

# RAMAN IDENTIFICATION OF PIGMENTS IN WALL PAINTINGS OF THE COLONIAL PERIOD FROM BOLIVIAN CHURCHES IN THE RUTA DE LA PLATA

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## Introduction

This interdisciplinary study was realized with the participation of different scientists from various disciplines: chemistry, conservation, art history and archaeology. All the specialists contributed in different aspects related to the aim of the project which included the iconographic and stylistic analysis of the visual representation, its historical and cultural contextualization, and the microscopic and physical-chemical characterization of the materials in the wall paintings of four churches on the Ruta de la Plata, Bolivia. This comprehensive approach was realized for the first time in the South Central Andean region with specialists from different countries: Bolivia, Chile and Argentina to exchange different experiences, but also knowledge of the painting practices during the colonial period. Materiality of visual art representation from the 16<sup>th</sup>-17<sup>th</sup> centuries exhibits a particular complexity related to the combination of practices and knowledge from the old world, mixed with European art traditions, including that from the local indigenous peoples of the Andean region. Bringing together all these different elements, obliges us to discuss, from an interdisciplinary approach, all physical-chemistry results obtained from the spectroscopic analysis to fully understand the original painting process employed inside the churches and possible later interventions, which were not always recorded, performed in the past.

### 1. Church wall paintings in the Ruta de la Plata

Between the 16<sup>th</sup> and 18<sup>th</sup> centuries, the *Ruta de la Plata* was one of the main axes of trade used by the Spanish colony for the circulation of raw materials and minerals throughout the Andes region. These resources were obtained from different mountain localities, such as Huancavélica in the Central Andes and Potosí in the Bolivian highlands from the South-Central region and then transported to the Royal Treasury of Spain from Arica harbor on the Pacific coast (Figure 1). This route represented, among its other uses, a significant network of roads for the commerce of silver minerals and other raw materials extracted from the Cerro Rico mine of Potosí [1]. However, the dynamism of the *Ruta de la Plata* declined significantly in the 18<sup>th</sup> century as a result of the reduced mineral production in Potosí and the preference for Buenos Aires as the new port for commercialization [2]. Important colonial cities were founded along the *Ruta de la Plata*, as well as the infrastructures necessary to support the hard displacement between the Andean highlands and the Pacific coast to the west. In each village, in the current territories of Bolivia and Chile, several churches were built to contribute to and promote the evangelization of the local indigene population. Inside the churches, murals were important supports for painting, iconography and illustrating various scenes from daily life, as they visually conveyed the ecclesiastical doctrine, seemingly without ignoring local realities.

The aim of the present work is to perform a Raman study and to identify pigments used in the wall paintings of four Bolivian churches of the *Ruta de la Plata* belonging to the period from the 16<sup>th</sup> to 18<sup>th</sup> century. With the present results, we intend to determine the color palette and to infer about the pictorial techniques used in this historical context, in the South-Central Andean region. They are the Santiago de Curahuara de Carangas church, with early 17<sup>th</sup> century paintings, which underwent restoration work during the 18<sup>th</sup> century [4]; the La Sacristía de Santiago de Callapa and San José de

Soracachi churches, whose characteristics, observed in the representations and architecture, allow their wall paintings to be dated to the second half of the 17<sup>th</sup> century [5]; and lastly, the Copacabana Andamarca church, whose wall paintings were executed in the late 17<sup>th</sup> century or beginning of the 18<sup>th</sup> century [6].

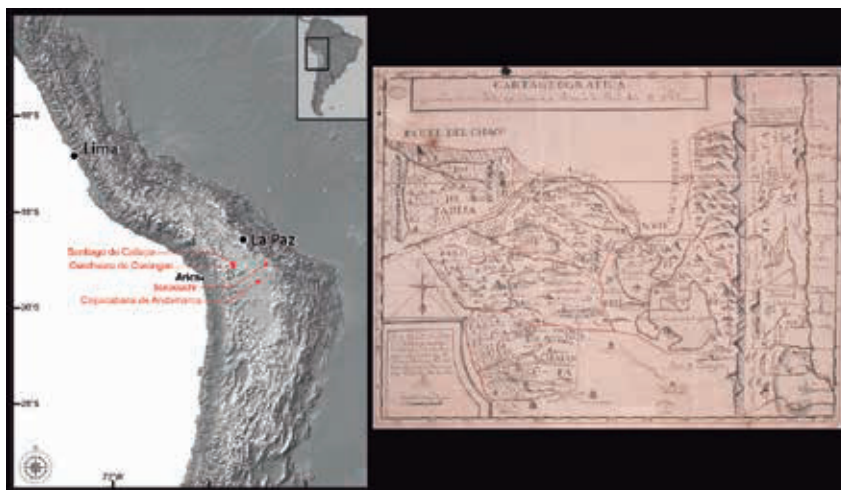


Figure 1. a) Map of the four colonial churches in the South Andean Region; b) Ancient map with the six parts of Potosí province, 1787. Archivo general de Indias. MP-Buenos Aires, 160 [3].

