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An imaging and spectroscopic methodology for in situ analysis of ceiling and wall decorations in Colonial missions in Northern Mexico from XVII to XVIII centuries

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Abstract

Almost three hundred Spanish colonial missions—or their remains—are scattered over the vast state of Chihuahua in northern Mexico. A few of them still display painted decorations on the wood ceilings and walls. The decorated areas vary greatly, from the whole ceiling of the main aisle to just a few square meters in a lateral chapel, and so does the conservation state of the paintings. In this context, the information regarding the paintings' composition plays a key role in the restoration and conservation processes. For the gathering of such information, we propose a combined methodology for a fast, non-destructive and non-invasive characterization of such paintings with a minimum of techniques. This methodology includes false color infrared imaging as a first approach to determine the composition of large areas of the paintings and the homogeneity of the materials used in the painted areas, followed by small area analysis by X-ray fluorescence and fiber-optics reflectance spectroscopy. This methodology was applied to characterize the elemental and molecular composition of the decorations for four missions in Chihuahua in a fast and specific manner, revealing the use of a mix of mineral and organic materials including indigo and cochineal, and detecting differences between the missions. The methodology presented here can be easily applied for the study of a wider number of missions in Chihuahua and other regions to provide outstanding information of materials, pictorial techniques and deterioration conditions.

Keywords: Non-destructive analysis, Mexican colonial missions, FORS, XRF, False color infrared imaging

Introduction

The colonization of the northern territories of Mexico began a few decades after the fall of Tenochtitlan in 1521 and was driven by the discovery of silver and gold deposits in the areas that are now part of the states of Chihuahua, Zacatecas, Durango and Coahuila in Mexico, and Texas, Arizona and New Mexico in present-day United States. The arrival of soldiers and settlers was accompanied by Catholic priests, mainly Jesuits, Franciscans and Dominicans, with the intention of preaching the Gospel to the indigenous population. In the following three centuries several hundred missions were built, located alongside small towns, military posts (presidios), mines and private estates [1, 2].

The Jesuit and Franciscan religious orders built around 280 missions in the state of Chihuahua, many of which have survived to the present day under different states of conservation. A few of them still preserve decorative paintings in the walls and wood ceilings [3]. In a previous study [4], samples from the polychromy of five

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Casanova-González *et al. Herit Sci*   (2020) 8:91

Page 2 of 14

of these missions were analyzed by Fourier Transform Infrared Spectroscopy (FTIR), Fiber-Optics Reflectance Spectroscopy (FORS) and Scanning Electron Microscopy (SEM), leading to the identification of iron-based pigments, copper-based pigments, possibly charcoal and, interestingly, indigo and cochineal.

Other studies on wall paintings have used a combination of in situ XRF and visible reflectance [5] or FORS spectroscopy [6] with micro sample acquisition on selected areas. The analysis of these microsamples with SEM–EDS, micro Raman, and FTIR spectroscopies, together with micro XRD and HPLC-ESI-TOF, allows a better characterization of the pigments used than the in situ techniques, and the identification of painting layers improves the understanding of the painting technique used. However, sampling should be avoided whenever possible when dealing with heritage objects. Also, as sampling is usually limited, important regions may be omitted and relevant information regarding the use of materials and pictorial techniques might be missed.

Over the last years, in situ analysis techniques have become a suitable alternative to conventional laboratory methods. Such techniques include X-ray fluorescence spectroscopy (XRF), Raman spectroscopy, FTIR and FORS, together with infrared reflectography, ultraviolet and visible imaging, false color infrared imaging (FCIR) and hyperspectral imaging. Different combinations of these techniques have been applied to the study of a wide variety of objects, including wall decorations in churches [6], illuminated books and manuscripts [7–10], dyes and pigments identification [11–13], pre-Hispanic wall paintings [14], Mexican colonial paintings [15, 16] and textiles [17, 18], among others. Nevertheless, there are few reported case studies on polychrome decorated wood ceilings using in situ spectroscopic methods [19, 20].
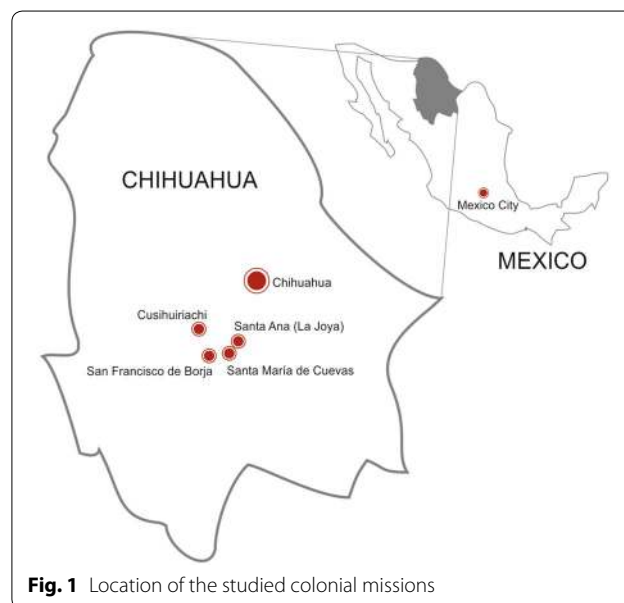
The combination of analytical techniques to be applied is not a trivial matter, it depends on the studied object and the objectives of the research. The chosen method must yield specific and high-quality information in a short period of time. In the case of objects where physical access is difficult, the equipment must also be light and highly portable. The latter is particularly important in the case of Mexico, where restoration and conservation projects are usually funded by public institutions with low budgets. In such scenarios, it is crucial to develop fast, precise and simple methodologies with a minimum of techniques, in order to overcome difficulties related to the lack of appropriate infrastructure and logistics, as well as tight time schedules. These methodologies should allow the study of large areas in a short time, providing a comprehensive identification of all the coloring

materials present. Moreover, the results from in situ analyses may be useful to establish an informed sampling strategy according to the objectives of the study and the deterioration conditions of the object.

Because of this difficulty in analyzing polychrome decorations that can be as high as ten meters above the ground, we propose a combined methodology for the non-destructive and non-invasive in situ characterization of painting materials from large areas in a short time. This methodology is based on the use of imaging and spectroscopic techniques with highly portable equipment: false color infrared imaging, X-ray fluorescence spectroscopy and fiber-optics reflectance spectroscopy.

