crystals were observed in other case studies, however not as clearly as in the green samples from Santa Maria de Cuevas. All green points analysed by XRF contain copper (Cu). Arsenic (As) was also detected as a minor component in the green areas only.

The spots analysed by XRF were also studied by FORS. Copper based green pigments such as malachite and copper resinate (copper salts of resin acids), were used as references in the FORS spectra. The spectra from the studied green spots of the SMC ceiling have a similar shape to that of malachite. The FORS spectra of the green spots from CUSI and ANA, however, were not always consistent with the FORS reference spectrum of malachite. The maximum reflectance of the green spots are at 547 nm but the absorption bands are centred at 735 nm while in malachite this band is at 800 nm (Bevilaqua, Borgioli, and Gracia 2010, 241). In these cases, FORS identification for malachite was not clear.

The wall painted frieze from SMC presents different green hues. As mentioned above, XRF analysis found copper as the prevalent element with arsenic was also detected. It is likely that this in this case that colour change is related to light exposure, for example, in the areas that are not directly exposed to the sunlight the colour of the leaves and birds are well preserved. The areas that are exposed to direct daylight from the window have changed the hue to a greenish blue colour (Figure 6).

ATR- FTIR spectra from the studied green samples confirmed the results of the non-invasive techniques. Absorption bands were found at the 1550–1350 cm^{-1} region, which are related to the carbonate asymmetric stretching vibrational mode. In addition, 890–670 cm^{-1} bending bands were observed, which are

typically found in hydrated carbonates such as malachite (Adrover García 2001, 38; www.irug.org). Although a correlation between the spectra acquired on the churches and the reference (malachite IMP00146 from IRUG database) was good, some discrepancies were also observed. In addition, spectra from the green samples were compared with that of the malachite obtained from the mines located in the geographic area of study and significant differences were found. Interestingly, when this same malachite was used to prepare the pigments applied in the mock-ups, a higher correlation with the spectra obtained from the case studies was observed.

A correlation of 97.78% between ATR-FTIR spectra from the green sample from Santa Maria narthex ceiling and the malachite prepared with indigo (1:1) (Table 2 MI.01) was found, whereas the correlation with the mixture pigment made with yellow reddish earth was only 56.36% (sample VAI. C), but 91.43% with the green from the nave ceiling. This could indicate that two different greens were prepared for the decoration of the nave and the narthex ceilings. Although absorption bands at both spectra are similar except for calcium carbonate bands at the narthex green spectra.

According to FCIR image interpretation, in Cusi-huirachi ATR-FTIR results confirmed that two different greens were applied on the ceiling. A 96.70% match between the green from a side panel (dark green at VIS light) and the green prepared with malachite, indigo and yellow earth (sample VAI.B) was found. Whereas, the light green from the central panels presented only a 53% correlation. Most likely, the light green was prepared by malachite (M) (90.19%) with some indigo (92.53%) over calcium sulfate hemihydrate. However, the correlation with the pigment mixture malachite and indigo (MI) was not conclusive (88,50%) (Figure 7).

In Santa Ana, FORS results indicated that the green colours of both areas (narthex ceiling and baptistery), were obtained with a mixture of malachite and an iron(III) hydroxide-oxide based pigment. Nevertheless, no indication of this iron(III) based pigment was observed in the cross sections. ATR-FTIR spectra show a Quick Compare software high correlation with local malachite (83.14/95%) but it is not conclusive.

3.2.2. Red & Red-orange

In the FCIR imaging technique, orange-red pigments such as red lead, vermilion and cadmium red, are reported with yellow hues. Iron(III) based pigments such as red ochre have been described in IRFC as: “verde bruno” (brownish green) (Bevilaqua, Borgioli, and Gracia 2010, 259); yellow (Moon, Schilling, and Thirkettle 1992, 49); and brown (Cosentino 2014, 9). In the case of SMC and ANA, the elements preserved their bright colour and appeared in IRFC images as a

Santa María de Cuevas
Upper frieze - wall paint

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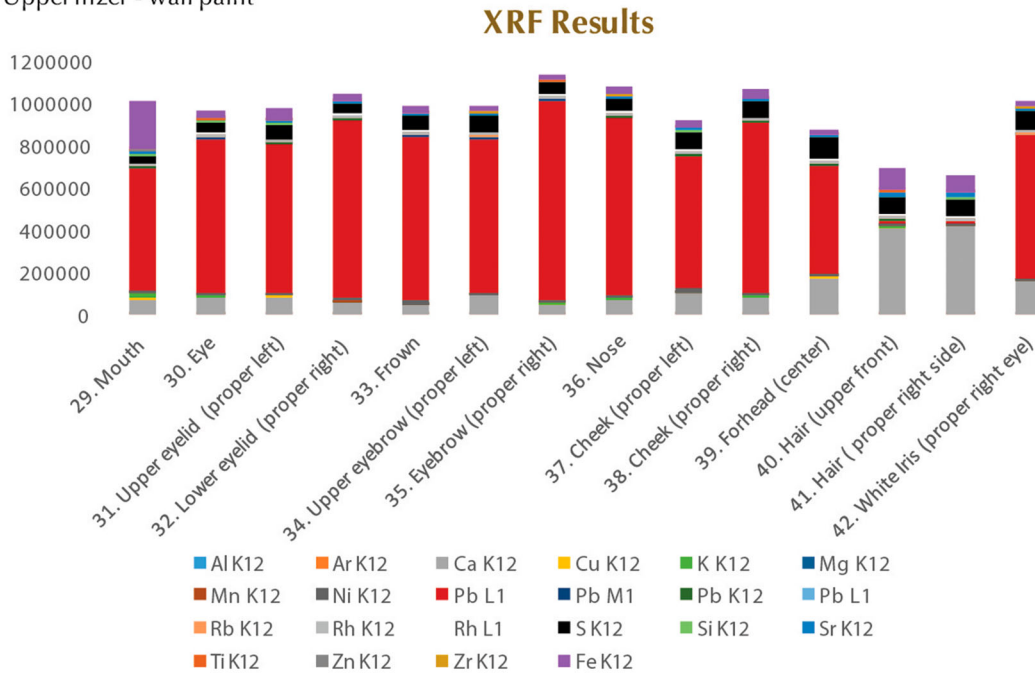


