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Romantic restorations in the Alhambra monument: spectroscopic characterization of decorative plasterwork in the Royal Baths of Comares

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Abstract

The polychrome plasterwork decorations of the Room of the Beds in the Royal Bath of Comares of the Alhambra monumental ensemble have been studied using Raman microspectroscopy and complementary techniques. This area keeps the testimony of the controversial restorations carried out in the 19th-century in an attempt to imitate the lost original appearance of the authentic Nasrid plasterwork. Raman spectroscopy and energy dispersive X-ray fluorescence (ED-XRF) have been employed to identify the pigments and extenders. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) has been used to gain additional information about the morphology of the painting layers. Additionally, infrared microspectroscopy provided insight into the nature of the organic materials employed as binders. Vermillion, synthetic ultramarine blue, hematite and carbon black were clearly identified in red, blue, brown and black decorations by Raman spectroscopy. Green decorations were executed with a copper-arsenic pigment that could not be unambiguously identified although the presence of Raman bands typical of arsenate stretching bands could point to alteration processes of

copper arsenite pigments. Regarding the execution technique, the pictorial layer was applied over a preparation layer of white lead that also contained barite using a proteinaceous binder. The presence of anglesite and other phases related to hydrocerussite alteration due to humidity and salts was also evidenced. Finally, a comparison of the materials found in this redecoration with those identified in original Nasrid decorations has been performed revealing noticeable differences in both the materials and the execution technologies.

Introduction

The Alhambra monumental ensemble is the most important surviving remnant of the medieval Islamic architecture in the Iberian Peninsula. Both fortress and residence, the Alhambra comprises palaces, guard rooms, courts, and gardens as well as workshops, baths, and a mosque.^[1] It was included in the UNESCO World Heritage List in 1984 due to its universal beauty and exceptional expression of Moorish and Andalusian culture. The citadel was mainly built by the Nasrid dynasty, the last Muslim rulers in Spain, during the 13-15th centuries. However, the Alhambra now is the result of many changes, interventions and restorations carried out throughout its history. Shortly after the Christian conquest in 1492, some areas were redecorated according to the Renaissance style and several constructions were made to adapt the complex to the new military needs and the Christian customs.^[2] After some periods of abandonment and the Napoleonic occupation between 1810 and 1812, the state of conservation of the Alhambra was particularly alarming. The Monument was then re-discovered thanks to the romantic travelers and writers who started to promote the need of preserving it.^[3] The first modern consolidation and restoration works inside the Nasrid palaces were accomplished long before the institutionalization of the protection of historical monuments in Spain. Starting in 1828 and lasting until 1907, the interventions carried out by the Contreras family

followed the restoration ideology predominant in Spain at that time, the *violletiana* school, and recreated whole areas, mostly without any conclusive archaeological or documental evidence.^[4] Particularly, the works of Rafael Contreras (between 1847 and 1889) became very famous and also controversial. He was named the “ornamental restorer” because of his esthetical interventions redecorating many areas with vivid colors in an attempt to return the oriental aspect to the palaces.^[5] This study focuses on his redecoration of the Room of the Beds of the Royal Bath of Comares in the context of a new intervention of this space, which is being carried out by the Council of the Alhambra and Generalife. The investigation of the materials employed in the Contreras’s redecoration will surely help conservators and will provide a better historical knowledge of the past interventions allowing a comparison with the original decorations still preserved in the Monument.

