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Gold in the Alhambra: study of materials, technologies, and decay processes on decorative gilded plasterwork[†]

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A complete study of the decayed gilded decorations of the stalactite vaults in the Hall of the Kings in the Alhambra complex (Granada, Spain) has been carried out for the first time. Preliminary investigations were carried out *in situ* using a portable Raman spectrometer and enabled the identification of tin (II) oxide in the black areas nearby the golden flakes. This suggested the presence of an altered tin foil. Then, a comprehensive characterization of these decorations was achieved through the use of complementary nondestructive techniques working on microsamples. Two main metallic structures were identified by means of scanning electron microscopy coupled to energy dispersive X-ray spectroscopy: (1) a thin (1–2 μm) gold leaf (probably original), and (2) redecorations with a laminated structure formed by a gold leaf placed over a thicker (10–15 μm) tin foil. Synchrotron Fourier-transform infrared microspectroscopy revealed the use of proteinaceous glue to fix the gold leaf directly on the plasterwork, whereas in the case of the laminated structures, either glue or a natural resin was found. Raman microspectroscopy provided insight into the main decay processes affecting the gildings: the detachment of the metals due to the alteration of the organic materials employed as adhesives (forming calcium oxalates) and the oxidation of the tin foil. In addition, two technologies of false gilding have been encountered. One was based on a tin foil tinted to look like gold by means of a varnish (composed of a drying oil and a natural resin), and the second was made up with a tin–copper alloy (bronze) that appears severely degraded to copper oxalate and tin (II) oxide, as revealed by Raman microspectroscopy. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: gilding; plasterwork; tin; calcium oxalate; Alhambra

Introduction

Analytical sciences play an important role in the preservation of our cultural heritage by providing essential information about the materials employed originally or in different interventions as well as decay products. Furthermore, the investigation of the composition of artworks also contributes to the comprehension of the technologies used in ancient times, as well as of their transfer and diffusion in time across geographical areas. When dealing with cultural heritage investigations, the principle of minimal impact must always be considered. For this reason, it is of crucial importance the close cooperation between scientists of several branches and conservators to understand the capabilities of each analytical technique and which reliable results it is possible to obtain for a specific purpose.

In this multidisciplinary context, this work is devoted to the study of the gilding decorations in the Hall of the Kings of the Alhambra. The Alhambra in Granada is one of the most visited monuments in the world and the best surviving example of medieval Islamic architecture. Founded as a fortress in the ninth century, it was enlarged by the Nasrids (1232–1492) until it became a veritable city in itself, containing palaces, mosques, baths, tombs, gardens, and quarters for artisans. The Alhambra became a Christian court in 1492 after the conquest of the city of Granada, and further palaces and Christian chapels were added to the complex in the centuries since. Thus, the Alhambra not only comprises buildings conceived or modified during the Islamic period but also later additions and interventions, which responded to functional adaptations, stylistic restorations, and conservation needs. These interventions began with the conquest and have continued to the present day.[1]

The gildings that decorate many spaces of the Alhambra are poorly studied, and previous works have been restricted to isolated fragments of plasterwork and carpentry.[2,3] Here, we will

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address a complete study of the gildings of the Hall of the Kings trying to find the optimal combination of analytical tools that can provide a comprehensive understanding of the evolution of gilding technologies and the alteration of these decorations throughout the history of the Alhambra.

The chemical characterization of gilding decorations is a complex task for conservation scientists. Samples are intrinsically heterogeneous at the microscale and are composed of mixtures of organic and inorganic materials that may have undergone chemical modifications and aging.[4–6]