When these four churches were first constructed they belonged to the Archbishopric of La Plata, in the ecclesiastical jurisdiction of the old Viceroyalty of Peru, and later, from the 18<sup>th</sup> century, to the Viceroyalty of La Plata [4]. The synod of 1772-1773 shows clear concern about the role of paintings and sculptures in these ecclesiastical buildings [4]. After clearly recommending the use of iconographic programs that the faithful could read like a book, the text refers to the possibility that the meaning of a Christian image could be altered by the presence, even if hidden, of images or material objects associated with ancient local indigenous practices. This led to the integration of particularities into the pictorial program which were characteristic of the various local indigenous communities so that they contributed to evangelization transfer from the old European world [7]. The iconographic and stylistic analysis of the images painted on various programs on the interior walls of the churches, show these variabilities. However, the analysis of the materiality of these paintings can also complement our knowledge of the pictorial and symbolic practices of the colonial period in the South Andes Region. Artists commissioned for the realization of mural paintings might have had access to products transported and sold throughout the *Ruta de La Plata*, but they certainly had access to their own local knowledge [7]. Knowledge of the materials involved in artistic or cultural heritage can, moreover, contribute to understanding the ancient colonial and Andean technologies and pictorial techniques. Finally, it can also aid conservators and restorers in making decisions regarding the planning and restoration of these historical monuments.

Information on the color and pigments used in the wall paintings of the *Ruta de la Plata* churches can be obtained through several scientific techniques, including spec-

troscopic analyses which are the most frequently used in heritage science [8,9]. Raman spectroscopy is one of the most powerful spectroscopic tools employed due to its unique properties; it is a non-destructive technique; no sample preparation is required and it displays characteristics of reliability and specificity [10-15]. Raman spectrometers have become the instrument of choice when analyzing archaeological materials and pigments on art works [16]. It is also amenable to *in-situ* analysis, based on the development of fiber optics technology [17-19]. Most Raman spectrometers are today coupled with microscopes, thus making it possible to observe the sample and scan the spectrum from a micrometric area [20, 21]. The use of micro-Raman spectrometers gives information on the microstructure of analyzed samples also by improving spatial resolution. Nevertheless, its major disadvantage lies in the formation of undesirable fluorescence, which is an accompanying phenomenon when measuring diverse materials and is difficult to forecast. The main applications of Raman in heritage studies concern the identification of pigments and dyes on different supports. Pigments together with binders or agglutinant and extender, generally of mineral origin, are added to a paint mixture to improve or slightly modify some of its properties, such as diluting it or giving it additional body or, finally, to increase the quantity of paint. The analysis of these substances provides important information about materials, artists, artistic schools or technological knowledge and evolution [22].

## 2. Experimental

### 2.1 Sample collection

Forty-four samples, measuring 0.5-1.0 mm<sup>2</sup>, were collected in September 2012. They were taken from selected wall paintings following internationally accepted procedures [23]. Samples were organized according to the different colors displayed in the artworks. Figure 2 displays details of the artworks indicating the points where the samples were collected. 20 samples were taken from the Cuarahuara de Carangas church (CDC); 5 from the Santiago de Callapa church (STC), while from the San José de Soracachi church (SRC) 11 samples were selected. In total, six colors were identified. Finally, 8 samples were taken from the Nuestra Señora de Copacabana de Andamarca (CPC) church.

### 2.2 Microscopy measurement

Optical microscopy data were acquired with a trinocular stereoscopic microscope Optika, model SZM-2 LED, with a total magnification of 90x. Recorded images (Figure 3) were calibrated by referencing one rule of 0.10 mm with divisions of 0.01 mm; the scaling was performed so that the displayed images were in the 0.01-0.02 mm range.

Figure 3 shows some of the micro-samples from the churches described above. The size of the investigated samples, as well as the distribution of the colored pigment in each micro-sample can be observed in Figure 3.

### 2.3 Raman measurements

Raman spectra were recorded on a Raman RenishawInVia Reflex apparatus, equipped with 532, 633, and 785 nm laser lines for excitation, a Leica microscope and