In particular, false color infrared imaging was first developed for astronomy [21] and later applied to other fields [22], including cultural heritage analysis [23]. In Mexico, FCIR has been applied to the analysis of XVI century easel paintings and pre-Hispanic ceramic objects [24]. Ongoing investigations deal with the application of FCIR to a wider variety of materials, which include polychrome glazes, murals and decorative tiles. The information provided by FCIR can be linked to the presence of specific materials, including pigments and dyes, thus providing information on the homogeneity of materials present in large surfaces, and allow a more precise selection of areas for further spectroscopic analyses.

The proposed methodology was applied in the study of four colonial missions, Santa María de Cuevas, Cusihuiriachi, San Francisco de Borja and Santa Ana La Joya, all located in the state of Chihuahua (Fig. 1) and dated between 1674 and 1723 [4]. These missions contain some of the best conserved wall and wood ceiling polychrome

Fig. 1 Location of the studied colonial missions

Casanova-González *et al. Herit Sci*   (2020) 8:91

Page 3 of 14

decorations among those found in northern Mexico, and they are part of a wider conservation project led by Misiones Coloniales de Chihuahua A.C. [3]. Santa María de Cuevas probably possesses the most important painted ceiling in the state, covering the main aisle of the mission, along with wall paintings and other decorated areas. All four missions were analyzed in a work week of field studies.

The main objective of this work is to assess the capability of the proposed methodology to obtain information about the painting materials in a quick manner with a minimal set of highly portable analytical techniques. A secondary objective is to provide art historians and art restorers with relevant information regarding the composition of the pictorial layers, in order to gain a better understanding of the painting technique used and for planning future restoration and conservation projects.

Materials and methods

In the methodology followed, false color infrared imaging has been used to gather general information of the whole painted surface, and for the selection of specific areas for a more specific elemental (XRF) and molecular (FORS) analysis of the painted surfaces using battery operated, hand-held equipment. Most images were acquired from the ground level, while simple scaffoldings were used to access the higher regions for the spectroscopic analyses.

False color infrared imaging (FCIR)

Visible and near infrared (NIR) images where captured with a Sony Handycam HDR-PJ760V10 camera. NIR images where captured in *Nightshot* mode with an external IR 720 filter to eliminate the contribution of visible light. The photographed areas were illuminated using two Lowel Tota halogen lamps (3200 K). To generate the FCIR images, the visible and NIR images where processed with Photoshop CC (Adobe Inc., California, USA) following the procedure described in [24].

FCIR, along with XRF and FORS, were first applied in the analysis of a painted reference mock-up. The reference consists of a wood panel, prepared and painted according to XVI century recipes, with twenty-five different pigments and dyes applied over a gypsum preparation layer. Details on this painted reference mock-up can be found elsewhere [25]. FCIR and XRF analysis results have been published before [16, 24], along with a detailed characterization by Raman and SERS spectroscopies.

Fiber-optics reflectance spectroscopy (FORS)

A portable FieldSpect-4 (ASD Inc., Colorado, USA) was used to acquire visible, NIR and shortwave near infrared (SWIR) reflectance and absorbance (log[1/R]) spectra. A handheld probe was used which is placed in contact with the surface. A D65 illuminant provides illumination over the whole spectral range. The analysis area is about 1 cm^2 and spectra where obtained with a 0.2 s integration time. In absorbance mode, data is processed with the Kubelka–Munk algorithm [26, 27]. Calibration was performed using a certified reflectance standard (AS-02035-000CSTM-SRM-990-362, ASD Inc).

For analysis purposes, the visible and NIR regions are presented together in a zone named visible-near infrared (Vis–NIR). Vis–NIR ranges from 300 to 1000 nm and SWIR ranges from 1000 nm to 2500 nm. Inflection points in all spectra were determined using the first derivative of the spectrum, generated using the Origin Software (OriginLab Corporation, Northampton, USA).

X-ray fluorescence spectroscopy (XRF)

Elemental information was acquired with a Tracer-III SD (Bruker) handheld spectrometer equipped with a rhodium X-ray tube. Acquisition conditions were 40 kV, 11 µA and 30 s integration time. The acquired spectra were processed with the software Spectra Artax v.7.4.6.1 (Bruker) in order to measure the X-ray intensities from the specific elements. The analyzed surface is an ellipse with major and minor axes of approximately 9 and 7 mm, respectively.

Results and discussion

Santa María de Cuevas

The mission of Santa María de Cuevas presented an impressive decorated ceiling covering the main aisle, a small painted ceiling located at the entrance, both supported on independent wood panels and rafters, and a frieze on the top of the supporting walls (Fig. 2).
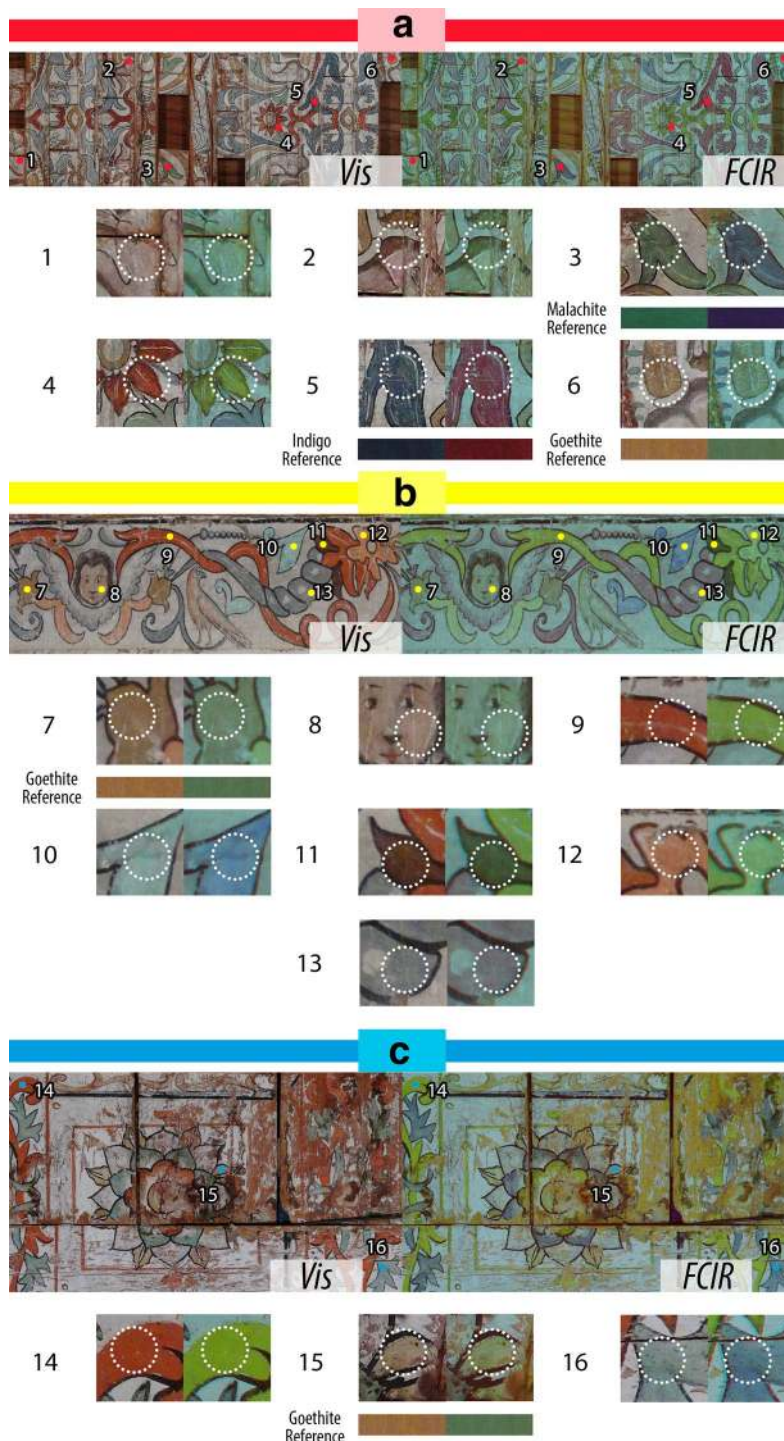
False color infrared imaging

