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

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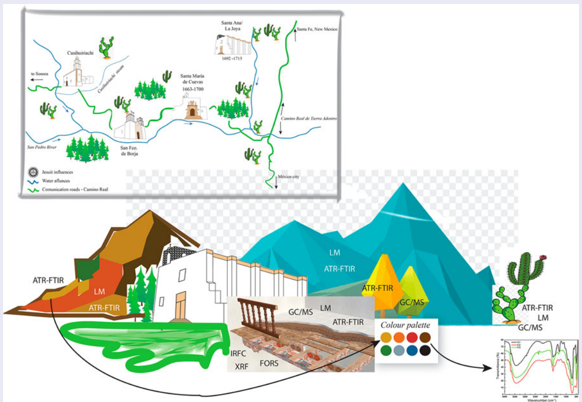
ABSTRACT

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 for ATR-FTIR, LM and GC/MS laboratory analyses. A survey of natural resources were also studied by ATR-FTIR and LM to elucidate the natural occurrence of a select number of materials found 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 identifying those materials that were available locally, due to their natural occurence in the surrounding areas of the churches, and differentiating them from those 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), Cusihuiriachi (CUSI), San Francisco de

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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 the churches' 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 Suffructicosa* 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 (*Opunita*) 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 through the trade routs 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 previously (Muñoz-