Figure 6. XRF chart from the studied points from the angel face and images from the wall paint upper frieze. It is possible to observe the green malachite from the leaves and birds that have faded into a light blue colour. (E. Casanova, Instituto de Física, Universidad Nacional Autónoma de México, 2016; images: K. Muñoz-Alcocer, 2004; 2016).

bright yellow with some tendency towards a greenish. The areas that were affected by humidity and that have black stains, produce a yellow brownish colour

in FCIR. Again, based on references mentioned before, the red areas from these ceilings are more likely to be made of iron(III) oxide based pigments.

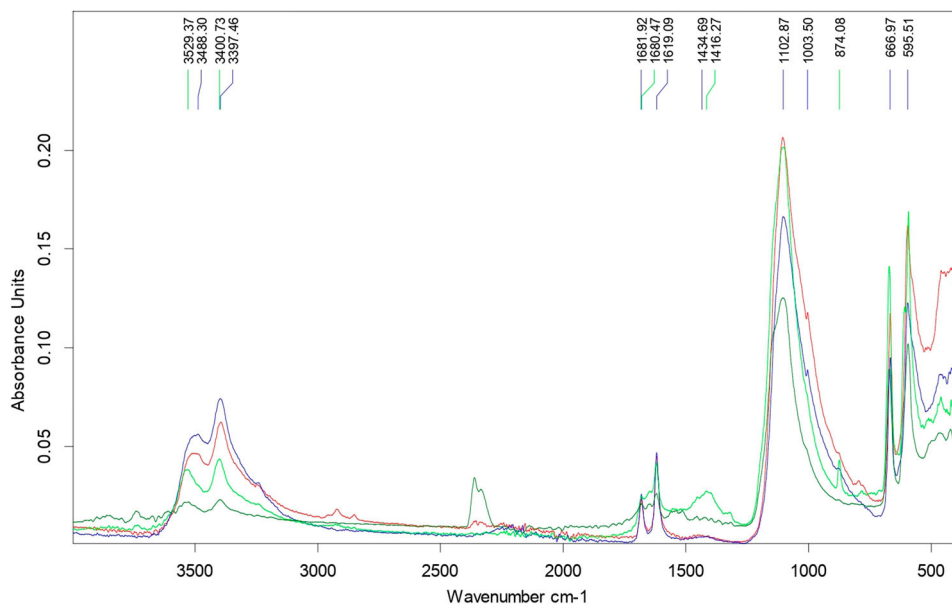


Figure 7. ATR-FTIR spectra from the narthex green sample from Santa María de Cuevas narthex ceiling (light green line), nave ceiling (dark green line) and the prepared pigments VALC (red line) and MI (blue line) (D.Maldonado, K. Muñoz Alcocer, 2018).

In the case of the wall paint from Santa Maria de Cuevas, XRF detected iron as a major element in the red botanic motifs of the frieze, and lead in the pigment used to render the lips and faces of the two angels. The differences between brightness in the red from ceiling and the red from the botanic ornaments of the frieze are most likely due to the support used. According to studies, organic binders do not affect the change of tone or colour in IRFC images, but the concentration of the pigment does (Moon, Schilling, and Thirkettle 1992, 49). This can be clearly seen as in the FCIR image of the nave ceiling where the intensity of the hue varied according to the degradation of the colour paint. The angel faces were not sampled as in general these areas are in good condition.

XRF analysis indicate that the red from the Cusi-huirachi and San Francisco de Borja polychrome ceilings presents lead as the major element, which could be associated with the presence of minium. The FORS spectra of those two ceilings confirmed the presence of minium, presenting a reflectance inflexion point at 565–575 nm in accordance with the reference data (Aceto et al. 2012a, 2012b, 2014). In conjunction with these findings and the verification of minium in the ceiling, there were a few cases in which another inflexion point at 580–585 nm is present in addition to the main inflexion point at 570 nm (Leona and Winter 2001). This finding can be related with the presence of small quantities of vermilion in the red pigment (Figure 8).

Both red colours from CUSI ceiling (flowers and structure) show a yellow – brownish yellow in IRFC imaging with some hue differences (Figure 4b). As in San Francisco de Borja, the red appears to have two subtle hues depending on the concentration of the pigment used. The red in the triangular motifs is an

intense orange applied as one layer, whereas the pigment in the flower motifs was applied in two layers. Both reds appeared yellow in IRFC with some hue differences as well (Figure 4c).

