

The Sibyls from the church of San Pedro Telmo: a micro-Raman spectroscopic investigation[†]

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The series of the Sibyls from the church of San Pedro Telmo is one of the most important groups of paintings of Argentine colonial art. Ten of the paintings were performed in the 18th century, while those corresponding to the Delphic and Tiburtine Sibyls were painted in 1864 during the first restoration of the series in Buenos Aires. There is a controversy regarding the origin of this remarkable group of paintings pointing to an Andean workshop or a Spanish source. In this study, Raman microscopy in combination with scanning electron microscope energy-dispersive X-ray spectrometer analysis and HPLC has successfully identified the materials employed in the manufacture of the paintings. The Raman analysis revealed the presence of a mixture of barium sulfate, lead white, and calcite in the preparation layers of the 19th century Sibyls in contrast to the clayish ground layer in the 18th century paintings. Traditional pigments such as vermilion, lead white, orpiment, indigo, ultramarine blue, and Prussian blue were readily identified by Raman microscopy. The presence of a madder lake in one of the 18th century Sibyls strongly suggests their Spanish origin in accordance with historical data. The identification of synthetic ultramarine blue in the Tiburtine painting is the first report of this blue pigment in Argentine colonial art. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: pigments; micro-Raman spectroscopy; colonial art; HPLC; SEM-EDS

Introduction

The series of the Sibyls, belonging to the church of San Pedro Telmo in Buenos Aires, is one of the most important groups of paintings of Argentine colonial art. It is essentially based, from the iconographic point of view, on engravings by Crispijn de Passe.^[1] These 12 paintings, one of the few complete series, depict the Sibyls prophesying on episodes of the life of Christ. Some controversies related to the origin of this remarkable group divided the positions between an Andean workshop and a Spanish source.^[2–4] Ten of the paintings were performed in the 18th century, while those corresponding to the Delphic and Tiburtine Sibyls were painted in 1864 during the first restoration of the series performed in Buenos Aires in order to possibly replace the originals because of their poor state of conservation. After the cleaning process, carried out in a recent restoration in 2005, the difference between the relatively limited palettes used in the original Sibyls in contrast with the colorful one employed in the two 19th century copies was evident. However, the cleaning also made clear the skillful execution technique exercised during the creation of the 18th century group.^[1]

The aim of the present work was to contribute to the study of this colonial series by characterization of its palette in order to add to the elucidation of its origin, pictorial technique, and deterioration patterns. Also, a comparison between the 18th and 19th century palette was carried out to evaluate the evolution in pigment uses within the region. Therefore, a set of samples taken from four of the paintings (Fig. 1, Table 1) were studied by micro-Raman spectroscopy in order to identify the pigments and components from the pictorial and preparation layers. Complementary information was obtained by light microscopy, high-performance liquid chromatography (HPLC), and scanning electron microscope energy-dispersive X-ray spectrometer (SEM-EDS) analysis.

Experimental

Sampling was carried out during the restoration process and after careful examination of the paintings with different imaging techniques in order to distinguish original from repainted areas. A discussion with conservators and art historians was also taken into account in selecting sampling areas. After photographic documentation, microsamples were mounted in methacrylate transparent resin (Subiton), and polished cross sections were prepared according to traditional techniques. Observation and photography of the samples' cross sections were achieved using a Leica DM EP microscope equipped with visible and ultraviolet light sources in the normal and polarized modes. Images were recorded with a Leica DFC280 camera using Leica Application Suit 4.0 software to acquire and process them (Fig. 2).

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Figure 1. Sampling positions on the 18th century Sibyls (a) Samia and (b) Libica and on the 19th century Sibyls (c) Delphic and (d) Tiburtine. The paintings' sizes are 117.5 × 92.5 cm.

Elemental chemical analyses of the layers of the cross sections were obtained by using a field environmental SEM Zeiss Supra 40 coupled with an EDS microanalysis INCA X Sight, Oxford Instruments. Several measurements were performed on selected areas or certain grains of each layer of the samples.