As a preliminary technique, FCIR is useful for narrowing down possible pigments and selecting representative areas for further spectroscopic analysis. In this first approach, FCIR images from all of the areas analyzed (Fig. 3) suggested the presence of the pigments goethite, malachite and indigo (Table 1), whose color change corresponded with those found in previous studies [24].

After the FCIR software process (Table 1), dark yellow areas changed to green, indicating the presence of goethite, green areas changed to blue, indicating the use of a malachite-based green, and greyish-blue areas changed to a very distinctive red hue, usually attributed to indigo. The presence of indigo was previously reported for the same areas by Muñoz-Alcocer et al. [4]. Pink, brown and red areas did not correspond to any of the references used for comparison (Table 1).

In each of the three painted areas, FCIR images displayed a homogeneous distribution of colors, and thus of
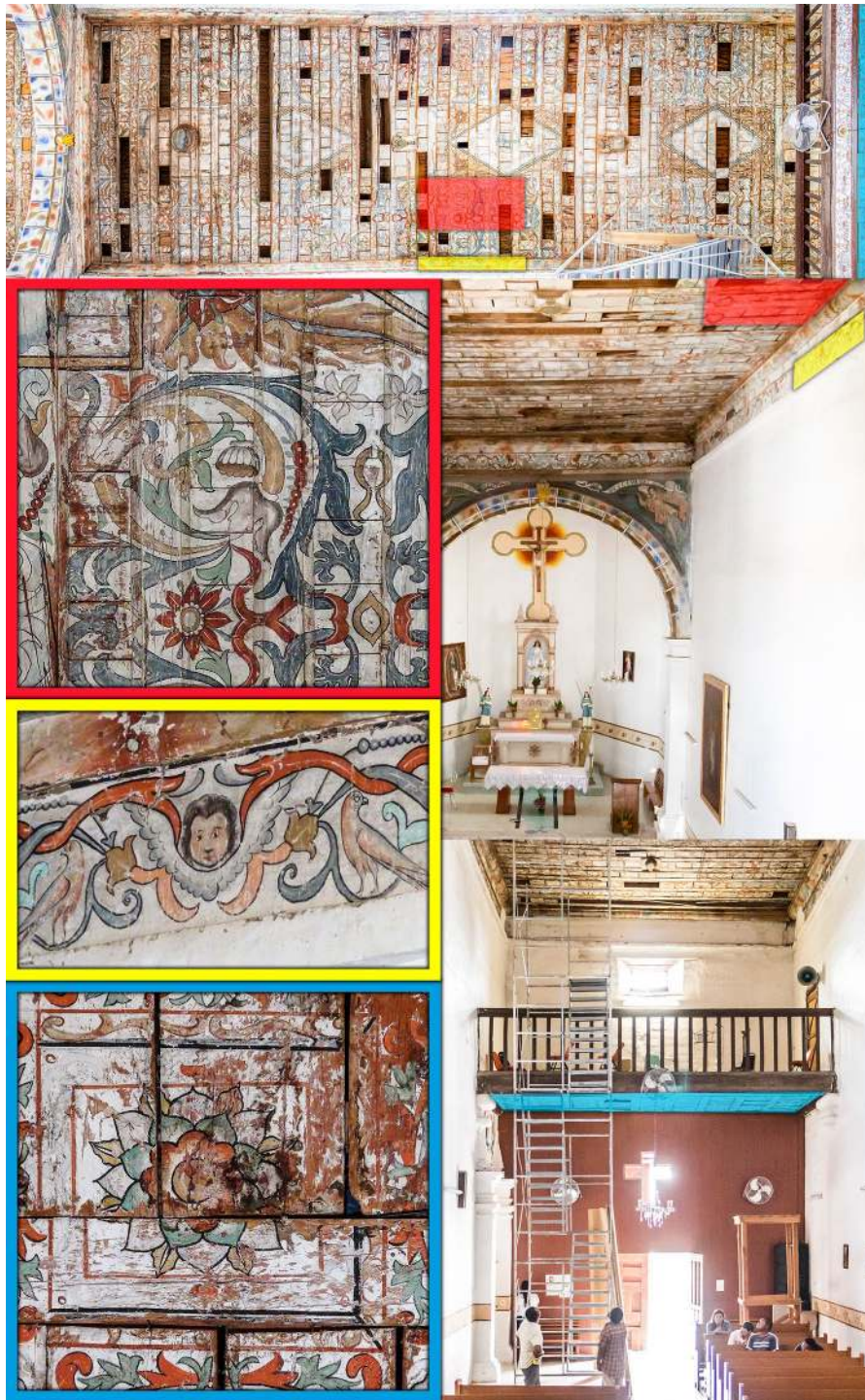
Fig. 2 Images of the decorated ceilings at Santa María de Cuevas. Red squares: Detail from the ceiling; Yellow squares: Detail from the frieze; Blue squares: Entrance ceiling