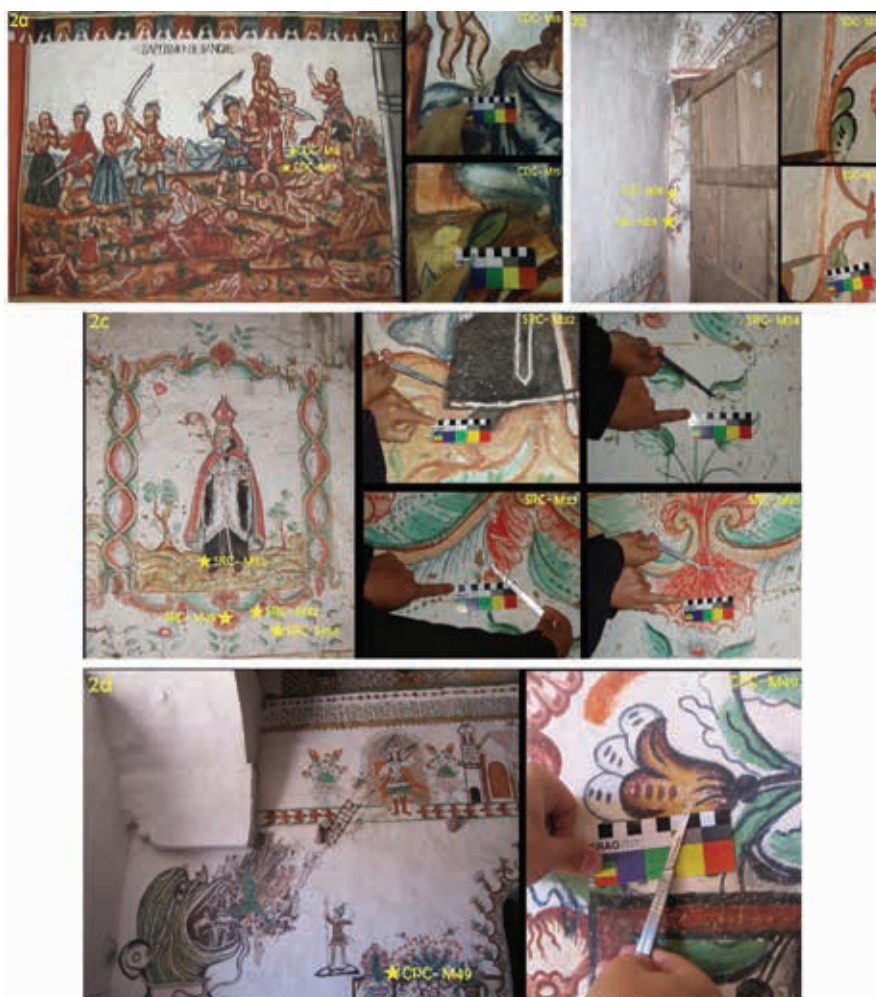


Figure 2. Details and sampling points of wall painting inside churches: A) Curahuara de Carangas (CDC); B) Sacristía de Santiago de Callapa (STC); C) San José de Soracachi (SRC) and D) Copacabana de Andamarca (CPC).

an electrically cooled charge-coupled device detector. The instrument was calibrated using the 520  $\text{cm}^{-1}$  line of a Si wafer and a 50x objective. The resolution was set to 4  $\text{cm}^{-1}$  and 1-5 scans of 10-50 s each were averaged. Spectra were recorded in the 1800-200  $\text{cm}^{-1}$  region. Spectral scanning conditions were chosen to avoid sample degradation and photo decomposition. The best results were obtained using the 785-nm laser line and a power range of 10-100 mW on the sample. Data were collected and plotted using the programs WIRE 3.4, GRAMS 9.0 and OriginLab Pro 2016.





Figure 3. Microscopic images of representative coloured samples from: A) Santiago de Curahuara de Carangas (CDC); B) Sacristía de Santiago de Callapa (STC); C) San José de Soracachi (SRC) and D) Copacabana de Andamarca (CPC).

### 3. Results

#### 3.1 Raman spectrum of pigments

The artwork, code sample, color and pigments found in the samples are displayed in Table 1. The Raman band assignment of the samples is based on general Raman data [24-26], for dyes [25-31] and pigments [27, 32]. The spectra are shown as obtained and are illustrated along with the discussion.

Table 1. Sample code, color and pigments in wall paints of Curahuara de Carangas (CDC), Santiago de Callapa (STC), San José de Soracachi (SRC) and Nuestra Señora de Copacabana de Andamarca (CPC) churches.

Sample Code	Church	Color	Identification
CDC-M7	Curahuara de Carangas	Red	Cinnabar
CDC-M8	Curahuara de Carangas	Black	Carbon
CDC-M9	Curahuara de Carangas	Green	Copper phthalocyanine
CDC-M10	Curahuara de Carangas	Green	Copper phthalocyanine
CDC-M11	Curahuara de Carangas	Red	Cinnabar
CDC-M12	Curahuara de Carangas	Black	Carbon
CDC-M13	Curahuara de Carangas	Yellow	Benzimidazolone
CDC-M14	Curahuara de Carangas	Black	Carbon
CDC-M15	Curahuara de Carangas	Green	Copper phthalocyanine
CDC-M16	Curahuara de Carangas	Red	cinnabar
CDC-M17	Curahuara de Carangas	White	No result
CDC-M18	Curahuara de Carangas	Blue	Indigo
CDC-M19	Curahuara de Carangas	Green	Copper phthalocyanine
CDC-M20	Curahuara de Carangas	Red	No result
CDC-M21	Curahuara de Carangas	Blue	Indigo
CDC-M22	Curahuara de Carangas	Blue	Indigo
CDC-M23	Curahuara de Carangas	Red	Cinnabar
CDC-M24	Curahuara de Carangas	Green	Copper phthalocyanine
CDC-M25	Curahuara de Carangas	Brown	No result
CDC-M26	Curahuara de Carangas	Green	Antlerite
STC-M27	Santiago de Callapa	Black	Carbon
STC-M28	Santiago de Callapa	Green	Antlerite + Kronhnikite
STC-M29	Santiago de Callapa	Red	Hematite
STC-M30	Santiago de Callapa	White	Gypsum
STC-M31	Santiago de Callapa	Blue	Phthalocyanine
SRC-M32	Soracachi	Black	carbon
SRC-M33	Soracachi	Blue	Indigo
SRC-M34	Soracachi	Green	Antlerite + gypsum
SRC-M35	Soracachi	Red	Cinnabar
SRC-M36	Soracachi	White	Gypsum
SRC-M37	Soracachi	ocher	Goethite + gypsum
SRC-M39	Soracachi	Green	Antlerite
SRC-M40	Soracachi	Brown	No result
SRC-M41	Soracachi	Yellow	Goethite + gypsum
SRC-M42	Soracachi	Black	Carbon
CPC-M43	Copacabana	orange	No result
CPC-M44	Copacabana	Green	Antlerite
CPC-M45	Copacabana	Black	Carbon
CPC-M46	Copacabana	Blue	Indigo
CPC-M47	Copacabana	pink	No result
CPC-M48	Copacabana	purple	Hematite + gypsum
CPC-M49	Copacabana	Yellow	$\beta$ -naphthol + anhydrite
CPC-M50	Copacabana	White	Rutile

### 3.2 Santiago de Curahuara de Carangas church

The red sample CDC-M7 in Figure 4A displays a Raman spectrum with bands at 253, 311 and 354  $\text{cm}^{-1}$  which were ascribed to cinnabar (HgS) in agreement with data from RRUFF [32]. These bands are assigned to  $\nu$ HgS vibration modes and are orientation dependent. Samples CDC-M11, -M16 and-M23 show the same Raman bands as CDC-M7.