To address these challenges, we propose a combination of different analytical techniques that can provide elemental, molecular, and morphological information. Thus, in order to obtain information about the composition of the different metallic layers and their thickness and microstructure, scanning electron microscopy coupled to energy dispersive X-ray spectroscopy (SEM-EDX) has been demonstrated to be useful.[7] However, scarce information about the mode of adhesion of the metal leafs onto the substrates has been reported up to date.[8,9] This information is especially relevant for the elucidation of the basis of the recipe used by the craftsman to create the gildings. Although the identification of organic materials employed in work of arts can be attempted using chromatographic techniques coupled to mass spectrometry,[10,11] sampling preparation is extensive and time-consuming. Vibrational spectroscopic techniques such as Fourier-transform infrared (FTIR) and Raman spectroscopy can be useful in this sense because they can provide molecular information (namely, the identification of diverse molecular groups: organic/inorganic, crystallized/amorphous), without extensive sample preparation. In this context, synchrotron radiation-based FTIR (SR-FTIR) microspectroscopy is an emerging technique[12] with the extra potential derived of the properties of the synchrotron source, which are high brightness, offering high signal-to-noise ratio even using reduced spot size without long acquisition times and enhanced lateral resolution. The fast identification of different organic compounds in works of art using SR-FTIR has been successfully reported in the last years.[13–16] Finally, Raman spectroscopy appears as one of the most suited methods to investigate cultural heritage materials because of its unique advantages, particularly the invaluable ability to analyze the objects in a completely noncontact and nondestructive way.[17] In the last years, this technique has been demonstrated to be very useful to identify not only the materials intentionally used by the artists but also several decay products from pigments and metals in works of art.[18–21] In this way, by combining the results provided by several microanalytical techniques applied in a nondestructive way on the same microsamples, we will maximize the information that can be obtained from the gildings minimizing the impact on the artwork.

Experimental

Instruments and methods

The *in situ* studies were carried out with a portable innoRam spectrometer (B&WTEK Inc, Newark, NJ, USA) covering a Raman shift of 65–2565 cm^{-1} when using a 785 nm excitation laser. The spectral resolution is about 2 cm^{-1}. It was equipped with a fiber optical probe head attached to a video microscope, motorized in the *x*–*y*–*z* axes with remote control. A 20× long-distance objective lens was used providing a laser spot size about 85 μm in diameter.

Raman spectra for raw samples (without any sample preparation) and polished thin sections were recorded on a Renishaw (in Via Reflex) spectrometer equipped with a Peltier-cooled charged-coupled device detector coupled to a Leica microscope. The 520.7 cm^{-1} peak of a silicon standard was employed for calibration. The 785 nm diode and 514 nm ion Ar lasers were used as excitation sources. Laser power was always set to the minimum in order to avoid sample damage (typically 1–3 mW). The spectral resolution is better than 1 cm^{-1}. Using a 50× magnification objective, a spatial resolution of about 2 μm can be achieved.

Preliminary observation of the samples was performed using a stereomicroscope Leica M205C with a continuous zoom magnification from 7.8–160×, coupled to a Leica DFC495 digital camera with 8 Mp charged-coupled device. The petrographical study on polished thin sections (embedded in epoxy resin) was carried out using an Olympus BH-2 optical microscope equipped with digital camera.

Scanning electronic microscopic study of samples, both raw and polished thin sections, was carried out with a Carl Zeiss field emission scanning electron microscope model SUPRA40VP. Images in both secondary electron and backscattered electron modes were obtained. The use of variable pressure enabled the investigation of nonconductive specimens in their natural uncoated state in the case of polished thin sections. In this way, the thin sections can be further investigated by other spectroscopic techniques. Qualitative, semiquantitative, and mapping analyses of selected areas of the samples were performed by EDX.

Fourier-transform infrared spectra were obtained with a Nicolet NEXUS IR spectrophotometer coupled to a Nicolet continuum IR microscope with a mercury cadmium telluride detector cooled with liquid N_2 with a measuring range from 650 to 4000 cm^{-1}. Both the conventional Globar source and SR from beamline IRIS at BESSY II (Helmholtz-Zentrum Berlin) were employed. Typical apertures were 50×50 μm and 10×10 μm for Globar and synchrotron sources, respectively. Micrometric samples selected under stereozoom, were first placed and pressed in the diamond cell, and then only one window of the cell was used for the measurement. The FTIR spectra were recorded at 4 cm^{-1} resolution.

Site of study and description of samples

The Hall of the Kings consists in a large vestibular room covered with seven stalactite vaults, named V1 to V7 from the southern to the northern side. Three big squared vaults alternate with four rectangular of smaller size. This space represents a magnificent example of Islamic 'stalactite vaulting', whose decoration consists of vertical gypsum prisms applied one over another and joined in multiple different arrays resembling stalactites of a cave (*mocarabes*) (Fig. S1, Supporting Information). This Hall has suffered at least two previous interventions during the 19th and 20th centuries to consolidate the structure of the vaults. Structural damage, probably due to the seismic activity of the area, was especially relevant in V1 and V7.

