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Raman and FT-IR microspectroscopies reveal medieval Hispano-Muslim wood painting techniques and provide new insights into red lead production technology

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Abstract

This paper describes the study of two Nasrid polychrome wooden ceilings from the Alhambra monumental ensemble using vibrational spectroscopic techniques. The study is focused on the identification of the constituent materials and execution techniques used employing non-invasive and non-destructive scientific investigation methods. Information about both inorganic (pigments) and organic (binders and coatings) materials has been obtained without the need for time-consuming procedures. A complex stratigraphy involving the use of a protective priming layer of red lead covered with animal glue and white lead was revealed. The identification of Raman signatures of different lead oxide compounds, including lead-tin oxide (Pb_2SnO_4), in the priming layer, allowed us to hypothesize the synthesis of red lead (Pb_3O_4) from litharge (α-PbO), a common by-product of the cupellation process used since antiquity for silver production. Furthermore, the pigments employed in hidden drawings found in the reverse of the wood pieces of one of the ceilings were also studied and compared with those found in the visible external face.

Keywords: pigments, Pb_2SnO_4, Pb_3O_4, polychrome wood, μ-FTIR

Introduction

The investigation of the materials employed by the artists in the context of cultural heritage has evolved in the last years trying to find the more convenient analytical techniques to provide as much information as possible with the less invasive intervention,[1–3]. Vibrational spectroscopies are among the most adequate approaches because of their multiple advantages in comparison with other spectroscopic or chromatographic analytical techniques. For example, the molecular and structural information provided by infrared and Raman spectroscopies yields more conclusive results than those obtained if just the elemental composition is retrieved. In addition, infrared and Raman spectroscopies are very suitable for the study of artistic heritage items because they are not destructive, which allows working on the same micro-samples to get more complete results. They constitute a very interesting option since they also provide information not only about inorganic materials but also about organic compounds, with much less intensive sample preparation[4] in comparison with chromatographic methods. The size and amount of the sample required, particularly for Raman microspectroscopy, are scarce and the measurements can be carried out directly without sample preparation. Thus, Stanzani et al[5] demonstrated that with the use of different excitation lines for Raman spectroscopy and in combination with FTIR, it was possible to identify almost all the ingredients of a 16th-century wood panel painting. Furthermore, Raman micro-spectroscopy allows quick and non-invasive measurements and it is even possible to work *in situ* employing portable instruments without taking samples.[6] Although working with portable Raman *in situ*, usually is only possible to examine the most superficial layer, in certain cases, stratigraphy could be accessed in areas where the external layer has been detached.[7]

The above-mentioned benefits of both Raman and infrared microspectroscopies are exploited in this work to gain information about the richly painted carved wooden

ceilings typical of the medieval Hispano-Muslim architecture. Wooden ceilings have a long tradition in the Hispano-Islamic area attaining their greatest splendour during the Nasrid period. They have been mostly studied from a stylistic point of view, being scarce the scientific investigations aimed at the identification of materials and techniques employed in their decoration.[8] The objects of study are two polychrome panelled wooden ceilings located in the Alhambra monumental ensemble (Granada, Spain). It is the best-preserved monumental complex representative of the medieval Islamic architecture in the Iberian Peninsula. Built and decorated by the Nasrid dynasty during the 13-15th centuries, it was included in the World Heritage (UNESCO) in 1984.

Experimental

2.1 Description of the site of the study

The wooden ceilings that embellished the Hall of the Abencerrages and the Hall of the Two Sisters (Figure 1a and b) were studied; both of them were built during the reign of Muhammad V in the 14th century. These ornamental plane ceilings with interlace decoration, called a*lfarje ataujerado*, are characteristic of the medieval Islamic architecture. They are formed by several pieces of wood nailed to a supporting structure forming geometric patterns.

The wooden ceiling of the Hall of the Abencerrages is located in the central zone of the south gallery connecting the entrance to this hall with the Court of the Lions. This intricate woodwork is composed of eight-point stars placed in the center and interlaced with other polygonal pieces (*zafates)*. The pieces (Figure 1c) are decorated with vegetable motifs carved and painted with white, red and black colours over a background also decorated with red, blue, and green colours. The *alfarje* belonging to the Hall of the Two Sisters is located in the east room of this hall. In this case, the pieces are just polychromed without carved decorations. The geometrical composition is around a central circle with eight-point

stars.

