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Micro-Raman spectroscopy of carbon-based black pigments[†]

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Carbon-based black pigments are a wide group of dark-colored materials, which are classified according to the starting material used and their method of manufacture. Raman spectroscopy is an ideal technique for the characterization of carbonaceous matter: crystalline carbon materials present well-defined peaks, which can be easily assigned; amorphous carbon materials, on the other hand, show broad bands between 1300 and 1600 cm^{-1}. The aim of this work was the discrimination between carbon-based pigments by micro-Raman spectroscopy. Five carbon-based pigments provided by Zecchi (lampblack, ivory black, bistre, bitumen, and graphite), two humic-earth materials [Van Dyck (Kremer) and Earth of Kassel (Zecchi)], and a commercial wood charcoal were studied. Raman spectra of all the samples showed the characteristic bands at approximately 1580 and 1350 cm^{-1}; however, a clear difference in position, width, and relative intensity could be observed for most of the samples. The resulting analysis showed that micro-Raman spectroscopy allowed the discrimination of most of the reference pigments and allowed the identification of carbon-based black pigments in two South American colonial paintings dated from the early 18th century. Copyright © 2012 John Wiley & Sons, Ltd.

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Keywords: carbon-based pigments; micro-Raman spectroscopy; art and archaeology; colonial art

Introduction

Black and dark-colored pigments can be found in all types of artwork, such as archaeological artifacts, rock art, easel, and wall paintings.[1–3] There is a wide variety of sources for these pigments, depending on the materials and the techniques of manufacture used by different cultures.[3–5] Within the variety of black pigments, carbon-based ones form a very diverse group that includes several subgroups, such as crystalline carbons, flame carbons, chars, cokes, and black earths. Their names are often confused because each discipline labels the materials according to different categories.[1,6,7] The classification proposed by Winter[1] is chosen in this work because it is based on the starting material used for the manufacture of the pigment.

An unambiguous identification of carbon-based pigments used in art and archaeology still remains a challenge owing to the variety of sources and manufacturing processes used in their preparation. Traditionally, X-ray diffraction, scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS), or a combination of these techniques, are applied to pigments characterization.[1,2] However, in the last decades, vibrational spectroscopic techniques, such as infrared and Raman spectroscopy, have played an important role not only in scientific laboratories but also in museums and archaeometry laboratories.[2,8–10] These techniques allow the identification of organic and inorganic compounds, as crystalline and amorphous structures, with a small sample requirement.[9–11] In particular, Raman spectroscopy is a very useful technique for pigment characterization.[9] A great number of libraries are available to identify a variety of materials used in art and archaeology.[9,12–15] Although many pigments, resins, and binders have been characterized by Raman spectroscopy[12–15] and the presence of a carbon-based pigment can be easily assessed by Raman, there were no attempts to discriminate between carbon-based black pigments from different origins by spectral analysis.

Raman spectroscopy is an ideal non-destructive technique for the characterization of a variety of carbon materials such as diamond, graphite, amorphous carbon, coals, nanotubes, and fullerenes.[16–21] This technique is sensitive to crystalline and amorphous structures, allowing the study of highly disordered materials, such as carbon-based pigments.

The Raman spectrum of crystalline graphite consists of a narrow band at 1580 cm^{-1} corresponding to the zone center E_{2g} mode known as G band (‘graphite’), which is assigned to the in-plane stretching vibration mode. On the other hand, the Raman spectrum of disordered or microcrystalline graphite, also known as glassy carbon, presents an additional band around 1350 cm^{-1} known as D band, often called the ‘disorder’ band, attributed to a zone

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boundary graphite mode with A_{1g} symmetry.[22–25] In amorphous carbon, the Raman spectrum corresponds to a vibrational density of states and is characterized by broad bands around 1550 and 1350 cm^{-1},[22,26] together with the second order bands in the 2200–3400 cm^{-1} region attributed to overtones and combinations of graphitic lattice vibration modes.[16,23,27] It is now well established that Raman spectra of carbonaceous matter are sensitive to the degree of disorder or crystallinity of samples and that several spectral parameters such as G and D band positions, relative intensities, and band widths provide structural information and have helped to discriminate between samples from different origins, in some particular cases.[17–21] On the other hand, there is still some controversy around the use of D and G bands as representative of changes in the structure of amorphous carbon.[18]

In this work, seven carbon-based black pigments used in art and as references for archaeometric studies, together with a sample of commercial vegetable charcoal, were studied by micro-Raman spectroscopy. The samples showed similar spectra despite their different origins. The aim of this study was to find relevant parameters to distinguish between carbon-based pigments by micro-Raman spectroscopy and to extend this approach to the identification of carbon-based black pigments in two colonial paintings dated from the early 18th century.