Sampling locations were carefully selected on the basis of the knowledge of the conservators about the whole monument, a detailed observation and considering the results of the noninvasive investigations. In this way, a compromise between the selection of representative areas while ensuring that sampling was minimal and confined was reached. Fifteen samples of the golden decorations and their remnants were carefully collected in the minimum quantity (flakes of ~1–2 mm long). The samples showed golden, black, yellow-orange, and violet areas. It is important to note that, in some cases, the metal layers became detached from the substrate when taking the samples because of the poor conservation state of the gildings, and the underlying preparation layers were lost. Furthermore, the samples were small and extremely fragile being necessary in occasions to consolidate them using an acrylic resin (Acrysil).

Results and discussion

A preliminary investigation of the gildings in the Hall of the Kings was carried out *in situ* before sampling using a portable Raman instrument. This study was part of a wider project carried out in close cooperation with the conservators during a recent intervention that allowed reaching decorations otherwise inaccessible because of the height of the vaults. A complete description of the characteristics of the different colored pigments that decorate the stalactite vaulting and their conservation state has been described elsewhere.[22]

In contrast with the rest of the polychromy, which was relatively well preserved, the gilding decorations suffer from severe decay, and only remnants can be found mainly in protected and hidden areas. In these motifs, remarkably brilliant rests can be observed together with blackened areas. In some places, the altered gilding remnants appear covered by a white layer that shows in some places a distinct light violet color.

All Raman spectra recorded in the black areas near the golden remnants presented two sharp and intense bands located at 110 and 208 cm^{-1}. The identification of the compound responsible for this Raman features through the usual databases of artistic materials[23–25]did not succeed. In fact, in many cases, the spectral region less than 200 cm^{-1} was not available because of the limitations of traditional notch filters. Here, the improved edge filter of the portable spectrometer that allowed the acquisition of Raman spectra from 65 cm^{-1}. We could attributed these two bands to the Eg$^{(1)}$ and A_{1g} vibration modes of the tetragonal crystal structure of SnO, respectively.[26] In Fig. 1, the spectra obtained from the black areas of the gildings are shown together with those of tin oxides standards for comparison. The presence of this compound has been previously reported in other works of art where tin foil was present.[27] These results suggest that tin was employed in the gildings, although the presence of other metals cannot be excluded from this study.

In orange areas, only strong fluorescence signals were recorded, which could be indicative of the presence of organic compounds employed as binders. The spectra recorded from the substrate and also from the white covering observed in many places corresponded to gypsum, even when trying to focus on the violet areas. No useful Raman spectra were obtained from the golden flakes.

In order to gain more information about the original composition and stratigraphy of the gildings, several samples were taken from representative areas. These samples were classified according to the observations under stereozoom that revealed the different layers constituting the gilding. In most of the samples, a bright golden metallic layer appeared over a black one. This sequence seemed to be always adhered to the substrate by means of a layer of amber color, and in some samples, it was replicated, one over the other. In addition, sometimes, the bright golden metallic layer was adhered to the gypsum substrate by the amber-colored layer, and no blackening was observed. In the outer surface, many samples showed a light violet aspect, whereas the observation under stereozoom revealed a white layer with dark particles embedded. Finally, the samples from V7 did not show any bright golden layer, and one of them had a greenish appearance.

The study with SEM-EDX revealed in many samples the presence of a laminated structure with a gold layer over another one of tin (Fig. 2). Unfortunately, the fragility of the samples caused the detachment of the gypsum substrate together with the adhesive layer during the preparation of the polished thin sections.

The average thickness of the gold leaves was 1–2 μm, whereas the underlying tin foil was always thicker (10–15 μm). The gold leaf is very pure showing only minor impurities of silver. In some samples, this laminated structure Sn—Au appeared twice, one over the other. Furthermore, the tin layers appeared much altered in some areas showing an expansion in volume, leading to thickness of about 50 μm. In these areas, the massive metallic aspect of the tin evolved to a fibrous appearance with acicular crystals. The investigation of these altered areas with Raman microspectroscopy confirmed the presence of SnO as degradation product of metallic Sn. Even when at ambient conditions, the common crystalline phases in the Sn—O system[28] are the rutile-type SnO_2 and the litharge-type SnO; here, only SnO was clearly detected. Apart from these laminated structures Sn—Au, some samples presented a very pure gold leaf located below. When found, this leaf was always the deepest metallic layer, and it usually appears discontinuous (Fig. S2, Supporting Information).