Casanova-González *et al. Herit Sci*   *(2020) 8:91*

Page 5 of 14

Fig. 3 False color infrared images from Santa María de Cuevas. A and C correspond to areas from the ceilings (main aisle and entrance respectively), while B is related to the frieze painting. Details of the FCIR color change in the different areas are included. Where appropriate, the visible and FCIR images of malachite, indigo and goethite references are also included

Casanova-González *et al. Herit Sci* (2020) 8:91

Page 6 of 14

Table 1 False color infrared analysis from Santa María de Cuevas

	Samples		Probable identification
	Visible	FCIR	
1 (Pink)			–
2 (Dark pink)			–
3 (Green)			Malachite
4 (Red)			–
5 (Blue)			Indigo
6 (Dark yellow)			Goethite
7 (Dark yellow)			Goethite
8 (Incarnate)			–
9 (Red)			–
10 (Green)			Malachite
11 (Brown)			–
12 (Orange)			–
13 (Blue)			Indigo
14 (Red)			–
15 (Dark yellow)			Goethite
16 (Green)			Malachite

the materials used. This information was used to select smaller areas of ceiling and wall decorations for further spectroscopic analysis, as they presented the best access options for our equipment, and contained a representative sample of the pigments identified by FCIR in the larger area.

X-ray fluorescence spectroscopy

A background of calcium and sulfur was found in all areas, with an almost constant Ca/S ratio regardless of color, suggesting a gypsum ground layer. In the main ceiling painting, two types of red were identified, displaying different hues. The first (henceforward referred to as red 1; points 4, 9 and 14 on Fig. 3) contains high amounts of iron, probably related with red earths or iron oxides (Fig. 4). In the second red (red 2; points 1 and 2 on Fig. 3), no particular elements related to red pigments were identified—such as Fe, Hg, As, Pb—thus indicating the use of an organic dye (Fig. 4).

High iron contents were also present in the dark yellow and brown areas (Fig. 4), indicating the possible use of ocher. Some orange and black analysis points also presented a high iron content, which could be related with the application of several painting layers. However, as no samples were collected, we cannot ascertain this hypothesis.
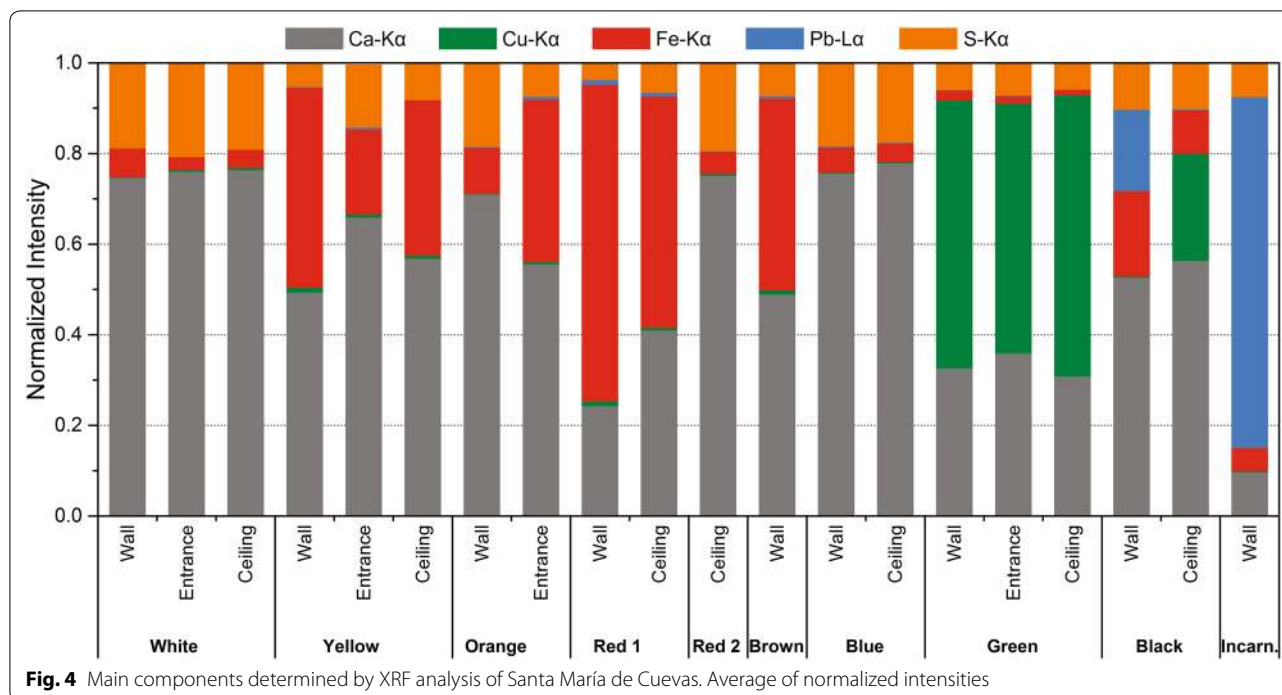
Copper content was elevated in green zones, reinforcing the assumption of the use of malachite as inferred from FCIR. In all the blue areas analyzed, Ca and S were the main elements detected (Fig. 4), revealing the use of an organic dye, probably indigo as suggested by FCIR.

Of interest was the detection of lead, found exclusively in the black hair and incarnate of the cherub faces from the wall decorations. In particular for the incarnate, XRF analysis revealed a slight increase in tin content when compared with other colors, which together with the detection of lead could suggest the use of lead white, lead–tin yellow, minium, or a mixture of them. Under these conditions, elemental analysis alone cannot confirm any of these possibilities.

Fiber-Optics Reflectance Spectroscopy

The results from the FORS analysis are summarized in Table 2 and some relevant spectra are also shown. As in XRF and FCIR analysis, FORS spectra of red areas showed the presence of two different reds. The spectra from the iron-containing red 1 areas were similar to those of our iron oxide references, particularly hematite, with reflection maxima at 613 and 745 nm (Fig. 5a).