In this sense, it is remarkable that even when the decorative revetments of the Alhambra have been widely studied from the historical and stylistic point of view, scientific investigations related to the materials are still scarce. First studies devoted to the analysis of the characteristic polychrome Nasrid decorative plasterwork or *stucco* of the Alhambra were performed on samples taken from different areas of the palaces and using mainly SEM-EDX to identify the pigments and the execution technologies.^[6] Later, our group performed a wide *in situ* study in the Hall of the Kings of the Lions Palace using portable Raman instrumentation.^[7] *In situ* studies were complemented with laboratory investigations on selected microsamples.^[8] These studies provided valuable information about diverse phenomena affecting the decorations with the identification of degradation forms of pigments like cinnabar, minium, and azurite. Furthermore, a complete study of the characteristic of gilding decorations including diverse execution technologies and alteration forms was also carried out.^[9] All of these previous studies focused on the

original Nasrid polychrome works and some Christian redecorations of the early period. Up to date, no studies have been carried out on the 19th-century restoration works, which are now also part of the Alhambra's history, as the one presented in this investigation. Here, we propose the use of Raman spectroscopy including both portable and benchtop approaches in a smart combination with other analytical techniques like X-Ray Fluorescence (ED-XRF), infrared microspectroscopy and SEM-EDX, to identify pigments, extenders, preparation layers, alteration products and organic binders.

Experimental

Description of the site of study

The Room of the Beds (Fig. 1) is located in the Royal Bath of Comares Palace in the Alhambra. This bath was funded by the sultan Yusuf I (1333-1354)^[10] according to the importance of the baths in the Islamic culture. The baths or *ḥammām* were used for cleaning as well as a therapeutic, relaxing, purification and meeting place. The Room of the Beds was the reception and dressing room of this bath where people chatted about politics and everyday issues. This site presents severe humidity problems not only because of its ancient use as a bath but also due to the underground location and the roof leaks that caused infiltration of rainwater. This fact induced the deterioration of polychrome of the plasterworks decoration and turned the whole structure very unstable. The earliest recorded interventions date already in early Christian period. Much later, during the 19th century, it was carried out one of the most relevant works of restoration of Contreras family in the Alhambra.^[5] They began with the intervention of Jose Contreras who removed the panels of original plasterwork that remained disassembled for more than a decade.^[11] Afterward, in the period of 1848-1866, Rafael Contreras undertook the redecoration of the room with the construction of new decorative elements, combining the use of copies of the original disassembled motifs, copies from different

spaces of the Nasrid Palaces, and carving new designs according to the needs. These motifs, decorated by the painter Santiago Ferraro Grissi, were based in an esthetical, whimsical and colorful restoration trying to imitate the original Nasrid aspect.^[5] Unfortunately, the humidity problems are still present, and the redecoration of Contreras is now suffering from lack of adhesion of the pigments. That is why the Alhambra Council took part in a new intervention during the last years trying to consolidate the decoration. During this intervention, restorers took some microsamples by scrapping off the polychrome plasterwork that we studied for this work. Ten microsamples were considered, two of each one of the colors that can be found in the room, namely red, blue, green, brown and black.

Figure 1

Instrumentation and measurements

X-ray fluorescence spectra were registered with a handheld ED-XRF analyzer Niton XL3t GOLDD+ (Thermo Fisher Scientific Inc.) equipped with a Rh tube anode of 45 kV and 40 μ A maximum and a Geometrically Optimized Large Drift Detector (GOLDD). The instrument is provided with multiple programmable excitation filters that are optimized for specific ranges: main (40kV), low (20kV) and light (10kV) ranges. A collimator is provided to reduce the standard sample spot of 8 mm to 3 mm. An integrated CCD camera allows visualizing the measurement area. “Mining and soils” measurement method was used as it is optimized to detect elements from Mg to U at levels higher than 1%. Around 40 measurements were made.

Raman spectra were registered either with a portable Raman microspectrometer innoRam (B&W TEK Inc., Newark, USA) or a Renishaw inVia Raman Confocal Microscope. The first one was employed for the *in situ* measurements. It is equipped with a 785 nm excitation laser (300 mW), and a CCD detector thermoelectrically cooled to -20 ° C.

Acquisition spectral range is defined to 65-2565 cm^{-1} . A 5-meter-long fiber optic probe connected to a video microscope (20x objective) is mounted on a motorized accessory in the X-Y-Z axes that allows different positioning and orientation. More than 120 spectra were recorded.