Experimental

Carbon-based reference pigments were supplied by *Zecchi, Belle arte e restauro* [graphite (GRZ), lampblack (LBZ), bistre (BSZ), bitumen (BTZ), ivory black (IBZ), and Earth of Kassel (EKZ)] and by *Kremer Pigmente* [Van Dyck (VDK)]. For comparison purposes, a sample of algarrobo (*Prosopis sp.*) charcoal (CWC) was included. Table 1 lists sources and characteristics of the studied reference carbonaceous materials.

Furthermore, two microsamples were extracted from black areas of the figure of Leviathan in a wall painting (sample A) and an easel painting (sample C) from the churches of Copacabana de Andarmarca and Caquiaviri, Bolivia, respectively (Fig. 1). Both paintings, dated from the early 18th century, represent the eschatological themes of death, judgment, glory, and hell.[28] The pictures of the Last Four Things together with the manufacture of South American polychrome sculptures are part of what has been identified as the process of evangelization done under the Spanish domain.[29]

Raman spectra were recorded on a LabRAM HR Raman system (Horiba Jobin Yvon), equipped with two monochromator gratings and a charge coupled device detector. A grating of 1800 g/mm and hole of 100 μm resulted in a spectral resolution of 1.5 cm^{-1}. The spectrograph was coupled to an imaging microscope with 10×, 50×, and 100× magnifications. The Ar laser line at 514.5 nm was used as excitation source and was filtered to give a laser fluence or density power at the exit of the objective lens varying from 0.1 to 2 W/mm^2. Several measurements were performed, adjusting the laser fluence to 0.5 W/mm^2, to ensure that the heating produced by the laser was minimized and that the sample was not altered. Typically, for a 50× magnification, the spot size diameter was about 2–3 μm. To register the Raman spectra of the references, we randomly took ten different points from each pigment under the same conditions. Each spectrum was averaged over four scans corresponding to a collection time of 30 s. Raman spectra of both colonial painting samples were registered in the same conditions as for the reference pigments, collecting spectra from ten different points in each sample.

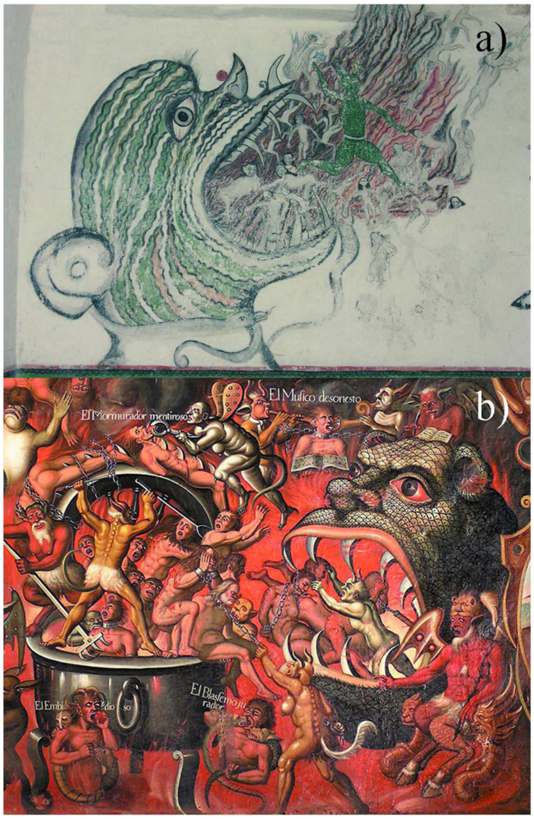

Figure 1. a) Detail of the figure of Leviathan in a wall painting from the church of Copacabana de Andarmarca (sample A); b) detail of the figure of Leviathan in the easel painting *Infierno* (1739) from the church of Caquiaviri (sample C).