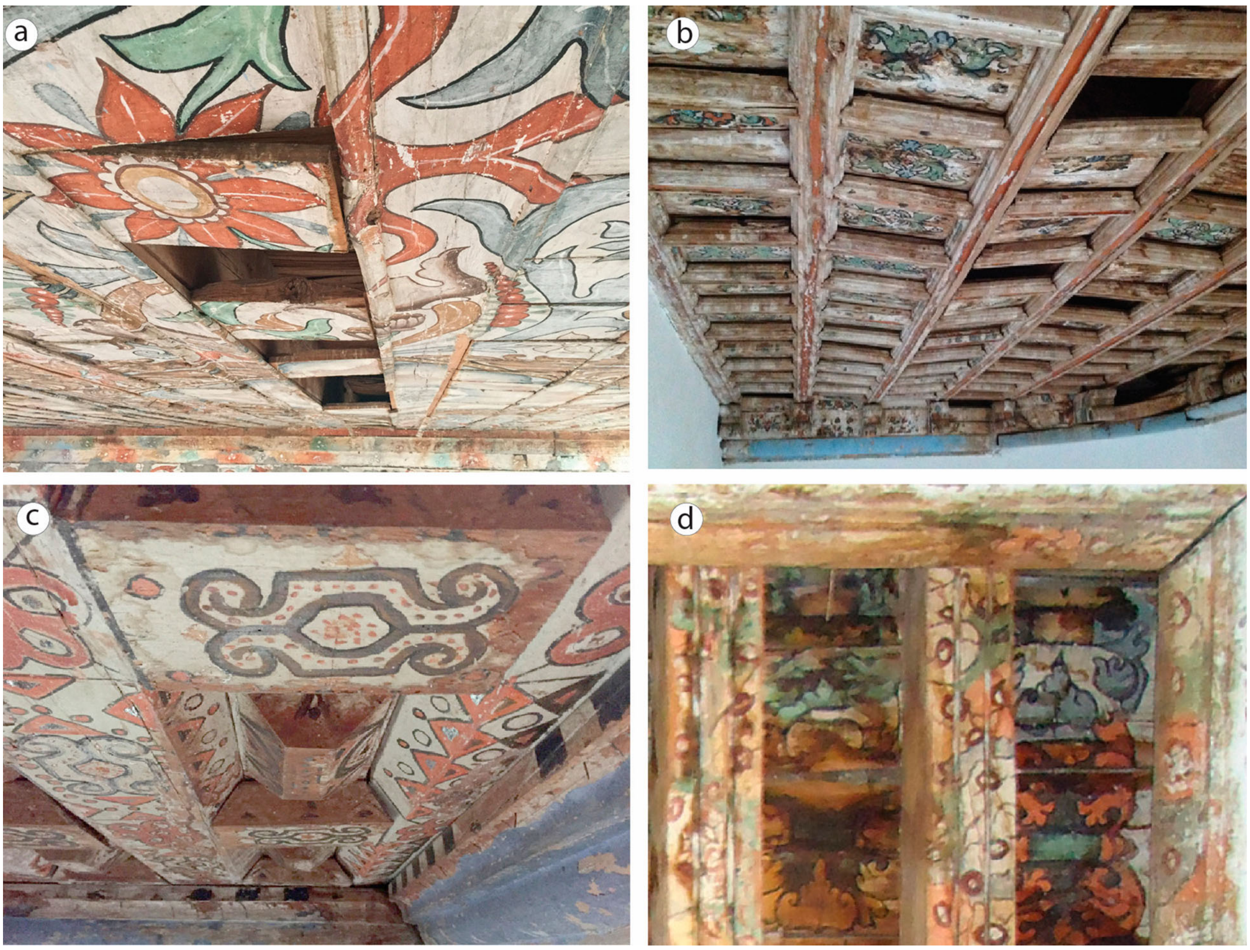


Figure 1. Detail of the polychrome wooden ceilings from Santa Maria de Cuevas (a); Cusihuiriachi (b); San Francisco de Borja (c) and Santa Ana de la Joya (d). K. Muñoz Alcocer, 2015.

Table 1. Invasive and non-invasive techniques used to characterize *in situ* spot tests and microsamples of the four sites studied.

Santa Maria de Cuevas

Analitical techiniques		Nave & Presbitery									Narthex						
		W	G	[yellow]	[red]	[pink]	[brown]	[blue]	[green]	[black]	W	G	[yellow]	[red]	[brown]	[dark green]	[black]
Non-invasive	IR-FC	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	XRF	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓
	FORS	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓
Invasive	LM	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	ATR-FTIR	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	RAMAN					✓		✓									
	GC-MS		✓		✓		✓										

Cusihuiriachi

Analitical techiniques		Chapel									
		W	G	[yellow]	[orange]	[dark red]	[pink]	[blue]	[light green]	[green]	[black]
Non-invasive	IR-FC	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	XRF	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	FORS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Invasive	LM	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	ATR-FTIR	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	RAMAN						✓	✓			
	GC-MS		✓							✓	✓

San Francisco de borja

Analitical techiniques		Baptistery						
		W	G	[white]	[yellow]	[dark red]	[brown]	[black]
Non-invasive	IR-FC	✓	✓	✓	✓	✓	✓	✓
	XRF		✓	✓	✓	✓	✓	✓
	FORS		✓	✓	✓	✓	✓	✓
Invasive	LM	✓	✓	✓	✓	✓	✓	✓
	ATR-FTIR	✓	✓	✓	✓	✓	✓	✓
	RAMAN					✓		
	GC-MS			✓		✓	✓	✓

Santa Ana de la Joya

Analitical techiniques		Presbitery & Narthex									
		W	G	[yellow]	[orange]	[dark red]	[brown]	[grey-blue]	[dark slate]	[green]	[black]
Non-invasive	IR-FC	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	XRF	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	FORS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Invasive	LM	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	ATR-FTIR	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	RAMAN							✓			
	GC-MS		✓			✓		✓			

Alcocer, et al. 2017b). Results indicated that indigo was either mixed with gypsum (as *ad hoc* Maya blue pigment) or applied directly to the gypsum ground surface following the European technique (Cennini 1954; Doerner 1984). As for cochineal, two sources were used: domesticated cochineal from Lanzarote (Spain), and sylvan cochineal collected at Santa Maria de Cuevas town. In FTIR spectra, very little correlation difference was detected between the domesticated (96%) and the sylvan cochineal (97%) mixed with alumina (3:1) FTIR spectra. Nevertheless, alumina was identified as mordant (Muñoz Alcocer 2018).

The current paper establishes the correlations found using ATR-FTIR between the collected natural resources and the identification made by the multianalytic studies of other colours such as green (malachite and mixture of malachite, indigo and green & yellow earth), red-orange (minium) and black (carbon and iron oxide). Local resin-gums, which could have been used as binders in the polychrome wooden ceilings of the four case studies were also analysed.

2. Materials and methods

The analysis of micro samples together with *in situ* measurements in SMC, CUSI, SFB and ANA was carried out. Samples from collected regional materials such as malachite, lead, yellow, black and red earths were analysed and used for mock-up preparation. The indigo used was from a family of dyers in Oaxaca, who continue to make the dye using traditional methods. The dyes as well as the raw materials used in their manufacture, were also analysed for comparison purposes before they were used in the mock-ups. The sample preparation and analytical methods are presented in two sub-sections: micro-invasive and non-invasive analysis techniques in microsamples from the case studies, and regional materials and mock-ups.

2.1. Case studies

Non-invasive in situ study for actual case studies and analysis of samples. In 2015 samples were taken from the four case studies. In 2016, IRFC images were registered and spectroscopic measurements by XRF, FORS were carried out at the same areas where samples had been taken (Aceto et al. 2012a; Aceto et al. 2012b; Appolonia et al. 2009; Bacci et al. 2009; Mounier et al. 2014; Leona and Winter 2001). Table 1. Summarizes the points and samples considered in the multi-analytical study in the four sites SMC, CUSI, SFB, ANA.