The black color in sample CDC-M8, Figure 4B is identified as carbon material [32]. The same component was identified in samples CDC-M12 and CDC-M14.

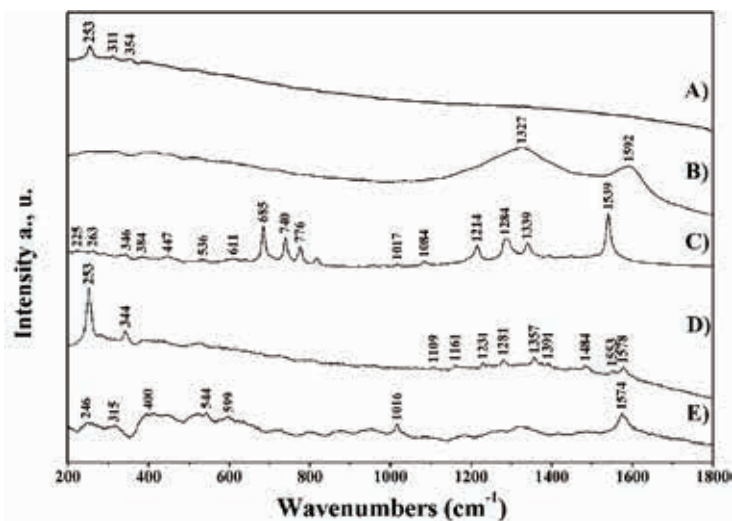


Figure 4. Raman spectrum and sample codes of the: (A) red; (B) black; (C) green; (D) yellow gold and; (E) blue samples of the Curahuara de Carangas church wall paint.

In Figure 4C, the green areas in sample CDC-M9 are dominated by copper phthalocyanine (CuPc). Bands in the spectrum, mainly those at 1539, 776, 740 and 685  $\text{cm}^{-1}$ , are consistent with the presence of CuPc. as bands at 1339 and 776  $\text{cm}^{-1}$  involve isoindole moiety, while the macrocycle ring deformations are expected in the 300-450  $\text{cm}^{-1}$  range. The green material itself was determined to be phthalocyanine green, a copper-based pigment first synthesized in 1928 [33]. Phthalocyanine green, C<sub>32</sub>H<sub>0</sub>-2N<sub>8</sub>Cl<sub>14</sub>-16Cu, was indexed as Cl:74260 in 1971 [33]; it is usually adsorbed on an aluminum hydrate base to form a deep vivid green color that is used as a substitute for viridian. The permanent pigment is unaffected by light, heat, and chemicals. Samples CDC-M10, CDC-M15, CDC-M19 and CDC-M24, show the same Raman bands as CDC-M9, clearly indicating a recent intervention on the Curahuara de Carangas church wall paintings.

The Raman spectrum of the sample CDC-M9, (Figure 4C), is highly coincident with that reported by Chaplin et al. [34] for a green phthalocyanine. In their work, authors concluded that in the case of the screen alone, in a large painted leather screen and two illuminated title pages in 17th century books of ordinances of the Worshipful Company of Barbers, London, a restoration in the 1980s was carried out with different pigments: hematite, phthalocyanine green, rutile, and a mixture of azurite, malachite and barium sulphate. No bands of the green perchlorinated copper phthalocyanine Cl:74250 reported by Scherrer et al. [25] were detected. The present result indicates that restoration work was performed on the wall painting including the phthalocyanine component in the green areas.

The yellow gold sample CDC-M13, Figure 4D, displays a Raman spectrum, identical to that reported by Scherrer et al. [25] for the PBr 25 Cl:12510 monoazo pigment benzimidazolone. This compound is accompanied by the vermilion pigment HgS displaying bands at 253 and 344  $\text{cm}^{-1}$ [35]. The bands of the monoazo pigment benzimidazolone at 1578 and 1553  $\text{cm}^{-1}$  are ascribed to  $\nu\text{N}=\text{N}$  modes and the bands at 1484,



1391 and 1357  $\text{cm}^{-1}$  are  $\nu\text{CC}$  ring vibrations, the last two belonging to the naphthalene ring following Lutzenberger et al. [36]. A deformation of the benzoimidazole ring is assigned to the band at 1281  $\text{cm}^{-1}$ . *Para*-disubstituted ring breathing is ascribed to the band at 1231  $\text{cm}^{-1}$ . The band at 1161  $\text{cm}^{-1}$  could be assigned to a CO vibration of the imidazole ring moiety. A CH deformation is attributed to the band at 1109  $\text{cm}^{-1}$ .

The blue sample CDC-M18 displays a Raman spectrum (Figure 4E) characterized by a group of weak relative bands at 1574, 1016, 599, 544, 400, 315 and 246  $\text{cm}^{-1}$ . The first two bands are highly coincident with the equivalent of indigo dye ( $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ ), following Baran et al. [37]; the band at 1574  $\text{cm}^{-1}$  is assigned to a coupled  $\nu\text{C}=\text{C}/\nu\text{CO}$  mode. The very weak band at 544  $\text{cm}^{-1}$  is probably a benzene ring out of plane bending. The band at 246  $\text{cm}^{-1}$  also observed by Leona et al. [38] is a five-member ring out-of-plane bending mode. The band at 1016  $\text{cm}^{-1}$  is an out of plane CH deformation. Indolic ring modes are expected in the 300-400  $\text{cm}^{-1}$  range.

### 3.3 Sacristía de Santiago de Callapa church

The Raman spectrum of the black pigment in the sample STC-M27, (Figure 5A), displays large D (defects) and G (graphitic) bands at 1338 and 1582  $\text{cm}^{-1}$ , respectively; they are ascribed to  $\nu\text{CC}$  modes of a carbon material [32].