In the ATR-FTIR spectra from Cusi-huirachi red samples from the coffered ceiling wood structure (beams) confirm the presence of minium (absorption bands at 521s, 455s and 398s cm^{-1}) and gypsum (Bevilaqua, Borgioli, and Gracia Rodríguez 2010, 221; Hunt et al. 1950). However, the presence of minium in the red flowers that decorate the board panels was not ascertained. ATR-FTIR spectra were also compared with those collected from a rock acquired from local lead mines. The rock contains a high concentration of minerals containing lead, such as red lead. On this sample absorption bands similar to those observed in the painted samples were found, but they were not sufficient to determine the presence of minium. Due to the strong absorption band at the region (1150s, 1106s, 1096s, 1000md, 782p cm^{-1}), comparisons were also made with iron(III) oxide based sediment collected a few kilometres from the church, and with commercial pigments. Comparison of the absorption bands indicated that the red flowers were painted with minium with iron(III) oxide based sediments.

3.2.3. Black

Black coloured materials were used in the four case studies to outline the botanic ornaments and figures. The analysis of these black areas was difficult due to the fact that black hue is mostly overlapping other colours.

XRF and FORS techniques obtained almost similar results in the four case studies. The elements detected by XRF were most likely representative of the background colour beneath the black line, while in areas where black was not overlapping another colour,

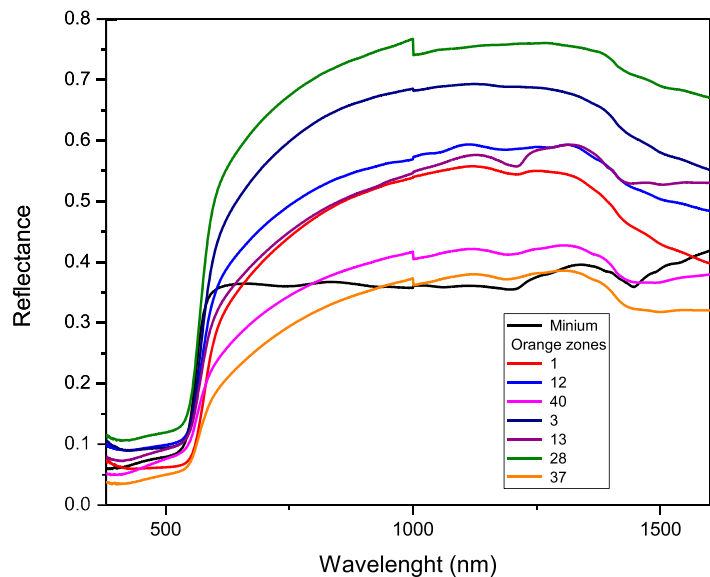


Figure 8. Detail view from San Francisco de Borja polychrome ceiling and FORS spectra from the red-orange studied points. Minium reference (black line) red-orange spots studied (colour lines). (M.A Maynes, Institut of physic, Universidad Nacional Autónoma de Mexico, 2016).

elements were also present at the ground layer. However, an increase of iron, manganese and potassium was observed in some cases. No identification of the black pigment was determined by FORS. These results could indicate that carbon black was used at the polychrome ceiling of the four case studies. Nevertheless, ATR-FTR spectra indicated that a mixture with carbon black (burnt wood) and local black earth had been used to prepare the black, especially at ANA, which will be explained in more detail.

A clear European influence can be seen in the use of black to delineate the figures, as the colour chosen in pre-Hispanic times for this purpose was red, usually manufactured from earth pigments. In this same sense, the Pre-Columbian mural paintings that have been preserved in Mexican territory do not contain evidence of the use of black to create volume in the figures represented (Vázquez de Ágredos Pascual et al. 2018). Therefore, both uses of black refer to European influences in the field of Mexican mural painting that was developed in Colonial times. The tone of umber could vary from blue-grey to a dark brown depending on the area (Figure 4).

One black sample from Santa Ana was observed under the stereoscope. The paint layer appeared compact, made of well adhered powdery black particles. Also visible were small green, red, and yellowish crystals mixed with the black particles and with white-transparent crystals. These particles are not regularly present in carbon black samples. Based on the reported characteristics, the black pigments found at Santa Ana de la Joya appeared to be made with iron oxide minerals (Figure 9).

In two of the three black spots studied by XRF, manganese was detected between the major elements with calcium and iron, including an increase of sulphur and potassium in comparison with those found at the ground layer. The measurement of the third spot was made in a black stain existing at the dark blue colour. The elements found at this spot are the same ones

that present in the blue studied spots (Ca, S, Fe). According to the elements found at the two black spots, the use of iron – manganese oxide as black pigment is not considered (Pitarch et al. 2014). FORS spectra were not conclusive.

The same black sample observed under the stereoscope was studied by ATR-FTIR. Absorption bands related to calcite were detected from the background, similar to the ground layer. The ATR-FTIR spectrum presents O-H stretching bands at 3524 and 3398 cm^{-1} and a weak broad band at 3115 cm^{-1} . Si-O absorption bands (Derrick, Stulk, and Landry 2015, 117) were also identified (1642p). In addition, the spectrum presents strong absorption bands at the 500–400 cm^{-1} range that could also be related to the presence of iron oxide materials. Based on these correlations with iron oxide pigments, ATR-FTIR results are in correspondence with those obtained by XRF elemental analysis.

For corroborating the obtained results, the spectrum was compared with commercial iron oxide pigment from Windsor & Newton and with local black earth collected in the region of study. The spectra from the black panel present similar high correlation with both references. The commercial pigment maintained a higher correlation (Quick compare 93/95%) than the local raw black earth (90%). In addition, the spectrum from the black sample was compared with burnt wood, and a high correlation (88%) was found, but not as high as was detected with iron oxide pigments. However, we should consider that a possible mixture of both organic and inorganic materials was used to produce the black pigment at Santa Ana de la Joya (Figure 10).

