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An authentication case study: Antonio Palomino *versus* Vicente Guillo paintings in the vaulted ceiling of the Sant Joan del Mercat church (Valencia, Spain)

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In 1695, the Valencian artist Vicente Guillo was engaged in painting the vault of the Sant Joan del Mercat church in Valencia, Spain. After preliminary work was carried out, his contract was cancelled. In 1697, Antonio Palomino, renowned for the publication of his technical treatise entitled *El Museo Pictorio y Escala Optica*, was finally selected as the painter in charge of decorating the vaulted ceiling of Sant Joan del Mercat. This paper reports an analytical study focused on the characterisation and discrimination of the palette and painting procedures used by Palomino and Guillo in the frescoes of Sant Joan del Mercat. For this purpose, Raman spectroscopy combined with light microscopy, scanning electron microscopy–X-ray microanalysis, voltammetry of microparticles, X-ray diffraction, Fourier transform infrared spectroscopy and gas chromatography–mass spectrometry has been employed.

The use of gypsum as stucco material for the ground layers contrasts with the recommendations made by Palomino in his treatise about the convenience of using slaked lime-sand mortars according to traditional fresco recipes. Although lead-based pigments were not traditionally recommended for frescoes because of their empirically known alterations when subjected to strong alkaline fresco medium, both Guillo and Palomino used them. Palomino, probably supported by his personal experience as a painter, recommended and used Naples yellow, which has been found in a good state of preservation. In contrast, white lead areas found on Guillo's paintings have transformed into lead oxides. Other pigments found in the vaulted ceiling such as smalt, goethite, haematite, azurite and malachite have also undergone substantial changes because of the extreme temperature conditions to which they were subjected in the church.

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

Keywords: light microscopy; scanning electron microscopy–x-ray microanalysis; voltammetry of microparticles; Raman spectroscopy; Antonio Palomino; Vicente Guillo; wall painting; colour palette; pigment; binding medium

Introduction

Scientific disciplines play an essential role in providing research advice and guidance to archaeologists, historians, curators and conservators on several areas including historical and archaeometrical studies as well as on determining the feasibility, appropriateness and effectiveness of their conservation treatments. This situation is clearly reflected in the specialised literature where one can find a large number of papers that have focused on the scientific study on works of art.[1–12]

This is the case of the paintings evaluated in the present work, namely, the frescoes executed on the vaulted ceiling of Sant Joan del Mercat church in Valencia, Spain. In 1695, the Valencian painter Vicente Guillo was commissioned by the Valencian *Cabildo* to paint the vault of Sant Joan del Mercat church. After an initial painting campaign in the vaulted ceiling of the central nave, his contract was cancelled, and in 1697, Antonio Palomino was finally selected as the painter in charge of decorating the vaulted ceiling. Despite Palomino having to remove most of the frescoes painted by Guillo in order to develop his own artistic programme, some of Guillo's original paintings remained in the lower part of the vault.[13]

Vicente Guillo Barcelo (1645–1698) was an active Valencian artist in charge of the wall decorations of many churches in the Valencian region. This artist also executed oil paintings and altarpieces.

Antonio Palomino (1655–1726) can be considered one of the most outstanding baroque Spanish painters of the 17th and 18th centuries in both oil and fresco techniques. In 1688, he was appointed Court Painter to King Carlos II. In the period between

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1697 and 1702, Palomino was based in Valencia, where he executed several important frescoes, including those in the Sant Joan del Mercat church. Palomino is particularly renowned for the publication of the art treatise, entitled *El Museo Pictorio y Escala Optica*[14] (1715–1724), on the theory and practice of painting, which provides relevant information on painting techniques and is also an important archive of biographical material for art historians. The third volume, entitled *El Parnaso español pintoresco laureado*, includes 226 biographies of painters. Thus it can be considered the most important compendium concerning Spanish artistic historiography. The technical volumes that describe the materials and methods used for preparing paints, binding media and varnishes constitute a unique text, which shows the painting procedures commonly used during this artistic period. In particular, the fourth chapter of the seventh book in Volume II offers an accurate description, step by step, of the Italian technique of *buon fresco*. Moreover, in the ninth and tenth chapters of the ninth book in this volume, Palomino describes the iconographic programme that he developed in the Sant Joan del Mercat church.

The analytical study of Palomino's paintings in the Sant Joan del Mercat church offers a unique case study that enables an accurate comparison between the materials and painting techniques theoretically established by the artist in his treatise and the real work executed on the vaulted ceiling.

A second area of interest in this analytical study arises from the extensive vandalism that took place during the Spanish Civil War (1936–1939). During this period, seven fires were lit in the church in an attempt to destroy the frescoes. Thus, the recognition of unusual alteration products formed from the pigments, as well as from substrate and ground layers, has been another important aim of the scientific study carried out on the frescoes at Sant Joan del Mercat along with the analytical identification of pigments and painting materials, a problem that has been partially solved in prior works.[15–18]

As a continuation of this research, this paper reports the findings of a further and a more comprehensive analytical study that has centred on the discrimination of the palette and painting procedures used by Palomino and Guillo on the frescoes in the Sant Joan del Mercat church. The great damage suffered by the frescoes prevents art historians from performing a confident discrimination on the basis of stylistic analysis. The chemical-analytical study carried out has provided conservators, in charge of the Sant Joan del Mercat frescoes, a way of differentiating between the parts of the vaulted ceiling painted by each artist, through the identification of their specific materials and techniques. This scientific study was conducted using a multi-technique approach, which included Raman spectroscopy combined with light microscopy, scanning electron microscopy–X-ray microanalysis, voltammetry of microparticles, X-ray diffraction, Fourier transform infrared (FTIR) spectroscopy and gas chromatography–mass spectrometry.

Experimental section

Multi-technique approach

Seven instrumental techniques have been applied for the analysis of the Sant Joan del Mercat frescoes: light microscopy (LM), scanning electron microscopy–X-ray microanalysis (SEM-EDX), FTIR spectroscopy, Raman spectroscopy, X-ray diffraction (XRD), voltammetry of microparticles (VMP) in square wave mode and gas chromatography–mass spectrometry (GC-MS). In particular, VMP is a solid-state electrochemical technique recently developed by Scholz *et al.*[19,20], which is based on the abrasive attachment of a few nanograms of the sample to the surface of an inert electrode (typically, a paraffin-impregnated graphite electrode) in contact with a suitable electrolyte where the sample is not soluble. Because of its inherently high sensitivity and the requirement of minimal amounts of the sample, it has been applied to the identification of electroactive species in art objects including metals, ceramics, glass, textiles and paintings as well as archaeological artefacts, as recently reviewed.[21,22]

For analytical purposes, the relevant point to emphasise is that the position (peak potential, E_p) and the shape of the voltammetric peaks are representative of the mineralogical composition of the sample and are also influenced by the shape and size distribution of the particles, so that the electrochemical identification of the pigment can be derived from E_p and the shape-characterising parameters previously obtained from reference minerals and pigments with known compositions.[23]

The techniques used in the present study satisfy the important criteria for the archaeometric analysis of painting materials such as high sensitivity and minimum amount of sample required for the analysis (all of them in the range of μg or ng). On the other hand, this multi-technique approach, which includes microscopy, spectroscopic, spectrometric, electrochemical and chromatographic techniques, enables a complete and complementary analysis of the paintings. This includes a morphological examination from the microscopy techniques, elemental composition of pigments and grounds from SEM-EDX, crystallographic and mineralogical composition from XRD, molecular and functional characterization of pigments and binding media from FTIR and Raman spectroscopy, identification of electroactive species and speciation studies from VMP and the accurate identification of binding media and other organic compounds present in the paintings from GC-MS. The complementary data obtained from these methods provide a comprehensive image of the materials and techniques used by the two painters as well as the damage sustained by the materials and, therefore, inform about conservation problems and conditions required for the preservation of the surviving paintings.

