

Document downloaded from:

<http://hdl.handle.net/10251/133376>

This paper must be cited as:

Fuster-López, L.; Muñoz-Alcocer, KM.; Pizarro-Medina, A.; Picollo, M.; Bartolozzi, G. (2016). Pre-hispanic pigments and Italian renaissance designs at Spanish colonial missions churches in Northern Mexico. *Color Research & Application*. 41(3):289-293.
<https://doi.org/10.1002/col.22028>



The final publication is available at

<https://doi.org/10.1002/col.22028>

Copyright John Wiley & Sons

Additional Information

Pre-Hispanic Pigments and Italian Renaissance Designs at Spanish Colonial Missions Churches in Northern Mexico

Karla Muñoz-Alcocer,^{1,2*} Laura Fuster-López,²
Andrea Pizarro-Medina,³ Marcello Picollo,⁴
Giovanni Bartolozzi⁴

¹Misiones Coloniales de Chihuahua A.C., Laboratorio de Patrimonio Historico, Chihuahua, Mexico

²Dpto.Conservación Y Restauración de Bienes Culturales, Universidad Politécnica de Valencia, Valencia, Spain

³Dpto. Bioingeniería, Tecnológico de Monterrey Campus Chihuahua, Chihuahua, Mexico

⁴“Nello Carrara” Institute of Applied Physics of the National Research Council of Italy (IFAC-CNR), Sesto Fiorentino, Firenze, Italy

Received 13 October 2015; revised 16 December 2015; accepted 17 December 2015

Abstract: This article presents the early ATR-FTIR and FORS results of the analysis carried out in five polychrome wooden ceilings from different Jesuit Spanish colonial mission churches. These mission churches date between 1674 and 1723 and are located in the rural villages of Santa Maria, Cusihuirachi, Coyachi, La Joya, and Rosario in the Northern Mexican State of Chihuahua. The decorative motifs in all five church sites were executed using a similar color palette and painting technique although the pictorial quality differs from one site to the next. The samples collected from the interior of the La Asunción de Santa María de Cuevas are of considerable importance as this site is one of the most significant models of colonial architecture, containing some of the oldest examples of colonial figurative art in Northern Mexico. The scope of this research is to identify and compare the pigments and techniques used in the decorative surfaces of these five selected mission churches. Preliminary FTIR results have unexpectedly determined the presence of indigo and cochineal (not traditionally used among Chihuahua natives) and possibly a mixture of both to produce different tones to decorate the wooden ceilings and choirs of the five missions studied. © 2016 Wiley Periodicals, Inc. Col Res Appl, 00, 000–000, 2015; Published

Online 00 Month 2016 in Wiley Online Library (wileyonlinelibrary.com). DOI 10.1002/col.22028

Key words: color identification; ATR-FTIR; FORS; mayan blue; carmine; Spanish colonial missions; polychrome wood

INTRODUCTION

The nonprofit Misiones Coloniales de Chihuahua A.C (MCC) have been carrying out several research projects in collaboration with national and international institutions for the last years to preserve 17th and 18th century Spanish Colonial churches found throughout Northern Mexico.¹ The current project aims to achieve several different research goals including: 1) the creation of a natural resources database to aid in understanding the regional materials that were available to artists working in these remote regions during the 17th and 18th centuries, 2) the study of the iconography and iconology of the pictorial designs in each church, and 3) the chemical characterization of the materials and techniques used to create these painted interiors in an effort to develop appropriate conservation strategies.

Out of 283 documented Spanish Colonial churches, there are only five that are decorated with wall paintings and polychrome wooden structures: Santa Maria (wall paintings, choir, paneled and beam ceilings), Cusihuirachi (paneled ceiling), Coyachi (door and frame), La Joya

*Correspondence to: Karla Muñoz-Alcocer (e-mail:karmuoa@doctor.upv.es)

