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# Raman spectroscopy in the diagnosis of the wall painting *History of Concepción*, Chile

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Pigments and fresco-related materials from the wall painting *Historia de Concepción* by Gregorio De La Fuente in Concepción, Chile were identified by Raman microscopy. The pigments were compared with those obtained from the artist's studio, and results allowed inference about subsequent interventions. Materials coming from processes such as salt efflorescence were also studied. The results contribute to the diagnosis of the current conservation state of the wall painting for its future restoration. Copyright © 2011 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: Raman spectroscopy; wall painting; work of art; pigment identification

# Introduction

Material recognition and/or characterization are important steps in the study of objects associated with cultural heritage. By knowing the different chemical species present in a work of art, valuable information can be obtained. This information can lead to knowledge of the object and, in the process, to a better comprehension of its conservation as a whole. Also, in some cases it could help restorers to take the best options in terms of the procedures to be carried out on the object. Vibrational spectroscopy, a well-known structural analysis tool, with the infrared (IR), Raman and surface-enhanced Raman scattering, as well as the recently developed Raman instrumentation, has been extensively used in conservation science.<sup>[1–4]</sup>

The benefits of Raman spectroscopy are obvious, as only a minimal amount of sample is usually needed. Even better, in many cases the data can be collected *in situ* (where the object is located)<sup>[5]</sup> or upon the object itself. The spectral data collection process is also nondestructive,<sup>[6]</sup> which is an enormous advantage over other methods for molecular identification. Also, the degradation products of pigments<sup>[7]</sup> can be recognized, giving information about the causes of deterioration.

In a recent publication, Donais *et al.*<sup>[8]</sup> used a portable X-ray fluorescence (XRF) spectrometer and portable Raman spectrophotometer to study pigments found on the fresco at the Coriglia, Castel Viscardo excavation site near Orvieto, Italy. Numerous fresco samples were analyzed. The identified pigments included vermillion, red ochre, yellow ochre, terre verte, Egyptian blue, and hematite. Appolonia *et al.*<sup>[9]</sup> combined FORS, XRF, and Raman spectroscopy in the study of mural paintings in the Aosta Valley (Italy). On the basis of the information obtained, the palette was found to be composed of typical fresco pigments such as calcite, azurite, malachite, vermilion, and red and yellow ochre.

Raman microscopy was selected as one of the analytical techniques chosen to analyze different materials related to the wall painting *Historia de Concepción* by Gregorio de la Fuente (1910–1999) (Fig. 1a–c), under the project *Estudio Diagnóstico del* 

Estado de Conservación del Mural Historia de Concepción para su Restauración y Mantención.

The scope of the present analysis concerns three aspects: (1) to support the characterization of the technique used to paint this artwork, which is said to be a fresco, rarely used in Chile; (2) to document the materials employed in the artwork, because due to any damage caused by an earthquake to the building and to the wall painting itself, the risk of losing this artwork is real; and (3) to infer about the different processes that may be the cause of the strong pulverization affecting the painting layer, by identification of the decay products. Because of some visually notorious interventions made by Gregorio De La Fuente in 1987, pigments from his studio were collected and analyzed, in order to compare them with those obtained from the wall painting.

The data obtained are an important part of a set of analytical results that became crucial to better understand this wall painting, and are part of the scientific base expected to contribute to the diagnosis of the current conservation state of the wall painting for its future restoration.

## Experimental

The wall painting, originally called *Latidos y Rutas de Concepción*, was painted between 1943 and 1946, in the former Main Train Station of Concepción, Chile. The building passed through a period of abandonment before it was recovered to host the Regional Government of Bío Bío. The recent earthquake of February 27, 2010, inflicted even more damage to the wall painting, which is made of a mortar arrangement fixed to

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Figure 1. Wall painting *Historia de Concepción*, left (a), central (b) and right wall (c).

the wall. The total area of the painting is about  $258 \text{ m}^2$ , and a restoration by the author himself was carried out in 1987.