Hierarchical cluster and principal component analysis (PCA) were performed by open source statistic analysis software PAST (Hammer, Ø., Harper, D.A.T., and P. D. Ryan, 2001. PAST:

Table 1. Reference pigments

Reference sample name	Subgroup	Commercial name and reference number	Manufacturer
GRZ	Crystalline carbon	Graphite – 1300	Zecchi
LBZ	Flame carbon	Lampblack	Zecchi
BSZ	Flame carbon	Bistre – 1200	Zecchi
BTZ	Coke	Asphaltum (bitumen) – 098	Zecchi
IBZ	Coke	Ivory black – 979	Zecchi
CWC	Chars	Commercial wood charcoal	Unknown
VDK	Black earth	Van Dyck – 41000	Kremer
EKZ	Black earth	Earth of Kassel	Zecchi

Paleontological Statistics Software Package for Education and Data Analysis. Palaeontologia Electronica 4(1): 9 pp.http://palaeo-electronica.org/2001_1/past/issue1_01.htm).

Results and discussion

Analysis of reference carbon-based pigments by Raman spectroscopy

Reference carbon-based pigments from different sources showed similar Raman spectra with characteristic first-order bands in the range 1300–1600 cm^{-1}. Figure 2 shows one representative spectrum for each reference. Two broad and overlapping bands with intensity maxima at approximately 1580 cm^{-1} (G band) and 1350 cm^{-1} (D band) were observed. Nevertheless, each spectrum revealed distinctive features. Position, width, and relative intensity of D and G bands were analyzed for each sample. The full width at half maximum (FWHM) of D and G bands (ω_D and ω_G) increases with higher degree of disorder, and other overlapping bands may appear between the D and G bands.[22,27] It must be considered that when a sample contains extra compounds presenting Raman bands in the 1000–1900 cm^{-1} region, the parameter values can be affected. For example, if iron oxides were present, a broad band at 1320 cm^{-1} could overlap the D band and affect the fitting procedure.[30] On the other hand, the presence of characteristic bands of certain components may contribute to the identification of a carbon-based pigment. This is the case of sample IBZ (ivory black), which shows a very weak band around 965 cm^{-1}, characteristic of the phosphate-stretching mode of hydroxyapatite.[12] However, this band is not always easy to observe, considering its low intensity compared with carbon bands (Fig. 2h)).

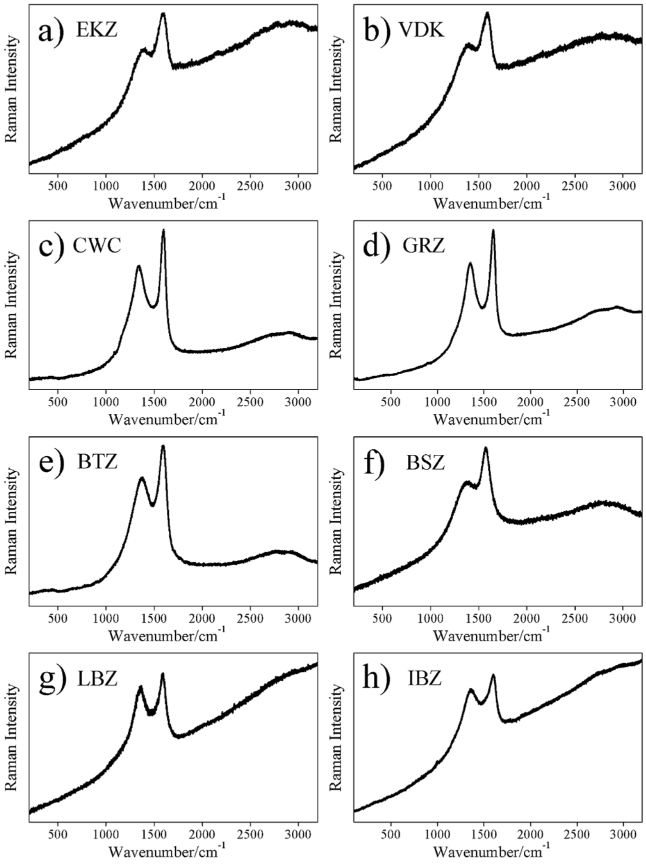

Figure 2. Micro-Raman spectra of carbon-based pigments: a) Earth of Kassel (EKZ); b) Van Dyck (VDK); c) *Prosopis sp.* charcoal (CWC); d) graphite (GRZ); e) bitumen (BTZ); f) bistre (BSZ); g) lampblack (LBZ); h) ivory black (IBZ).