2.2. Mock-ups and local materials

The local materials collected were observed under the microscope and analysed with ATR-FTIR. Representative mock-ups were made for the characterization of ground layers, colour pigments, and dyes. A ground made of calcium sulphate ($CaSO_4$) and calcium sulphate hemihydrate ($CaSO_4$. ½ H_2O) was applied to two pine wood panels. Two different painted areas were created for each panel: in one area the paint layer was applied with no binder (in order to obtain a clear interpretation of the colour palette). In the other hand, the resin-gum, tascate (*Juniperus deppean),* was used as a binding medium in order to determine its use as a binder at the selected polychrome wooden ceilings.

Malachite, indigo, green and yellow earth were used in the production of pigments to explore the use of either green earth, malachite or a mixture of malachite, indigo and yellow or green earth in the green areas studied at Santa Maria de Cuevas, Cusihuiriachi and Santa Ana (Figure 2). The identification of the red-orange (minium), black, and ground layer was made by ATR-FTIR spectra comparisons with lead (Pb) from local mines, local earths (brown, red and black), as well as burnt wood gypsum, lime, and tascate resin that were collected around the selected case studies.

Local water sources were used in the production of pigments and mock-ups as their geographical proximity to the case study was likely noted and utilized by the original artists. Outflow water from the mines located near the mining town of Cusihuiriachi merge with water from the confluence of the San Pedro River and a smaller local stream, making them a readily available source both in the past and now. The

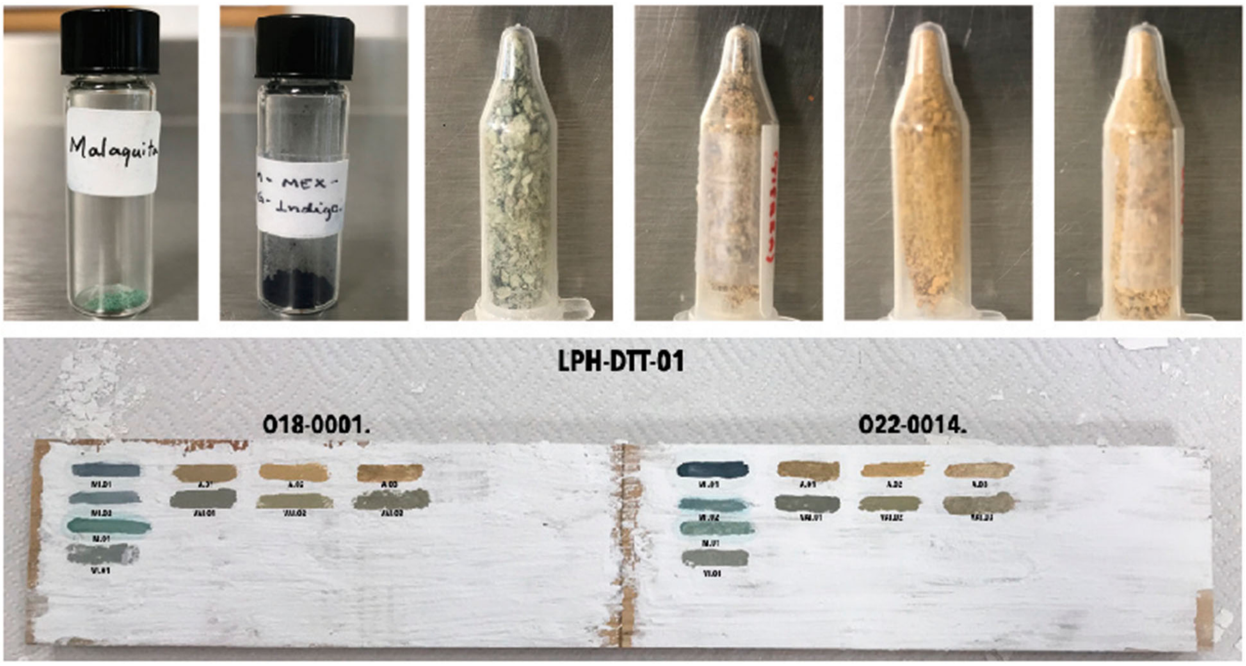


Figure 2. Characterization of the green colours from Santa María de Cuevas and Cusihuiriachi ceilings. View of the materials used and the mock-ups prepared with their identification number.

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 (IRFC). 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 µA for 30 s per region. All spectra were processed with the software

Table 2. Materials used in the elaboration of the representative mock-ups for the characterization of ground layers, colour pigments, and dyes.