Figure 1

2.2 Pieces of study and micro-samples

The ceilings of both halls were disassembled during the conservation works carried out by the *Wood materials restoration workshop* of the Council of the Alhambra and the Generalife. This allowed a non-invasive investigation with a portable Raman spectrometer without the need to use scaffolding to reach the ceiling. The optic probe and the microscope head of the portable Raman spectrometer were attached to an extensible bar, which allowed recording Raman spectra of the different pieces placed over a table. Eighteen polychrome geometric pieces were analysed on the obverse and reverse before they were restored. Surprisingly, the reverse of some pieces revealed some pictures and sketches. The drawings found showed flowers, fantastic animals and human figures or faces (Figure 1d). In the obverse, crackling, fissures in different patterns and detaching were clear signs of deterioration of the painting layer.

To complete the results achieved and to enable the study of the stratigraphy of the polychrome work, five small samples (less than 1 mm) were taken from some pieces of the *Alfarje* of the Hall of Abencerrages (see Table 1S, supporting information).

2.3 Instrumentation and measurements

Non-invasive measurements were carried out with a portable Raman microspectrometer innoRam (B&W TEK Inc., Newark, USA) provided with a 785 nm excitation laser with a maximum of power of 300 mW and a CCD detector thermoelectrically cooled to -20ºC. The spectral range is from 65 to 2565 cm^{-1}. The fibre optic probe is connected to a video microscope with a 20x magnifying objective coupled to a motorized accessory which allows moving in the X-Y-Z axes. Laser power less than 10 mW and different exposition times and a number of accumulations were employed adapting the acquisition conditions to the sample behaviour.

The same acquisition variables were considered for the measurements in the laboratory, which were carried out with a Renishaw inVia Raman confocal micro-spectrometer equipped with a CCD detector camera refreshed by Peltier system (-70ºC) and four objectives (5x, 20x, 50x, 100x). Laser power was adjusted paying special attention to avoid sample degradation, being below 5 mW and 10 mW for 514 nm (green) and 785 nm (red) excitation laser, respectively.

An FTIR 6300 spectrometer coupled to an FTIR IRT-7000 microscopy with a mercury cadmium telluride (MCT) detector from JASCO (Tokyo, Japan) was employed to further investigate the presence of organic materials in the samples. Spectra were registered in the spectral range 750-4000cm^{-1} with a microscope provided of an objective lens of 16x magnification. The number of scans was around 130 and the aperture was modified depending on the sample. Micrometric samples selected under stereo zoom were placed in a Spectra-Tech micro-compression cell with diamond windows (Thermo Scientific, USA) to register the spectra in transmission mode.

Results and discussion

Characterization of the external decoration of the wooden pieces

The wooden pieces were richly decorated mainly in red, blue and green colour in the obverse. This is the external part that can be seen when the ceiling is assembled in its original position. A summary of all the results found in the obverse of the pieces can be found in Table 1.

The decoration was first investigated with the portable instrument. A high fluorescence background was found in all the spectra recorded suggesting the presence of organic compounds. For this reason, only pigments giving strong Raman signals could be clearly identified. This was, for example, the case of cinnabar (HgS) in the red areas, with the characteristic Raman bands at 255, 285, 344 cm^{-1}. The spectra recorded in the blue-greyish decorations were characterized by a weak feature at 548 cm^{-1} and a complex pattern in the region from 1000-2000 cm^{-1} that could be related to natural lapislazuli [9,10] as it will be discussed later. Furthermore, access to deeper layers was only possible in small areas where the superficial layer was lost. This allowed the detection of red lead (Pb_3O_4) with bands at 121, 147, 389 and 548 cm^{-1} in the cracked part of one piece with external blue decoration.