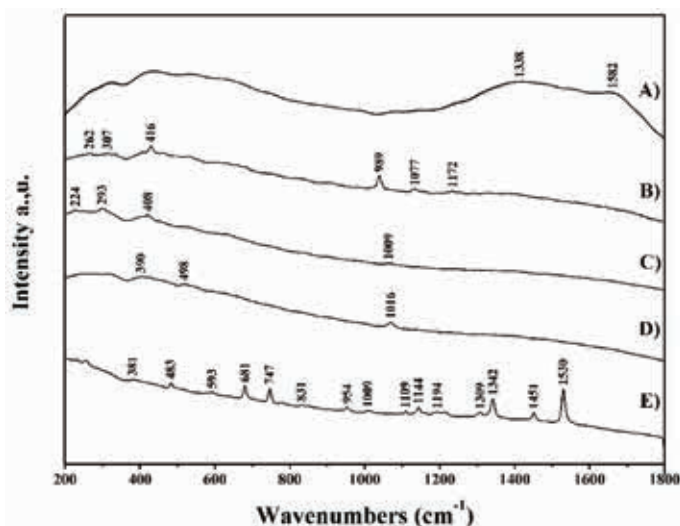


Figure 5. Raman spectrum and sample codes of the: (A) black; (B) green; (C) red; (D) white and (E) blue samples of the Santiago de Callapa church wall paint.

Sample STC-M28 in Figure 5B, displays a green coloration. The Raman spectrum shows bands at 1172, 1077, 989, 416, 307 and 262  $\text{cm}^{-1}$ . These bands are characteristic of copper sulphate salts, probably from minerals antlerite  $\text{Cu}_2\cdot 3\text{SO}_4(\text{OH})_4$  or / plus krohnkite  $\text{Na}_2\text{Cu}(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$  and brochantite  $\text{Cu}_4\text{SO}_4(\text{OH})_6$  [32]. The most intense band at 989  $\text{cm}^{-1}$  is assigned to a  $\nu\text{symSO}_4$  vibration, while the weak band at 1077  $\text{cm}^{-1}$  is the corresponding asymmetric mode [39]. The band at 1172  $\text{cm}^{-1}$  is a  $\nu\text{symSO}_4$  mode, while the band at 416  $\text{cm}^{-1}$  is a doubly degenerate  $\nu_2$  symmetric  $\text{SO}_4$  bending mode. The band at 262  $\text{cm}^{-1}$  is probably a lattice vibration [40].

The Raman spectrum of the red sample STC-M29 in Figure 5C contains bands at 1009, 408, 293 and 224  $\text{cm}^{-1}$ . The last three bands are highly coincident with vibrations of hematite [32]; the bands at 408 and 293  $\text{cm}^{-1}$  are assigned to the  $E_g$  mode while the last is ascribed to an  $A_{1g}$  mode [18]. The weak band at 1009  $\text{cm}^{-1}$  is ascribed to gypsum  $\text{CaSO}_4$  probably used as filler.

The white pigment STC-M30 in Figure 5D is probably gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , displaying Raman bands at 1016, 498 and 390  $\text{cm}^{-1}$ . The first band is the  $\nu_1\text{SO}_4$  mode, while the second is the  $\nu_2\text{SO}_4$  mode; this assignment is highly coincident with data by Liu et al. [41]. The band at 390  $\text{cm}^{-1}$  is a  $\nu_2$  bending mode following Frost et al. [42].

The intense blue pigment in sample STC-M31, (see Figure 5E), displays characteristic Raman bands of a phthalocyanine polycycle. In fact, the most probable compound is classified as PB 16:6 Cl: 74160:6 with strong bands at 1530, 1342, 747 and 681  $\text{cm}^{-1}$ ; these bands can be ascribed, following Basova et al. [30], to the  $\nu\text{CN}$ ,  $\nu\text{CC}$ ,  $\nu\text{CuN}/\delta\text{CNC}$  and  $\delta\text{CNC}/\nu\text{CN}$  modes, respectively. According to historical information, phthalocyanines were discovered in the early 1900s [43], thus the only way to explain this coloration is related to recent interventions or restoration of the wall painting.

### 3.4 San José de Soracachi church

The Raman spectrum of the black pigment from sample SRC-M32, Figure 6A, is quite similar to that observed in the case of the Santiago de Callapa and Nuestra Señora de Copacabana de Andamarca church samples; the Raman spectrum with bands at 1341 and 1580  $\text{cm}^{-1}$  corresponds to a carbon material. Carbon was also identified in sample SRC-M42.

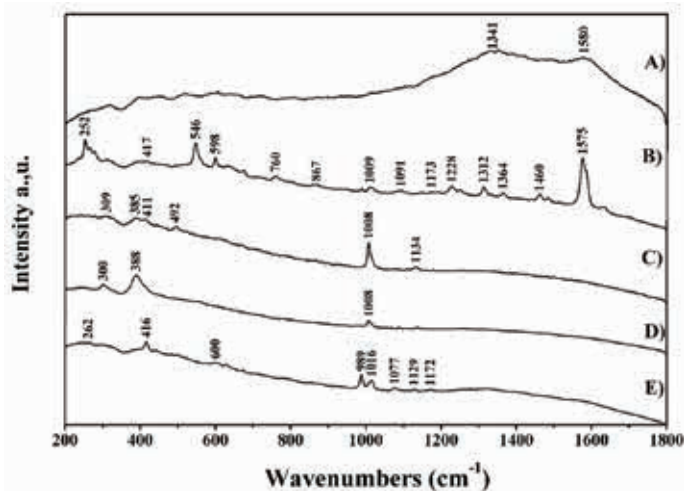


Figure 6. Raman spectrum and sample codes of the: (A) black; (B) blue; (C) white; (D) red ochre and (E) green samples of the San José de Soracachi church wall paint.