Raman spectra were recorded using a LabRAM HR Raman system (Horiba Jobin Yvon), fitted with 1800 grooves per mm and a 1024 × 258-pixel charge-coupled device detector, resulting in spectral resolution of 1.2 cm⁻¹; the spectrograph was coupled to an imaging microscope with 10×, 50×, and 100× objectives. Typically, for a 50× magnification, the spot size diameter was about 2–3 μm. Two different laser excitation sources were used (λ_0): 514.5 nm (Ar⁺) and 632.8 nm (He–Ne). It is well known that some compounds present different response depending on the excitation line. Each sample was analyzed using the most suitable laser. Excitation lines were filtered to give a laser density power at the sample varying from 70 to 160 kW cm⁻². Several measurements were performed, adjusting the laser density power, in order to ensure that the heating produced by the laser was minimized and the sample was not altered. To register the Raman spectra of

the samples, several different points from each pigment were randomly taken under the same conditions. Each spectrum was averaged over four scans corresponding to a collection time of 30 s. To improve some Raman spectra that exhibited a strong luminescent background, the smoothing tool from LabSpec software was applied. The baseline correction tool from the same software was also used with different polynomial fitting regarding each spectrum.

Analytical HPLC with diode array detection (HPLC-DAD) was carried out on a Gilson 506C HPLC system using a Phenomenex Gemini 5-μm column (25-cm × 4.6-mm internal diameter). Gradient elution was performed using two solvents, A, MeOH and B, 1% (v/v) aqueous orthophosphoric acid. The gradient started with 36% A during 5 min and was raised to 90% A within 10 min, followed by 20 min at this condition. Solvents utilized in the HPLC were filtered through a 0.2-μl filter prior to use. The flow rate was 0.8 ml min⁻¹. Hydrolysis of samples S-3 and L-4 was performed following the procedure described previously.^[5] The reference sample of madder lake (Madder Lake, genuine, 37200-B) was supplied by Kremer Pigmente.

Results and discussion

Preparation layers

Light microscopy examination of cross sections of the samples revealed different preparation layers in the 18th and 19th century

Table 1. List of pigments and preparation layer materials determined		
Sample (color)	Pigments	Preparation layer
18th century Sibyls		
S-1 (green; repaint)	Ultramarine blue, As_2S_3 , lead white	Clay
S-2 (red)	Vermilion	Clay
S-3/S-5 (red)	Madder lake	Clay
S-4 (blue)	Indigo, lead white (upper layer), Prussian blue, cerussite (bottom layer)	Clay
L-1 (green; repaint)	Ultramarine blue, As_2S_3 , lead white	Clay
L-2 (white)	Lead white	Clay
L-3 (red)	Vermilion	Clay
L-4 (orange)	As_2S_3 , organic yellow lake	Clay
19th century Sibyls		
D-1 (red)	Vermilion	Barium sulfate, lead white, calcite
D-2 (carnation)	Vermilion, lead white	Barium sulfate, lead white, calcite
T-1 (blue)	Ultramarine blue	Barium sulfate, lead white, calcite
T-2 (red)	Vermilion	Barium sulfate, lead white, calcite

Sibyls (Fig. 2(a) and 2(b), respectively). SEM-EDS analysis of the preparation layer of the red sample (L-3) taken from the hat of the Libica Sibyl, 'Fig. S1 (Supporting Information)', indicated the presence of silicon as the major element together with minor amounts of calcium, aluminum, potassium, sulfur, and magnesium. This elemental composition suggested the use of a clayish ground layer, which was in accordance with the high fluorescence depicted in the Raman spectrum that prevented material identification by this technique. Analysis by SEM-EDS of the preparation layers of the 19th century Sibyls, Tiburtine and Delphic, 'Fig. S1 (Supporting Information)', showed the presence of barium, calcium, sulfur, and lead as the major elements, together with iron and silicon. The Raman spectrum obtained for the preparation layer of the red sample (T-2) from the Tiburtine Sibyl (Fig. 3) consisted of a mixture of barium sulfate ($BaSO_4$) with its characteristic band at 989 cm^{-1} , lead white ($2PbCO_3 \cdot Pb(OH)_2$) with two bands at 1049 and 1055 cm^{-1} , and calcite ($CaCO_3$), which gives rise to a band at 1085 cm^{-1} .^[6] The mixture of barium sulfate and lead white is in agreement with the typical composition of commercial 19th century ground paints.^[7–9] Calcite was commonly mixed with lead white in ground paint preparations.