A description of the reagents, the instrumentation and the experimental conditions employed in performing the analyses is presented as supporting information.

Samples studied

The fresco paintings studied were applied to the central nave of the Sant Joan del Mercat church as result of a substantial restoration campaign, which took place at the end of the 17th century and the beginning of the 18th century. According to the standards of this historical period, the internal space of the church was substantially modified by covering the former gothic system and building a new vaulted ceiling, which was slightly parabolic, resulting in the redefinition of a more complex formal system in the most pure baroque style.[13] In the 20th century, during the Spanish Civil War (1936–1939), several fires were deliberately ignited in the interior of the church. As a result of this, the paintings were seriously damaged. The study performed has focused on the original paintings that still remain at the entry of the central nave (at approximately 200 m^2). The rest of the paintings (at approximately 400 m^2) were subjected to restoration works in the 1960s. During the restoration process, the frescoes were taken off and reinstalled in the vault after a drastic repainting treatment that notably altered the original paintings.

The results reported in this paper are part of a study, carried out between 2004 and 2006, devoted to the characterization of the materials, the discrimination between the parts of the vaulted ceiling painted by A. Palomino and by V. Guillo, the characterization of the artistic techniques of the two painters and the identification of the damage exhibited by the paintings caused by the fire of 1936 as well as by natural ageing. For this purpose, over 80 samples were excised from the remaining original paintings placed in the vaulted ceiling, which covers an area of approximately 200 m^2. The overall painted surface was divided into 32 sections or quadrants (approximately 6 m^2) in order to have a systematic graphic register of the paintings (Fig. S1). Several samples were excised from each section so that a complete picture of the materials, techniques and damages could be obtained. Sampling points were randomly chosen in each section in an attempt to characterise the materials and artistic techniques used by the two artists. In parallel, a number of samples were intentionally taken from areas of the paintings that exhibited damage.

It is interesting to note that because the poor state of preservation of the paintings, it was difficult to determine which parts of the vaulted ceiling were painted by Palomino and which parts could be attributed to Guillo. On the other hand, no mention of Guillo's frescoes has been found, apart from an unspecific reference in which there were instructions for them to be placed in the lower parts of the vault.[24] Therefore, samples were classified according to the section from which they were taken and their colour. During the excision process, the samples taken from the lower part of the vaulted ceiling, close to the *lunettes*, were tentatively attributed to Guillo according to the scarce historical information available. It should be noted that this assignment was provisional until further confirmation was made possible through analytical results. Figure S1 shows the distribution of spatial sections on the vaulted ceiling with an indication of the zones of the vault, in which Guillo's and Palomino's paintings were apparently located.

Results and discussion

Ground layers

An interesting discovery that emerged from this study is the discrimination between Guillo's and Palomino's wall-painting techniques on the basis of the particular ground technique of the latter. Table S1 summarises the results obtained with Raman spectroscopic analyses, combined with SEM-EDX, XRD and FTIR, performed in the substrate grounds of the paintings in the vaulted nave of the Sant Joan del Mercat church. According to the analyses, Guillo constructed the ground layer following the traditional method for making frescoes where a previously prepared paste of slaked lime is mixed with sand or some other inert material in order to form a dense mortar which hardens because of the well-known reaction of moist calcium hydroxide with carbon dioxide present in the air to re-form cohesive calcium carbonate. Analyses performed using different instrumental techniques confirmed the use of slaked lime and quartz-rich sand in agreement with what Palomino established in his treatise. Thus, calcite and quartz were identified as major components of most of the samples analysed. Nevertheless, small amounts of unreacted calcium hydroxide were identified in several samples through its characteristic signature near 790 cm^{-1} in the Fourier Transform-Raman spectrum.[25] The presence of this compound is explained by the slow rate at which calcium hydroxide reacts with carbon dioxide, in the atmosphere, inside the *intonaco* after contraction of the pores takes place. The latter is due to the formation of dense calcium carbonate crystals on the surface of the *intonaco*, which then results in a significant decrease of the diffusion of this gas from the air into the ground. Sometimes, it is observed that lumps of unslaked lime can find their way into the painting ground, which then gradually become slaked and, eventually, form pustules of calcium carbonate.

A more elaborate technique of constructing ground layers was used by Palomino, typically including three different strata. Palomino used gypsum in the inner substrate ground layer. This material was subjected to a dehydration process during the 1936 fires, so anhydrite is the major compound now found in the intermediate ground layer (*arriccio*). Hemihydrated gypsum has also been found to some extent in this layer. The inner ground layer (*arenato*), which was not so intensely affected by the fires, is mainly composed of gypsum together with a small amount of quartz-rich sand. It is interesting to remark that Palomino did not recommend the use of gypsum at all for making ground layers in fresco painting. In contrast, in his treatise, he proposed the traditional fresco method of ground preparation based on the use of slaked lime sand-based mortars. The excellent mechanical and working properties of gypsum were probably well known to Palomino, so he decided to use this material in the inner ground layers, in an innovative way, in an attempt to suppress irregularities in the brick fabric of the vault. The uniform surface obtained was ready for the application of an outer ground layer, the *intonaco*, which was composed of slaked lime and sand. In this layer, the pigment was fixed during the ground setting.

It is interesting to note that after the wall was prepared through the application of the two internal ground layers, Palomino probably drew a sketch, which consisted of a preliminary rough drawing of a simple outline, to assist him in making the final painting. This sketch was made with a red earth pigment (*sinopia)*, dissolved in water and applied on the *arriccio* surface.[26] Sustaining this hypothesis, the *sinopia* was identified in a number of samples as a thin layer applied on the top of the intermediate ground layer. Analysis with SEM-EDX confirmed the iron(III) oxide red composition of this particular *imprimatur*.

Alkaline chlorides were identified in a number of samples of the *intonaco*, suggesting that according to Palomino's reported technique, sand from the *Pinedo* and *Nazaret*, beaches that were adjacent to Valencia, was used. In the procedure described in Palomino's treatise, sand is mixed with quicklime and allowed to slake by adding the appropriate amount of water.

Other minerals have been found in the *intonaco* as common impurities of mortars, which accompany the sand and lime, mainly, potassium feldspars and, more rarely, aragonite, dolomite, calcium phosphate, strontium sulphate, titanium oxide, iron oxide and clayey materials. Additionally, carbon black, associated to the fires, was also identified.

Hexahydrite ($MgSO_4.6H_2O$) and nitre (KNO_3) have been identified through XRD and FTIR as efflorescences formed in a particular section of the paintings that was subjected to the presence of abundant moisture caused by poor insulation and reduced protection by the roof, which resulted in covering the painted vault and windows at that point. Nitre was formed as a result of the migration of NO_3^- ions formed from the rather large amounts of pigeon excrements accumulated in the accessible space between the roof and the vaulted ceiling. Hexahydrite was formed in several wet zones located beside a restored area over an unglazed window (*lunette*) in the lower part of the vaulted nave. Mechanisms of salt formation here can be ascribed, in this case, to dampness as well as to the various materials used during a later restoration, in particular, concrete and gypsum plaster. In parallel, efflorescent deposits of gypsum were found through SEM-EDX on the surface of the *intonaco*, which extended further over the paintings. This compound was probably formed as result of the reaction between SO_2, present in the atmosphere as a pollutant, and calcium carbonate through the well-known degradation mechanism of limestone rocks and calcite-rich mortars.[27]

An important result of this study is that it provides significant information about how the particular methodology in making fresco paintings developed by Palomino has noticeably affected the painting's behaviour during the 1936 conflagrations. Thus, the gases formed in the internal ground zones, owing to the high temperatures achieved during the series of seven fires, displaced the paint layer and, subsequently, produced the detachment and loss of large areas (spallation) of the fresco.