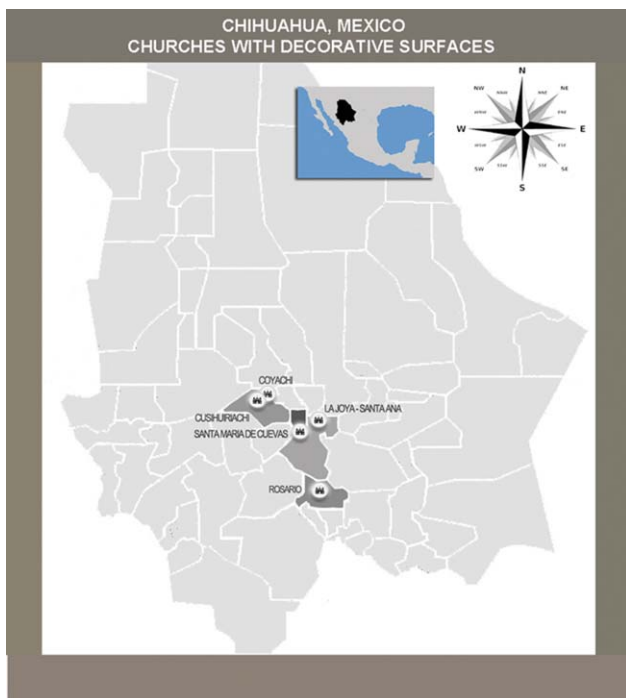


Fig. 1. Map of the state of Chihuahua. Location of the five Spanish colonial churches with polychrome wooden ceilings and choirs.

(beam ceiling and choir), and Rosario (wall paintings, choir, and paneled and beam ceilings) (Fig. 1). Since Santa Maria de Cuevas contains a unique polychrome wooden ceiling and it is considered to be the oldest example of colonial figurative art in Northern Mexico (Fig. 2), considerable attention was devoted to this site during the early stages of the project (Munoz-Alcocer Karla, Suarez Wendy, *et al*, Project Planning Report, J. Paul Getty Grant program. Unpublished 2003). The additional four churches were selected because of their similarities with Santa Maria and are referred in this article for comparison purposes.

MATERIALS AND METHODS

A total of 62 samples were collected from the wall paintings and the upper panel ceiling from the Santa Maria church over four separate sampling sessions (2001, 2003, 2006, and 2015). In addition, 15–18 samples were taken in 2015 from each polychrome ceiling at the other four churches. Each sample consisting of paint layer(s), ground, and support was documented in detail as summarized in Table I (Fig. 3).

A Bruker ALPHA-P FTIR spectrophotometer equipped with a Platinum attenuated total reflection (ATR) sampling module (diamond crystal) was used to collect spectra in the range of $7500\text{--}375\text{ cm}^{-1}$. Spectra were elaborated with Quick Compare OPUS software. ATR–Fourier transform infrared spectroscopy (FTIR) spectra obtained were compared to the spectral library of traditional and natural resources materials (cochineal, azurite, malachite, lead, natural earths, etc.) created at LPH—

Laboratorio de Patrimonio Histórico (Joint laboratory run by Tec Monterrey Campus Chihuahua and Misiones Coloniales de Chihuahua A.C.).

Fiber Optic Reflectance spectroscopy (FORS) measurements were carried out on a panel of the polychrome Nave Ceiling of Santa Maria de Cuevas in the UV–Vis–NIR (350–2200 nm) spectral range by using two Zeiss spectroanalyzers (models MCS 601 UV/VIS and MCS 611 NIR 2.2 WR, respectively), equipped with optical fibers and a $8^\circ/8^\circ$ probe-head, on approximately a 2-mm diameter spot.² A 99% Spectralon[®] diffuse reflectance standard was used to calibrate the system.

RESULTS AND DISCUSSION

In this article, the study of some of the pigments found in the selected mission churches is presented. The results of ATR–FTIR on Santa Maria samples were consistent with the previous technical studies (Smithsonian Museum Conservation Institute Internal Reports (2001–2006). Unpublished. The report presents FTIR, SEM–EDA and XRD analytical studies from Santa Maria de Cuevas ceiling and wall paint decoration. The pigment identification was as follows: Green—cooper based green pigment, Blue light/dark—Indigo, reds and brown—Iron Oxide with some traces of organic. Yellow: Iron Oxide ochre. No organic binder was identified with GC, FTIR. Anhydrite



Fig. 2. Santa María de Cuevas mission church polychrome ceiling.

TABLE I. Distribution of samples studied.