Water source	Wood	Ground	Code	Malachite (g)	Indigo (g)	Green earth (g)	Yellow earth (g)	water (Drops)	Vinegar (drops)
San Pedro river water PH-DTT-01 022–0014	Pine wood	$CaSO_4 + H_2O$ 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
			VAI.A	–	0.01	0.2	0.2	6	4
			VAI.B	–	0.01	0.2	0.2	6	4
			VAI.C	–	0.01	0.2	0.2	6	4
Cusihuiriachi steam water LPH-DTT-01 018–0001		$CaSO_4 + H_2O$ 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
			VAI.A	–	0.01	0.2	0.2	6	4
			VAI.B	–	0.01	0.2	0.2	6	4
			VAI.C	–	0.01	0.2	0.2	6	4

Spectra Artax v.7.4.6.1 (Bruker) in order to measure the X-ray intensities.

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 cm^2 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 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 under 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 resource 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 correspondece with the results from the other analytical studies. 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) analyses 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 transestherified 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 analyses 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 ad 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 20̊C/min until 210, then 2̊C/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.

Gyspum is present in the ground layer of Santa Maria's nave ceiling, at Cusihuiriachi, and at San Francisco de Borja. Anhydrite and hemihydrate sulfate (Hunt et al. 1950, 427), are also present in some FTIR spectra. In Santa Maria, some weak bands (875, 711 cm^{-1}) of calcium carbonate ($CaCO_3$) were detected as well in some spectra from the ground layer. Calcium carbonate (1429s, 872sh, 712psh cm^{-1}) was used as the main ground component at the narthex ceiling of Santa Maria. In addition, absorption bands related to anhydrite (670msh, 614p, 593msh cm^{-1}) and hemihydrate sulphate (3600p, 3440p, 1151ms, 1120sh, 1690p, 667def, 466p cm^{-1}) and dihydrate (3544m, 3407m, 3250br, 1109, 490p, 414psh cm^{-1}) 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 the 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 cm^{-1}) 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 Cusihuiriachi (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 in the ground layer of Santa Maria de cuenvas, but not in the ground layer of the other case studies (CUSI,SFB,ANA) (Figure 4).

3.2. Paint layers: pigments and dyes

3.2.1. Green

The visual comparison between the VIS image and FCIR allows the identification of some hue changes

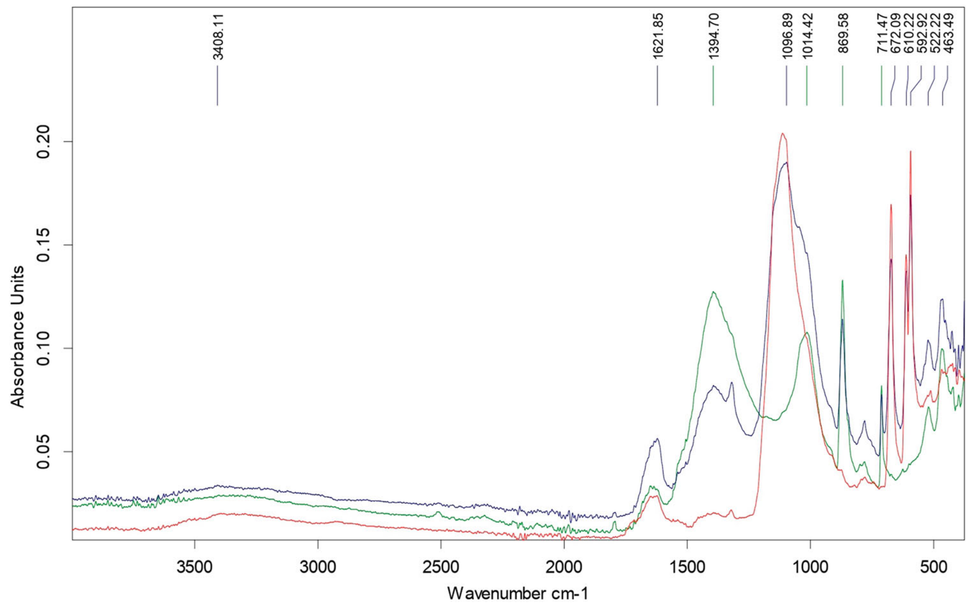


Figure 3. ATR-FTIR spectra from the blue (B.T.02) (blue line), red-orange (VM.01) (red line), and ground layer (B.T.04) (green line) from Santa Ana de la Joya narthex and baptistery ceiling. Differences can be observed with the calcium carbonate ground layer absorption bands (peaks on blue) and those from the blue and orange samples spectra, where calcium sulfate absorption bands 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 in the gypsum ground layer prepared without tascate resin-gum (b). K. Muñoz-Alcocer, 2018.

in the green colour. In comparison to other colours, green is the colour that changes the most. This 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), Cusihuiriachi (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, Santa Marias' 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 ($Cu_2CO_3(OH)_2$). 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 Cusihuiriachi, appeared in FCIR with a light blue hue suggesting the presence of a copper

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

based green pigment. Also of note are areas that have 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, while arsenic was also detected. It is likely that in this case the 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 in 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, since absorption bands from both spectra are similar except for calcium carbonate bands at the narthex green spectra.