3.3. Binding media in grounds and painted layers

Ground and coloured samples from the case studies were analysed by GC-MS using the two methods, as previously described. Generally, samples were very tiny.

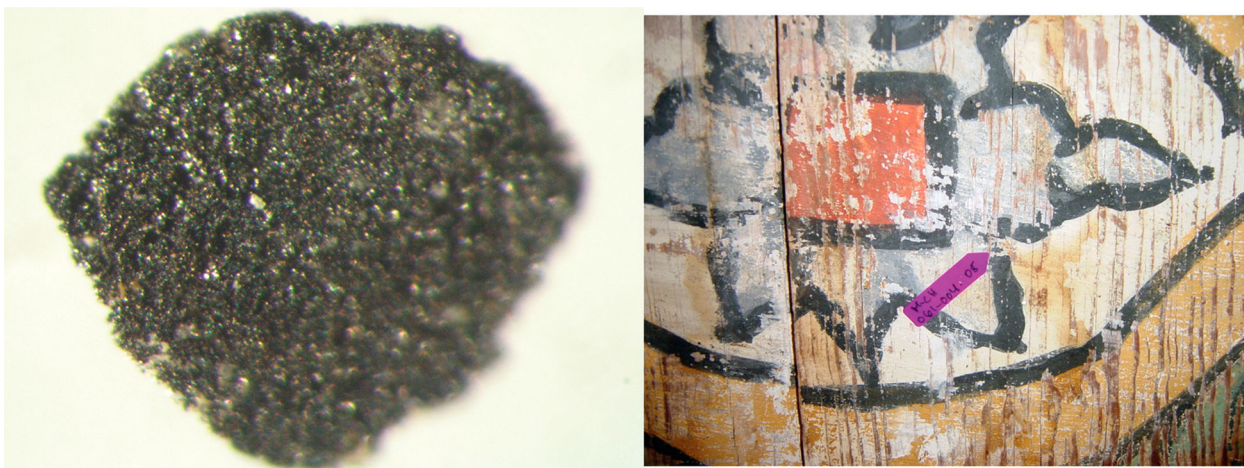


Figure 9. Black sample from Santa Ana de la Joya narthex under the microscope and image from the area in which the sample was taken (K. Muñoz-Alcocer, 2018).

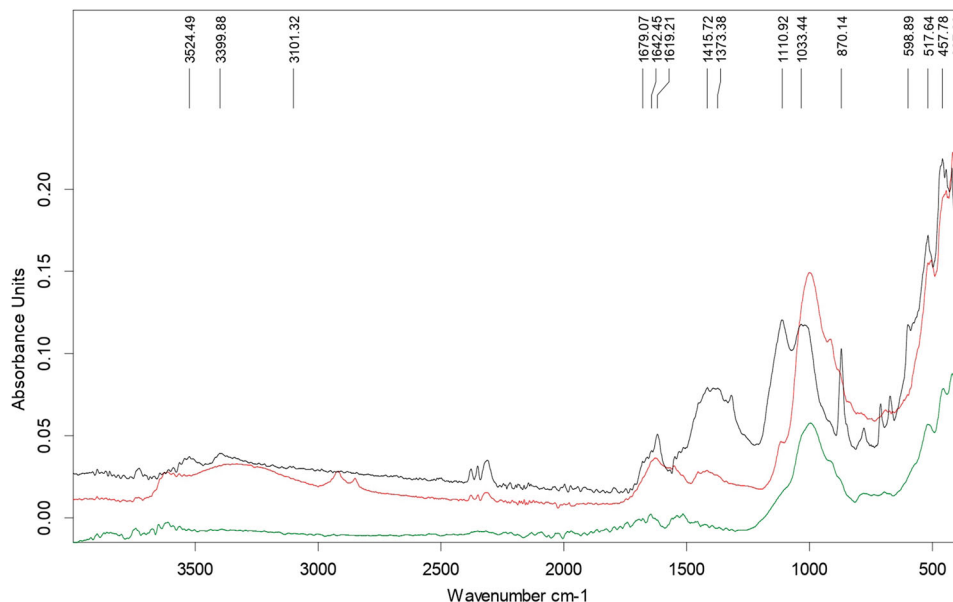


Figure 10. Comparison ATR-FTIR spectra between the black sample B.T.06 (spectrum in black line), local black earth RM.04 (red line) and burnt wood (green line). K. Muñoz Alcocer & A. Pizarro, LPH, 2015.

3.3.1. Santa Maria de Cuevas

The organic fraction of the ground samples contain traces of lipidic compounds (fatty acids such as palmitic and stearic acids, glycerol), proteinaceous material (amino acids such as alanine, valine, glycin) and carbohydrates (rhamnose, arabinofuranose, arabinose, glucose and gluco-pyranose). Very little variation was found with the colour samples.

The chromatograms obtained from SMC proteins and polysaccharides are similar to the ones detected in the resin-gum of the tascate tree collected in the region around this church. Although the identification needs further analysis, there is a favourable correspondence between the identified compounds (Figure 11).

3.3.2. Cusihuiachi

The organic portion from the Cusihuiachi samples analysed with both GC-MS methods was very limited. Traces of fatty acids (in particular myristic, palmitic and stearic acids) were identified. The use of drying oils is excluded because of the lack of dicarboxylic acids – typical of the oxidation and polymerization of siccative oils. Their occurrence is likely due to the presence of fatty compounds, such as animal fats.