The areas presenting the apparently organic red 2 (inferred from XRF results, as no significant elements were detected) were strongly faded—displaying a pink and dark pink color-, making it difficult to acquire good quality spectra. It was still possible to identify the colorant using a combination of absorption maxima at 520 and 560 nm (Fig. 5b), with the inflection point of the reflectance spectra—located at 586 nm—strongly supporting the presence of carminic acid, the main component

Casanova-González *et al. Herit Sci* (2020) 8:91

Page 7 of 14

Fig. 4 Main components determined by XRF analysis of Santa María de Cuevas. Average of normalized intensities

Table 2 Results of the FORS analysis in Santa María de Cuevas

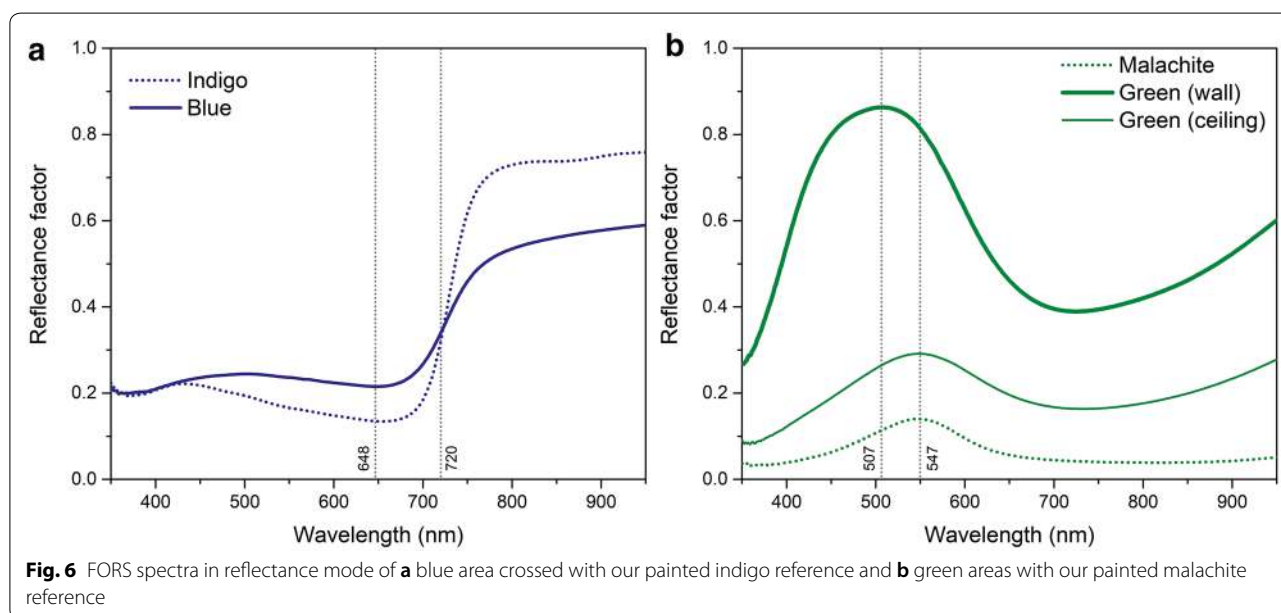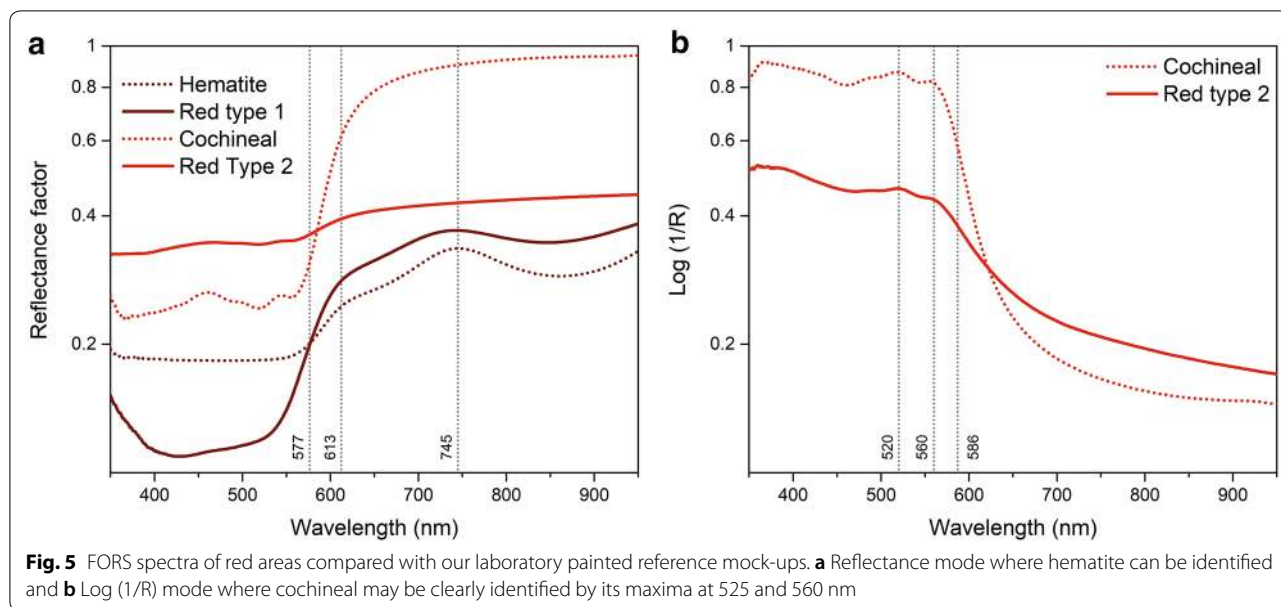| Color	Average spectral features (maxima position)		Pigment identified
	Reflectance (nm)	Absorbance (nm)	
White		1446, 1491, 1539, 1752, 1944, 2178, 2217, 2268	Gypsum
Dark yellow	550*, 601, 771	475, 893	Ocher
Orange	567*, 621, 742	523, 845	Iron oxide
Blue	516, 720*	648	Indigo
Brown	571*, 747	506, 847	Iron oxide-rich earth
Incarnate	565*, 619, 737	525, 844	Minium
Green (wall)	501–582	725	Malachite + a blue pigment, probably indigo
Green (ceiling)	547	734	Malachite
Red 1	577*, 613, 745	526, 847	Hematite
Red 2	586*	520, 560	Cochineal

*Inflection point

found in cochineal. This identification of cochineal is supported by historical information, since FORS allows to dismiss the presence of plant-based red dyes such as Brazilwood or madder, but not to discriminate between insect-based dyes (cochineal, lac, kermes) [28]. Cochineal was the most common red insect-based dye used in Mexico during the Novohispanic period [29].