Mission	Location	Number of samples	Analysis	Institution	Date
Santa Maria	Polychromed wooden ceilings, choir Decorative wall paint	32 Samples	LM XRD SEM-EDA, FTIR GS/MS	Museum Conservation Institute (Smithsonian Institution, Washington DC)	2001–2006
	Polychromed wooden ceiling (1 panel)	27 Picks	FORS	IFAC-CNR (Florence, Italy)	2015
Santa Ana	Polychromed beams ceiling	12 Samples	FTIR	LPH (Chihuahua, Mexico)	2014–2015
	Polychromed wooden choir	5 Samples	LM XRD SEM-EDA, FTIR	Museum Conservation Institute (Smithsonian Institution, Washington DC)	2006
Huejotitan	Polychromed wooden altarpiece	4 Samples	LM SEM-EDX	UNAM (Instituto de Investigaciones Esteticas)	2012
		19 Samples	LM FTIR GS/MS	Museum Conservation Institute (Smithsonian Institution, Washington DC)	2001–2006
Santa Rosalia	Polychromed wooden ceilings—decorative wall paint	4 Samples	FTIR	LPH (Chihuahua, Mexico)	2014–2015
Cusihuirachi	Polychromed wooden ceiling	22 Samples			
Coyachi	Polychromed wooden door	12 Samples			
Rosario	Polychromed wooden ceiling, choir Decorative wall paint	18 Samples			
Carichi	Wooden columns and beams (some polychromy under overpaint)	11 Samples			
S. Fco. de Borja	Polychromed wooden ceiling	12 Samples			
Satevo	Wall paint	10 Samples			
Total samples	156 Samples/picks				

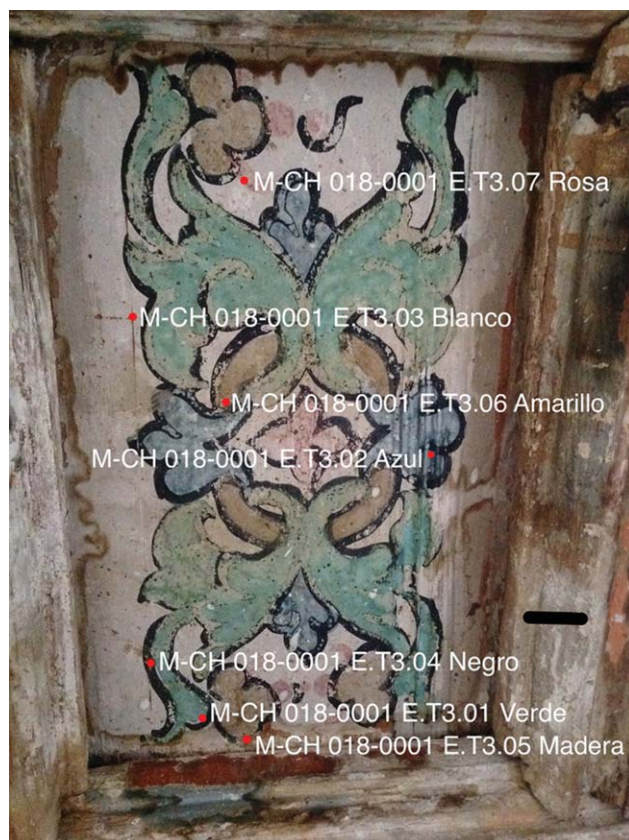


Fig. 3. Polychrome ceiling of Cusihuirachi with samples location.

and gypsum were used as ground for the wall paintings and the polychrome ceiling. FORS spectra obtained from the white ground of the center of the panel showed the presence of absorption bands at around 1700–1750 nm owing to the first overtones of the aliphatic C—H_n stretching which could be associated to the presence of a binding medium. Black pigments were tentatively identified as charcoal black by using FTIR as no spectral features related to other black pigments were found. Yellow, brown, and some of the red areas mainly consisted of iron hydroxide/iron oxide pigments, recognized by their typical absorption bands in the range of 900–400 cm⁻¹.^{3,4} FORS detected a copper-based green pigment mixed with lead white in lighter green passages. Copper-based green pigments, such as malachite, have a broad and structured absorption band centered at 700–900 nm corresponding to d–d transitions in an approximately square planar geometry, whereas lead white shows the typical strong and sharp absorption band at 1450 nm due to the first overtones of the O—H stretching. ATR–FTIR analysis of red and blue passages revealed the presence of cochineal and indigo, respectively. FORS analysis on the polychrome wood panel from the Santa Maria ceiling^{4,5} confirmed the presence of carmine red lake and probably Mayan blue. The latter presents an intense absorption band in the region of 420–730 nm that corresponds to the π – π^* electronic transition of the indigo dye that is responsible for the blue color. The anthraquinone chromophores of the carmine red lake, instead, show absorption bands in the visible region related to the lowest energy n – π^* electronic transition, attributed to