#### Sample collection

Samples were collected in January 2010. Samples of dimensions  $0.5-1 \text{ mm}^2$  were collected with a brush and scalpel from the wall painting, and selected by two criteria: get samples of the main colors displayed in the artwork; and collect samples from zones where it is suspected that, according to historical data, they were altered after its creation. Figure 1(a-c) displays the whole painting, showing the spots from where the samples were collected. Pigments from De La Fuente's studio were also collected to compare them with the analyzed samples. The main identified species are described in Table 1. The selection criterion was the color observed in the artwork.

#### Spectroscopic measurements

Raman spectra from samples of the pigments, the superficial salts, and the contaminated areas were collected using a Renishaw micro-Raman System 2000 with 785 and 633 nm laser lines and a Leica microscope. The incident radiation was focused on the spot to be analyzed through a  $50 \times$  objective. The spectra are reported from 100 to 1800 cm<sup>-1</sup>, as no conclusive bands were observed above this range. The samples were exposed for 10 s to the laser beam, taking 1-5 accumulations. Spectral data of the organic material in the whole spectral range is available on request. The laser power was set in the range 1-10%, obtaining a maximum power on the sample of 0.14 mW. General scan conditions were chosen in order to avoid sample photodecomposition or photobleaching. The Fourier transform infrared (FTIR) spectra in KBr pellets of samples 7 and 16 (from the studio) were registered by using a Perkin-Elmer series 2000 apparatus. The spectra were registered with a resolution of 4 cm<sup>-1</sup>. This spectrometer operates with a deuterated triglycine sulfate (DTGS) detector.

# **Results and Discussion**

The spectra obtained were compared with published data<sup>[10-13]</sup> and online libraries.<sup>[14,15]</sup> The results are summarized in Table S1 (Supporting Information), indicating the color, the corresponding mineral, the formula, and the main Raman bands. The spectra are shown as obtained and are illustrated along with the discussion.

The predominant pigments in the present artwork are mostly metal oxides, in agreement with that observed in other similar artworks.<sup>[16]</sup> Moreover, calcium carbonate is identified by its Raman spectrum, displaying the characteristic symmetric stretching mode near 1090 cm<sup>-1</sup>.<sup>[17,18]</sup> This information, along with historical data, the cross-section of the wall painting, and the absence of organic binders, provide confirmation that the artwork is a fresco.

The samples to be identified are classified according their color. Some physical and chemical characteristics, along with Raman spectral information, are displayed in Table S1.

#### **Red samples**

Raman spectroscopy has been used to identify pigment mixtures.<sup>[19-21]</sup> Red samples (Table 1) are mainly iron(III) oxide, also called hematite. Some mixtures of hematite and minium (lead(II,IV) oxide) have been observed (Fig. 2), and are recognized by the characteristic Raman bands of Fe(III) and Pb(II,IV) oxides. Hematite stretching bands corresponding to the Fe-O bond are observed at 222 and 494 cm<sup>-1[22]</sup>; the deformation modes are assigned to the bands at 240, 290, 407, and 612 cm<sup>-1</sup>, following Legodi et al.<sup>[23]</sup> The Pb(IV)–O stretching mode is observed at 548 cm<sup>-1</sup>, while the O-Pb(IV)-O deformation mode corresponds to the band at  $118 \text{ cm}^{-1}$ ; the stretching Pb(II)–O is ascribed to the band at  $147 \text{ cm}^{-1}$ , in agreement with Bussotti *et al.*<sup>[24]</sup> It has been shown that minium should not be used for the fresco technique,<sup>[25]</sup> as dismutation reactions occur in acid and alkali media,<sup>[26]</sup> producing PbO<sub>2</sub> (plattnerite). Here, PbO<sub>2</sub> was not detected spectroscopically. Fortunately, hematite, which is highly compatible with any binder and largely used in all kinds of paintings, does not display collateral reactions in the present artwork (collateral reactions as those concerning blackening process<sup>[27]</sup> or those mentioned above for minium). On the basis of XRF data, it can be proposed that iron-containing molecular species are the ones mainly responsible of the red color in areas from where no