Table 1

Nevertheless, the information provided by the portable instrument in the obverse of the pieces was, in general, very limited by the strong fluorescence. Thus, microsamples were taken for further investigation in the laboratory. Looking at these samples under the microscope, a superficial layer with waxy and yellowish appearance was always observed. In fact, this layer was probably causing most of the difficulties in achieving information with the portable instrument. Focusing on this topcoat, together with some spectral features of the corresponding pigments, the characteristic Raman bands of beeswax were detected at 1065, 1133, 1298, 1423, 1445, 2857, 2893 cm^{-1}[11] (see Figure 2a). FTIR

microspectroscopy confirmed the identity of this topcoat. As can be seen in Figure 2b the infrared spectrum shows bands corresponding to C=O stretching (1737 cm^{-1}) and CH stretching vibrations of hydrocarbonated long chains (2850 and 2917 cm^{-1}), typical of waxes[12]. This wax finishing was probably applied with a protective role against humidity during the intensive restoration works carried out by Torres Balbás in the first half of the 20th century,[13] a period during which wax-based treatments were popularized among restorers.

Figure 2

Regarding the pigments, the study in the laboratory confirmed the presence of cinnabar as red pigment. In the case of blue decorations, the Raman spectra differ depending on the wavelength (785 or 514 nm) employed for excitation, as can be seen in Figure 3.

Figure 3

In both cases, the bands at 258 and 548 cm^{-1}, which can be assigned to the bending and symmetric stretching vibration of the blue radical anion S_3^- responsible for the intense blue color of ultramarine pigments (both natural and synthetic), are observed. Additionally, in those spectra recorded using 514 nm as the excitation source, the first and second overtones of the stretching vibration at 1093 and 1640 cm^{-1} are also visible due to the resonance of the chromophore group at this excitation wavelength.[14] Using this laser, we also identified weak bands located at 390, 667 and 1010 cm^{-1} that could be attributed to an accessory mineral, diopside ($CaMgSi_2O_6$), commonly present in lapis lazuli rock together with the blue lazurite ($Na_7Al_6Si_6O_{24}S_3$), which points to the natural origin of the pigment.

When excitation at 785 nm is employed, interestingly, the most intense spectral features observed are bands at 1290, 1485, 1533 and 1806 cm^{-1}. Despite being so narrow that could be misinterpreted as Raman features, these bands have been demonstrated to be due to the luminescent emission arising from other components of lapis lazuli rock excited only when

785 nm laser is employed.[10,15] These features, due to mineral impurities, can be used to distinguish easily the natural pigment from synthetic ultramarine blue.[8] In fact, in some of the spectra recorded, the characteristic band of lazurite at 548 cm^{-1} was almost imperceptible (see Figure 3) which points to the use of a pigment with many impurities. The reason could be the poor quality of the raw lapis lazuli stone (not very rich in lazurite) or the use of a second-grade pigment obtained during the purification process.[16] This is in agreement with the greyish blue tonality observed macroscopically and the identification of diopside (with excitation at 514 nm). In fact, when the blue samples were observed microscopically few intense blue grains were seen in contrast with the presence of many partially blue and transparent particles. Focusing on blue particles, the intensity of the Raman band at 548 cm^{-1} increased.

Finally, when we investigated the sample taken from the green decoration (Z-8V), we found that in fact, it was blue under the microscope. Grains with different blue tonalities were observed (Figure 1S, supporting information). In this case, apart from lapis lazuli identified in the brilliant dark blue crystals, another blue pigment, azurite ($2CuCO_3 \cdot Cu(OH)_2$), was detected in the pale blue grains using the 514 nm laser. It seems that both pigments were applied together since no signs of superimposed layers was found. This mixture has been also reported on plasterwork in other locations in the Alhambra[17] and may have been used to save costs due to the high value of natural lapis lazuli or to change the tonality.

Characterization of the preparation layers

The analysis of the microsamples allowed for the investigation of the stratigraphy of the paintings using confocal Raman microspectroscopy and FTIR microspectroscopy even when the possibility of preparing embedded cross sections was not considered. First, the visual inspection under the stereomicroscope revealed always an orange preparation layer

applied on the wood support and sometimes an additional white layer under the pigments (see Figure 4a).