To obtain quantitative parameters from the Raman spectra of the samples, we applied conventional fitting procedures based on Lorentzian and Gaussian profiles.[16,20] The baseline was fitted using a straight line in the 1000–1900 cm^{-1} range, to minimize the number of parameters involved, using the spectrometer software (LabSpec5). Table 2 shows the averaged parameters over ten spectra for each sample (references and painting samples); errors were calculated taking into account the fitting errors and the statistical deviation over the ten measurements.

The D band position (x_D) showed a larger range of values (from 1345 to 1394 cm^{-1}) than the G band (x_G) (from 1578 to 1603 cm^{-1}). Regarding the bandwidth of the D band, we observed that ω_D showed values above 180 cm^{-1}, characteristic of amorphous carbonaceous materials.[21] Samples of bistre (BSZ) and bitumen (BTZ) showed the highest ω_D values (334 and 299 cm^{-1}, respectively). According to the manufacturer, pigment BSZ is prepared from wood soot, whereas pigment BTZ is a complex mixture of aliphatic and aromatic hydrocarbons. Both samples showed an amorphous morphology by SEM.[31] Regarding the bandwidth of the G band, ω_G presented a narrower range of values from 67 to 116 cm^{-1} with graphite (GRZ) and charcoal (CWC) showing the lowest values (67 and 75 cm^{-1}, respectively).

To compare the features of the spectrum for each reference pigment, we plotted the FWHM of bands G (ω_G) and D (ω_D) *versus* the positions (x_G and x_D) of each band (Fig. 3a), b)). As observed in both figures, the pigments can be distinguished by their parameters, and certain materials can be grouped helping in their identification. For example, samples GRZ and CWC show the lowest values of ω_G (Fig. 3 a)), and they occur at the lowest frequencies of x_D (Fig. 3 b)), which indicates that they have the highest degree of graphitization among the reference pigments. The parameters of BTZ and BSZ are quite different from those of the other samples, placing these pigments in distinguishable areas in both figures. Lampblack (LBZ) and ivory black (IBZ) can be readily distinguished from Van Dyck (VDK) and Earth of Kassel (EKZ) on the basis of D band position (Fig. 3 b)). LBZ and IBZ have different origins, but both show organized structures at a nanometric level, as observed by earlier studies by SEM.[31] Finally, the dark earths, VDK, and EKZ show very similar parameters in accordance with the presence of amorphous carbon matter as humic substances, which are the main components of organic matter in soils and are responsible for their dark color.

Table 2. Raman spectral parameters: full width at half maximum (ω_G and ω_D) and positions (x_G and x_D) of G and D bands

Sample	x_D (cm^{-1})	ω_D (cm^{-1})	x_G (cm^{-1})	ω_G (cm^{-1})	I_D/I_G
EKZ	1382 ± 3	228 ± 7	1592 ± 2	98 ± 3	0.63 ± 0.10
VDK	1381 ± 4	237 ± 10	1593 ± 3	106 ± 6	0.70 ± 0.13
CWC	1345 ± 2	258 ± 4	1594 ± 1	75 ± 3	0.74 ± 0.08
A	1354 ± 3	269 ± 6	1595 ± 1	80 ± 3	0.74 ± 0.12
GRZ	1351 ± 3	188 ± 18	1598 ± 1	67 ± 2	0.78 ± 0.13
BTZ	1394 ± 3	299 ± 11	1603 ± 2	102 ± 3	0.79 ± 0.06
BSZ	1360 ± 3	334 ± 13	1578 ± 4	116 ± 5	0.85 ± 0.09
LBZ	1357 ± 2	215 ± 7	1585 ± 2	104 ± 4	0.91 ± 0.06
C	1364 ± 2	265 ± 6	1594 ± 2	114 ± 3	0.93 ± 0.09
IBZ	1358 ± 2	274 ± 5	1593 ± 2	102 ± 4	0.94 ± 0.09