Analyses of the green paint film by both methods identified a major presence of protein and polysaccharides. The same components were identified in the black samples. As seen for Santa Maria de Cuevas' case study, the GCMS outcomes for Cusihuiachi have a similar correspondence with the results from the tascate tree exudate.

3.3.3. Santa Ana de la Joya

In general, there were no organic components identified as weak peaks, nor were any peaks identified in the C–H region $2990-2850\text{ cm}^{-1}$ in the ATR-FTIR spectra from

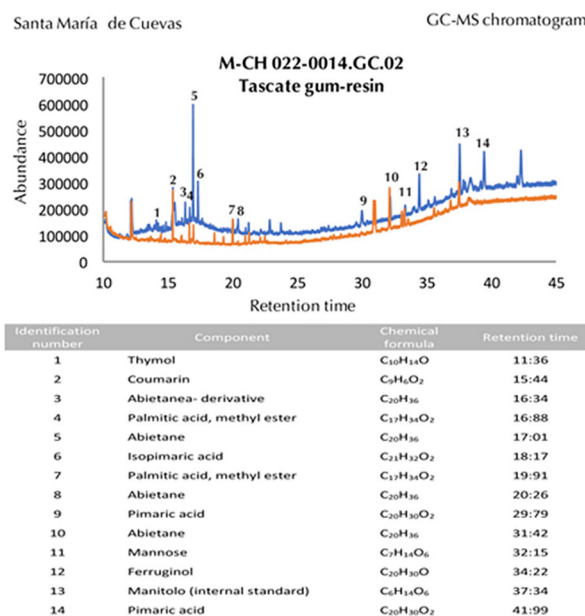


Figure 11. GC-MS chromatogram from the ground sample from the panel DT1 (orange line) and the tascate gum (blue line) analysed by the protein method. The table lists the compounds found in the tascate gum-resin. Performed by F. C. Izzo, P. Consoli & L. Giorgi, 2018.

Santa Ana de la Joya. GC-MS was undertaken for two samples in order to determine the presence of a protein as a binder. The samples studied, one from a green layer, and one from a blue layer, were analysed by the protein method. The spectra presented similar components. Traces of protein and polysaccharides were detected; however, the identification was not possible due to the noise present in the chromatogram. As for San Francisco de Borja, all the ATR-FTIR stretching bands were detected in the region of $2990-2850\text{ cm}^{-1}$, indicating the presence of organic molecules. However,

the identification was not possible due to the lack of certain absorption bands related to resins and or oils.

3.3.4. San Francisco de Borja

GC-MS was undertaken for six samples, in which traces of fatty acids were detected in the ground layer. However, a major presence of proteinaceous and polysaccharide components was also identified. Unfortunately, these analyses were unable to confirm the presence of hydroxyproline as a marker for animal glue. The red sample presented a similar chromatogram to that of the ground layer, showing a major presence of polysaccharide over that of protein. In contrast, the brown pigment showed a significant presence of lipid components mostly related to animal lipids. However, in this case the findings were related to a pigment component and not to the binder.

4. Discussion and conclusions

This study demonstrates the local and European influences in the decorative programme of the Mission churches of Santa Maria de Cuevas, Cusihuiachi, San Francisco de Borja and Santa Ana de la Joya. Results from this study show that these influences impacted the design and decorative artistic vision for these interiors, and particularly influenced the selection of raw materials that made the decoration of the polychrome ceilings in these churches possible.

Tascate trees grow in abundance throughout the study area. Several research accounts have been published on the oils that can be obtained from the tascate leaves and branches (Conabio 2000). However, no reference was found about the use of the exudate as a binder for decorative purposes. A significant characteristic of this tree's exudate is a natural property that repels insects and termites. The use of this material as a binding medium makes perfect sense in the conservation of the ceiling wood. The ground layer has mostly the same characteristics, with minor differences. This could indicate that the resin-gum was applied in the stucco or ground preparation layer.

The components found by GC-MS at the ground layer were also found in the painted layers which could indicate the use of the same gum as binder. In order to determinate the presence of tascate gum at the ground and paint layers, mock-ups were prepared using gypsum, tascate resin-gum and water from the river that runs through the town of Santa Maria. This result was also corroborated by the ATR-FTIR technique as the spectra collected on two samples showed a strong correlation (96%) with the resin-gum reference spectrum. However, further analysis is needed to determine if this resin-gum was applied only at the ground layer or if it was also used as a binder to prepare the coloured material (Figure 12).

The palette is quite similar in all case studies, except for San Francisco de Borja, which is limited to yellow, red, brown-turnsole and black. The absence of green, pink and blue at San Francisco de Borja was not because the artist had no access to these pigments and dyes but because colours were selected as a function of the style of the ceiling structure (Muñoz Alcocer 2018, 419).

Red lead pigment was chosen to paint the ceilings of Cusihuiachi and San Francisco de Borja instead of mixing red and yellow ochre to obtain an orange-red colour, even though they are found in great abundance around these churches. The brightness of red lead was perhaps the reason why it was used in both ceilings.

The presence of mineral lead has been documented in CUSI and SFB. Other red-orange hues, such as those found in the marble imitation paint technique from the beams in Santa Ana and Santa Maria, were made by mixing red ochre and yellow ochre with gypsum. The red and brown from the polychrome ceiling of these two missions were made of red ochre as well. A European influence was also detected in the selection of pigments for the stylistic decoration, as in the ceiling of San Francisco de Borja, upon which red lead was used instead of a local earth. This ceiling seemingly has only Spanish and Italian influences (Muñoz-Alcocer et al. 2017b), since the structure, polychrome design, and pigments come from European style canons. This is opposed to the other case studies, where a fusion of local and European style features and materials was found.