Figure 4

Considering the white layer, all Raman spectra recorded were characterized by a huge fluorescence background that hindered the observation of clear Raman bands. However, spectra of fair quality could be obtained after a careful selection of the measurement conditions (50x and 100x magnification objectives and taking profit of high confocality) enabling the identification of white lead ($2PbCO_3 \cdot Pb(OH)_2$) which is characterized by a strong band at 1053 cm^{-1} [18–20]. This lead carbonate hydroxide is equivalent to the naturally occurring hydrocerussite but due to the scarcity of the mineral, white lead has been synthesized since the antiquity, being the first evidence from the Roman period.[21] Apart from its use as a white pigment, it is well known the use of white lead in artworks as a ground to provide luminosity to the pigments because of its high reflective index.[22,23] In fact, a small feature at 1053 cm^{-1} was observed in many spectra of the different colours identified. Furthermore, some small additional Raman bands (weak and broad) were observed in the spectra recorded in this white layer (see Figure 4b). They can be attributed to C-H bending (1450 cm^{-1}), amide I vibration (1668 cm^{-1}) and C-H stretching (2884 and 2949 cm^{-1}) of proteins[11,24] (Figure 4b). This proteinaceous material, employed as binder, is probably responsible for the strong fluorescence background observed.[25] These findings were confirmed by the results obtained using infrared microspectroscopy. In Figure 4d, the infrared spectrum recorded in the white layer shows a broad band at 1398 cm^{-1} due to CO_3^{2-} stretching of white lead together with typical bands of proteins. These can be better seen in areas where the organic binder was isolated from the pigments with the help of the diamond compression cell. Thus, a broad band centred at 3310 cm^{-1} due to NH stretching vibrations (Amide A), Amide I (mainly associated with the stretching vibrations of the C=O bond) at

1654 cm^{-1} and Amide II (primarily involving bending vibrations of the N—H bond) at 1533 cm^{-1}were clearly identified.[26] These findings are in agreement with the results obtained using gas chromatography coupled to mass spectrometry (GC-MS) which revealed the use of animal glue as the main binder.[27] Here, the use of vibrational spectroscopy has allowed for the identification of the type of binder in a very fast way and without any sample treatment. Of course, the information obtained by GC-MS was more specific and allowed the detection of additional organic materials as polysaccharide gums, but a time-consuming sample treatment was necessary to extract the different fractions of the organic material.

Another example of how the vibrational spectroscopy helps in the identification of organic binders is also shown in Figure 4d. In this case, a natural resin was detected by its infrared spectra with a strong band at 1728 cm^{-1} and additional features in the C-O stretching region (1164, 1064 and 1029 cm^{-1}). These bands are typically associated with natural resins formed by complex mixtures of esters and polyesters of polyhydroxy acids. These features strongly resemble those obtained by our group in gilded decorations on plasterwork in the Alhambra[28]. In certain false gildings, we found tin foil tinted to look like gold by means of a varnish composed of oil and natural resin. Thus, we can hypothesize that some areas of the ceiling were decorated with tin-based false gildings and these could be remains of the mordant employed to fix the metal or the varnish.

Regarding the orange layer, the microscope observations revealed that it was always applied directly on wood support. The major phase identified was the red-orange pigment red lead (Pb_3O_4) as can be seen in Figure 4c. The only previous scientific study about polychrome carpentry in the Alhambra[8] also hypothesized the presence of this pigment for priming wood. However, using SEM-EDX, the authors could only identify Pb. Although they proposed the use of the intensity of the Pb Mγ spectral line to discriminate among red (oxides) or white (carbonates), the identification of red lead was not

unequivocal. Here, the use of Raman spectroscopy provides full evidence of the use of red lead in the priming layer, probably as a protective treatment against insects, fungi, and mold[21]. In addition, in the previous work, Cardell *et al*. proposed that synthetic minium (red lead) produced from the heating of white lead was used. They based their assumption on the presence of white grains identified as the incompletely roasted white lead just by visual observation with the petrographic microscope under polarized light. Here, with the use of Raman spectroscopy, we were able to get complete molecular and structural information even without the need for sample preparation. Thus, we identified (see Figure 4c) not only red lead (Pb_3O_4) but also massicot (orthorhombic β-PbO) (with bands at 142, 287 cm^{-1}) and lead-tin oxide (Pb_2SnO_4) with characteristic bands located at 127, 194, 456 cm^{-1}[29,30] in the ground layer. Furthermore, changes observed in the relative intensity of the band at 147 cm^{-1} could also be attributed to the presence of litharge (tetragonal α-PbO)[29] although in this case, the results are not conclusive due to the overlapping with red lead bands. All these are pigments employed in medieval times, being litharge and lead-tin oxide yellow, and massicot red-orange.[31] However, these findings have not an easy explanation since the idea of an intentional mixture with red lead to achieve a specific colour makes no sense if we think they were used in a ground layer completely hidden. Therefore, it is more probable that their presence is accidental, maybe as degradation products or as remains of incomplete reactions during the synthesis of red lead. Massicot and litharge presence could be explained by considering the traditional process of white lead calcination to obtain the red lead. Heating white lead first produces litharge, which finally with temperatures about 470º and in an oxidative environment, generates Pb_3O_4. Massicot can appear as a consequence of an excess of the temperature (>500º) during the roasting process.[32] Thus, non-homogenous heating during the manufacturing process of red lead allows explaining the presence of both compounds. However, it cannot explain the