According to FCIR image interpretation, in Cusihuiriachi 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 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 ochrehave 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

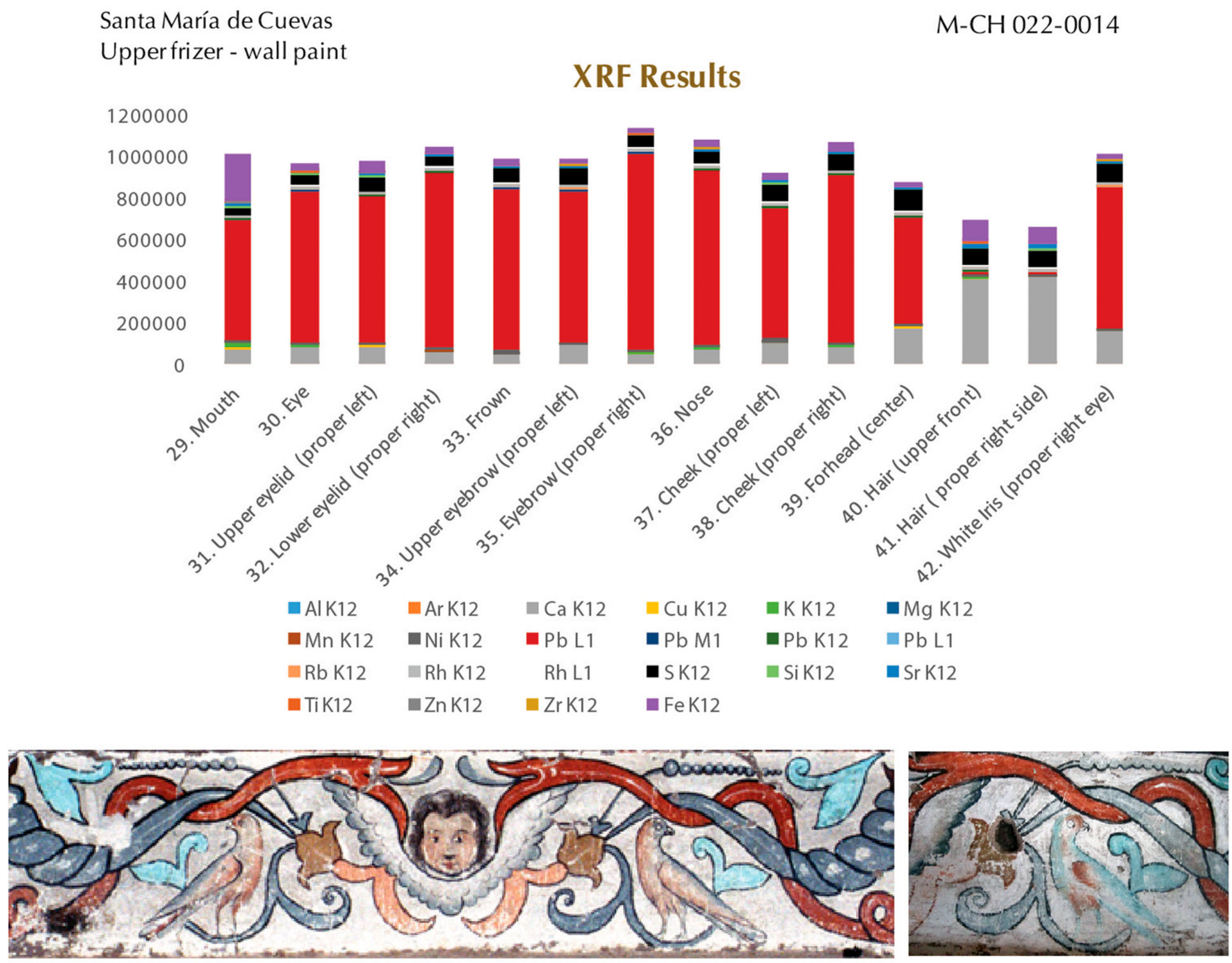


Figure 6. XRF chart from the studied spots from the angel face and images from the wall paint upper frieze. It is possible to observe the green malachite from the leaves and birds that have faded into a light blue colour. (E. Casanova, Instituto de Física, Universidad Nacional Autónoma de México, 2016;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