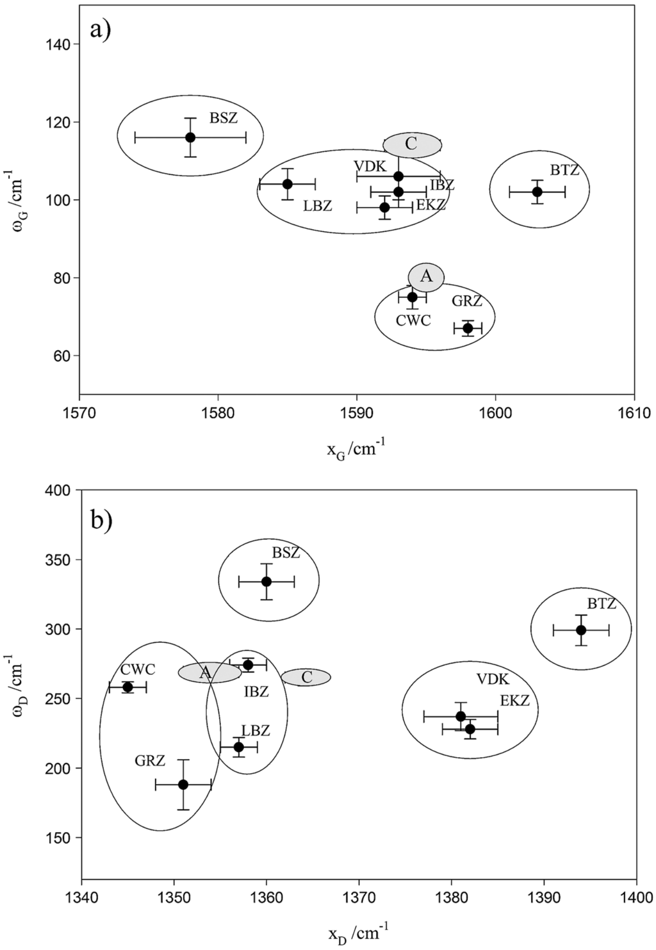

Figure 3. a) Full width at half maximum *versus* position from G band for all samples (ω_G *vs* x_G); b) full width at half maximum *versus* position from D band for all samples (ω_D *vs* x_D).

The intensity ratio of bands D and G (I_D/I_G) is an often used parameter to indicate the level of graphitization of a material.[16] However, this parameter is influenced by several phenomena that lead to disorder in carbonaceous materials.[6] In Table 2, the carbon-based pigments were arranged according to the increasing value of I_D/I_G. It has to be taken into account that these pigments belong to different categories of carbonaceous material. Pigments IBZ and LBZ showed the highest values (0.94 and 0.91, respectively) reflecting a certain degree of order in the system as observed in previous studies on soot from different origins.[21,32] On the other hand, the dark earths EKZ and VDK showed the lowest values (0.63 and 0.70, respectively) in accordance with their lamellar and irregular morphology as observed previously by SEM.[31]

Application on artwork samples

The combined analysis of Raman spectral parameters was applied to the identification of carbon-based black pigments in two colonial paintings. Measurements were made in the same conditions as for the references. Raman spectra of samples A and C (Fig. 4) showed D and G broad bands characteristic of amorphous carbon. To determine the source of each carbon-based pigment, we obtained Raman spectral parameters and compared them with those of the references in the corresponding graphics. The values of I_D/I_G ratio for samples A and C (0.74 and 0.93, respectively) (Table 2) indicate different sources for both carbon-based pigments. Samples A and C differ significantly in D band position (1354 and 1364 cm^{-1}, respectively) and in G band FWHM (80 and 114 cm^{-1}, respectively).

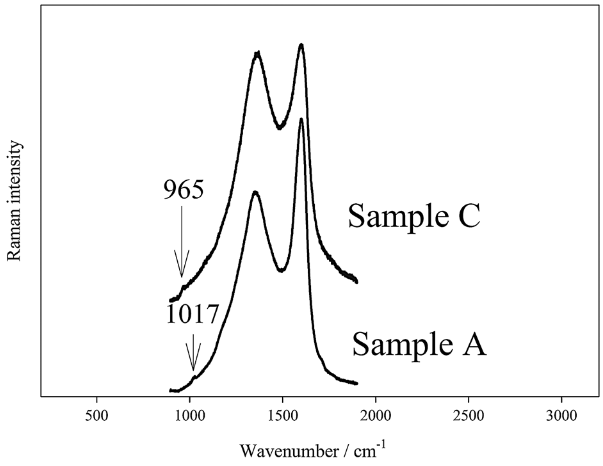

Figure 4. Micro-Raman spectra of black pigment samples A (Andamarca) and C (Caquiaviri).