The artistic influences of the New World were detected in the identification of yellow, pink, and blue dyes in Santa Maria de Cuevas (carmines and indigo), Cusihuiachi (plant dye, carmines, indigo), and Santa Ana de la Joya as reported in previous publications (Muñoz-Alcocer et al. 2016, 2017a, 2018).

Historic references suggest that malachite, azurite and turquoise minerals, broadly employed in Mesoamerica since ancient times (Williams & Weigand 1995), were commercialized by the Mogollón culture (1000 BC - 1350 AD) (Haury 1936). The use of malachite as pigment has been registered in central México since Late Pre-classic times (ca. 300 BC - 300 AD). It is presumable that its use was known within northern populations (Vázquez de Ágredos-Pascual et al. 2018). However, no reference on the use of malachite or azurite by Tarahumaras Indians has been found (González Rodríguez 1972; Pennington 1963). Thus, it is reasonable to say that these polychrome ceilings evidence the first use of malachite as a pigment in Chihuahua.

Finally, black used as contour lines is present in all the case studies. In Santa Ana, umber was used to create the shape and volume in the decorative motifs, and in Borja, it was included as part of the decoration in alternating black and white squares. The identification of

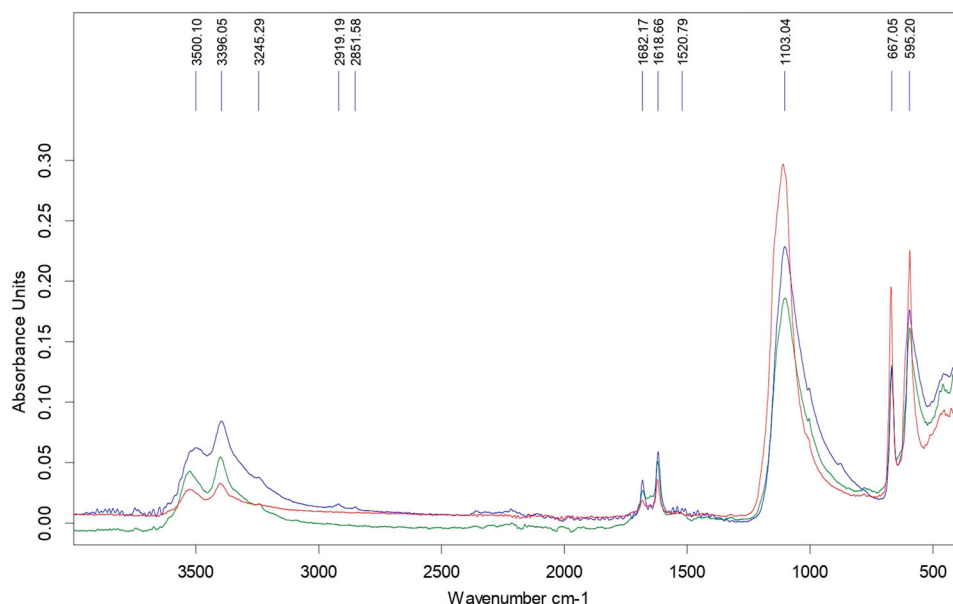


Figure 12. ATR-FTIR spectra from Santa Maria de Cuevas nave ground layer (red line), presbytery ground layer (green line), and the prepared ground layer calcium sulfate anhydrite mixed with tascate resin-gum (blue line).

black pigments is complex. XRF and FORS did not provide a clear identification. The presence of manganese in low concentration in the XRF data discarded the possible presence of manganese black. ATR-FTIR spectra indicate that in most of the case studies a mixture of organic and inorganic components was made to produce the black pigments. A major presence of iron oxide was detected at Santa Maria de Cuevas' presbytery, however some correlation was also found with burnt wood (79%). In Cusihiuriachi a higher spectral correlation was found with both local black earth (89-91%) and burnt wood (91-93%). In San Francisco de Borja, different correlations were obtained between the two black samples. However, in the black sample from the moulding, in which the black material is found separated from other colours, a high correlation with both, local black earth (91%) and burnt wood (92%), was obtained. In Santa Ana, a low correlation (88%) with carbon black was found in comparison with the other case studies. Presence of silicate materials were found, obtaining a high correlation with local black earth (93%). As mentioned above, iron-oxide black compound was used as pigment until the early twentieth century, which does not correspond to the time period of the ceilings studied. Perhaps through the use of red and brown earth in the region in concert with local knowledge of iron-oxide pigment preparation in pre-Hispanic times for ceramic in Paquimé (Bishop et al. 1998; Rakita and Cruz Antillón 2015; Kindel 2019; Triadan et al. 2018) and in the Tarahumara community (Pennington 1963), a black pigment was prepared. However, further analysis is needed to determine this, since conclusions cannot be extracted from the few samples studies.

In conclusion, the results presented reveal that polychrome wooden ceilings and decorative walls at Santa

Maria de Cuevas, Cusihiuriachi, San Francisco de Borja, and Santa Ana de la Joya are the evidence of the two principal Jesuit characteristics. First, the adaptation of their own paradigm (*il modo nostro*) to create an architecture that brings local influences together with their own cultural background and conception, as both a religious order and bastion of Spanish culture (Sale 2003). The second is the interest in creating meaningful and magnificent spaces for conversion and evangelization, not only for the new Christians, the natives, but also for the religious Spaniard community that was settling and building a new life on the other side of the ocean (Tellechea and González 2007; González Rodríguez 1995).