Blue paint areas

Light microscopy examination of the cross section of the blue sample (S-4), detached from the tunic of the Samia Sibyl, showed two strata in the pictorial layer (Fig. 2(c)). Analysis by Raman spectroscopy of the upper blue stratum indicated the characteristic bands of indigo at 539 , 594 , 759 , 1145 , 1247 , 1308 , 1361 , 1462 , 1573 , and 1693 cm^{-1} together with those of basic lead carbonate at 1054 and 1055 cm^{-1} (Fig. 4(a)).^[6] This blue dye obtained from plants of the family Papilionaceae was used for developing the chiaroscuro and the details of blue surfaces.^[10]

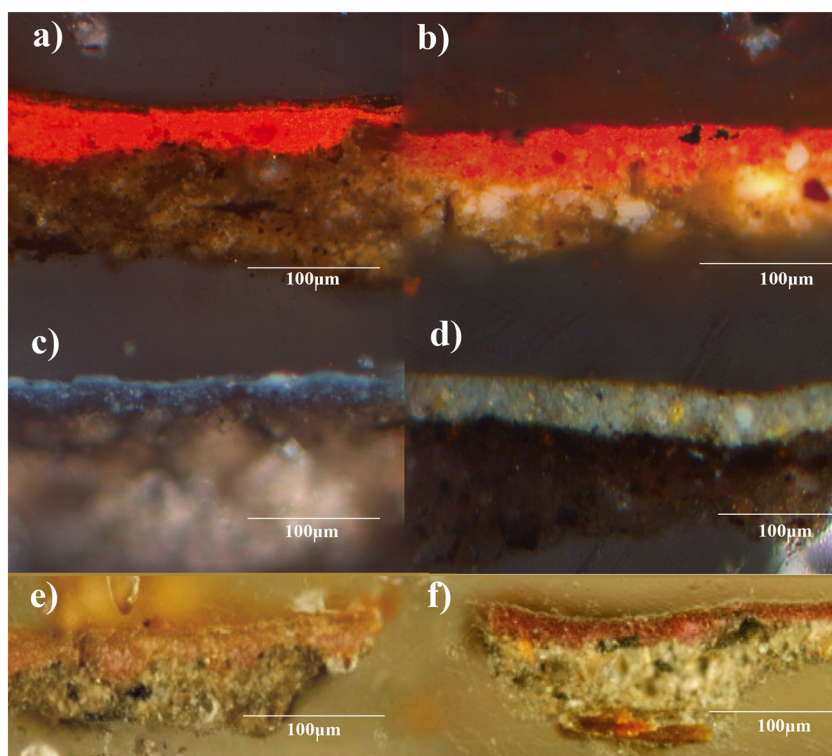


Figure 2. Cross sections of samples L-3 (a), T-2 (b), S-4 (c), L-1 (d), S-3 (e), and S-5 (f) under visible polarized light (200 \times). The stratigraphy of T-2 is the only one corresponding to a 19th century Sybil.