The forms of adhesion of the metal foils can be investigated through the identification of the organic materials present. However, the recording of useful Raman spectra of the organic layers was impossible because of the strong fluorescence interference observed. FTIR provided this information by analyzing selected micrometric subsamples of the different layers. The use of synchrotron was crucial for detecting the presence of different organic

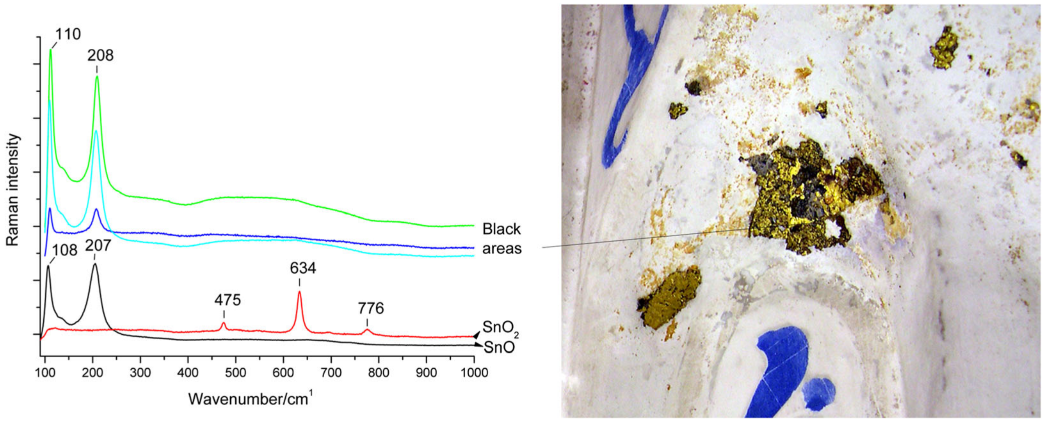

Figure 1. Comparison of Raman spectra of SnO and SnO_2 standards and spectra recorded *in situ* from black areas in vaults V2, V3, and V7. Detail of remnants of gilding decorations.

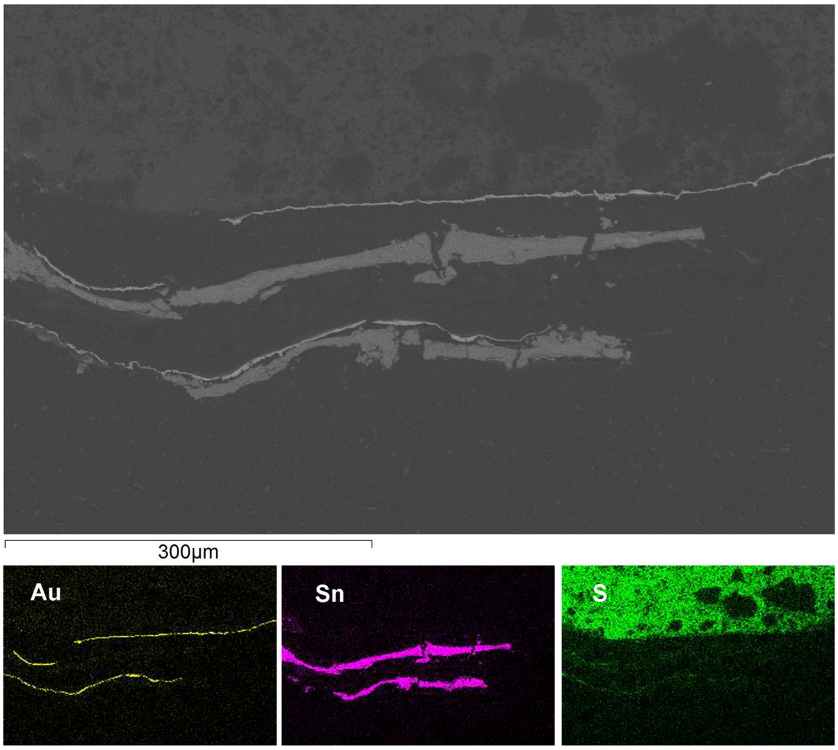

Figure 2. Scanning electron microscopy (SEM) images (backscattered electrons mode) taken from a sample of V4. SEM-energy dispersive X-ray elemental maps corresponding to Au, Sn, and S in false color.