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Disclosure statement

No potential conflict of interest was reported by the author(s).

Notes on contributors

Karla Muñoz-Alcocer has a PhD on Conservation and Restoration of Cultural Heritage at the Universidad Politécnica de Valencia, Spain. Founded the interdisciplinary project “A Mission for Chihuahua: Its Colonial Missions” serving as director of the nonprofit Misiones Coloniales de Chihuahua since 2000. In 2011 establish the first laboratory focused on science conservation research of cultural heritage in Northern Mexico. Over seven years worked at the Smithsonian Institution as conservator and director of the project *Imaginería de Las Californias* which studied the Spanish colonial polychrome sculpture from Southwest of United States and northern Mexico. Currently she works as professor at Tecnológico de Monterrey Campus Chihuahua.

Laura Fuster-López is an Associate Professor in the Department of Conservation and Restoration of Cultural Heritage at the Universitat Politècnica de València (Spain). Graduated in Fine Arts, specializing in Conservation and Restoration of Cultural Heritage from UPV, Faculty of Fine Arts, Valencia (Spain). In 1999. In 2006 she got her PhD with honors in Conservation and Restoration of Cultural Heritage from the same university. Since January 2005, she has been lecturing as Associate Professor in the BA and MA program on Conservation and Restoration of Cultural Heritage at UPV. In 2011 she was appointed (tenured) Professor. In 2007 she set up the research line: “Study of the mechanical and dimensional properties of cultural materials” at UPV. Since then, her main focus has been the study of both the structural behavior of cultural materials and the failure mechanisms they experience in time in order to take more informed conservation decisions and to design appropriate conservation strategies. Currently she is the coordinator for the ProMeSA Project: “Study of the mechanical and dimensional properties of commercially manufactured paint films and their influence in the physical and chemical degradation of modern and contemporary paintings” (2017–2019) granted by the Ministerio de Economía, Industria y Competitividad (MICINN/FEDER) – Programa Estatal de Fomento de la Investigación Científica y Técnica de Excelencia, Subprograma Estatal de Generación del Conocimiento (HAR2016-75131-P). The Project is run in collaboration with several international universities and research institutes and in partnership with Museo Picasso in Barcelona. Since 2011 she is Board Member of the European Network for Conservation Restoration Education (ENCoRE) as well as Assistant Coordinator of the Education and Training Working Group of the International Council of Museums- Committee for Conservation (ICOM-CC). Finally, since 2017 she is the coordinator of Conservation 360°, a series of multi- and interdisciplinary books on current themes in the field of Conservation of Cultural Heritage that are intended to provide a general overview of the state of the art, research and concepts in the field of the preservation of cultural heritage.

Ma. Luisa Vázquez de Ágredos-Pascual is D. Phil. in Geography and History (Universidad de Valencia 2006) and D. Phil in History of Art (Universidad

Politécnica de Valencia 2007). Her research focuses on archaeometric and cultural studies of Maya mural painting. Recently, in order to understand their compositions and cultural significances, she has concentrated on physical-chemical analysis of the colors, aromatics and drugs in Pre-Columbian Mesoamerica and other ancient cultures. She is author of numerous articles in specialized journals, such as *Archaeometry*, *Journal of Archaeological Science*, *Journal of Cultural Heritage*, *Analytical Chemistry*, book chapters and books in prestigious publishing, such as Universidad Nacional Autónoma de México, the British Archeological Reports, Cambridge University Press, New Mexico University Press, among others.

Francesca Caterina Izzo graduated in “Chemical Sciences and Technologies for the Conservation of Cultural Heritage” at Ca’ Foscari University of Venice with a thesis related to Contemporary Italian Mural Painting. During her European PhD, she did a 1-year internship at RCE (Amsterdam), collaborating with the Modern Oil Project. From 2012 she is an academic researcher in Conservation Science for Contemporary Art in Venice, focusing on the study of contemporary paintings and Design objects.

Marcello Picollo, Ph.D. in Photonics from the University of Eastern Finland (UEF), Faculty of Science and Forestry, Joensuu (Finland) and graduated in geology from the University of Florence, is a researcher at the Institute of Applied Physics “Nello Carrara” of the National Research Council of Italy (IFAC-CNR), Florence. He has been working on spectroscopic investigations of works of art since 1991 and his main research focus is on artists’ material characterization using non-invasive spectroscopic and imaging techniques.

Giovanni Bartolozzi is a fellow at the Institute of Applied Physics Nello Carrara of the National Research Council of Italy (IFAC-CNR), Florence. He has been involved for many years in pharmaceutical and agrochemical drug discovery research. From 2011 he has been working on identification and characterization of artists materials using both invasive and non-invasive spectroscopic techniques. Lately he has been involved in a research project dealing with fiber optic pH sensor.

Jose Humberto Vega, PhD, was born in Chihuahua, Mexico, his specialty is Botany. He obtained his Doctorate with Cum Laude mention in 2014 from the Autonomous University of Nuevo León. Currently, he is dedicated to teaching and research and has been assigned since 2016 to the Faculty of Zootechnics and Ecology of the Autonomous University of Chihuahua. His research areas are about plant diversity in arid zones and forest in northern Mexico and plant taxonomy. The author currently has five scientific articles indexed in international impact journals, three articles in peer-reviewed journals and has directed four bachelor’s level theses. Dr. Vega is Coordinator of the Grassland Plants Identification Club, which competes annually in different parts of the United States, recently obtaining 3rd place for Mexico. Finally, the Teacher-researcher is the curator of the HUACH-HER Herbarium of the Autonomous University of Chihuahua.