Paint layers

Common pigments in both Guillo's and Palomino's colour palettes

The pigments composing the colour palette for fresco painting are listed by Palomino in his treatise.[14] They are classified into two groups: mineral pigments and *calcinados* (artificial) pigments. *Ocre claro* (light ochre) and *ocre oscuro* (dark ochre), *tierra roja* or *almagra* (red earth), *albin* (iron oxide red), *pavonazo* (burnt red ochre), *tierra de Venecia* (Italian umber, reddish), *tierra del Viejo* (umber), *tierra verde* (green earth), *tierra negra* (wad) and *bermellón mineral* (cinnabar) are included in this mineral group. Whereas *esmalte* (smalt), *negro carbon* (carbon black), *ocre quemado* (burnt ochre), *hornaza* (Naples yellow), *vitriolo romano* (Roman vitriol), *vitriolo quemado* (burnt vitriol) and *bermellón* (vermilion) are designated as artificial pigments.

Although Palomino does not include any white pigment in the list of pigments suitable for fresco painting, he makes, in further paragraphs of his treatise, the recommendation of using slaked lime, maturated for 4 months, as a white pigment for *fresco*.[14]

A number of these pigments, commonly present on the colour palettes of Guillo and Palomino, were found widely spread in the vaulted ceiling of Sant Joan del Mercat. The results obtained after evaluating a selection of the most representative samples are summarised in Table 1. The results obtained from the complete set of samples analysed are presented as supporting information in Table S2. A description of the characteristic X-ray emission lines, Raman bands and electrochemical peaks used for identifying inorganic materials and pigments in this study, is also presented as supporting information in Table S3.

Black. A carbon-based black pigment of vegetable origin (charcoal) has been used by Guillo and Palomino in the frescoes of Sant Joan del Mercat. This pigment was obtained from a carbonisation process with limited supply of air. During this process, the particles of pigment retain the cellular morphology of the starting material. The recognition of a carbon black pigment, assignable to a vegetable-based or plant-based origin in several samples of the fresco painting, has been achieved by means of Raman spectroscopic signatures, (Fig. 1), where the D and G bands of amorphous sp^3 and sp^2 carbon can be seen at 1590 and 1320 cm^{-1}, respectively.[28] It is not possible from the Raman spectrum to differentiate between carbon that has been used as a pigment and a darkening agent deliberately added to other pigments, commonly red and blue, and the deposition of soot through incense and candle burning during church services. However, optical microscopy permitted evaluation of the distribution of carbon particles in the pigment layers and allowed differentiation between the uneven aggregation points due to the accidental deposition of soot and the more homogeneous distribution resulting from admixture with other pigments. The Raman spectrum shown in Fig. 1 confirms the organic, vegetable origin of the carbon pigment used by Guillo and Palomino because an alternative source of black pigment obtained from the calcination of bones or ivory, known as bone black or ivory black, leaves a phosphate signal in the spectrum at 960 cm^{-1}.[29]

Iron oxide pigments. Following Eastaugh *et al.*,[30] Gettens and Stout,[31] Colomban *et al.*[32] and Grygar *et al.*,[23] the mineralogy of earth pigments permits the identification of four main groups of raw and manufactured materials (Table S4): (1) iron(III) oxide reds; (2) red ochres; (3) yellow ochres; and (4) umbers and wads.

Raman spectra of the red pigments from Palomino's frescoes show the presence of iron oxide pigments of two classes. First is one highly crystalline (haematite) with narrow spectral bandwidths and main signatures appearing at 227, 293 and 1310 cm^{-1} accompanied with moderate and weak bands at 610, 412 and 246 cm^{-1} (*vide infra*, Type 1) (Fig. 2(a)). Second is another class of reddish pigment, which exhibits bands in the 650–685 and 520–550 cm^{-1} ranges and has been associated with amorphous iron oxide structures characteristic of ochres and red ochres (goethite and lepidocrite-rich) (*vide infra*, Type 2) (Fig. 2 (b)), as well as with magnetite formed from thermally treated haematite (*vide infra*, Type 3).[32]

In a parallel study, characteristic X-ray energy emission lines from Fe were identified in the spectra recorded on individual grains of these pigments, confirming that iron oxides are the main components of these pigments.

On the other hand, square wave modes were obtained from these samples while in contact with 0.10 M HCl. The main electrochemical process involving iron oxides and hydroxides can be described as a proton-assisted reductive dissolution yielding Fe^{2+} ions in a solution. Semiderivative convolution of voltammograms permits the discrimination of four types of responses.

In Type 1 pigments, a peak appearing at −425 mV prevails, and it is associated with crystalline haematite (Fig. S2(a), Table S3). This pigment is correlated with the iron(III) oxide red pigment, the Spanish haematite (*albin*), included in the group of mineral pigments recommended by Palomino in his treatise. Weak signals accompanying the main feature are ascribed to the disordered or amorphous portion of iron oxides, reductive dissolution of magnetite and hydrated haematite accompanying crystalline haematite.

In Type 2 pigments, the haematite peak at −425 mV is accompanied by overlapping peaks at −50 and −150 mV, producing a voltammetric profile similar to that displayed by the red ochre and yellow ochre reference pigments, which is associated to hydrated goethite (Fig. S2(b)). A larger peak at +700 mV, preceded by a weak signal at +450 mV, denotes the presence of manganese oxide minerals in most of these samples. This group of samples has been correlated with the light and dark ochre pigments mentioned by Palomino in his treatise.

Simultaneously, characteristic X-ray energy emission lines from Fe and Si were mainly identified in the spectra from coloured individual grains and mineral aggregates from the cross-sections of these samples, suggesting that anhydrous and hydrated iron oxides, as well as quartz, were the main components of these samples. The characteristic X-ray spectrum of clay was detected in a number of samples. Manganese (Mn), associated with manganese oxides,

Table 1. Summary of inorganic compounds identified in the paint layers and grounds of the frescoes in the *Sant Joan del Mercat* Church

Quadrant	Samples*	Pigments and inorganic materials identified		Analytical techniques used				
		Paint layer	Grounds	SEM-EDX	VMP	FTIR	Raman	XRD
$C1_3$	P-A1B	Green earth, azurite, smalt	—	√	√	√	√	—
	P-V8	St. John white, malachite, smalt, Naples yellow	—	√	√	√	√	—
$C1_6$	P-I1[a]	—	Major: calcite, quartz. Minor: potassium feldspar, clayey minerals, aragonite, calcium phosphate, carbon black, strontium sulphate, titanium oxide, iron oxide, dolomite, alkaline chloride	√	√	√	√	—
$C1_8$	G-V1	Malachite	—	√	√	√	√	—
$C1_9$	G-A1	Smalt	—	√	√	√	√	—
$C1_{14}$	P-AR1[b]	—	Red earth	√	√	√	√	√
$C1_{15}$	P-N1	Umber/wad	—	√	√	—	—	—
$C1_{16}$	G-R1	Iron oxide red, red earth	—	√	√	√	√	—
	G-M2A	Umber/wad	—	√	√	—	—	—
$C2_1$	G-M2B	Burnt ochre/red ochre	—	√	√	√	√	—
	G-AM1	Light ochre/dark ochre	—	√	√	√	√	—
$C2_3$	P-TR6	Iron oxide red, red earth	—	√	√	√	√	—
	P-TR7A	Burnt ochre/red ochre	—	√	√	√	√	—
$C2_5$	P-TR2A	Light ochre/dark ochre	—	√	√	√	√	—
$C2_6$	P-E1[d]	—	Major: gypsum. Minor: anhydrite, quartz	√	—	√	√	√
$C2_7$	P-D1	Gold foil	—	√	√	—	—	—
$C2_8$	G-B1	St. John white	—	√	—	√	√	—
$C2_9$	G-N1	Carbon black	—	—	—	—	√	—
$C2_{15}$	P-AR2[c]	—	Major: anhydrite. Minor: hemihydrate, gypsum	√	—	√	√	√
$C2_{16}$	G-B2	Lead white	—	√	√	√	√	—
	G-I1[a]	—	Major: calcite, quartz. Minor: aragonite, dolomite	√	—	√	√	√

SEM-EDX, scanning electron microscopy–X-ray microanalysis.
VMP, voltammetry of microparticles.
FTIR, Fourier transform infrared.
XRD, X-ray diffraction.
* P, sample attributed to Palomino; G, sample attributed to Guillo.
[a] Sample of outer ground, *intonaco*.
[b] Sample of intermediate ground, *sinopia*.
[c] Sample of intermediate ground, *arriccio* mortar.
[d] Sample of inner ground, *arenato* mortar.

was identified less frequently, as well as Ba and S associated with barite. This last result was also confirmed through Raman spectroscopy (Fig. 2(b)), where the characteristic sulphate stretch appeared at 981 cm^{-1}.