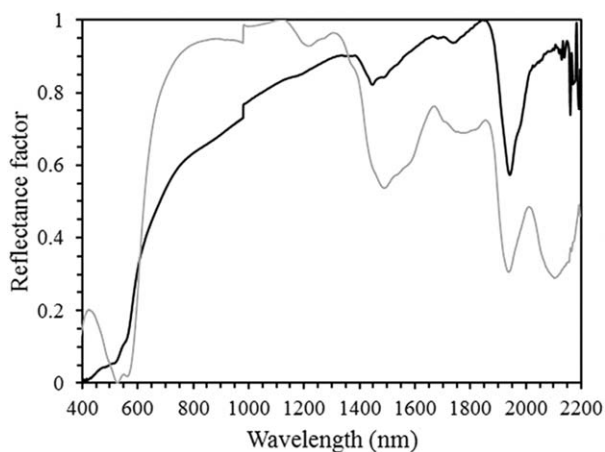


Fig. 4. FORS spectra of Santa Maria violet-pink sample (M-CH 022-0014.DT1.12, black curve) and of a cochineal reference on paper (gray curve); the arrows indicate the position of the two sub-bands that were used to identify the cochineal-based pigment.

the conjugated double bonds and characterized by a significant charge-transfer contribution, and the $n-\pi^*$ electronic transitions of the carbonyl groups (Fig. 4).⁶⁻⁸

FTIR spectra of samples collected from Santa Maria were found to share certain characteristics with samples collected from church sites in other villages: the spectra corresponding to blue, green, yellow, and pink samples from sites in Cusihiuriachi, Coyachi, and Rosario showed a 92–98% correlation with spectra obtained from Santa Maria samples (See supporting material on the website.).

In addition, it might be possible that the yellow sample from Cusihiuriachi is associated with the presence of a cochineal-based material as its IR spectrum matches to 97% with those recorded on two samples from Santa Maria (Fig. 5), which contained carmine. Even if cochineal-based colors are usually associated to red hues, from cochineal powder colors with different hues than red can produce orange and yellow tones when an acidic component, such as acid fruits (lemon and orange), plants with acid properties (esp. *Ionoxalis trineuris*), or even

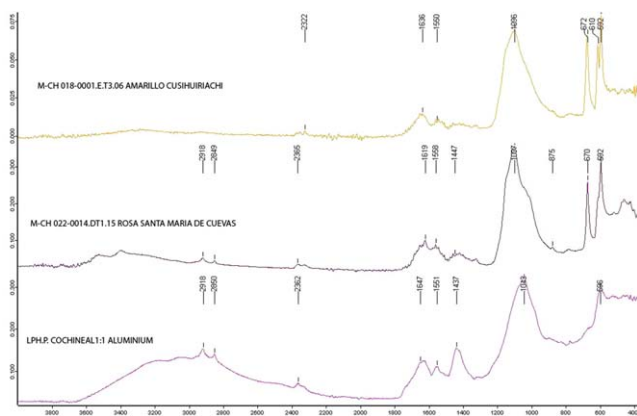


Fig. 5. ATR-FTIR spectrum of Santa Maria violet-pink sample (M-CH 022-0014.DT1.15), Cusihiuriachi yellow sample (M-CH 018-0001 E.T3.06) and cochineal prepared 1:1 with alumbre (alumina).

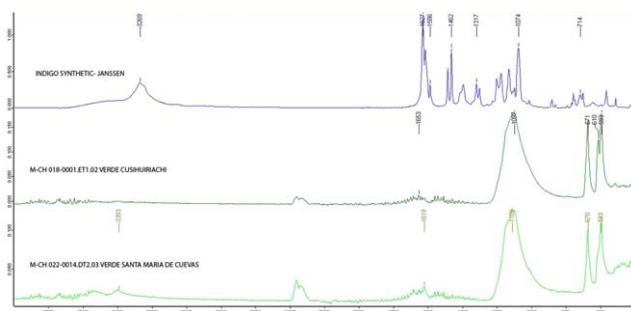


Fig. 6. ATR-FTIR spectrum of Santa Maria green sample (M-CH 022-0014.DT2.03), Cusihiuriachi green sample (M-CH 018-0001.E.T1.02), and synthetic indigo-Janssen.

urine, is added to the hydrated cochineal. Furthermore, purple colors are obtained when alkaline materials, such as ashes, are mixed to the hydrated cochineal. The results also suggest that green passages could be a possible combination of Mayan blue and carmine (with a still unknown acid component) due to the of absorption bands attributable to indigo and to carmine in the FTIR spectra.^{9,10} Comparing the IR spectra recorded on Cusihiuriachi green pigment with those on Santa Maria blue and pink-violet ones, a high percentage of match was found as 94% match for the blue and 93% for the pink-violet, respectively (Fig. 6). This combination of pigments was also found in Coyachi (located several kilometers from Cusihiuriachi).