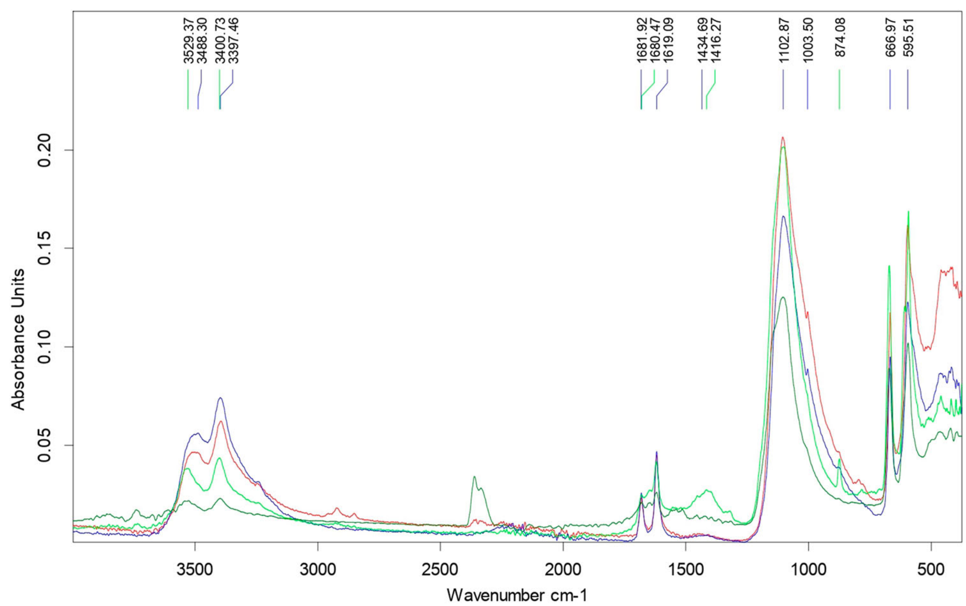


Figure 7. ATR-FTIR spectra from the narthex green sample from Santa Maria de Cuevas narthex ceiling (light green line), nave ceiling (dark green line) and the prepared pigments VAI.C (red line) and MI (blue line) (D.Maldonado, K. Muñoz Alcocer, 2018).

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 previous 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 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 analyses indicate that the red from the Cusihuiriachi 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's 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 Cusihuiriachi 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 an 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 combined with ironIII 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, the

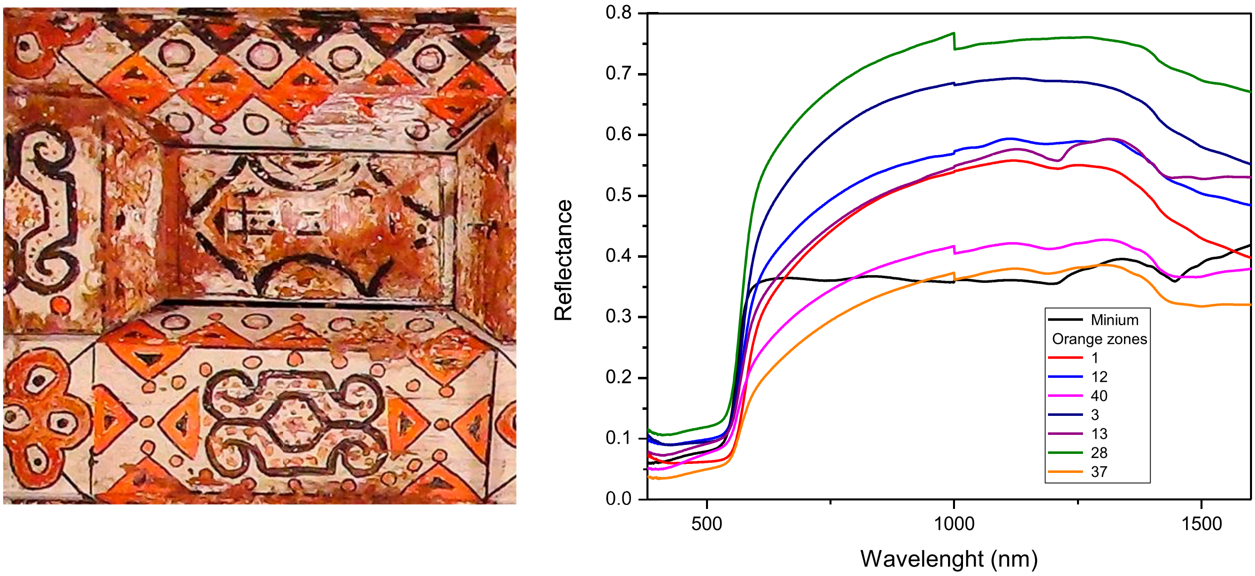


Figure 8. Detail view from San Francisco de Borja polychrome ceiling and FORS spectra from the red-orange studied spots. Minium reference (black line) red-orange spots studied (colour lines). (M.A Maynes, Institut of physic, Universidad Nacional Autónoma de Mexico, 2016).

elements detected were probably associated to 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 are 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 cm^{-1}). In addition, the spectrum presents strong absorption bands in 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.