The broadening of the spectra and the lower intensity of the 520 and 560 nm bands may be related with the

degradation process of the colorant. This behavior may explain the shift of color to brown hues observed in the corresponding areas.

XRF analysis of greyish-blue areas from the ceilings and walls did not show the presence of any elements that could be related to such hue, since calcium and sulfur were the main elements detected. FORS spectra also suggest the use of indigo, based on the inflection point near 720 nm in the reflectance spectra and a wide absorption

Fig. 5 FORS spectra of red areas compared with our laboratory painted reference mock-ups. **a** Reflectance mode where hematite can be identified and **b** Log (1/R) mode where cochineal may be clearly identified by its maxima at 525 and 560 nm

Fig. 6 FORS spectra in reflectance mode of **a** blue area crossed with our painted indigo reference and **b** green areas with our painted malachite reference

band centered at 648 nm (Fig. 6a), in accordance with the spectra of indigo references and recent studies on Mexican codices [10]. The absence of clay-related elements in the XRF spectra, the high amounts of Ca and S detected and the presence of gypsum bands on the FORS spectra ruled out the use of Maya blue and pointed to a gypsum base, closer to the European tradition [30–33].

Copper-containing green areas resulted in FORS spectra closer to malachite in the ceilings, with the reflectance maximum at 547 nm, similar to our reference spectra of the mineral (Fig. 6b). In the walls, the acquired spectra displayed a wide interval in this reflectance maximum, from 501 to 582 nm. This may indicate the use of different mixtures to achieve varied hues of green, with blue pigments or dyes—such as indigo—being used for the areas displaying a blue-shift of the reflectance maximum of malachite (Fig. 6b). It is important to note that the best preserved areas were chosen for analysis, and, to the best of our knowledge, no restorations or repaints have been carried out in the analyzed areas, making any possible interference of modern pigments highly unlikely.

Casanova-González *et al. Herit Sci*   (2020) 8:91

Page 9 of 14

For the identification of yellow areas, FORS analysis of four references were compared, two inorganic and two organic: orpiment (As_2S_3), ocher (α-FeO(OH)), *palo azul* (*Cyclolepis Genistoides*) and weld (*Reseda luteola*). Although FORS spectra of yellow colors can be difficult to differentiate, the inflection points of the spectra acquired on the ceilings of the main aisle and in the walls are located around 550 nm, closer to the value determined for ocher (558 nm) and in agreement with the high amounts of iron detected by XRF. The reflection maxima—around 601 nm and 771 nm—are also close to those observed for the ocher reference, at around 606 and 767 nm (Fig. 7a). Orange areas, on the other hand, yielded FORS spectra that could be related to an iron oxide, with reflectance bands at 621 and 742 nm (Fig. 7a). The brown color used on the walls could be an iron oxide-rich earth pigment, as indicated by the FORS spectra showing a 571 nm inflection point and 731 nm reflectance maximum (Fig. 7a).

FORS spectra of the cherub incarnate (Fig. 7b) present in the wall decorations allowed the identification of minium, in accordance with the elemental analysis from XRF. The reflectance spectra of the incarnate areas showed a distinctive 565 nm inflection point, very close the value of 561 nm reported for minium [34].

When the spectra corresponding to all the colors observed are compared (Fig. 8), gypsum bands are clearly visible in all of them at 1446, 1491, 1539, 1752, 1944, 2178, 2217 and 2268 nm [35, 36], thus confirming the use of a gypsum base in the walls and ceilings of Santa María de Cuevas. Gums or proteinaceous binders were not
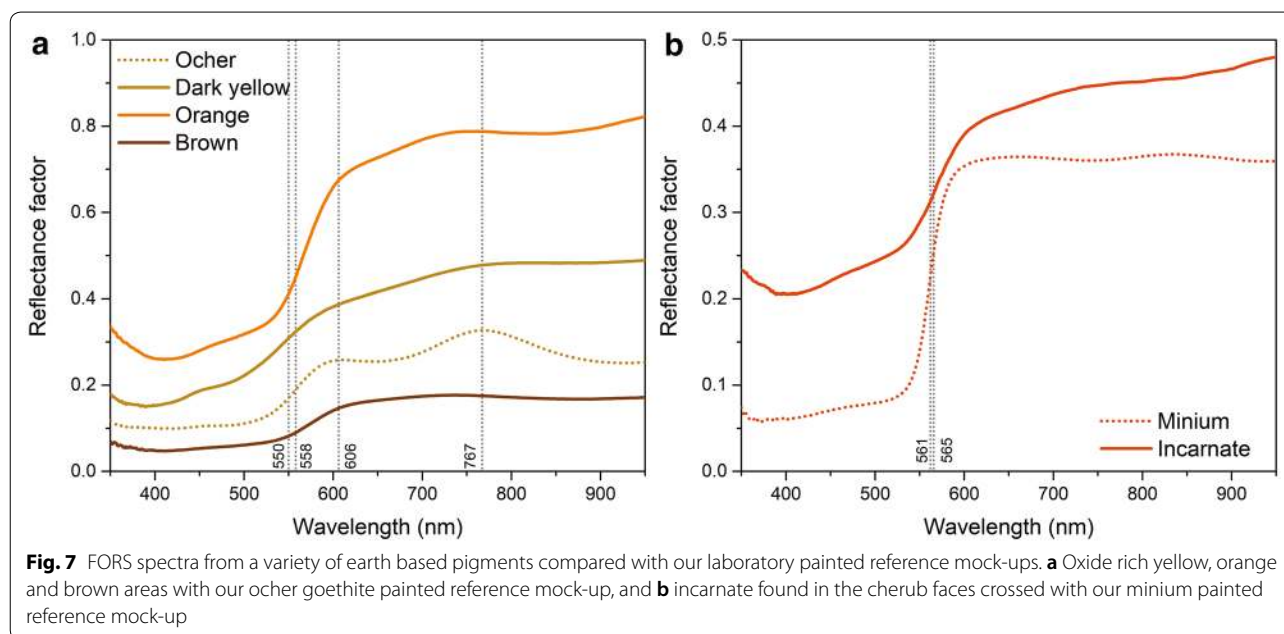
detected, since neither the broad absorption at 2100 nm related to polysaccharides [37, 38], nor the absorption features of carbonyl (near 2050 nm) or amide (near 2175 nm) groups of proteins [36, 39] or the stretching and bending modes of methylene from the triglycerides (2285 and 2350 nm) present in egg yolk [36] were observed. Water vibrations from gypsum in the NIR region, especially the one at 2178 nm, related to the stretching and bending modes of hydroxyl groups, [35, 36] can mask the signal of proteins and impede their identification.
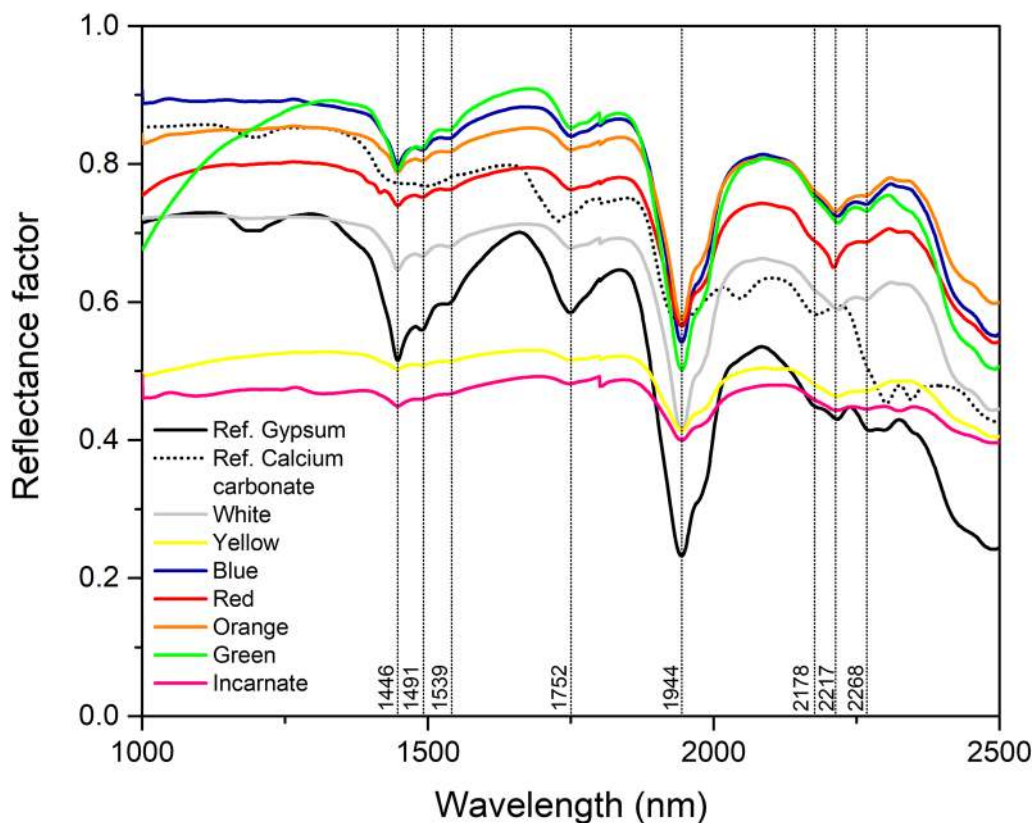
Comparison of the four missions