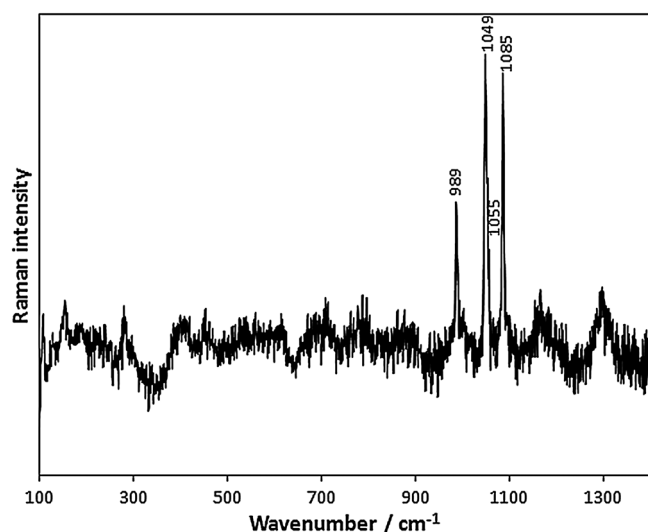


Figure 3. Raman spectrum of the mixture of lead white, calcite, and barium sulfate in the preparation layer from sample T-2.

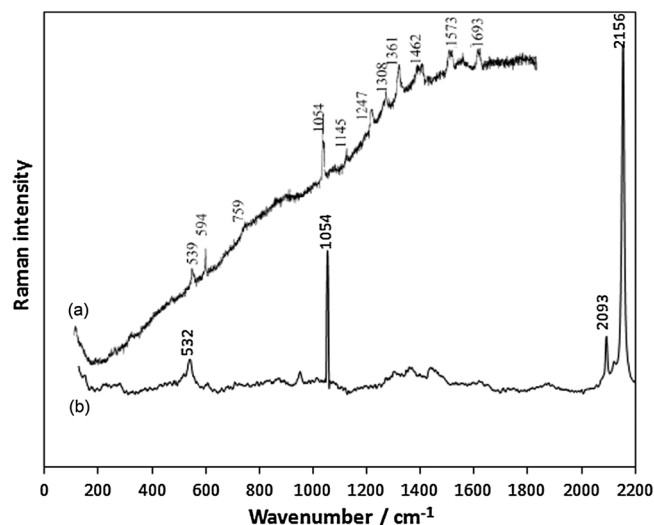


Figure 4. Raman spectra of blue pigments from sample S-4. (a) Upper stratum (indigo and lead white) and (b) bottom stratum (Prussian blue and cerussite).

The Raman spectrum of the bottom blue layer showed the characteristic bands of Prussian blue at 532, 2093, and 2156 cm^{-1} together with a strong band at 1054 cm^{-1} assigned to cerussite (PbCO_3 ; Fig. 4(b)). Basic lead carbonate and cerussite can be easily distinguished by Raman spectroscopy. Basic lead carbonate presents two strong bands at 1049–1055 cm^{-1} , while cerussite shows one strong band at 1054 cm^{-1} .^[12] The identification of basic lead carbonate and cerussite in the same painting sample is not uncommon because of variations in the composition of lead white pigments according to manufacturing processes.^[13] Prussian blue is a hydrated iron hexacyanoferrate complex, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$, that was synthesized for the first time by Diesbach in Berlin in 1704.^[14] Indigo and Prussian blue, the latter not before than 1770, have been the pigments most employed in the workshops of Cuzco in the 18th century, followed by azurite and smalt,^[15,16] but they were also extensively used in European art.^[10,14]

The blue paint sample that was taken from the feather of the hat from the Tiburtine Sibyl (sample T-1, Fig. 1) consisted of a mixture of ultramarine blue, with very well defined bands at 258, 546, and