A third type of pigment (Type 3) is recognised through the characteristic voltammetric behaviour. These samples exhibit a well-developed, isolated peak at 0.0 mV, preceding the more intense peak of the haematite (Fig. S2(c)). This response does not fit with the patterns displayed by the reference iron pigments and can be attributed to the superimposition of the peaks of haematite and magnetite. This last material consists of a well-defined peak at 0.0 V.[33] This response suggests that Type 3 samples, consisted of iron oxide pigments, submitted to a significant thermal stress under non-oxidising conditions. Characteristic X-ray energy emission lines from Fe were mainly identified in the spectra from dark individual grains and mineral aggregates, confirming that magnetite is present in these samples at a significant level. Characteristic clay profiles for the X-ray emission lines were detected in a number of reddish-pigmented grains. Once more Mn, associated with manganese oxides, was identified less frequently, as well as Ba and S associated with barites.

The results obtained suggest that, in this third type, pigments that have been thermally altered during their preparation such as burnt red ochre *pavonazo*[34] or *ocre quemado* (burnt ochre)[35], as well as those that had undergone thermal alteration during the 1936 fires, are included. It has already been stated that Raman spectra indicated both types of haematite pigments, which were identifiable in the frescoes.

Interestingly, in a number of analysed earth pigment-based samples, an additional peak appeared at −550 mV (Fig. S2(b)). This can be attributed to the presence of lead in the sample. Simultaneously, Pb signals appeared in the X-ray spectra obtained from some aggregates of iron oxide minerals present in the analysed paint cross-sections. This supports the presence of traces of this element accompanying the iron oxide mineral that has been suggested by the VMP data.

Voltammograms corresponding to Type 4 pigments exhibited features associated with iron oxides and hydroxides, manganese

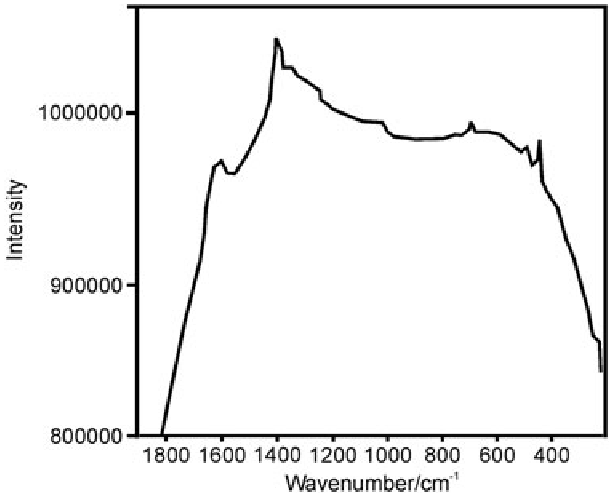

Figure 1. Raman spectrum from a black area in Sample G-N1 corresponding to Guillo's frescoes, 785 nm excitation, 50× objective, 10 scans accumulated, 2 cm^{-1} spectral resolution, wavenumber range 300–1850 cm$-^{1}$. The signatures of amorphous carbon at 1310 (sp^3 hybridised) and 1590 cm^{-1} (sp^2 hybridised) and the absence of a phosphatic mode at 960 cm^{-1} are indicators of a compound of plant carbon origin.

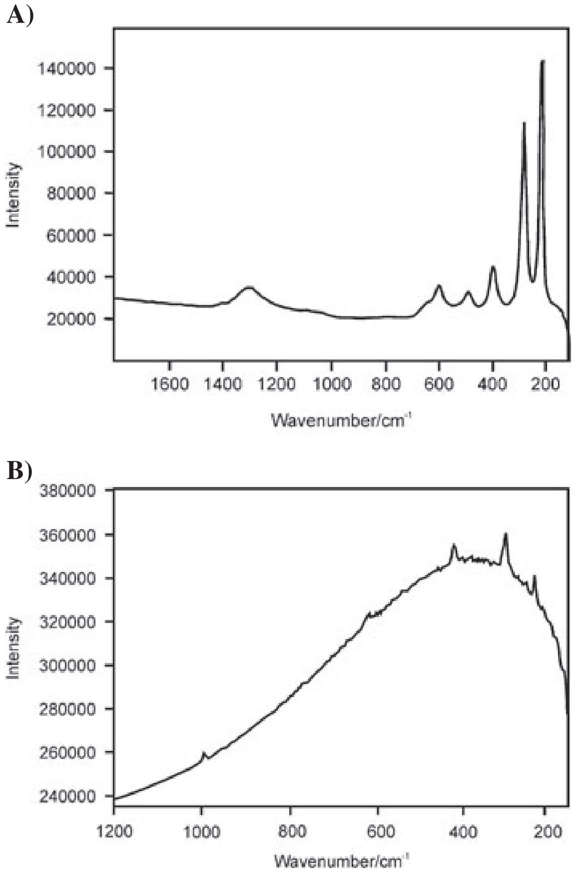

Figure 2. Raman spectrum of haematite-rich pigment used by Palomino found in Sample P-TR6: (a) highly crystalline and pure mineral pigment, and (b) thermally processed haematite. Both spectra were recorded using a 785 nm excitation and a 50× objective. The presence of a weak feature arising from the symmetric stretching band of sulphate in barites is observed in the *b* spectrum at 987 cm$-^{1}$.

oxides and Pb associated with iron oxide minerals. Characteristic X-ray emission lines from Mn were identified in the X-ray energy spectrum of individual grains and mineral aggregates appearing in the paint layers of these samples. Weak signals of Ba and S were also present in the spectra of manganese oxide, suggesting that barium sulphate, most probably, accompanies this oxide as a minor component. The Raman spectrum (Fig. 3) showed a broad band at 637 cm^{-1}, characteristic of manganese oxides such as pyrolusite. The higher content of manganese oxides and the homogeneous dark colour exhibited by the paint layer in the cross-sections enabled us to correlate these samples with the pigments *tierra negra* (wad), *tierra de Venecia* (Italian umber) and *tierra del Viejo* (umber), listed by Palomino in his treatise.

Blue. Smalt has been identified in most of the blue, green and mulberry samples analysed from the frescoes. This pigment is easily recognised through optical microscopy because of its characteristic appearance under plane-polarised light. This pigment fractures when crushed with a pronounced conchoidal form because of its glassy structure, so that the particles have characteristically curved fractured surfaces with concentric pressure ridges. Angular shards with curved particle boundaries are also easily observed (Fig. S3 (a)). SEM-EDX analysis shows the characteristic emission lines of Co, As, Si, K, Ca and Fe (Fig. S3(b)). The complementary electrochemical detection of blue smalt (cobalt silicate) has been based on the appearance of an anodic stripping peak at −100 mV. It is interesting to note that Palomino, according to his treatise, suggests combining smalt with iron oxide red in order to obtain a mulberry colour. No evidence of indigo was observed in our analyses despite the recommendation of the artist that this pigment should be added to smalt to darken it. In contrast, some samples are evidently combinations of smalt-azurite-Naples yellow (PA4B) and smalt-azurite-green earth (PA1B) (Table S2).