The same methodology was also applied to the three remaining missions. In this section a comparison of the results obtained is made (Table 3). In order to simplify their discussion, spectral data are not shown.

Red and blue areas of Cusihuiriachi presented a similar composition to that of Santa María de Cuevas, where indigo, cochineal and gypsum were identified. In contrast, the colorant used for the blue hue at Santa Ana La Joya could not be identified with the techniques used. Elemental analysis did not point to any blue inorganic compound and the FORS spectra were not conclusive to suggest the presence of any pigment or dye.

The use of malachite—probably from local origin [3]—for the greens was also determined in Cusihuiriachi and Santa Ana La Joya, with a probable addition of a yellow dye at the second mission. Yellow colors presented the major differences between the four missions. While ocher or some type of yellow earth seem to be the

Fig. 7 FORS spectra from a variety of earth based pigments compared with our laboratory painted reference mock-ups. **a** Oxide rich yellow, orange and brown areas with our ocher goethite painted reference mock-up, and **b** incarnate found in the cherub faces crossed with our minium painted reference mock-up

Fig. 8 Near infrared FORS spectra in reflectance mode from all of the analyzed colors, crossed with our calcium carbonate and gypsum reference ground layers. The characteristic gypsum bands were identified as the corresponding ground layer

material used at Santa María de Cuevas and Santa Ana La Joya, lead was found in San Francisco de Borja and an unidentified organic dye was possibly used for the yellow hues in Cusihuiriachi. The presence of this organic yellow dye was inferred from the XRF results, due to the absence of diagnostic elements typically related to yellow pigments, since the FORS spectra obtained from these areas were inconclusive.

Orange colors from both San Francisco de Borja and Cusihiriachi were achieved with the use of minium, while at Santa Ana La Joya iron-based compounds were used. Copper-containing compounds were used for the brown hues in San Francisco de Borja, which differs from Santa María de Cuevas.

While the black areas of Santa María de Cuevas and San Francisco de Borja consisted mainly of copper-containing colors—with the exception of the cherubs in the first one, where lead was detected—the materials used for this color at Santa Ana La Joya are manganese-enriched earths, as deduced from the elemental characterization. The presence of copper and lead in these areas could be related with the presence of degradation products of Cu/Pb based pigments. Further analyses are

needed to determine if this is the case, applying a wider set of techniques including Raman and FTIR spectroscopies, among others.

Although FORS spectra were not conclusive in the identification of a gypsum background in San Francisco de Borja and Cusihuiriachi, its presence was suggested by the XRF results. From the FORS information the presence of calcium carbonate might be inferred, but the spectra are not conclusive.

The Ca/S intensity ratios from the analyzed areas (ranging from 4.5 to 5.0, respectively) was compared with those obtained from gypsum and anhydrite references under the same analysis conditions (3.64), the difference may be due to either the presence of a second Ca-containing compound—such as calcium carbonate—or to a stronger absorption of the 2.3 keV photons from sulfur, related to the presence of heavier elements (such as Pb or Cu) in the upper pictorial layer, which are absent in the mineral sample. However, the XRF intensity of Pb and Cu in the analyzed white areas of both missions were not high enough to quench the detection of sulfur X-rays. Thus, the presence of calcium carbonate is more probable. The mineral composition of the gypsum and calcium

Table 3 Comparison of results obtained from all four missions analyzed, displaying the main elements detected by XRF and its molecular identification by FORS. Color codes are explained in the notes below the table.