To corroborate the results obtained, the spectrum was compared with a 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 the use of a mixture of both organic and inorganic materials could have been 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

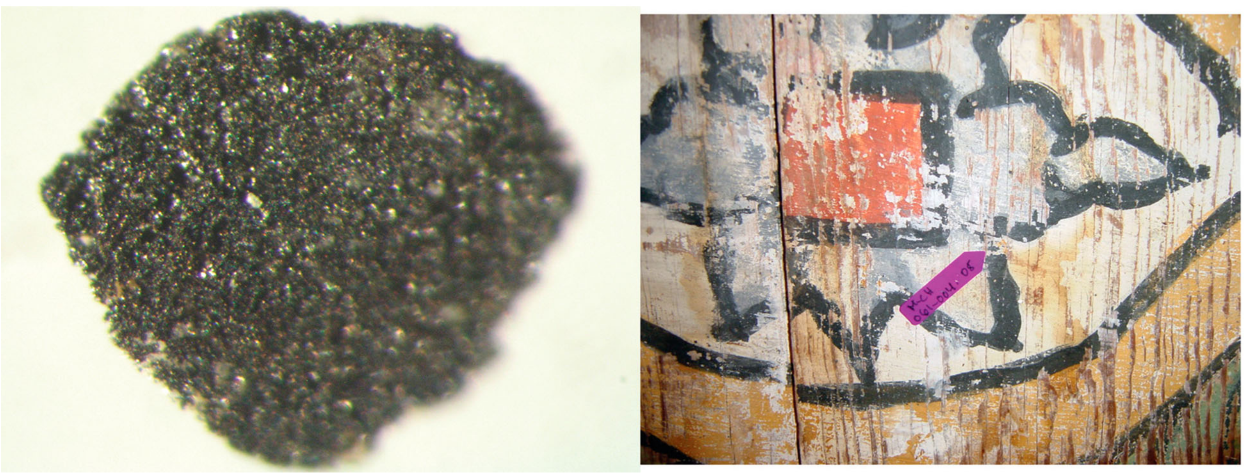


Figure 9. Black sample from Santa Ana de la Joya narthex under the microscope and image from the area in which the sample was taken (K. Muñoz-Alcocer, 2018).