A thin layer composed of fine grains of ultramarine blue was identified in one specific sample (PA4B). SEM-EDX analysis of this sample showed its characteristic profile of X-ray emission lines containing Na, Al, Si, S, K and Ca. This pigment was found applied over an inner layer of smalt-azurite-Naples yellow. The fact that this pigment has only been found in a single sample sustains the hypothesis of the presence of unrecorded repainting in this zone of the vault.

In general, smalt was found to be in a poor state of preservation because of the high temperatures the paintings were exposed to and the severe preservation conditions prevailing in the church after the fires. Thin fractures were observed in the

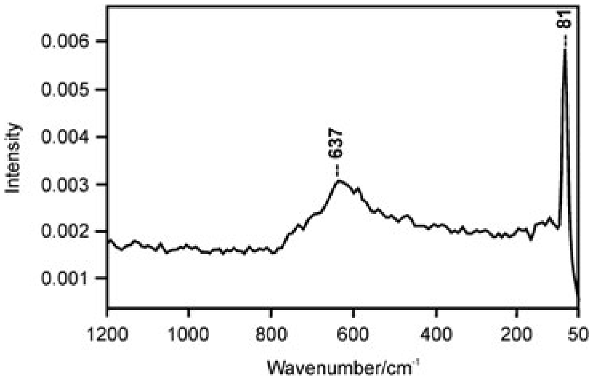

Figure 3. Raman spectrum of pyrolusite-rich pigment found in Sample P-N1 corresponding to Palomino's frescoes, 1064 nm excitation, 8000 scans, 8 cm$-^{1}$ spectral resolution.

external region of the grains (Fig. S3(a)). Nevertheless, the leaching process reported by Santopadre and Verità[36] in the Italian fresco paintings from the 17th century, characterised by the formation of a thick weathered layer followed by crizzling and corrosion of the glass surrounding the fractures and the extraction of Co(II) ions in the external part of the pigment grains, was not observed in Palomino's frescoes (Fig. S3(b)). This behaviour contrasts with the rapid degradation undergone by smalt because of alkali excess in the glass composition, reported by several authors, which results in the change of its colour from blue to greenish-grey.[36–41] Leaching of potassium from the glass network[37], extraction[38] or depletion[39] of Co(II) ions from the glass network, diffusion into the surrounding organic binder and weathering of the surrounding binder[40–42]have all been adduced as the main processes responsible for the loss of stability of this pigment. Figure S3(c) shows a grain of smalt from a 17th century painting from the Saint Joseph Church in Taormina (Italy), in which linseed oil was used as the binding medium. Lixiviation of the Co from the periphery of the grain has resulted in the absence of Co(II) ions in this external zone of the glass, as can be seen in the X-ray energy spectrum depicted in Fig. S3(d), in contrast with the internal core of the grain where the presence of Co(II) attached to the glass network has been confirmed (Fig. S3(e)).

Green. The presence of malachite was clearly identified by means of Raman spectroscopy in areas of the frescoes attributed to both Palomino and Guillo (see Table S3). Raman spectroscopy provided a definite way to discriminate between the basic copper carbonates, malachite and azurite. The Raman spectrum in Fig. 4 shows, among others, intense bands at 268, 433, 509, 553 (lattice modes for Cu(II)), 753, 1085 and 1492 (carbonate stretching vibrations) cm^{-1}, characteristic of malachite,[43] that correspond to a sample located in the lower part of the vault which has been associated with Guillo.

Electrochemical analysis confirmed the presence of copper carbonate hydroxide through the appearance of a main reduction peak at -100 mV, followed, in a reverse scan, by an anodic stripping peak at -25 mV, characteristic of copper products.[44] The presence of copper carbonate hydroxide was also clearly observed in the FTIR spectrum, which showed the characteristic band at 1478 cm^{-1} associated with the fundamental stretching vibration of the carbonate group in the copper carbonate hydroxide.

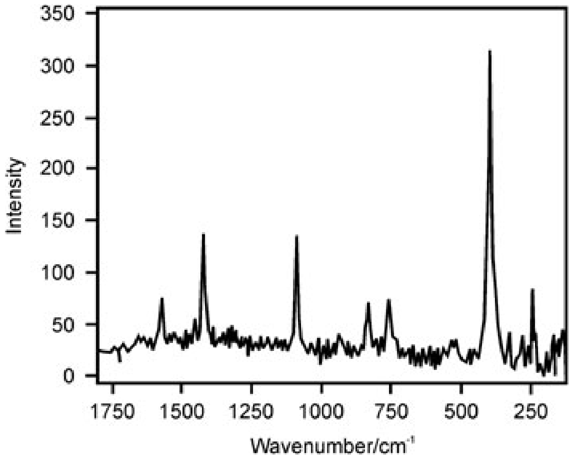

Figure 4. Raman spectrum of malachite pigment used by Guillo, found in Sample G-V1, 785 nm excitation, 20× objective, 2 cm^{-1} spectral resolution, wavenumber range 150–1800 cm$-^{1}$.

Discrimination between Palomino's and Guillo's paintings

Red. No evidence of the use of any characteristic red colour, apart from iron oxide red, was found in the samples analysed from the Sant Joan del Mercat church. Thus, red areas did not provide a way to discriminate between the materials employed by the two artists under investigation. It is interesting to mention that Palomino includes vermilion in his treatise as a component of his fresco colour palette despite the fact that this pigment was considered not suitable, according to the traditional artistic technique, because of its alteration in strong alkaline media. To avoid this alteration, Palomino recommended not to apply this pigment directly on the *intonaco* and proposed interposing an intermediate paint layer made with red earth. Although vermilion was not found in the analytical study of the San Joan del Mercat paintings, this pigment was identified through S and Hg X-ray emission lines in the SEM-EDX measurements of red samples from other fresco paintings by Palomino in the Basílica of the Mare de Déu dels Desemparats (Table S2). Thus, there is experimental evidence that Palomino, in agreement with his treatise, used this pigment in his fresco technique. It is probable that Palomino did not use vermilion in the Sant Joan del Mercat church, and later, he changed his mind and added it to his palette because the paintings in the Basílica of the Mare de Déu dels Desemparats were executed after the Sant Joan del Mercat paintings. The absence of this pigment in the Sant Joan del Mercat church frescoes can also be ascribed to the small percentage of original paintings that remained after the fires of 1936 to which we have had access for analysing.

Blue and green pigments. Azurite has been recognised in some samples from the upper areas of the vault of Sant Joan del Mercat, but it was always combined with other pigments. The characteristic features of this pigment were recognised in the Raman spectra of the blue samples at 1557 (carbonate antisymmetric vibration ν_3), 1459/1430 (carbonate stretching vibrations) and 401 cm^{-1} (lattice modes for Cu(II)).[43]

This pigment has been associated with Palomino's palette. In some samples corresponding to the blue areas of the paintings, azurite appears to be mixed with smalt and green earth, whereas in the green zones, combinations of azurite, smalt and Naples yellow have been found. Additionally, in most of the green samples studied, an inner paint layer composed of earths, diluted at different levels by calcite, was also found. It is interesting to note that azurite and malachite were not included by Palomino in his list of key pigments for a fresco palette, and he did make accurate comments concerning the specific problems of copper pigments when they are applied with the fresco technique. Nevertheless, Palomino establishes, in other part of his treatise, that malachite, in particular, can be used in frescoes in combination with green earth in order to avoid its alteration during the setting of the fresco. Palomino also suggests the addition of milk as an organic binder in order to minimise the degradation of malachite in the fresco. Traces of amino acids have been recognised in one of the analysed samples containing azurite and earths, but the low levels of these compounds hindered the assignment of the proteinaceous medium identified as casein. Nevertheless, the discovery of this organic binder in the frescoes confirms the practical use, by Palomino, of the technique recommended in his treatise.