1091 cm^{-1} ,^[11] and lead white with a weak band at 1055 cm^{-1} in the Raman spectrum (Fig. 5(a)). Lazurite was obtained from lapis lazuli by a laborious extraction procedure of the blue particles. It is a complex sulfur-containing sodium aluminum silicate, $(\text{Na,Ca})_8(\text{AlSiO}_4)_6(\text{SO}_4, \text{S}, \text{Cl})_2$, that may be accompanied by some natural impurities, such as diopside ($\text{CaMgSi}_2\text{O}_6$), forsterite (Mg_2SiO_4), calcite (CaCO_3), and pyrite (FeS_2).^[17,18] Because of the high cost of good-quality ultramarine, the pigment had been often reserved for painting the robes of Christ and the Virgin. In 1828, an artificial ultramarine was synthesized by Jean-Baptiste Guimet and adopted by European artists. Lazurite and synthetic ultramarine blue may be differentiated by optical microscopy according to the size and morphology of their particles. Synthetic pigment particles have a rounded shape, and they are small and very uniform in size, ranging from 5 and up to 10 μm in diameter. Their size is smaller than lazurite, although some time, synthetic particles can form aggregates when they are not well dispersed in the medium.^[19] In contrast, lazurite particles are larger, 20 to 50 μm , with size depending on the source. For instance, lazurite particles from Afghanistan have a similar size than the synthetic ones (5–10 μm); however, they have a more variable shape, and their morphology presents well-defined sharp edges.^[17] In the present case, the size of the particles was calculated (around 500 measurements taken from the blue stratum), and the average diameter was under 10 μm . The morphology showed uniform particles mostly rounded with just some particles with relatively sharp edges. In addition, in our sample, the granules are opaque in accordance with those from synthetic ultramarine blue.^[18] Considering these data and the fact that this painting was manufactured in 1864, it is highly probable that synthetic ultramarine had been used as the blue pigment.

The green paint areas

Light microscopy examination of the cross section of the green sample (L-1; Fig. 2(d)) taken from the garland of the Libica Sibyl revealed a mixture of blue and yellow pigments in the green layer. The Raman spectrum of the blue particles indicated the presence of ultramarine blue (main bands at 258, 546, and 1091 cm^{-1}). The yellow component showed a Raman spectrum with bands at 137, 155, 203, 293, 312, 354, and 383 cm^{-1} characteristic of orpiment (As_2S_3),^[11] Fig. S2 (Supporting Information). In addition, SEM-EDS

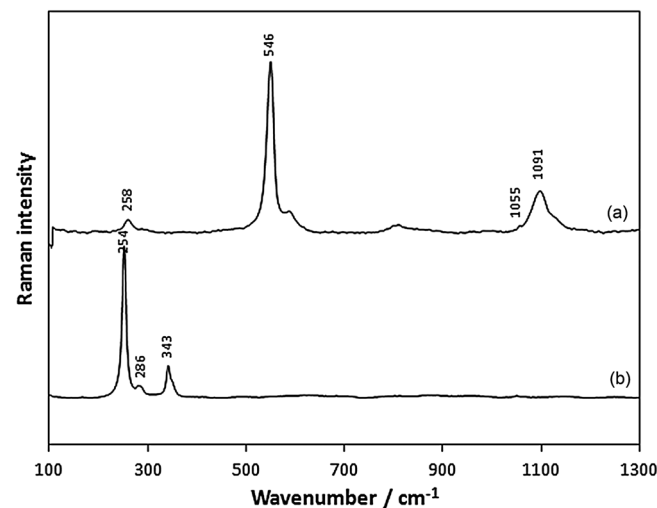


Figure 5. Raman spectra of (a) ultramarine blue and lead white in the blue layer from sample T-1 and (b) vermilion in the red layer of sample S-2.

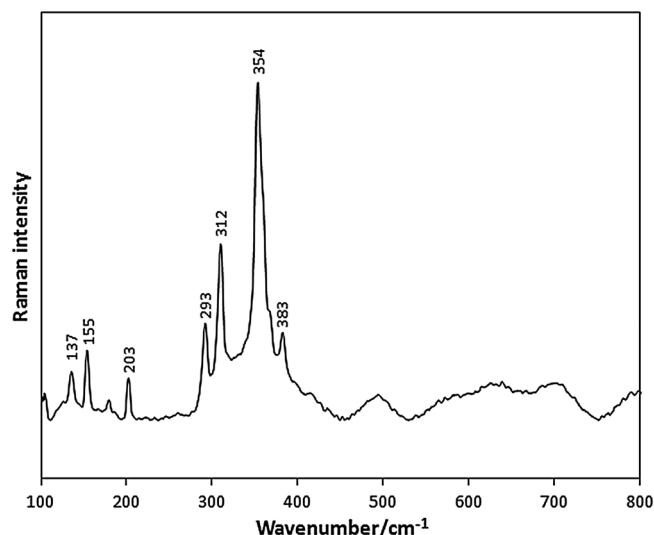


Figure 6. Raman spectrum of orpiment in the orange layer from sample L-4.