The same excitation laser of 785 nm is available in the Renishaw inVia Raman confocal micro-spectrometer that is equipped with a CCD detector camera refreshed by Peltier system (-70°C) (CICT, Universidad de Jaén). Four objectives (5x, 20x, 50x and 100x) can be used which allow changing the laser spot from 1 to 300 μm .

Acquisition conditions like the exposition time and the number of accumulations were adapted to the characteristics of each sample to get good signal-to-noise ratio in the spectra. The laser power was always less than 10 mW in order to prevent sample damage. Infrared spectra were recorded in the range 4000 to 750 cm^{-1} using a Jasco Fourier transform infrared (FT-IR) 6300 spectrometer coupled to an IRT-7000 microscope. The microscope is provided with a nitrogen cooled MCT detector. 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. A 16x Cassegrain objective was used. Typical acquisition parameters were 50x50 μm aperture, 4 cm^{-1} resolution, and 200 scans.

A MERLIN (Carl Zeiss SMT AG) Field Emission Scanning Electron Microscope of high resolution (FESEM) that allows obtaining secondary electron (SE) and retro dispersive electrons (EBS) images has been employed. The equipment has two detectors for the elemental microanalysis, an energy dispersive X-ray spectroscopy detector (EDS) Oxford Inca Energy 350X-MAX 50 and a WDS detector Oxford Inca Wave 500. The samples were metalized with carbon.

Results and discussion

Pigments identification

Red and blue decorations were easily characterized by using the portable instruments. ED-XRF spectra identified mercury and sulfur in the red color. The presence of mercury sulfide (cinnabar or vermillion) was further revealed by the characteristic Raman bands at 255, 285 and 344 cm^{-1} (see Fig. 2). The distinction between natural cinnabar or synthetic vermillion is challenging. Both pigments have been employed since the antiquity being cinnabar the natural mineral and vermillion the synthetic form manufactured in Europe since the 8th century. The absence of clear signals of elements like Fe or Si in the ED-XRF spectra due to impurities of bitumen or clays is not enough to affirm unambiguously that synthetic vermillion was used.

Figure 2

Synthetic ultramarine blue was identified by the most characteristic Raman band of lazurite at 548 cm^{-1} (see Fig. 2). In this case, it was possible to attribute the blue color to this synthetic pigment instead to natural lapis lazuli due to the absence of the intense luminescence pattern (additional bands around 1300, 1500 and 1800 cm^{-1}) of mineral impurities that characterize the natural rock when using 785 nm as the excitation source.^[12] The synthetic pigment was first synthesized in the 19th century and it was widely employed due to its cheaper prize comparing with the natural lapis lazuli. It is basically a complex sulfur-containing sodium aluminosilicate ($\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$) with blue color due to the spectral range of absorption of the sulfide ions S^{2-} and S^{3-} .^[13]

No useful Raman spectra were obtained with the portable instrument for green, brown and black decorations. Thus, the corresponding microsamples were studied in the laboratory. Nevertheless, in the case of the green motifs, the identification of the elements

using the portable ED-XRF instrument was extremely useful. Copper and arsenic were mainly detected (Fig. 3 b) therefore the use of pigments like Scheele's green or Emerald green that were widely employed during the 19th century^[13] could be hypothesized. However, the Raman spectra obtained from the green microsamples (see Fig. 3 a) with a dominant band at 860 cm⁻¹ did not match the reported Raman spectra of either of these two pigments. Scheele's green presents bands at 135, 370, 780 cm⁻¹, and Emerald green is a copper acetoarsenite that shows a more complex Raman spectrum with dominant bands at 242, 371 and 950 cm⁻¹ together with the characteristic pattern of acetate in the region of ~1400 cm⁻¹.^[14] The presence of the latter could be discarded by the absence of typical bands of acetate. On the other hand, the band at 860 cm⁻¹ in the here recorded spectra is more similar to those bands reported for several basic copper arsenate minerals like cornwallite (Cu₅(AsO₄)₂(OH)₄) and attributed to the symmetric stretching vibration of the arsenate anion (AsO₄³⁻).^[15,16] It must be taken into account that Scheele's green is considered a mixture of several compounds belonging to the copper arsenite pigment group and depending on the recipe for the synthesis, it may contain different predominating forms that could also include copper arsenate forms.^[13] On the other hand, the presence of arsenate ions could also be the result of degradation phenomena affecting the copper arsenite pigment. However, an unambiguous identification of the green pigment has not been possible.