Interestingly, VMP supplied evidence that the copper pigments were accompanied, in a number of samples, by copper(II) oxide, tenorite (CuO) and/or the copper(II) trihydroxychlorides atacamite/paratacamite, ($Cu_2(OH)_3Cl$) and, more rarely, copper(I) chloride, nantokite (CuCl). Azurite and malachite yield a reduction peak at −100 mV, whereas nantokite yields a reduction peak at −350 mV. In turn, tenorite produces a prominent reduction at −600 mV, whereas copper(II) trihydroxychlorides exhibit a unique reduction process at −150 mV. Results obtained with LM and SEM-EDX were in good agreement with those of VMP and Raman spectroscopy. The grains of azurite exhibited black and dark greenish colour because of the reactions that transformed this pigment into CuO, CuCl and $Cu_2(OH)_3Cl$. The X-ray energy spectrum obtained from the black grains presented characteristic emission lines of copper, or copper and chlorine. The presence of copper chlorides and copper trihydroxychlorides in the vault paintings of Sant Joan del Mercat can be attributed to the combined action of high humidity and chloride ions from the sand used by Palomino and, secondly, to the marine aerosol (Valencia is 4 km far the Mediterranean sea) on the surviving pristine copper pigments during the post-fire period. On the other hand, the presence of tenorite has been associated with the thermal degradation of azurite and malachite during the 1936 fires.

Green earth (pigment of natural origin mainly composed of the minerals celadonite and glauconite) was also identified in a number of samples from Palomino's frescoes. This pigment was identified through the characteristic Raman band exhibited by celadonite and glauconite structures at 145 cm^{-1}, ascribed to the internal vibrations of the octahedra MO_6 formed with the metal atoms placed in the inter-tetrahedra layer, as well as by the bands at 685 and 635 cm^{-1} caused by the vibrational modes of the SiO_4 tetrahedra. Signals at 1085, 1007 and 636 cm^{-1} are correlated with calcite, gypsum/anhydrite and anatase, respectively, which are frequent impurities of this natural pigment.[45]

White. No white pigment was identified in the white areas of Palomino's frescoes. Microscopic analysis by means of LM and SEM showed the application of a thin layer of calcium carbonate on the previously applied *intonaco* ground. Raman and FTIR spectroscopy confirmed the use of this material as a pigment. In other areas of the frescoes, the signature of slaked lime (a broad feature centred at 790 cm^{-1} with associated bands at 1086, 712 and 281 cm^{-1} formed from its reaction with moist atmospheric carbon dioxide) were also observed in the 1064-nm excitation of the Raman spectra. It is well known that the paste form of the slaked lime, called St. John's white, kept moist in pits for several weeks, was traditionally used by Italian artists as a white pigment for fresco painting. The long-term exposure to air, with occasional regrinding with water, of this material yields a pigment suitable for use without the need of an organic binder. Palomino also described these procedures in his treatise. Thus, the results obtained in the analysis of Palomino's frescoes at San Joan del Mercat are in good agreement with his recommendations according to the Italian tradition for fresco painting.

Raman spectra of samples from the areas of the paintings attributed to Guillo exhibited characteristic bands ascribed to white lead; the basic lead carbonate corresponding to the mineral hydrocerussite ($2PbCO_3.Pb(OH)_2$). In particular, a sharp and intense band at 1051 cm^{-1} associated with the carbonate stretching vibration and a weak band at 415 cm^{-1} ascribed to PbO modes were recognised in the Raman spectra. Interestingly, the presence of a weak band at 681 cm^{-1} suggests that neutral lead carbonate ($PbCO_3$, cerussite) could be present as a minor component of Guillo's white lead.[46]

Square wave modes from Guillo's samples show two main reduction peaks at −100 and −550 mV, accompanied by stripping oxidation peaks at +50, −25 and −450 mV. This voltammetry denotes the presence of a small amount of a copper pigment accompanying the lead pigment in these white samples. The peak at −550 mV exhibits a broad profile, suggesting the presence of a mixture of lead compounds. A comparison of the voltammetric parameters for this peak with those of the reference lead pigments suggests that a mixture of white lead and lead oxide is present in Guillo's samples; the latter was probably formed as result of the thermal alteration of the pristine white lead during the 1936 fire.

Gilding. The presence of gold metal foil was detected by means of VMP by the appearance of anodic peaks at approximately +250 and +1100 mV in contact with 0.10 M HCl, corresponding to the electrochemical oxidation of gold to $AuCl_4^-{}_{(aq)}$, Au_2O_3 and AuO(OH).[47–49]

A specific reference to the method for applying gold leaves in fresco painting is made in Chapter V of Book VI, Volume II of the Palomino treatise, where he describes the procedure for preparing a mordant for fixing the gold foil to the fresco surface. Colophony and wax are added to a previously prepared varnish (*barniz de guadamecileros*) of unspecified composition. Palomino indicates that linseed oil can be used if this varnish is not available. In Palomino's recipe, the aforementioned products are dissolved in turpentine, and the mixture is slowly heated until a viscous fluid consistency is obtained. GC-MS analysis of samples from the gilding applied by Palomino in the frescoes revealed the presence of drying oils together with colophony in the gold mordant, as summarised in Table S5. The compounds appearing in the chromatogram confirm that Palomino worked in the Sant Joan del Mercat church according to the method described in his treatise. The use of wax was sustained by the peak area ratio of palmitic and stearic fatty acids, as well as by the presence of a significant amount of hydrocarbons of high molecular weight such as nonacosane (C_{29}) and hentriacontane (C_{31}).[50]

Yellow. The presence of Naples yellow has been confirmed unambiguously by Raman spectroscopy (characteristic bands at 140, 330, 450 and 510 cm^{-1}), SEM-EDX and VMP in 17 samples extracted from different fragments of the original painting in the upper part of the vault. Naples yellow has a cubic pyrochlore structure ($Pb_2Sb_2O_7$) in which some metal atoms such as Sn, Zn and Fe can replace Sb and take octahedral coordination. As stated by Colomban *et al.*,[51–53] replacement of Sb atoms by other metal atoms results in a shift of the intense peak that appears at 140 cm^{-1} in the Pb-Sb binary structure and is associated with lattice vibrations of the Pb cation and vibration of the Sb cation with respect to the Sb-O sublattice. Another change observed in the Raman spectra of metal-substituted lead antimonates is the significant decrease of the most intense band at 510 cm^{-1}, ascribed to the totally symmetric elongation of the SbO_6 octahedra.[54,55]

Raman spectra of the yellow samples containing this lead antimonate pigment (Fig. 5) confirmed the presence of unmodified Naples Yellow through the intense band at 510 cm^{-1} and the band at 140 cm^{-1}. These two features enable the identification of Palomino's yellow pigment as Naples yellow discarding the lead-tin yellow or other solid solutions containing metal atoms partially replacing Sb. The absence of Sn, Zn or Fe signals in the X-ray energy spectra obtained from the yellow grains present in these samples sustained the result provided by Raman spectroscopy. Additionally, voltammetric profiles confirmed the presence of Naples yellow in these fragments of paintings ascribed to Palomino, as denoted by the prominent reduction peak at −570 mV, of characteristic profile, accompanied by the corresponding anodic stripping peak at

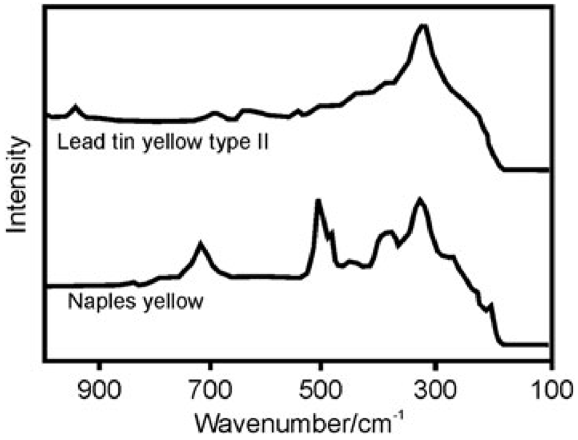

Figure 5. Raman spectrum of lead-tin yellow type II, used as reference pigment in this study (upper spectrum), and Naples yellow used by Palomino in Sample P-AM8 (lower spectrum), 785 nm excitation, wavenumber range 100–1000 cm^{-1}, 1 scan, 20× objective.