Mission	White	Blue	Green	Yellow	Orange	Brown	Red	Black
Santa María de Cuevas	Ca, S Gypsum	Ca, S **Indigo** Gypsum	Cu **Malachite** + **Indigo** Gypsum	Fe, K, Si **Iron oxide** Gypsum	**Minium** (Incarnate)*	Fe, K, Si, Mn **Iron oxide** Gypsum	Fe, K, Si, Pb* **Iron oxide** **Cochineal** Gypsum	Cu, Pb* Gypsum
San Francisco de Borja	Ca, S Gypsum[†]	-	-	Pb Yellow dye [†] Gypsum[†]	Pb **Minium** Gypsum[†]	Cu Oxides Gypsum[†]	-	Cu Gypsum[†]
Cusihuiriachi	Ca, S Gypsum [†] Gypsum	Ca, S **Indigo** Gypsum	Cu **Malachite** Gypsum	Probable dye Gypsum[†]	Pb **Minium** Gypsum[†]	-	Ca, S **Cochineal** Gypsum[†]	-
Santa Ana La Joya	Ca CaCO$_3$	Ca, S Blue dye[†] CaCO$_3$	Cu **Malachite** + Yellow dye CaCO$_3$	Fe, K, Si **Iron oxide** CaCO$_3$	Fe, K, Si **Iron oxide** CaCO$_3$	-	-	Ca, Fe, Mn Mn-enriched earth CaCO$_3$

Blue: Used by native Tarahumara population; Green: Probably introduced by Spanish missionaries from central or southern Mexico; Red: Probable European origin

[*] *Cherubs*

[†] Not clearly identified by FORS

carbonate references was confirmed by Fourier Transform Infrared Spectroscopy (data not shown).

Finally, calcium carbonate was identified in all the analysis points of Santa Ana La Joya. In this mission, XRF measurements displayed minor amounts of sulfur, but only CaCO$_3$ bands were observed in the FORS spectra. The Ca/S XRF intensity ratio in this mission is around 52, ten times higher than the ratio determined for the other three missions.

To sum up, the painting materials used at Santa María de Cuevas and Cusihuiriachi have a very similar composition, with some differences in the green, yellow and red colors. San Francisco de Borja shares a gypsum background with the first two, but differs in the pigments' composition. Santa Ana La Joya presents the biggest contrast with the other three missions, from the background to the selection of pigments and dyes.

Some possible interpretations may be pointed out from the comparison of palettes, backgrounds and raw materials [40–42] for the four missions dated between 1674 and 1723 [4]. The similarity of the palettes and the same ground layer may indicate that Santa María de Cuevas and Cusihuiriachi were painted around the same time,

while the palette changes observed for San Francisco de Borja may correspond to a different period of painting and to a change in the availability of raw materials. It could also correspond to a different choice of materials, corresponding to the economic boom of the town, as is displayed in the European construction technique employed in the ceiling. On the other hand, the use of a diverse background in Santa Ana La Joya and the change of palette in this site indicate a later different period of painting—and probably painters—with the use of local raw materials for the organic blue and the yellow, and orange and black colors (earth pigments). The economical restrains for carrying out the decoration of this site—a visiting mission—should be considered when compared to the other three missions that were significantly richer due to their status and the available resources from mining.

The presence of indigo and cochineal in geographical areas so far away from their known production regions, as well as the presence of minium (usually related to a European origin) [29, 43], is an indication of the active commerce routes established within the New Spain and with Europe. Soon after 1521 a vigorous trade was

Casanova-González *et al. Herit Sci* (2020) 8:91

Page 12 of 14

established between the Americas and Europe, including the exportation of cochineal, but also redwoods, indigo, logwood, yellow fustic and annatto [44] from the new World to the old one. In the opposite direction this included the import of other painting materials, such as lead white, blue powders, brushes, cord, linseed oil and Spanish canvas [45].

The combination of indigo and cochineal with a gypsum background is a common European technique, which has also been identified in mural paintings of other colonial churches in Central Mexico [46]. The use of indigo over a gypsum background has also been reported in polychrome wooden sculptures from Paraguay [47] and in an Andean church from Northern Chile [48, 49]. In this last case, cochineal was also found, together with orpiment, vermilion, smalt, antlerite, hematite and charcoal.

Conclusions

A combined methodology for a fast and in situ analysis of large painted surfaces using false color infrared imaging, X-ray fluorescence and fiber-optics reflectance spectroscopies was presented. This methodology was successfully applied in the study of four colonial missions in northern Mexico. The use of portable and light equipment allowed the examination of difficult to reach areas and the study of all four missions in just 5 days of field studies, achieving a comprehensive identification of the pigments and dyes used, as well as the preparation base. This methodology avoids or minimizes the need for sampling, providing outstanding data for a suitable choice of representative testing areas of the decorations and can be applied with a reasonably simplicity to a wide range of similar painted decorations that are yet to be studied in Mexico and elsewhere.

Limitations of the methodology are related to the identification of organic dyes, mainly yellows, the identification of binders and the precise characterization of paint layers. The use of appropriate comparative references is a requirement for a correct identification of the painting materials. This is specially the case of the yellow dyes [50].

Overall, gypsum was identified as the ground layer in three churches and calcium carbonate in the remaining one. This result may correspond to a later period of painting for Santa Ana La Joya and/or to less available resources to carry out the decoration of this site. Pictorial layers were characterized by the presence of malachite (alone or combined with a dye) in the green areas, the use of organic blues and cochineal. Minium was found in three churches, while iron oxide was identified in two of them. Main variances were found for yellow, brown and black hues, where the selection of materials was notably

different. This information is fundamental for future restoration and conservation efforts and provides data to make out the periods of painting and the use of imported and local raw materials for the colors.

Authors' contributions
ECG: conceptualization, methodology, investigation, in situ analyses, formal analysis, visualization, writing—original draft, editing; MAMR: in situ analyses, formal analysis; AM: investigation, formal analysis, visualization, writing—original draft; IRC: in situ analyses, formal analysis, visualization; MAGB: laboratory analyses, formal analysis; JLRS: conceptualization, methodology, investigation, supervision, writing—original draft; editing, funding acquisition, project administration; KMA: historical investigation; coordination and support on in situ analyses. All authors read and approved the final manuscript.

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Casanova-González *et al. Herit Sci*   (2020) 8:91

Page 13 of 14

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