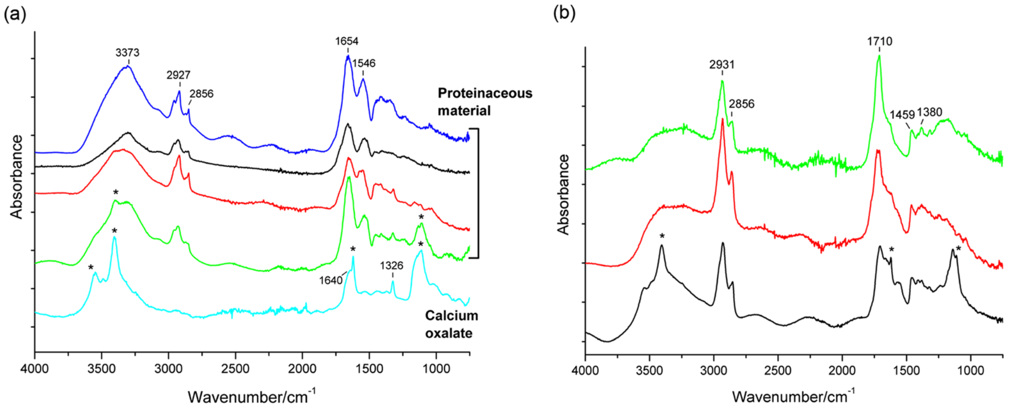

Figure 3. Fourier-transform infrared spectra of organic materials from different samples of gilding decorations (a) proteinaceous materials (b) natural resins. Spectral features of calcium oxalate are also present in some cases. Bands of gypsum substrate are marked with (*).

compounds mixed in the same samples together with low amounts of degradation compounds (with micrometric sizes).

Focusing in the organic layer used to adhere the metals to the substrate, the FTIR spectra recorded in most of the samples showed two strong bands at 1654 and 1546 cm^{-1} (Fig. 3(a)). They can be attributed to amide I and amide II bands, the two most prominent vibrational bands of proteins. The amide I band is due almost entirely to the C O stretch vibrations of the peptide linkages, whereas the amide II band derives mainly from in-plane NH bending and from the CN stretching vibration. Furthermore, there is a prominent, broad maximum in the region of 3300 cm^{-1}, typical of N—H bond stretches in proteinaceous materials. These features were observed for all samples with a gold leaf over the gypsum substrate but not for all the samples with the laminated structure of gold leaf over tin foil.

In some of these samples with Sn—Au laminated structure, the recorded FTIR spectra showed a rather different profile (Fig. 3(b)). The strongest and most characteristic band was observed at ~1710 cm^{-1}. It was accompanied by well-defined CH bands at 2931 and 2856 cm^{-1}. These strong spectral features at the carbonyl and hydrocarbon stretching frequencies are typical of natural resins. Furthermore, the wavenumber of the bands can provide information about the type of resin. Although it is difficult to assign the spectral features to a particular type of resin, the position of the bands observed in these samples could correspond with those of shellac,[29] an insect resin secreted by the lac bug that consist in a complex mixture of esters and polyesters of polyhydroxy acids.

In addition, calcium oxalates were identified by means of the characteristic infrared bands[30] at 1620 and 1320 cm^{-1}.

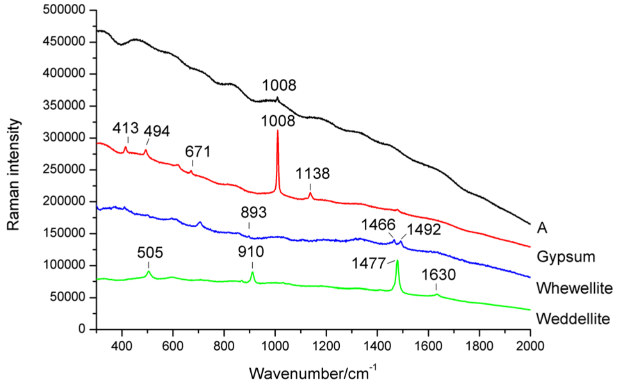

Figure 4. Raman spectra obtained in the laboratory on microsamples of gilded decorations. The strong fluorescence contribution from organic materials (A) together with the spectra of gypsum substrate and calcium oxalates in the forms of whewellite and weddellite are shown.