−510 mV.[40] This result was also confirmed by the X-ray energy spectra obtained from grains of this pigment that exhibited, exclusively, emission lines of O, Pb and Sb.

Hornaza is included within the artificial pigment group of the fresco colour palette in Palomino's treatise. In addition, in the glossary of terms included at the end of the treatise, this material is described as a light yellow colour made in the potters' furnace and used for glazing.

In specialised literature, *hornaza* has been associated with the lead-based yellow pigment *giallolino* mentioned in a number of old treatises.[56] Nevertheless, *giallolino* is an archaic and ambiguous word that has been ascribed to:[57] (1) an artificial yellow lead oxide analogue of massicot; (2) the artificial yellow pigment mentioned in recipes 272 and 273 of the Bolognese manuscript, which involves calcination of lead and tin (recipe 272), or calcination of those mixed with minium (recipe 273); (3) natural yellow mineral pigment found in the neighbourhood of volcanoes; and (4) artificial lead antimonate yellow prepared by roasting mixtures of lead and antimony oxides or salts, as described by Cipriano Piccolpasso[58] and used as a colouring agent for majolica glazes.

Use of these lead-based yellow pigments for painting in the 17th century has been reported in literature.[56,57] A prior mention of a pigment named *giallolino*, which is recommended for fresco painting, is found in the Ceninno Cennini's treatise.[59] Lead-tin-antimony yellow was most frequently used from the 15th to 17th centuries. Sandalinas and Ruíz-Moreno[60] have reported the use of this pigment in two paintings by the Spanish painter Velázquez, which were executed in Rome, as well as in a number of other 17th century Italian paintings.

The use of lead antimonate in paintings from the second quarter of the 17th century to the 19th century has also been reported.[56] This pigment has been identified earlier in two paintings by Lorenzo Lotto of 1505 and 1547.[60] On the other hand, lead antimonate yellow came to be called Naples yellow in a treatise by Andrea Pozzo published in Rome in 1693–1700.[56]

The identification of Naples yellow in a significant number of samples from the fresco paintings in Sant Joan del Mercat suggests that the *hornaza* pigment, listed by Palomino in his treatise, is Naples yellow. Nevertheless, one cannot discard the idea that Palomino simultaneously used both pigments, lead-tin yellow and Naples yellow. Although in the analyses performed, only the latter was found.

The analysed samples exhibited no signs of thermal alteration, and lead oxide was not found where Naples yellow was identified, thus, demonstrating the excellent stability of this pigment not only when being used in the fresco technique but also after being subjected to drastic thermal conditions during the 1936 fires.

Conclusions

The combination of the proposed analytical techniques has provided complementary and substantial data for assessing the artistic techniques of Vicente Guillo and Antonio Palomino and for discriminating between the colour palettes of these two artists for the first time. Raman spectroscopy has been essential in identifying the pigments present in the Sant Joan del Mercat frescoes and for discriminating between malachite and azurite, the latter used exclusively by Palomino and not included in his fresco palette. VMP has enabled the identification of gold foil and, in combination with LM, SEM-EDX and various spectroscopic techniques, the recognition of several alteration products of the original copper and lead pigments used by Guillo and Palomino in the Sant Joan del Mercat paintings.

The results obtained have generally been in good agreement with the recommendations written by Palomino in his treatise. The exceptional use of gypsum as stucco material for internal grounds in the wall paintings has been recognised in the areas of the vaulted ceiling painted by Palomino. This practice contrasts with the recommendation made by Palomino in his treatise about the convenience of using slaked lime-sand mortars according to traditional fresco recipes. The results obtained suggest that Palomino's treatise was written on the basis of his wide knowledge of the classical texts on artists' techniques as well as on his personal experience as a painter, which led him to propose new materials and techniques in an attempt to improve the existing fresco painting practice.

Despite the statement that lead-based pigments were traditionally not recommended for frescoes because of their empirically known alterations when subjected to the strong alkaline fresco medium, both Guillo and Palomino used them. Palomino, probably supported by his personal experience as a painter, recommended and used Naples yellow, lead antimonate. Interestingly, no significant changes have been observed in this pigment after the 1936 fires, confirming its good behaviour when used in fresco paintings. In contrast, areas of Guillo's paintings where lead white was used exhibited a noticeable change in visual appearance because of the transformation of this pigment into lead oxides.

Similarly, azurite, a pigment not mentioned by Palomino in his treatise (apart from smalt and a mention to an unknown blue pigment called *ignoto*, no blue pigments are recommended by Palomino for frescoes), has been identified. Thus, proper discrimination between Guillo's and Palomino's paintings has also been possible because of the use of azurite by the latter.

Malachite has also been identified in the frescoes. This pigment, similar to azurite, is not included by Palomino in his list of key fresco pigments. Nevertheless, Palomino remarks upon the possible alterations that malachite can undergo because of the alkaline conditions of the fresco technique, and in this context, the artist suggests a combination of malachite and green earth and/or a proteinaceous medium in order to minimise the degradation of this copper pigment.

Some of the pigments found in the vaulted ceiling and included in the colour palette proposed by Palomino, according to the classical fresco treatises, have undergone substantial changes because of the extreme conditions to which they were subjected in the church. Thus, smalt exhibited thin fractures in the outer parts of the grains probably arising from the thermal variations that occurred in the paintings during the 1936 fires. The high temperatures achieved during the fires were also the cause of the transformation of goethite to haematite and haematite to magnetite and the transformation of azurite/malachite to tenorite in parts of the fresco. The presence of a high level of humidity has also resulted in the alteration of the original azurite/malachite to copper chloride (nantokite) and copper trihydroxychloride (atacamite/paratacamite).