# RAMAN SPECTROSCOPY

Table 1. Analyzed samples and identified species				
Color	Sample	Wall	Description	Identified species <sup>a</sup>
Red	M4	Central	Girl on bike	<b>Fe<sub>2</sub>O<sub>3</sub>, Pb<sub>3</sub>O<sub>4</sub></b> , CaCO <sub>3</sub>
	M6	Central	Apple	Fe <sub>2</sub> O <sub>3</sub> , Pb <sub>3</sub> O <sub>4</sub> , CaCO <sub>3</sub> , CaSO <sub>4</sub> · 2H <sub>2</sub> O
	M15	Central	Belt	<b>Fe<sub>2</sub>O<sub>3</sub></b> , C <sub>17</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> , CaCO <sub>3</sub> , CaSO <sub>4</sub> · 2H <sub>2</sub> O
	M21	Left	Plant	$Fe_2O_3$ , CaCO <sub>3</sub> , CaSO <sub>4</sub> · 2H <sub>2</sub> O
Blue	M7	Central	Kilt	Na <sub>8-10</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>29</sub> ]S <sub>2-4</sub> CaSO <sub>4</sub> · 2H <sub>2</sub> O, CaCO <sub>3</sub>
	M13	Central	Locomotive wheel	$Na_{8-10}[AI_6Si_6O_{29}]S_{2-4}$
	M17	Central	Kilt in fissure	<b>Na<sub>8-10</sub>[Al<sub>6</sub>Si<sub>6</sub>O<sub>29</sub>]S<sub>2-4</sub></b> , CaCO <sub>3</sub> , Cr <sub>2</sub> O <sub>3</sub> , CaSO <sub>4</sub> · 2H <sub>2</sub> O
	M19	Central	Rider soldier	Na <sub>8-10</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>29</sub> ]S <sub>2-4</sub> , CaCO <sub>3</sub> , CaSO <sub>4</sub> · 2H <sub>2</sub> O, SiO <sub>2</sub>
	M25	Left	Kilt	$Na_{8-10}[Al_6Si_6O_{29}]S_{2-4}$ , CaCO <sub>3</sub> , CaSO <sub>4</sub> · 2H <sub>2</sub> O, C
Green	M8	Central	Miner bonnet	$\textbf{Cr_2O_3}, Na_{8-10}[Al_6Si_6O_{29}]S_{2-4}, CaCO_3, SiO_2, CaSO_4 \cdot 2H_2O$
Yellow	M20	Central	Saddle	$\alpha$ - <b>FeO(OH)</b> , CaCO <sub>3</sub> , CaSO <sub>4</sub> · 2H <sub>2</sub> O
Black	M11	Central	Coal	C, CaCO <sub>3</sub> , CaSO <sub>4</sub> · 2H <sub>2</sub> O
White	M14	Central	Horseman belt	$CaCO_3$ , SiO <sub>2</sub> , CaSO <sub>4</sub> · 2H <sub>2</sub> O
Brown	M9	Central	Miner face	<b>Fe<sub>2</sub>O<sub>3</sub></b> , C, CaCO <sub>3</sub>
	M22	Left	Indian feet	<b>Fe<sub>2</sub>O<sub>3</sub>, C</b> , CaCO <sub>3</sub> , α-FeO(OH)
Colorless	M10	Central	Miner face	<b>Na<sub>2</sub>SO</b> <sub>4</sub> , CaCO <sub>3</sub> , CaSO <sub>4</sub> · 2H <sub>2</sub> O
	M12	Central	Locomotive front	Na <sub>2</sub> SO <sub>4</sub>

<sup>a</sup> Main colored compounds are in bold.



Figure 2. Raman spectra of iron(III) oxide (a), lead (II,IV)oxide (b), and their mixture (c), found on red samples.

samples were collected. XRF data are not shown in the present work; they are available on request.