The location of sample A in both graphics in Fig. 3 together with the I_D/I_G ratio suggests the use of wood charcoal as the black pigment. The value of I_D/I_G ratio for sample C was indicative of ivory black or a bone black pigment, in accordance with the position of C in Fig. 3, particularly 3b.

The statistical significance of carbon-based black pigments A and C identification was assessed by hierarchical cluster analysis and PCA taking into consideration the five parameters of Table 2 for reference and painting samples A and C.

Figure 5 shows the dendrogram plot of the hierarchical cluster analysis using a single linkage algorithm and Gower similarity measure. Two samples (BSZ and BTZ) did not readily cluster with any other samples. Two distinct clusters, one containing the black earths (VDK and EKZ), and another one containing the artwork samples A and C and reference pigments GRZ, CWC, LBZ, and IBZ were observed. The two tight subclusters, which include samples A and CWC, and samples C and IBZ, respectively, indicate a high degree of correspondence in each subcluster and is in accordance with

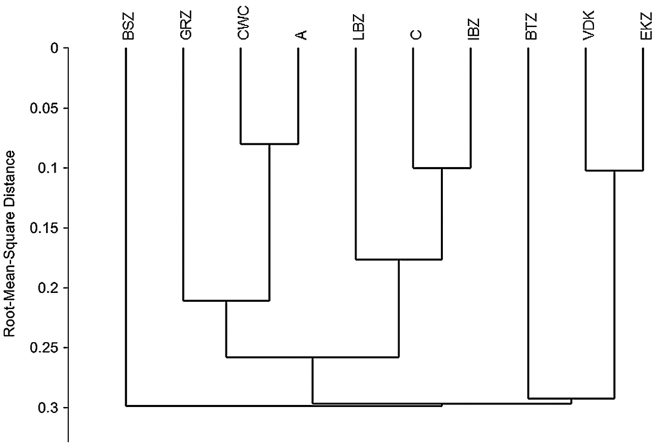

Figure 5. Dendrogram of the hierarchical cluster analysis of Raman spectral parameters of reference and artwork samples.

the proposal suggested earlier for the identification of the carbon-based pigment in both artwork samples.

The PCA scatter plot is shown in Fig.S1. The first two principal components (PC1 and PC2) account for 93.25% of the variance in the multidimensional data set (variance–covariance matrix). Samples A and C were located near references CWC and IBZ, respectively, in accordance with the dendrogram clusters.

The presence of wood charcoal in sample A was confirmed by SEM–EDS and Fourier transform infrared of the black pigment layer.[31] An additional weak band around 1017 cm^{-1} in the Raman spectrum of A (Fig. 4) is assigned to anhydrite ($CaSO_4$), which was present in the sample ground layer. Sample C presents a weak band at 965 cm^{-1} assigned to hydroxyapatite. The presence of phosphorous and calcium, as determined by EDS microanalysis, together with characteristic hydroxyapatite bands in the infrared spectrum confirmed the presence of a bone black pigment.[31]

Conclusions

In this study, we have demonstrated that despite the similar appearance of Raman spectra of reference carbon-based pigments, the combined analysis of spectral parameters determined by curve fitting allowed the discrimination of the pigments. For this purpose, various references have been analyzed to obtain the spectroscopic parameters that enabled the differentiation of the pigments. Our approach was extended to the identification of carbon-based black pigments in two colonial artworks from the early 18th century, which had previously been characterized as wood charcoal and bone black by SEM–EDS and Fourier transform infrared analysis.

It must be stressed that spectra acquisition conditions and fitting procedure are decisive to compare results. Equivalent methods are required, in both the development of a database and the measurement of the unknown samples, for the sake of comparison.

The unambiguous identification of pigments in works of art is important for understanding the technology used in the manufacture of the artwork as well as the available resources. This is relevant for our knowledge on Andean colonial art.

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Supporting information

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

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