CONCLUSIONS AND FUTURE PERSPECTIVES

The diagnostic campaign carried out in Santa Maria de Cuevas provided a base line for the study of polychrome wooden structures from similar Spanish colonial missions founded in late 17th century (1678–1700) in Northern Mexico. Preliminary FTIR results determined the presence of indigo and cochineal and possibly a mixture of both to produce different hues to decorate wooden ceilings and choirs in five mission churches in the Northern state of Chihuahua.

Additional FTIR analysis is currently being carried out in La Joya, Cusihiuriachi, Coyachi, and Rosario to complete the identification of materials and techniques in an attempt to confirm the presence of carmine and Mayan blue also in these sites. As these pigments had not been found in the region before, the next stage is intended to document the presence of *opuntia cacti* (on which cochineal insects usually live) as well as *indigofera tinctoria* plants in these territories. Equally relevant is the reconstruction of different mock-ups simulating the typical polychrome layered structures found in the churches and following traditional recipes, with the aim of correlating ATR-FTIR analysis of the natural compounds collected and of the pigments found in the actual samples considered. These results, in combination with the documentation of the art technology existing in such period, could contribute to determine if Mayan blue and carmine were already locally produced or if their use resulted from the

commercial trade existing between the central Mexico and the Northern territories.

ACKNOWLEDGMENTS

The authors are grateful to all the organizations and institutions in Mexico (Misiones Coloniales de Chihuahua A.C., Tec Monterrey Campus Chihuahua, Laboratorio de Patrimonio Histórico, Consejo Nacional de Ciencia y Tecnología—CONACYT, Instituto Nacional de Antropología e Historia—INAH, State Government of Chihuahua, as well as Local authorities and communities members of Carichi, Coyachi, Cusihiuriachi, Huejotitan, La Joya, Rosario, Santa Maria de Cuevas, Santa Rosalia de Cuevas, San Francisco de Borja, Satevo), USA (Smithsonian Museum Conservation Institute, J. Paul Getty Grant Program), Spain (Universidad Politécnica de Valencia), and Italy (IFAC-CNR in Firenze) that have contributed to the development of this study.

1. Márquez Zacarías Terrazas, *Misiones de Chihuahua Siglos XVII y XVIII*, Mexico D.F.: Consejo Nacional para la Cultura y las Artes; 2008. p 70–83.
2. Bacci M, Boselli L, Picollo M, Radicati B. UV, VIS, NIR Fibre Optic Reflectance Spectroscopy (FORS). In: Pinna D, Galeotti M, Mazzeo R, editors. *Practical Handbook on Diagnosis of Paintings on Movable Support*, European Project ARTECH, Firenze: Centro Di, Firenze; 2009. p 197–200.
3. Online database Infrared and Raman Users Group—IRUG, URL: <http://www.irug.org>.
4. Base de datos de Pigmentos Universidad de Valladolid, URL: http://goya.fmc.cie.uva.es/consultas/cons_ir.htm
5. Online Database IFAC-CNR of FORS spectra of pigments laid with a number of technique, URL: <http://fors.ifac.cnr.it>, Web October 19, 2015.
6. Bisulca C, Picollo M, Bacci M, Kunzelman D. UV-Vis-NIR reflectance spectroscopy of red lakes in paintings. In: *Proceedings of the 9th International Conference on Non-destructive Investigations and Microanalysis for the Diagnostics and Conservation of Cultural and Environmental Heritage*, Jerusalem, May 25–30, 2008; CD-Rom.
7. Vitorino T, Casini A, Cucci C, Melo MJ, Picollo M, Stefani L. Non-invasive identification of traditional red lake pigments in 14th-16th centuries paintings through the use of hyperspectral imaging technique. *Appl Phys A* 2015;121:891–901.
8. Leona M, Casadio F, Bacci M, Picollo M. Identification of the pre-Columbian pigment Maya blue on works of art by non-invasive UV-Vis and Raman spectroscopic techniques. *J Am Inst Conserv* 2004;43: 39–54.
9. Scheppe H. Indigo and woad. In FitzHugh EW, editor. *Artists' Pigments: A Handbook of Their History and Characteristics*, Vol.3. New York: Oxford University Press; 1997. p 81–108.
10. Scheppe H, Roosen-Runge H.. Carmine: Cochineal carmine and kermes carmine. In: Feller R, editor. *Artists' Pigments: A Handbook of Their History and Characteristics*, Vol. 1., Washington, D.C.: National Gallery of Art; 1986. p 255–298.