Toluidine red (PR3), an organic red pigment,<sup>[28]</sup> was identified by Raman spectroscopy<sup>[11]</sup> (Fig. 3). According to general vibrational charts,<sup>[29,30]</sup> bands at 1629 and 1503 cm<sup>-1</sup> are assigned to spectral modes of the NO<sub>2</sub> group and aromatic CC stretching. The band at 1452 cm<sup>-1</sup> is unambiguously ascribed to a CH<sub>3</sub> deformation mode. The N=N bond displays its band at 1402 cm<sup>-1</sup>. The strong bands at 1338 and 1325 cm<sup>-1</sup> are assigned to the asymmetric and symmetric stretching modes of the nitro moiety, respectively. Signals at 1221, 1190, and 1131 cm<sup>-1</sup> correspond to CH aromatic



**Figure 3.** Raman spectrum of sample M15 (a) and toluidine red structure (b). The marked bands are ascribed to barium sulfate.

deformation modes. The corresponding out-of-plane modes are assigned to bands at 1080, 844, 797, and 723 cm<sup>-1</sup>. Bands lower than 500 cm<sup>-1</sup> are in general difficult to assign; we propose that the bands at 379 and 337 cm<sup>-1</sup> are due to skeletal ring modes. Thus, the performed spectral assignment confirms the presence of toluidine red. The bands at 988, 616, and 453 cm<sup>-1</sup> are due to the barium sulfate used as filler in this pigment.<sup>[11]</sup>

## Blue samples

Blue pigments are vibrationally identified as ultramarine blue  $(Na_{8-10}[Al_6Si_6O_{29}]S_{2-4})$ , in agreement with the published data.<sup>[11]</sup> Ultramarine blue is a matrix composed by sodium aluminosilicate salts and sulfur anions  $(S_3^-, S_2^-)$ , and corresponds to synthetic lazurite, the substitute of natural *lapis lazuli*. The band observed at



Figure 4. Polished cross-section (a) and Raman spectrum (b) of sample M8.

547 cm<sup>-1</sup> is ascribed to the  $S_3^-$  ( $C_{2\nu}$ ) symmetric stretching mode; this molecular moiety is responsible for the blue color.<sup>[31]</sup> The  $S_2^$ anion (yellow) gives rise to the green tones associated with some ultramarine pigments. Because of its very low concentration in the blue pigments,<sup>[12]</sup> the corresponding  $S_2^-$  signal in the present case appears as a shoulder at about 580 cm<sup>-1</sup> with very weak intensity, Fig. S1a (Supporting Information). The color in ultramarine blue pigment is known to fade in acid and alkali media.<sup>[32]</sup> This fact contradicts what is observed in the wall painting.

#### **Yellow samples**

The yellow colors in the wall painting (Fig. S1b) are mainly due to  $\alpha$ -FeO(OH), in agreement with Correia *et al.*<sup>[13]</sup> and Bell *et al.*<sup>[10]</sup> which is called in its mineral form as goethite. This pigment is characterized by the Fe–OH symmetric deformation mode at 298 cm<sup>-1</sup>, the Fe–O–Fe/OH symmetric stretching at 386 cm<sup>-1</sup>, and the Fe–OH asymmetric stretching vibrations at 480 and 550 cm<sup>-1</sup>.<sup>[23]</sup> The band observed at 1091 cm<sup>-1</sup> belongs to calcite.

#### **Black sample**

Samples containing the black pigment display bands at about 1595 and 1319 cm<sup>-1</sup> (Fig. S1c), which are assigned to G and D1 stretching CC modes of amorphous carbon.<sup>[33,34]</sup> This pigment, called carbon black,<sup>[28]</sup> has been also used to give dark tones in some of the present samples. The absence of the band at 960 cm<sup>-1</sup>, which is attributed to symmetric stretching modes of the phosphate fragment in calcium phosphate,<sup>[35]</sup> suggests the vegetal origin of the coal in the fresco, although it cannot be excluded that it is of animal origin. The weak band observed at 1089 cm<sup>-1</sup> corresponds to calcite.