presence of lead-tin oxide, which only forms under oxidative calcination at temperatures above 650°C. We hypothesize an alternative process for the synthesis of red lead based on the roasting of litharge instead of white lead. The clue is in the origin of the litharge employed, which would come as a by-product originated from silver smelting in the cupellation process. The cupellation process is documented in the Hispano-Muslim territory (Al-Andalus).[33] This is the last stage in the production of silver and it follows the smelting of argentiferous ores (being galena the most common). Smelting silver-rich galena produces a silver-lead alloy. Cupellation relies on the fact that lead is more easily oxidized than silver. Once heated at high temperature (>650º) under oxidizing conditions, lead-silver bullion starts to melt and transforms into a foamy litharge cake on top of a relatively pure silver button. The formation of lead-tin oxide could happen during this process in tin-containing ores, as described for silver bearing jarosites mined during the Roman times in the Iberian peninsula.[34,35] Thus, the litharge cake obtained as a by-product can also contain lead-tin oxide. This cake could have been roasted at temperatures near to 500º C to produce the red lead and if the temperature was over 500ºC, some massicot was also formed[35]. This process could explain all compounds found together with red lead.

Interestingly, the presence of lead-tin oxide can also explain the identification of tin in the priming layer of red lead in Nasrid carpentry by Cardell *et al.* based on SEM-EDX.[8] In that case, due to the limited information provided by the elemental analytical techniques employed, its presence was attributed to powdered tin metal intentionally added by the artisans to get brighter polychromy. Here, the capacity of identification of Raman spectroscopy has allowed clarifying the presence of this element in the form of lead-tin oxide.

Characterization of the drawings found in the reverse of the pieces

Finally, we will discuss briefly the results of the analysis of the drawings found on the reverse of the thirteen pieces of the ceiling of the Hall of the Two Sisters. These pictures are very interesting because, up to our knowledge, the *alfarje* was never disassembled before, so it is possible to affirm that the materials of these drawings are totally original and free of any retouching, restoration or conservation treatment. Furthermore, the pigments are probably better preserved because they were not exposed to light and any other environmental agents. The drawings display a variety of forms, showing both real and fantastic human faces and bodies, animals, and schemes. The main colours employed for these hidden drawings were black and white but it is also possible to find yellow, red and orange colours. Stains with remains from brush strokes are also found, maybe as a result of cleaning the brush before changing the colour or just to see the result before applying it on the visible part of the piece.

In this case, all the measurements were carried out with the portable Raman spectrometer without the need of taking samples, because the pigments were applied directly above the wood without preparation layers and the spectra registered did not show any strong fluorescence or additional bands.

Typical spectra recorded can be seen in Figure 2S (Supporting information). Most of the pigments identified, namely cinnabar, white lead, red lead, and massicot, coincide with those found in the obverse, either in the external painting or in the preparation layers. The black colour which was widely used in these drawings was clearly identified as carbon black due to the two broad bands located at *ca.* 1300 cm^{-1} and 1600 cm^{-1}.[36] This pigment was probably used in the obverse for the contour lines of the different pigments but the fluorescence background did not allow a clear identification. Another pigment identified here but not in the obverse was the yellow pigment orpiment. Orpiment (As_2S_3) was identified thanks to the presence of intense Raman bands located at 67, 104, 135, 154, 178,

202, 293, 310, 354, 381 cm^{-1} [29]. The absence of this colour in the external face of the ceiling must be attributed to its instability. It has been reported that light affects this pigment turning it into white or colourless arsenolite (As_2O_3), a very weak Raman scatterer, which was not detected.[37] Curiously, blue drawings were not observed in the reverse despite this colour appeared abundantly in the obverse visible polychrome work.