analysis of the green layer indicated the presence of lead, in accordance with the identification of lead white by Raman spectroscopy, together with sulfur and arsenicum, 'Fig. S3 (Supporting Information)'. The same pigment composition was determined for the green pigment of sample S-1 taken from the garland from the Samia painting (Fig. 1). Taking into account that the blue pigments used in the manufacture of the Samia Sybil painting were indigo and Prussian blue and that synthetic ultramarine blue has been identified in the 19th century Tiburtine Sybil, it may be probable that the garlands in the 18th century Sybils were repainted during the first restoration of the series in Buenos Aires.

The red paint areas

In the red cloak of the Samia Sibyl, the examination of the cross sections of two samples, one from the highly faded area (S-3; Fig. 2(e)) and another from the border area beneath the frame (S-5; Fig. 2(f)), pointed to an organic red lake, which could not be identified by Raman spectroscopy. SEM-EDS analysis of the red layer of sample S-5 indicated lead, silicon, calcium, and sulfur as the major elements together with minor amounts of copper. This elemental composition suggests a lake of a calcium compound.^[20] A microsample from the unfaded red area was hydrolyzed for dyestuff identification with HPLC-DAD, 'Fig. S4 (Supporting Information)'. The organic dye found in the sample was a mixture of alizarin and purpurin, the main anthraquinone colorants of madder, which comes from the roots of *Rubia tinctorum*.^[20] Although red lakes have been used in colonial art, only carmine, the red lake obtained from cochineal, has been identified in paintings from the Andean region.^[3] Therefore, identification of a madder lake suggests a Spanish origin of the series in accordance with historical data.^[11]

Analysis by Raman spectroscopy (Fig. 5(b)) of the sample extracted from the red flower from the Samia Sibyl (S-2) indicated vermilion (254, 286, and 343 cm^{-1})^[11] as the intense red pigment, which was also identified in samples L-3, T-2, and D-1 as well as in a mixture with lead white in the finger carnation of the Delphic Sybil (D-2).

Orange paint area

Interestingly, the Raman spectrum obtained for the yellow layer of the cross section of sample L-4 (Fig. 1) consisted of bands characteristic of

orpiment (As_2S_3 ; Fig. 6).^[11] Nevertheless, the fading pattern of the orange area from the bottom of the painting pointed to an organic pigment used as a glaze, which could not be identified by Raman spectroscopy. Acid hydrolysis of a microsample gave a yellow solution, which was analyzed by HPLC-DAD, 'Fig. S5 (Supporting Information)'. The UV spectrum of the major peak in the chromatogram showed bands at 258 and 428 nm in accordance with the presence of an organic pigment. Nevertheless, further studies are required to assign its structure. Although orpiment has been identified in paintings from the Andean region,^[12,21] this is the first time that a yellow organic pigment is reported for colonial art.

Conclusions

The application of Raman microscopy in combination with SEM-EDS analysis and HPLC allowed the identification of the materials employed in the manufacture of the Sibyl paintings. Optical microscopy was useful to determine the painting technique. Raman spectroscopy proved to be very valuable in the identification of barium sulfate, lead white, and calcite in the preparation layers of the 19th century Sibyls in contrast to the clayish ground layer in the 18th century paintings as well as in the identification of traditional pigments as vermilion, orpiment, lead white, ultramarine blue, indigo, and Prussian blue. The identification of a madder lake in one of the 18th century Sibyls strongly suggests their Spanish origin. The identification of synthetic ultramarine blue in the Tiburtine painting is the first report of this pigment in a colonial artwork. Our Raman study offered new insights in the attribution of the origin of this outstanding group of paintings and contributed to increase our knowledge on colonial art.

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Supporting information

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