The blue in samples SRC-M33 and SRC-34, Figure 6B, displays a Raman spectrum characterized by bands at 1575  $\text{cm}^{-1}$ , a band at 546  $\text{cm}^{-1}$  and a multiple band at 252  $\text{cm}^{-1}$  plus other weak bands at 1460, 1312, 1228 and 1009  $\text{cm}^{-1}$ . This set of bands is

highly coincident with an indigo dye (C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>), following Baran et al. [37]. The band assignment has already been discussed in samples CPC-M46 and CDC-M18 for the indigo pigment.

The white sample SRC-M36 in Figure 6C displays a Raman spectrum with bands at 309, 385, 411, 492, 1008 and 1134 cm<sup>-1</sup> corresponding mainly to gypsum as in the case of the previously discussed sample STC-M30.

The red ochre sample SRC-M37 in Figure 6D contains bands at 300 and 388 cm<sup>-1</sup> corresponding to goethite Fe<sub>3</sub>O(OH) [32]; the additional band at 1008 cm<sup>-1</sup> belongs to gypsum. The band at 300 cm<sup>-1</sup> is a symmetric Fe-OH bending mode and the band at 388 cm<sup>-1</sup> is an antisymmetric stretching Fe-O-Fe/-OH mode [44]. The spectrum of the sample SRC-M37 is identical to that of the sample SRC-41.

The Raman spectrum of the green sample SRC-M34 is quite similar to that observed in samples SRC-M39, Figure 6E, in this same church and CPC-M44 of Nuestra Señora de Copacabana de Andamarca church. The green sample displays an intense band at 989 cm<sup>-1</sup> which is characteristic of the  $\nu_{\text{sym}}\text{SO}_4$  mode of the sulphate anion. The band at 1129 cm<sup>-1</sup> is a  $\nu_{\text{asym}}\text{SO}_4$  mode, while the band at 600 cm<sup>-1</sup> corresponds to asymmetric deformations of SO<sub>4</sub> [45]. The band observed at 416 cm<sup>-1</sup> is accompanied by shoulders at 409 and 420 cm<sup>-1</sup>; these bands were assigned to the  $\nu_2$  bending modes. The band at 262 cm<sup>-1</sup> is probably a lattice vibration [40]. The spectral profile of the SRC-M39 sample is highly coincident with the Raman spectrum of the antlerite mineral Cu<sub>2</sub>+3SO<sub>4</sub>(OH)<sub>4</sub> [32].

### 3.5 Nuestra Señora de Copacabana de Andamarca church

The basic copper sulphate minerals antlerite, brochantite, posnjakite and langite display characteristic bands in the 986-973 cm<sup>-1</sup> range [39]. The green sample CPC-M44, Figure 7A, displays an intense band at 973 cm<sup>-1</sup> which is characteristic of the  $\nu_{\text{sym}}\text{SO}$  mode of the sulphate anion.

The band at 608 cm<sup>-1</sup> corresponds to asymmetric deformations of SO<sub>4</sub> [45]; the bands at 478 and 318 cm<sup>-1</sup> are ascribed to  $\nu_{\text{Cu-O}}$  vibrations, following Lane [40]. An intense Raman band is observed at 415 cm<sup>-1</sup> with shoulder bands at 386 and 446 cm<sup>-1</sup>; these bands were assigned to the  $\nu_2$  bending modes by Frost et al. [42]. Other bands lower than 250 cm<sup>-1</sup> at 242 and 318 cm<sup>-1</sup>, are probably lattice vibrations [40]. The spectral profile of CPC-M44 is highly coincident with the Raman spectrum of the mixture of antlerite Cu<sub>2</sub>+3SO<sub>4</sub>(OH)<sub>4</sub> and brochantite Cu<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub> minerals [32].

The blue sample, CPC-M46, displays a Raman spectrum in Figure 7B, characterized by an intense band at 1575 cm<sup>-1</sup>, a band at 543 cm<sup>-1</sup> and a large and medium band at 253 cm<sup>-1</sup> plus other weak bands at 1460, 1364, 1313, 1228, 1015, 637, 600, 383, 314 cm<sup>-1</sup>. This set of bands is highly coincident with the indigo dye (C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>), as reported by Baran et al. [37]. The band at 1575 cm<sup>-1</sup> is assigned to a coupled  $\nu_{\text{C=C}}/\nu_{\text{CO}}$  mode, while the band at 543 cm<sup>-1</sup> is probably a benzene ring out of plane bending mode. The band at 253 cm<sup>-1</sup>, also observed by Leona et al. [38], is probably a five-member ring in-plane and out-of-plane bending mode. The band at 1460 cm<sup>-1</sup> is an aromatic  $\nu_{\text{CC}}$  mode and the band at 1364 cm<sup>-1</sup> involves the NH fragment and CH deformation modes coupled to  $\nu_{\text{CN}}$  vibrations. A six-member ring  $\nu_{\text{CC}}$  mode is ascribed to the band at 1313 cm<sup>-1</sup>. In and out of plane CH deformations are assigned to the bands at 1228 and 1015 cm<sup>-1</sup>, respectively. The N-H out-of-plane bending occurs at 637 cm<sup>-1</sup>. A CCOC deformation mode could be ascribed to the band at 600

cm<sup>-1</sup>. Indole ring modes are expected in the 300-400 cm<sup>-1</sup> range. Indigo is typically a natural dyestuff that has been extracted from the leaves of various indigofera species since ancient times; indigo has also been made synthetically since the late 19th century [33]. It can therefore not be excluded that the identified blue color may derive from a synthetic origin.