#### White sample

No white pigments were identified in the studied samples. The observed white color in sample M14 is due to calcium carbonate (band at 1089 cm<sup>-1</sup>), which is the binder used in this painting technique. Gypsum (CaSO<sub>4</sub> · 2H<sub>2</sub>O) was identified in the same sample (Fig.S1d) through the band at 1010 cm<sup>-1</sup>, which is ascribed to the symmetric stretching of the sulfate fragment.<sup>[11,36]</sup> Gypsum in the wall painting can originate from diverse processes. The contamination of the original materials used by the artist should be considered, as the required amounts of lime and sand were massive and thus their purity could not be ensured. Another factor

could be environmental pollution in the form of  $SO_x$  atmospheric gases, which in combination with humidity may unleash acid attacks.<sup>[27]</sup>

#### **Green sample**

The green pigment mixed with small amounts of ultramarine blue can be observed from a polished cross-section of the sample (Fig. 4a). The green color is due to the chromium(III) oxide (Cr<sub>2</sub>O<sub>3</sub>), the main green chromophore in this fresco. The asymmetry of the Raman band (Fig. 4b) observed at 550 cm<sup>-1</sup> shows contributions from both lazurite (at ~547 cm<sup>-1</sup>) and the chrome green ( $A_{1g}$ band at ~552 cm<sup>-1</sup>). The band at 348 cm<sup>-1</sup> belongs to the  $E_g$ symmetry species.<sup>[37,38]</sup> Additionally, another green compound was observed in this sample as well as on the blue samples M7, M13, and M17; this compound matches with the one found in a pot in the studio of the artist and its identification is discussed below.

#### **Brown samples**

Brown colors observed (Fig. 1) are produced with hematiteand goethite-containing earth pigments. Earth pigments are commonly mixtures of clay materials with different chromophores such as those found in this case (hematite or goethite).<sup>[28]</sup> Spectra (Fig. S2) obtained from samples M9 and M22 suggest that earth pigments could have been, in some cases, darkened with carbon black.

#### Other components

The observed saline efflorescence (samples M10 and M12) was found to be mostly sodium sulfate<sup>[14]</sup> (Fig. S3), also called thenardite. Efflorescence is mainly caused by water infiltrations from inside the supporting walls of the building, which carry these salts to the surface. This compound, highly water soluble, when affected by humidity and temperature variations, undergoes crystallization and dissolution cycles. The strong band at 996 cm<sup>-1</sup> is due to the sulfate symmetric stretch in thenardite.<sup>[39]</sup> The efflorescence causes an irreversible damage in the painting surface, generating loss of the paint layer.<sup>[16]</sup> On the other hand, quartz crystals (SiO<sub>2</sub>), which are part of the sand used to make the mortars (both *arriccio*, the inner layer, and *intonaco*, the outer layer), are largely observed on the wall painting surface. Its main Raman band can be seen at 463 cm<sup>-1</sup> and corresponds to an  $A_1$  symmetry mode. As the observed amount of sand on the surface is unexpectedly high for an *intonaco*,<sup>[16]</sup> we infer that the artist intentionally produced the rough surface in order to create an innovative texture in this painting, which is his first fresco. This fact could also accelerate the deterioration processes associated with water condensation on the wall painting surface because the roughness generates a larger surface of contact for water action.

The presence of gypsum, discussed before, and thenardite represents a critical situation for the integrity of the wall painting. These salts seem to be the responsible for the fading of color probably due to the formation of white gypsum microcrystals on the surface, and for the loss of the painting layer in the case of the saline efflorescence. Because of the presence of sulfate pollutants and the *intonaco* composition, the inorganic methods, such as nanolime<sup>[40-42]</sup> and Ferroni-Dini,<sup>[43]</sup> seem to be the most suitable to intervene the painting layer. These methods are being tested in a parallel research.