Conclusions

Raman spectroscopy has allowed the characterization of the polychrome decorations of the Nasrid wooden ceilings, identifying both the pigments and the execution technology. The use of benchtop microspectrometers was necessary to overcome fluorescence interference when studying the obverse of the pieces. The results have revealed an elaborated painting technique with several preparation layers each one with a different objective. The wood was first treated with red lead to protect it. Then, a white layer of white lead was applied to hide the intense orange colour of red lead and to give more luminosity to the pigments. Infrared spectroscopy has complemented the information contributing particularly to the identification of organic materials like animal glue employed as binders, a natural resin probably used as mordant for false gilding and beeswax at the topcoat. Particularly interesting was lead speciation in the red lead layer, with the identification of lead-tin oxide, massicot, and litharge. It helped to shed new light on ancient red lead production technology. These findings demonstrate the importance of using vibrational spectroscopic techniques that provide a unique fingerprint of the compounds present without the need for complex sample preparation procedures. Furthermore, the pigments employed in the hidden reverse drawings were easily identified with non-invasive measurements using portable Raman spectrometer without sampling. Some of the pigments matched those of the obverse but curiously natural lapislazuli was not found, probably because the artisans were aware of the cost of this highly precious pigment and reserved it strictly for the

external motifs.

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Figure captions

Figure 1. Images of alfarjes located in (a) Hall of the Abencerrages and (b) Hall of the Two Sisters. Typical geometrical wooden pieces (*zafates*) of the *alfarjes* (c) obverse and (d) reverse.

Figure 2. (a) Raman spectra of beeswax standard (1) and beeswax found in the top coat of red (2) and blue (3) samples. Raman features of red (cinnabar, C) and blue (lapis lazuli, L) pigments are observed. (b) Infrared spectra of beeswax (1) and topcoat of the samples (2).

Figure 3. Raman spectra of lapis lazuli pigment identified in the obverse of the zafates recorded with 514 nm (1) and 785 nm (2) and (3) excitation lasers focusing on different blue areas.

Figure 4. Study of the preparation layers. (a) Image of a red sample under the stereomicroscope where the white and orange preparation layers are observed under the red pigment. (b) Raman spectra registered in the white preparation layer: white lead (1), white lead and protein material (2) and standard of animal glue for comparison (3). Additional Raman features of pigments (*) found in both the pictorial and orange preparation layers are also observed. (c) Raman spectra of the materials found in the orange preparation layer: red lead/minium, (1), red lead/minium, M, and massicot (2), red lead/minium, M, and lead-tin oxide (3). (d) Infrared spectra of different organic materials identified in the wooden pieces: resin (1), protein material mixed with white lead (2) and protein material (3).

Table 1 Material identified in the obverse of the zafates wood pieces.

Area	Material	Raman bands (cm^{-1})	Laser (nm)	Portable
Red	Cinnabar	255, 285, 344	785	yes
Blue	Lapis lazuli	258, 548 (1020, 1215, 1290, 1485, 1533, 1806, 1965)*	785	yes
		258, 548, 580, 1093, 1640 (lazurite) 390, 667, 1010, 1635 (diopside)	514	no
Green	Azurite	248, 401, 762, 835, 1095, 1430, 1578	514	no
	Lapis lazuli	258, 548 (1020, 1215, 1290, 1485, 1533, 1806, 1965)*	785	no
		258, 548, 580, 1093, 1640 (lazurite) 390, 667, 1010, 1635 (diopside)	514	no
White preparation layer	White lead	1053	785	no
Orange preparation layer	Red lead	121, 147, 312, 390, 548	785	yes
	Lead tin oxide	127, 194, 456	785	no
	Litharge	147 (not confirmed)	785	no
	Massicot	142, 287	785	no
Topcoat	Beeswax	1065, 1133, 1298, 1423, 1445, 2857, 2893	785	no

* luminiscence bands