Fig. 3 a and b

In the black decorations, the characteristic Raman spectral signature of amorphous carbon showing broad bands at 1323 and 1592 cm⁻¹ (Fig. 2) was found. An additional small band located at 979 cm⁻¹ was also observed. The use of bone black could be considered attributing this band to phosphate stretching^[17] but the absence of phosphorous in both ED-XRF and SEM-EDX spectra discard this hypothesis. In addition, strong signals of

lead were also present in these spectra and probably correspond to deeper layers. This band was also present in the Raman spectra of the brown decorations so further investigation was needed and the results are presented in the next section. Finally, brown motifs also contained carbon black together with hematite (Fe_2O_3) as can be deduced from the ED-XRF (presence of iron) and Raman spectra. As can be seen, in Figure 2 Raman spectra of brown decorations showed the characteristic bands of hematite at 224, 251, 292, 413 and 614 cm^{-1} together with broad spectral features at 1323 and 1592 cm^{-1} typical of carbon black.

Execution technology and alteration processes

The extremely fragile state of the samples did not allow the preparation of cross sections to study stratigraphy. Nevertheless, a careful investigation of both sides of the flakes can provide useful information about the execution technology employed in this restoration of Contreras.

The white side of the detached flakes should correspond to the preparation layer of the painting and remains of the gypsum plaster support. The samples were studied using SEM-EDX and Raman microspectroscopy (see Fig. 4).

Figure 4

Lead, sulfur, and barium were detected by EDX spectroscopy in the thick white preparation layer. Using Raman spectroscopy several compounds were identified apart from the gypsum support (with bands at 413 , 492 , 671 , 1009 and 1135 cm^{-1})^[18], namely white lead, barium sulfate, and lead sulfate. The historical pigment white lead is composed of a mixture of two crystalline phases, namely, cerussite (PbCO_3) and hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) in variable proportions, being usually hydrocerussite the major form. It has been extensively used as the main compound in white grounds that

formed the undercoat onto which the paint was applied, providing more luminosity to the colors due to its high refractive index.^[19,20] However, both cerussite and hydrocerussite exhibit strong Raman bands at ca. 1053 cm⁻¹^[21,22] whereas the spectra registered in the preparation layer show an additional feature at 1057 cm⁻¹. This band could be attributed to degradation products resulting from the reaction of white lead with salt solutions forming Na or K bearing phases. According to literature, either NaPb₂(CO₃)₂OH or KPb₂(CO₃)₂OH can be responsible for the band observed at 1057 cm⁻¹.^[23,24] Raman bands at 462, 617, 647 and 990 cm⁻¹ correspond to barium sulfate^[25], which was employed since the early 19th century as an extender pigment.^[13,26] In fact, the mineral barite was one of the most common adulterants of white lead during the 19th century. Finally, lead sulfate (anglesite) was identified by the bands at 438, 450, 620 and 979 cm⁻¹.^[22,27] Lead sulfate can originate from the alteration of white lead in the presence of a sulfate-rich substrate (gypsum) due to the humidity of this room. However, the intentional presence of lead sulfate cannot be fully disregarded. This compound has been rarely used as a white pigment, although its use has been reported at the end of the 19th century and it has been found in some paintings of the same period as reported by Correia *et al.*^[28] Lead sulfate is furthermore the responsible for the band at 979 cm⁻¹ observed in the Raman spectra of black and brown motifs described above.