#### Pigments from the artist's studio

Eighteen pigments collected form De La Fuente's studio were analyzed, and they are listed in Table S2. Hematite was identified as the main chromophore in the red pigments. The difference between all of them is the quantity of clay material in the iron-containing pigments, which produce different red tones. The amount of clay on red pigments can be noticed by the fluorescence background observed in their Raman spectra. Yellow pigment is the same as the one found on the wall painting, i.e. goethite ( $\alpha$ -FeO(OH)). Two blue pigments were identified as copper phthalocyanine and ultramarine blue; the others could not be identified because of the amount of fluorescence produced when measured. Green pigments from the studio were not identified, but in the case of pigments 7 and 16 they correspond to the green compound mentioned in the green sample M8. This compound could not be found in any library or published work. Valuable vibrational information is extracted from its Raman and IR spectra (Fig. 5). Both spectra clearly show bands (988 cm<sup>-1</sup> in Raman and 1190, 1122, 1076, 983, 639, and 611 cm<sup>-1</sup> in IR)<sup>[11,14]</sup> ascribed to barium sulfate, an inert compound commonly used as filler; the presence of chromium(III) oxide in this mixture is then discarded. At least one additional organic component in the pigment is inferred from the observed most intense vibrational bands. In the Raman spectrum, these bands are at 349, 446, 470, 533, 670, 754, 883, 1025, 1081, 1152, 1260, 1354, 1362, 1478, 1520, and 1597 cm<sup>-1</sup>. In IR, the most intense bands are at 470, 730. 749, 827, 876, 933, 1301, 1355, 1388, 1445, 1506, and 1591 cm<sup>-1</sup>. This set of bands is closely related to a copper phthalocyanine complex following published data;<sup>[11,44-46]</sup> but they could not be fully ascribed to that specific pigment.

Brown and black pigments (1, 18, 9, 14), Table S2, are mixtures of iron oxides. Black pigments are mainly composed of iron(II,III) oxide (FeO-Fe<sub>2</sub>O<sub>3</sub>), also known as magnetite. The presence of magnetite can be noticed by the band at about 668 cm<sup>-1</sup>.<sup>[47]</sup> When black pigments are exposed to high laser power, they get oxidized, producing a red spot of hematite.

# Conclusions

The most relevant chromophores along with additional components coming from chemical and physical deterioration processes



Figure 5. Raman (a) and infrared (b) spectra of pigment 16 collected from the artist's studio.

of the wall painting *Historia de Concepción* were analyzed and identified by means of micro-Raman spectroscopy. The pigments found are mostly in agreement with those expected for a fresco, except for toluidine red and minium. Spectral information concerning mainly pigments and composition on the surface clearly corresponds to the fresco technique and therefore helps confirming historical data.

The particular intensity of some yellow and blue zones on the wall painting and the exact match with the pigments analyzed from the studio allow us to infer that at least these two colors were repainted by De La Fuente. Although there is no information that could confirm that pigments collected from the studio are the same as the ones the author used to paint or repaint this fresco, it is possible to argue that the pigments found in the studio are the same materials used by Gregorio De La Fuente during his later works and in the restoration carried out by him in 1987. Thus, the pigments found in this fresco should be considered for further analysis on his work.

The pollutants identified suggest that the strong pulverization observed in this wall painting may be due to the successive transformation of calcite into gypsum. Gypsum crystals are so large that they detach sand from the calcite matrix. The pulverization of the painting layer produced by this phenomenon appears on the whole surface in different degrees. This suggests that sulfate impurities were present in the original materials used by the artist, and support the possibility of external pollutants acting on some areas that appear more affected today. The activation of dissolution cycles of sulfate impurities started with a water wash procedure over the painting surface performed by the artist. Thus, we do not discard the possibility that humidity and contaminated materials along with the restoration made by the author in 1987 triggered an acid attack on the painting layer of the artwork. Pulverization continues as a result of the high humidity in Concepción, Chile.

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#### **Supporting information**

Supporting information may be found in the online version of this article.

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