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Supporting information

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

References

[1] M. R. Derrick, D. C. Stulik, M. J. Landry. Infrared spectroscopy in conservation science, Getty Conservation Institute, Los Angeles, **1999**.
[2] F. Casadio, L. Toniolo, *J. Cult. Heritage*, **2001**, *2*, 71.
[3] G. D. Smith, R. J. H. Clark, *Rev. Conserv.* **2001**, *2*, 92.
[4] F. Casadio, I. Giangualano, F. Piqué, *Rev. Conserv*. **2004**, *5*, 63.
[5] M. P. Colombini, F. Modugno, *J. Sep. Sci.* **2004**, *27*, 147.
[6] A. Spyros, D. Anglos, *Anal. Chem.* **2004**, *76*, 4929.
[7] H. G. M. Edwards, J. M. Chalmers (Eds.), *Raman Spectroscopy in Archaeology and Art History*, The Royal Society of Chemistry, Cambridge, **2005**.
[8] G. Bitossi, R. Giorgi, M. Mauro, B. Salvadori, L. Dei, *Appl. Spectrosc. Rev.* **2005**, *40*, 187.
[9] P. Vandenabeele, H. G. M. Edwards, L. Moens *Chem. Rev.*, **2007**, *107*, 675.
[10] R. J. H. Clark, *Appl. Phys. A* **2007**, *89*, 833.
[11] L. Bellot-Gurlet, S. Pagès-Camagna, C. Coupry, *J. Raman Spectrosc.* **2007**, *37*, 972.
[12] M. T. Doménech-Carbó, *Anal. Chim. Acta* **2008**, *621*, 109.
[13] P. Roig, I. Bosch, J. L. Alonso, M. T. Doménech, S. Muñoz. Proceedings of the 'Madrid en el contexto hispánico desde la época de los descubrimientos' *Meeting* Universidad Complutense de Madrid, Madrid, **1992**, pp. 1405.
[14] A. Palomino, *El museo pictórico y escala óptica*, Aguilar, Madrid, **1947**.
[15] M. T. Doménech-Carbó, F. Bosch-Reig, V. Peris-Martínez, J. V. Gimeno-Adelantado, *Quím. Anal.* **1997**, *16*, 273.
[16] A. Doménech-Carbó, M. T. Doménech-Carbó, H. G. M. Edwards, *Electroanalysis* **2007**, *19*, 1890.
[17] H. G. M. Edwards, M. T. Doménech-Carbó, M. D. Hargreaves, A. Doménech, *J. Raman Spectrosc.* **2008**, *39*, 444.
[18] A. Doménech-Carbó, M. T. Doménech-Carbó, H. G. M. Edwards, *Anal. Chem.* **2008**, *80*, 2704.
[19] F. Scholz, U. Schröder and R. Gulaboski, *Electrochemistry of Immobilized Particles and Droplets*, Springer, Berlin, **2005**.
[20] F. Scholz, B. Meyer, in *Electroanalytical Chemistry. A Series of Advances*, (Eds: A. J. Bard, I. Rubinstein), Vol. *20*, Marcel Dekker, New York, **1998**.
[21] A. Doménech, M. T. Doménech-Carbó, V. Costa, *Electrochemical Methods Applied to Archaeometry, Conservation and Restoration (Monographs In Electrochemistry)*, (Ed: F. Scholz), Springer, Berlin, **2009**.
[22] Electrochemistry for Conservation Science. (Ed: A. Doménech), *J. Solid State Electrochem.* **2010**, *14*(3), 347–503.
[23] T. Grygar, P. Bezdicka, D. Hradil, A. Doménech, F. Marken, L. Pikna, G. Cepriá, *Analyst* **2002**, *127*, 1100.
[24] J. A. Gómez Sanjuán, *Boletín del Centro de Estudios del Maestrazgo*, **1990**, *31*, 49.
[25] H. G. M. Edwards, D. W. Farwell, D. L. A. de Faria, A. M. F. Monteiro, M. A. Afonso, P. de Blasis, S. Eggers, *J. Raman Spectrosc.* **2001**, *32*, 17.
[26] R. Mayer, *The Artist's Handbook of Materials and Techniques*, 5th ed., Tursen Hermann Blume, Madrid, **1985**, pp. 60.
[27] M. Laurenci-Tabasso, M. Marabelli, *Il Degrade dei Monumenti In Roma In Rapporto all'inquinamento Atmosferico*, BetaGamma, Rome, **1992**.
[28] S. Potgieter-Vermaak, N. Maledi, N. Wagner, J. H. P. Van Heerden, R. Van Grieken, J. H. Potgieter, *J. Raman Spectrosc.* **2011**, *42*, 123.
[29] I. M. Bell, R. J. H. Clark, P. J. Gibbs, *Spectrochim. Acta, Part A* **1997**, *53*, 2159.
[30] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, *Pigment Compendium. Optical Microscopy of Historical Pigments*. Elsevier Butterworth-Heinemann, Burlington, **2004**.
[31] R. J. Gettens, G. L. Stout, *Painting Materials. A Short Encyclopaedia*, Dover, New York, **1966**, 34.
[32] F. Froment, A. Tournié, P. Colombian, *J. Raman Spectrosc.* **2008**, *39*, 560.
[33] V. B. Fetisov, A. N. Ermakov, G. M. Belysheva, A. V. Fetisov, V. M. Kamyshov, K. Z. Brainina, *J. Solid State Electrochem.* **2004**, *8*, 565.
[34] M. P. Merrifield, *Medieval and Renaissance Treatises On The Art Of Paintings*. Vol. *2*, Dover Publications Inc, New York, **1967**, chapter 5.
[35] L. Da Vinci, *Tratado de Pintura*, Akal, Madrid, **1995**, 426.
[36] P. Santopadre, M. Verità, *Stud. Conserv.* **2006**, *51*, 29.
[37] J. Boon, K. Keune, J. Van der Weerd, M. Geldof, J. R. J. Van Asperen de Boer, *Chimia* **2001**, *55*, 952.
[38] A. P. Hornblower, *Archaeometry* **1963**, *6*, 37.
[39] C. Altavilla, E. Ciliberto, *Applied Physics A*, **2004**, *79*, 309.
[40] J. Plesters, *Stud. Conserv.* **1969**, *14*, 62.
[41] B. Mühlethaler, J. Thissen, in *Artists' Pigments. A Handbook of Their History and Characteristics* (Ed: R. Ashok) Vol *2*, National Gallery of Art, Washington, **1993**, 113.
[42] R. Giovanoli, B. Mühlethaler, *Stud. Conserv.* **1970**, *15*, 37.
[43] R. L. Frost, W. N. Martens, L. Rintoul, E. Mahmutagic, J. T. Kloprogge, *J. Raman Spectrosc.* **2002**, *33*, 252.
[44] A. Doménech-Carbó, M. T. Doménech-Carbó, J. V. Gimeno-Adelantado, F. Bosch-Reig, M. C. Saurí-Peris, M. J. Casas-Catalán, *Fresenius J. Anal. Chem.* **2001**, *369*, 576.
[45] F. Ospitali, D. Bersani, G. Di Lonardo, P. P. Lottici, *J. Raman Spectrosc.* **2008**, *39*, 1066.
[46] R. J. Gettens, H. Kühn, W. T. Chase, in *Artists' Pigments. A Handbook of Their History and Characteristics* (Ed: R. Ashok) Vol *2*, National Gallery of Art, Washington, **1993**, 67.
[47] R. W. Andrews, R. M. King, *Anal. Chem.* **1990**, *62*, 2130.
[48] L. D. Burke, J. F. O'Sullivan, *Electrochim. Acta* **1992**, *37*, 588.
[49] A. Doménech-Carbó, M. T. Doménech-Carbó, X. Más-Barberá, *Talanta* **2007**, *71*, 1569.
[50] J. S. Mills, R. White, *The Organic Chemistry of the Museum Objects*, Butterworths, London, **1987**.
[51] M. Pereira, T. de Lacerda-Arôso, M. J. M. Gomes, A. Mata, L. C. Alves, P. Colomban, *J. Nano Research*, **2009**, *8*, 79.
[52] P. Colomban, G. Sagon, X. Faurel, *J. Raman Spectrosc.* **2001**, *32*, 351.
[53] B. Kirmizi, P. Colomban, B. Quette, *J. Raman Spectrosc.* **2010**, *41*, 780.
[54] F. Rosi, V. Manuali, C. Miliani, B. G. Brunetti, A. Sgamellotti, T. Grygar, D. Hradil, *J. Raman Spectrosc.* **2009**, *40*, 107.
[55] F. Rosi, V. Manuali, T. Grygar, P. Bezdicka, B. G. Brunetti, A. Sgamellotti, L. Burgio, C. Seccaroni, C. Miliani, *J. Raman Spectrosc.* **2011**, *42*, 407.
[56] H. Kühn, in *Artists' Pigments. A Handbook of Their History and Characteristics* (Ed: R. Ashok), Vol *2*, National Gallery of Art, Washington, **1993**, pp. 83.
[57] I. N. M. Wainwright, J. M. Taylor, R. D. Harley, in *Artists' Pigments. A Handbook of Their History and Characteristics*, (Ed: R. L. Feller) Vol. *1*, National Gallery of Art, Washington, **1986**, pp. 219.
[58] C. Piccolpasso. *Li tre Libri dell'Arte del Vasaio*, Annesio Nobili Editore, Pesaro, **1879**.
[59] C. Cennini, *El libro del Arte*, Akal, Madrid, **1988**, pp. 75.
[60] C. Sandalinas, S. Ruíz-Moreno, *Stud. Conserv.* **2004**, *49*, 41.