Finally, the small flakes were examined by infrared micro-spectrometry in order to identify the nature of the organic binders employed. Microsamples were placed in a diamond compression cell and flattened to achieve a path length thin enough for transmission measurements. As can be seen in Fig. 5, the typical spectral features of proteins were clearly identified with bands of amide I (1650 cm⁻¹), amide II (1545 cm⁻¹) and amide III (1336 cm⁻¹).^[29] These features can also be found in other spectra together with the characteristic absorption bands of gypsum (spectrum 1), calcium oxalate (1323

cm⁻¹) and pigments like ultramarine blue (spectrum 3). The presence of proteinaceous material can be compatible with the use of animal glue or white egg as a binder.^[30,31]

Figure 5

Curiously, an additional spectral pattern of organic material was found in the green samples. It corresponds to a yellowish layer that observed under the microscope shows a high elasticity when is pressed in the diamond cell. Apart from the already described protein bands, the typical lipid absorption bands located at 1733 cm⁻¹ (C=O of the ester group), as well as at 2850 and 2917 cm⁻¹ (CH stretching) can be observed in the spectrum. The use of whole egg could be hypothesized in this case.^[32]

Comparison with the original Nasrid polychrome plasterworks

As explained above, the restoration style of this period in the Alhambra tried to recreate the ancient beauty of the rooms but with limited knowledge of the materials and execution technologies employed by the Nasrid artists. In this context, it is interesting to note that the Room of the Beds is one of the unique examples where these kinds of restorations are conserved in the Alhambra. During the interventions carried out between 1923 and 1936 by Torres-Balbás most of these orientalist and romantic restorations of the mid-19th century were removed to emphasize the original Nasrid art.^[33] Here, we compare the results retrieved from the Room of the Beds with those of previous works on other Islamic spaces where Nasrid plasterwork is conserved. They include studies in the qubba Dar al-Manjara-l-kubra^[34], the Muslim university^[35] and the Partal palace^[6] in the Alhambra from the first period of the Nasrid art, together with other spaces in the Alhambra representative of the highest splendour of the Nasrid dynasty in the 14th century like the muqarnas of the Hall of the Abencerrages, the Hall of the Ambassadors, the Hall of the Mexuar^[6] and the Hall of the Kings.^[7-9]

The here presented results show that important differences can be found between the Nasrid art, as well as first Christian interventions, and the restoration works of Contreras, both in the materials and the execution technologies. First, Contreras applied a thick preparation layer of white lead over the gypsum plaster. In Nasrid art, the finishing layer of the plasterwork acts as the preparation layer for the polychromy. This delicate finishing layer is composed of very pure gypsum probably mixed with organic additives.^[36,37] An example of these differences is shown in Fig. 6.

Figure 6

Regarding the colors, black areas were always painted with carbon black but in the Room of the Beds, the use of lead sulfate as an extender is suggested. In the case of red, mercury sulfide was used in both cases. Nasrid artisans probably employed cinnabar^[6-8,34] considering the size and morphology of the grains, as can be seen in Fig. 6. The proximity of the mines of Almadén (Ciudad Real, Spain), the main source of cinnabar in the Mediterranean world, whose actual name comes from the Arabic word *al-ma'din* that means the mine^[13], support this statement. However, the natural or synthetic origin of the mercury sulfide employed in the Contreras' restoration cannot be confirmed. Blue decorations were originally painted with either azurite^[6,34] (in the early period) or lapislazuli^[6-8] whereas the restoration of the 19th century employed the cheaper synthetic ultramarine blue that was first synthesized in 1824.

In the case of brown decorations, it is worth mentioning that a similar color can be observed in other spaces of the Alhambra, i.e. the Hall of the Kings, however, it was not an intended color but the result of the darkening of the pigment red lead (Pb_3O_4) due to degradation to plattnerite (PbO_2).^[7] In contrast, here in the Room of the Beds, the brown color was produced intentionally by mixing hematite with carbon black. Hematite has been also found in the decorations of the early Nasrid period but as red color.^[34]

Finally, the green color is less employed in Nasrid plasterwork. In fact, it is sometimes the result of the degradation of the blue azurite like in the case of the copper hydroxychlorides found in the Hall of the Kings.^[7] In other locations, the presence of malachite has been reported.^[6] The pigment used in the restoration of Contreras was one of the typical poisonous 19th-century green pigments based on copper and arsenic.