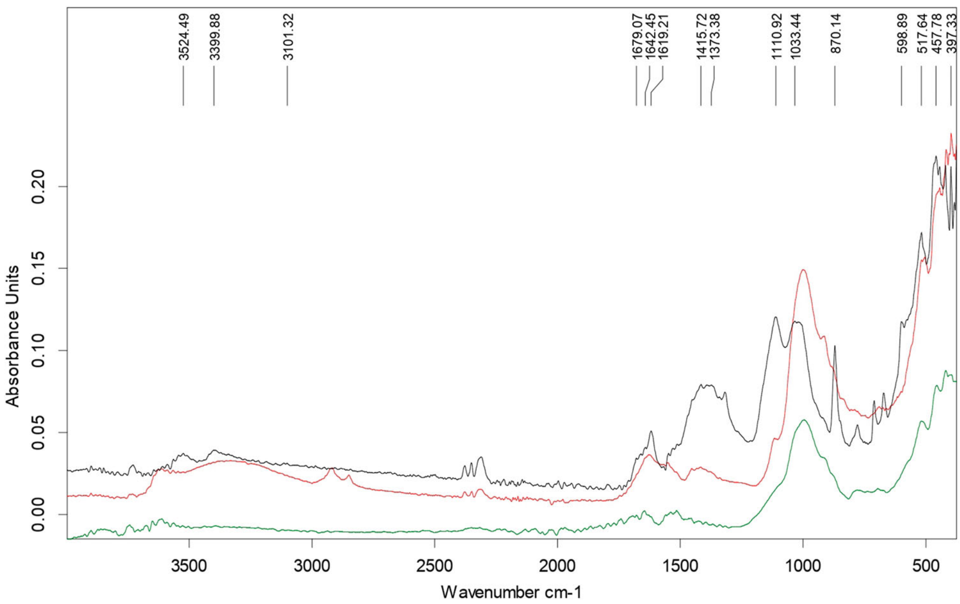


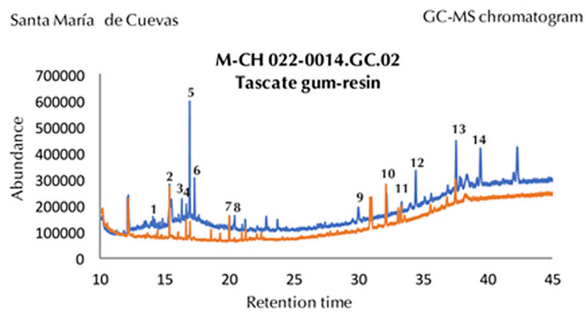
Figure 10. Comparrison between ATR-FTIR spectra from the black sample B.T.06 (black line), local black earth RM.04 (red line) and burnt wood (green line). (K. Muñoz Alcocer & A. Pizarro, LPH, 2015).

previously described. Generally, samples were very small.

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).



Identification number	Component	Chemical formula	Retention time
1	Thymol	$C_{10}H_{14}O$	11:36
2	Coumarin	$C_9H_6O_2$	15:44
3	Abietanea- derivative	$C_{20}H_{36}$	16:34
4	Palmitic acid, methyl ester	$C_{17}H_{34}O_2$	16:88
5	Abietane	$C_{20}H_{36}$	17:01
6	Isopimaric acid	$C_{21}H_{32}O_2$	18:17
7	Palmitic acid, methyl ester	$C_{17}H_{34}O_2$	19:91
8	Abietane	$C_{20}H_{36}$	20:26
9	Pimaric acid	$C_{20}H_{30}O_2$	29:79
10	Abietane	$C_{20}H_{36}$	31:42
11	Mannose	$C_7H_{14}O_6$	32:15
12	Ferruginol	$C_{20}H_{30}O$	34:22
13	Manitolo (internal standard)	$C_6H_{14}O_6$	37:34
14	Pimaric acid	$C_{20}H_{30}O_2$	41:99

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).

3.3.2. Cusihuiriachi

The organic portion from the Cusihuiriachi 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 Cusihuiriachi 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 cm^{-1} in the ATR-FTIR spectra from 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 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, Cusihuiriachi, 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 binding medium could explain the good condition of the wooden ceiling. 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 determine 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 Cusihuiriachi 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 observed 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 cannons. 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 (carmine and indigo), Cusihuiriachi (plant dye, carmine, 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.

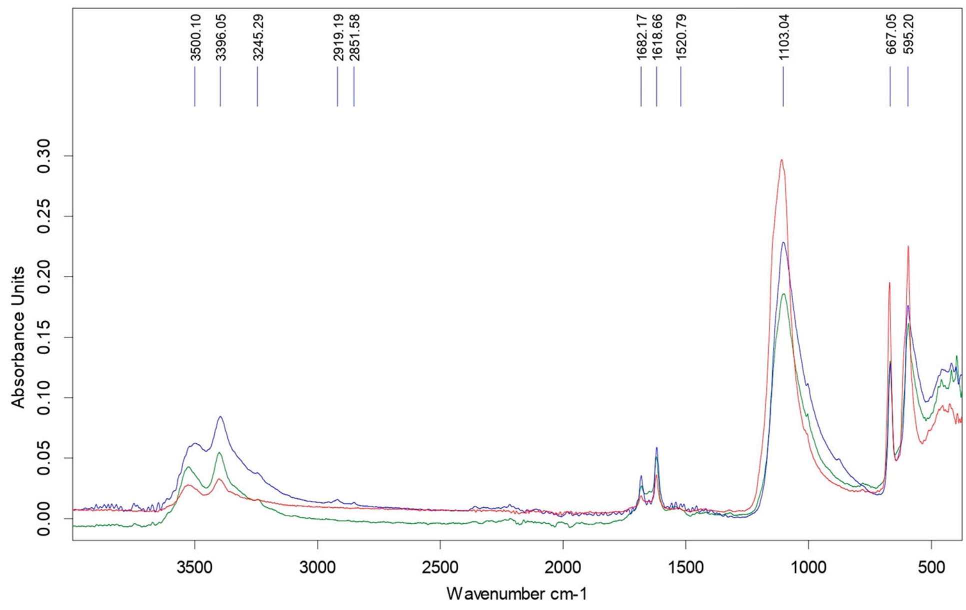


Figure 12. ATR-FTIR spectra from Santa Maria de Cuevas nave ground layer (red line), presbytery ground layer (green line), and the ground layer prepared with calcium sufate anhydrite mixed with tascate resin-gum. (blue line)

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 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 Cusihuiriachi 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.

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

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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.

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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 Tecnologico de Monterrey Campus Chihuahua, she speciaelized 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.

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