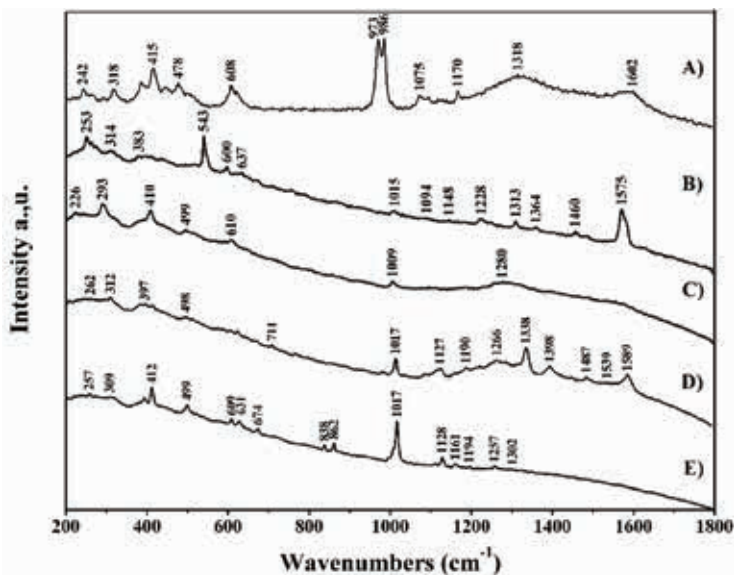


Figure 7. Raman spectrum and sample codes of the: (A) green; (B) blue; (C) purple; (D) pale red and (E) white samples of the Nuestra Señora de Copacabana de Andamarca church wall paint.

The Raman spectrum of the purple sample CPC-M48 in Figure 7C shows broad bands, in particular, at 226, 293, 410, 499, 610 cm<sup>-1</sup> which is coincident with the Raman signals of the hematite pigment [32]. Gypsum is also present in this sample displaying the characteristic band at 1009 cm<sup>-1</sup>.

The sample CPC-M49, pale red in color, displays a set of Raman bands in Figure 7D attributable to a synthetic azopigment, namely  $\beta$ -naphthol [25] mixed with gypsum [32]. In fact, the most intense bands of the azopigment are 1589 and 1338 cm<sup>-1</sup>, along with the medium bands at 1398 and 1127 cm<sup>-1</sup>. Weak bands are observed at 1487 and 1266 cm<sup>-1</sup>. The bands at 1017, 397 and 312 cm<sup>-1</sup> correspond to gypsum; analysis of these bands was done in the case of the Santiago de Callapa church. Three spectral features are characteristic of azocompounds:  $\nu$ N=N vibration (1380-1450 cm<sup>-1</sup>),  $\nu$ symC-N mode (1130-1200 cm<sup>-1</sup>) and  $\delta$ symC-N vibration (1160-1200 cm<sup>-1</sup>) [46]. The characteristic naphthalene band is identified at 1589 cm<sup>-1</sup>. The identification of the synthetic pigment suggests that the wall painting had undergone recent interventions or restoration; azopigments were originally synthesized in the last two decades of the 19th century [47].

Rutile (TiO<sub>2</sub>) was identified [32] in the white sample CPC-M50 (Figure 7E), displaying bands at 609 and 257 cm<sup>-1</sup>. Other bands at 1128, 1017, 862, 631, 499 and 412cm<sup>-1</sup> are ascribed to gypsum [32]. The strongest Raman spectrum of gypsum at

1017  $\text{cm}^{-1}$  corresponds to the symmetric  $\nu_1\text{SO}_4$  tetrahedral mode. Bands at 412 and 499  $\text{cm}^{-1}$  are assigned to the  $\nu_2$  symmetric bending, while the peak at 1161  $\text{cm}^{-1}$  corresponds to the  $\nu_3$  asymmetric stretching vibration mode. The bands at 631 and 674  $\text{cm}^{-1}$  are attributable to the  $\nu_4$  asymmetric bending vibration modes.

### **3.6 Raman spectra of components in the ground layer**

The strong band at 1008  $\text{cm}^{-1}$  is ascribed to the symmetric stretching mode of a sulphate group. This band appears in various samples. Several minerals containing the sulphate group could in principle be used as components of the preparatory layer of the mural paintings: alum-(K),  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  displays a band centered at 993  $\text{cm}^{-1}$  [32] while leightonite [32],  $\text{K}_2\text{Ca}_2\text{Cu}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ , displays a maximum at 1004  $\text{cm}^{-1}$ ; alunite  $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$  shows a band at 1020  $\text{cm}^{-1}$ . Gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , shows Raman bands at 1136, 1008, 671, 620, 494 and 415  $\text{cm}^{-1}$  [48], which is highly coincident with the observed signals in various present samples. This analysis indicates that the most probable component used in the preparation of the ground layer was gypsum. No organic binders were identified in the samples.