Conclusions

The study of one of the scarce remnants of the 19th-century interventions carried out in the Alhambra monument has provided valuable information about the materials and the execution technology employed by Rafael Contreras in the restoration of the Room of the Beds of the Royal Baths of Comares palace.

A combination of Raman spectroscopy and X-ray Fluorescence allowed the identification of the pigments of the main colors observed in the plasterwork decorations. Red and blue colors were easily identified with portable instruments but in the case of the green, black and brown motifs, more exhaustive analysis on microsamples was required. Particularly interesting was the case of the green color where the combination of both ED-XRF and Raman spectroscopies resulted decisive. Using only Raman spectroscopy it would have been very difficult to gain useful information because the recorded spectra did not match the spectrum of any green pigment. Thus, the identification of Cu and As by means of ED-XRF provided an important clue. Furthermore, starting from this point a detailed interpretation of the Raman features in the spectra allowed the identification of a copper arsenate compound, probably resulting from the alteration of the original green pigment. The results also showed the existence of a thick preparation layer above the gypsum support, which contained white lead mixed with barium and lead sulfates. Using infrared microspectroscopy, it was possible to identify proteinaceous material as the main binder. The structural information provided by Raman spectroscopy was also essential to

evidence diverse alteration processes related to the humid conditions of the Room of the Beads and affecting mainly the preparation layer. They involved dissolution/recrystallization processes forming alteration products like anglesite and Na and K bearing phases related to hydrocerussite that can play an important role in the detachment of the painting layer.

Finally, a comparison with previous studies on original Nasrid polychrome plasterworks revealed clear differences in the pigments and the execution technology employed. This information, apart from being helpful to plan future interventions in this space, contributes to understanding the complex history of a building like the Alhambra, which also includes its transformations through restoration projects that keep the testimony of the tastes, artistic and aesthetic intentions of different periods.

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Figure captions

Figure 1. A general vision of the Room of the Beds in the Royal Bath of Comares Palace in the Alhambra showing its polychrome plasterwork decoration.

Figure 2. Typical Raman spectra registered from the decoration of the Room of the Beds: (1) cinnabar/ vermillion, (2) synthetic ultramarine blue, (3) carbon black, (4) mixture of hematite and carbon black. (*) additional band at 979 cm^{-1} .

Figure 3. Typical (a) Raman and (b) ED-XRF spectra registered for the green decorations.

Figure 4. (a) Raman spectra obtained from the preparation layer from the Room of the Beds, showing spectral features of (1) gypsum substrate, (2) anglesite and white lead, (3) barite and white lead, (4) white lead and gypsum support (marked with *), (5) anglesite, barite and white lead. (b) SEM-EDX analysis of the preparation layer.

Figure 5. Infrared spectra from the samples of the Room of the Beds: (a) typical spectra recorded in different colors: (1) gypsum support, (2) proteinaceous binder, and (3) blue sample showing characteristic IR bands of gypsum support (marked with *) and proteinaceous binder. (b) additional organic material found only in green samples showing IR bands of both protein and lipid material.

Figure 6. Comparison of the redecoration by Contreras with original Nasrid plasterwork. SEM-EDX images of (a) a cross-section of an original Nasrid plasterwork sample from the Hall of the Kings and (b) front view of a sample from the Contreras intervention in the Room of the Beds using secondary (right) and retro dispersed (left) electron microscopy. In the Nasrid polychromy, two layers can be observed from bottom to top: gypsum finishing layer and cinnabar painting layer ($30\text{-}40\text{ }\mu\text{m}$). In the case of Contreras' redecoration, the thickness of the painting layer containing iron is lower (few microns)

and the thick preparation layer contains lead.