Diana Maldonado Escobar is a Biotechnology Engineer graduated from Tecnológico de Monterrey Campus Chihuahua, she specialized in Molecular Biology and also got a *Green Belt- Lean six sigma* certification, which has allowed her to grow up professionally in industrial quality field. During her career, she always show a lot of interest in subjects such as tissue culture, analytical chemistry and genetics,

she attend the *Biotechnology of plants in agri-food industry* course at Universidad Complutense de Madrid. Diana got involved in different student groups of biotechnology and she also provided professional social service in the Historical Heritage Laboratory where she contributed with scientific researches mainly sampling and using Fourier Transform Infrared Spectroscopy technique. Currently her professional objective is to continue developing in industrial quality and agricultural biotechnology area.

Alejandro Mitrani, B.Sc. in Physics (2008, UABC, Mexico), M.Sc. in Physics (2011) and Ph.D. in Material Science and Engineering (2017), both programs from the Universidad Nacional Autónoma de México (UNAM). He joined the National Laboratory of Sciences for the Research and Conservation of Cultural Heritage (LANCIC), of the Physics Institute, UNAM, for his Ph.D. studies in 2012, and has worked there as an Academic Technician since 2017. While at LANCIC, he has focused in the application of diverse spectroscopic and imaging techniques (such as XRF, PIXE, RBS, SEM-EDS, Raman, FTIR and FORS) for the non destructive, in situ study of a variety of Mexican cultural heritage materials (including ceramics, metals, gilded objects, glasses, lithic materials and paintings) with ages ranging from Prehispanic all the way to modern objects.

Dr Miguel Ángel Maynez, PhD is a member of the National Researchers System in Mexico City, working now in a post-doctoral position in the Aesthetics Institute in the Mexican National and Autonomous University (UNAM in Spanish). Originally formed as a chemistry Miguel Maynez finished in 2012 a master in Material Science and specialized in art material researcher in his doctoral degree. Dr. Maynez has worked with natural organic historical dyes, as a part of his research work he imitated Mexican pre-Hispanic and Colonial recipes taken from ancient codex and historical sources for one hand and for and other the by contemporary artisan workshops in different parts of Mexico.

Dr Edgar Casanova-González with a background on Radiochemistry (B.Sc., 2000 and M.Sc., 2006, ISCTN, Cuba) and a Ph.D. on Materials Science and Engineering by the Universidad Nacional Autónoma de México (UNAM), Mexico, he is currently a CONACyT Researcher at the National Laboratory of Sciences for the Research and Conservation of Cultural Heritage, at the Physics Institute of the UNAM. Over the last decade his research has been dedicated to the development and application of non-destructive and portable analytical techniques for the study of cultural heritage. Such techniques include Raman, SERS, FTIR, XRF and FORS spectroscopies, together with imaging methods, applied for the analysis of a wide variety of materials: lithic, panel, mural and easel paintings, manuscripts, ceramics, pigments and dyes and cave paintings, from pre-Hispanic period until modern times.

Isaac Rangel-Chávez graduated from the Bachelor of Design and Visual Communication at the Faculty of Arts and Design at UNAM. He is currently a student of the Master in Art History at the Faculty of Philosophy and Letters at UNAM. Linked to the National Laboratory of Sciences for the Research and Conservation of Cultural Heritage (LANCIC) with the thesis: "Methodology for the study of pigments and dyes in works of art and cultural heritage using the false color infrared imaging technique". Since 2016, he collaborates in the Imaging area of LANCIC-IFUNAM implementing the techniques of false color infrared imaging, UV-induced visible luminescence, infrared reflectography, thermal imaging, photogrammetry, orthoimage,

false color DStretch, photographic record of samples, materials of reference and study objects.


Dr Jose Luis Ruvalcaba-Sil studied Physics at the Sciences Faculty of the Universidad Nacional Autónoma de México (UNAM), and carried out his Ph.D. in the Laboratory of Analyses by Nuclear Reactions in Namur, Belgium. Since 1997, he has been research scientist and professor at the UNAM's Physics Institute. Head of the Pelletron Accelerator facility of this Institute from 2005, from 2014 he is the Head of the National Laboratory of Sciences for Research and Conservation of Cultural Heritage (LANCIC) of Mexico. In particular, his research has been focused on the application of non-invasive methodologies such as XRF, Raman, FTIR, FORS; and the development of spectroscopic instruments of XRF, XRD and PIXE for material characterization of Mexican cultural heritage collections from the pre-Hispanic period to Modern Art in the most important archaeological sites and museums of Mexico in collaboration with groups of UNAM, National Fine Arts Institute (INBA) and the National Institute of Anthropology and History (INAH).

ORCID

Karla Muñoz-Alcocer  <http://orcid.org/0000-0002-7259-5563>

Jose Humberto Vega  <http://orcid.org/0000-0001-7488-3334>

Laura Fuster-López  <http://orcid.org/0000-0001-7072-7190>

Ma. Luisa Vázquez de Ágredos-Pascual  <http://orcid.org/0000-0002-4433-8850>

Francesca Caterina Izzo  <http://orcid.org/0000-0001-9319-5094>

Marcello Picollo  <http://orcid.org/0000-0003-1012-6048>

Alejandro Mitrani  <http://orcid.org/0000-0002-0877-5033>

Edgar Casanova-González  <http://orcid.org/0000-0002-4574-9416>

Jose Luis Ruvalcaba-Sil  <http://orcid.org/0000-0003-1431-3019>

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