## **4. Discussion**

All spectroscopic results are summarized in Table 1 and contribute to identifying the palette of colors from the Colonial Period. Nevertheless, contemporary and modern paint was also identified and interpreted as used in possible recent restoration. In all the churches, the black pigment used to paint was identified as carbon. This material was widely used in the Colonial Period since it was easy to obtain [49-51]. Red paints correspond to hematite or cinnabar (vermillion). Both are historical colonial pigments identified in easel painting [52]. Indigo (CDC-M18, CDC-M21, CDC-M22, SRC-M33, CPC-M46) an important dying pigment was used as blue [53]. Red ochre (SRC-M37) and purple (CPC-M48) were separately identified as goethite and gypsum, and hematite, respectively; a combination of different proportions was probably used to obtain various tonalities [54]. The yellow sample (SRC-M41) was analyzed as a mixture of goethite and gypsum. Green pigments correspond to antlerite, a copper hydroxy-sulphate. Finally, anhydrite (calcium sulphate) [55] and rutile (titanium dioxide) were analyzed for the white paint. One case of pale red (CPC-M49) is particularly unusual and corresponds to a synthetic pigment used since the 19<sup>th</sup> century. One blue sample (CDC-M9) shows a phthalocyanine pigment which appeared at the beginning of the 20<sup>th</sup> century [54]. A similar pigment was identified in the Santiago de Callapa church (STC-M31) in the green paint. The yellow gold color (CDC-M13) corresponds to benzimidazolone, a synthetic pigment created in the 20<sup>th</sup> century.

The different pigments identified, correspond effectively to the Colonial Period. Artists used pigments commercially available at this time for painting on different supports, such as wood, easel painting and on church walls [50, 52, 57]. Some of these mineral and organic pigments have been known since pre-hispanic times, and include carbon, hematite, goethite, cinnabar, antlerite and indigo, showing some continuity from the local pre-Columbian pictorial tradition. These different coloring materials were also known and used in rock art (hematite, goethite, cinnabar and carbon), on vegetal fiber, leather (antlerite and copper mineral pigment) or textiles (for indigo) [55, 56,



58], among others. In contrast, four studied samples correspond to synthetic pigments developed in the late 19<sup>th</sup> century and early 20<sup>th</sup> century. The identification of these particular pigments allowed us to conclude that paints in the Curahuara de Carangas and Santiago de Callapa churches had undergone intervention and repainting, probably during past restoration. In the case of the Nuestra Señora de Copacabana de Andamarca church, restoration work was performed between 2005 and 2009 by the Bolivian and German governments.

## 5. Conclusions

Pigments of the four wall paintings of the Bolivian Andean highland churches Santiago de Curahuara de Carangas, Santiago de Callapa, San José de Soracachi and Nuestra Señora de Copacabana de Andamarca in Bolivia in the *Ruta de la Plata*, belonging to the Colonial Period, were identified and analyzed through optic microscopy and microRaman spectroscopy. Most of the original pigments correspond to colored mineral salts such as green from antlerite / krohnkite, red from hematite and cinnabar, white from rutile and red ochre from goethite; another blue color comes from the natural dyestuff indigo; black is obtained from carbon. Other pigments such as fully chlorinated copper phthalocyanine in the green areas, copper phthalocyanine in the blue areas,  $\beta$ -naphthol in the yellow areas and benzoimidazolone in the red areas were identified, suggesting old and recent interventions or restoration work. A filler / support such as gypsum was found in most samples. No organic binders were identified in the samples, but we cannot discard its use and its future analysis with complementary techniques. The present results are coincident with a recent painting analysis performed on the Copacabana de Andamarca church [50], where authors were able to identify organic binders which corresponded to precise recipes used in colonial times and painting techniques applied on church walls, namely an *a secco* technique. The present work remains open to other scientific analyses that complement and allow for further studies in other artworks enabling development of additional conservation protocols. These results also contribute to a discussion on continuity and innovation in relation to the palette of colors used since before the colonial period, an important dimension regarding technological knowledge regarding pigment use and production in the highlands of the South-Central Andean region.

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### Summary

Micro-Raman spectroscopy was used to analyze and identify pigments and determine the palette of color in wall paintings from four churches of the Colonial Period, in the Bolivian highlands. The ancient churches Santiago de Callapa, Curahuara de Carangas, Nuestra Señora de Copacabana de Andamarca and San José de Soracachi were constructed during the 17<sup>th</sup> and 18<sup>th</sup> centuries, around the important colonial *Ruta de la Plata*, between Potosí city and Arica harbor on the Pacific coast of South America. Most pigments used in the wall paintings correspond to inorganic minerals as well as to organic colorants. Fully chlorinated copper phthalocyanine (green), copper phthalocyanine (blue),  $\beta$ -naphthol (yellow) and benzoimidazolone (red), were identified in the corresponding colored areas suggesting subsequent recent interventions or restorations. Ground layer materials were also characterized. The present results allow for discussion of the pictorial techniques used in the Andean highland during the colonial period and allow conservators and restorers to make important decisions regarding the type of intervention to perform in the case of these important historical and patrimonial monuments.

### Riassunto

La spettroscopia Micro-Raman è stata utilizzata per analizzare e identificare i pigmenti e determinare la tavolozza di colori dei dipinti murali di quattro chiese risalenti al periodo coloniale, negli altopiani boliviani. Le antiche chiese di Santiago de Callapa, Curahuara de Carangas, Nuestra Señora de Copacabana de Andamarca e San José de Soracachi sono state costruite nel XVII e XVIII secolo, attorno alla coloniale Ruta de la Plata, tra la città di Potosí e il porto di Arica sulla costa del Pacifico, Sud America. La maggior parte dei pigmenti utilizzati nei dipinti murali si riferisce a minerali inorganici e coloranti organici. Il rame clorurato di ftalocianina (verde), il rame di ftalocianina (blu), il  $\beta$ -naftolo (giallo) e il benzimidazolone (rosso) sono stati identificati nelle corrispondenti aree colorate, suggerendo successivi interventi. Sono stati anche caratterizzati i materiali dello strato preparatorio. I risultati attuali permettono di discutere le tecniche pittoriche utilizzate nell'altopiano andino durante il periodo coloniale, permettendo inoltre ai conservatori e restauratori di prendere decisioni sul tipo di intervento che interessa questi importanti monumenti storici.