Furthermore, using Raman spectroscopy, it was possible to distinguish between the different forms of calcium oxalate.[31] As can be seen in Fig. 4, the Raman spectrum of the monohydrate (whewellite) shows two bands at 1466 and 1492 cm^{-1} assigned to CO symmetric stretching; whereas in this region, the dihydrate (weddellite) shows a unique band at 1477 cm^{-1}. Here, although both forms were found in all the samples associated to organic layers and in the nearby gypsum substrate, weddellite was much more abundant. It is interesting to note that calcium oxalates were not detected during the preliminary *in situ* investigations. This can be due to the lower sensitivity of the portable instrument and to the fact that oxalates were mainly found in the gypsum substrate below the organic binder and not in the surface of the samples. The formation of calcium oxalates has been reported in many wall paintings. Its origin is still not completely understood, and it has been attributed to degradation of binding media,[32] as well as to the attack of oxalic acid produced by lichens on calcitic substrates.[33] Here, the combination of a calcium-rich substrate (gypsum) with an organic layer (employed as binder to fix the metal leaves) probably suffering from both microbial and chemical degradation produced calcium oxalates. This is in agreement with the observations made by Lluveras *et al.*[16] on the calcium oxalate distribution on weathered gilding decorations.

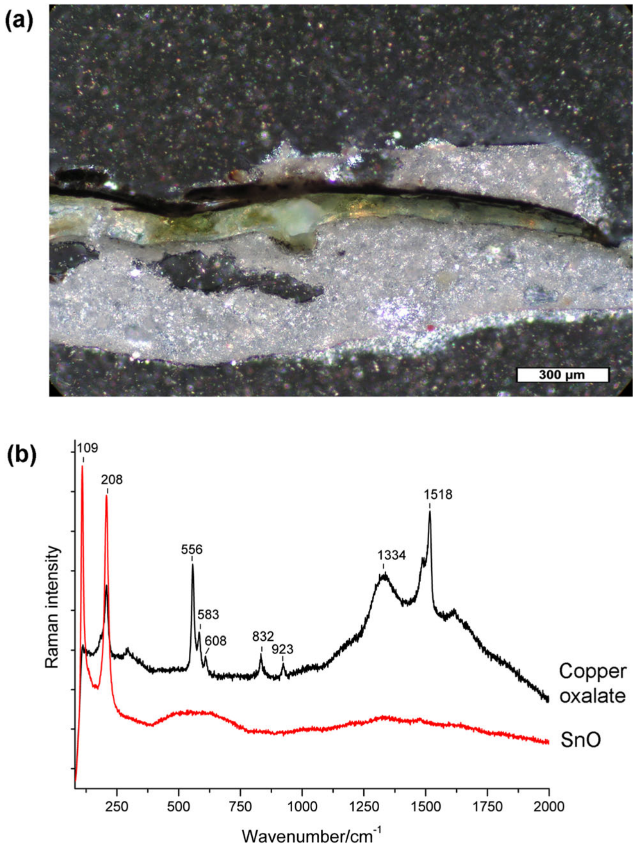

Figure 5. Petrographical microscopy image of a (a) thin polished cross-section and (b) Raman spectra showing the bronze degradation of samples taken from V7.

In the samples from one of the vaults (concretely V7), two more different types of gilding have been identified. In fact, these are false gildings because no gold is present. One case is formed by a tin foil covered by a thick organic layer of dark brown color (Fig. S3, Supporting Information). The FTIR spectra of this organic layer revealed a mixture of drying oil and a natural resin. Degradation products such as calcium oxalates and calcium carboxylates were also abundant. The tin foil appeared also degraded to SnO as revealed by Raman microspectroscopy. In one of the analyzed samples, up to three different tin layers can be found.

The second type of gilding found in this vault was based on bronze foil. This tin–copper alloy foil (10–12 μm) was much altered and showed a greenish color under optical microscopy (Fig. 5(a)). Degradation products of both metals have been identified. Apart from tin (II) oxide, copper oxalate with characteristic Raman bands at 558, 583, 610, 920, and 1516 cm^{-1} (Fig. 5(b)) was found. This compound has been previously reported to occur in bronze-based and copper-based pigments[15,34] as degradation product. Furthermore, FTIR spectra showing bands of proteins at 1656 and 1544 cm^{-1} together with those of calcium oxalate were recorded in the organic layer below the bronze foil.

Finally, the white gypsum covering that appears in many samples is observed above the different metal layers, independently of the type of gilding structure. Calcium oxalates as a result of the degradation of organic matter were also identified here by means of Raman microspectroscopy. This plaster layer was probably applied during the later restorations, carried out in the 19th century, with the purpose of hiding the black color because of the oxidation of the tin foil and the detachment of the gold leaves, providing a uniform white appearance.

Gilding technologies in the Hall of the Kings in the Alhambra

The identification of materials and degradation products achieved by the different analytical techniques can help in the elucidation of the gilding technologies used in the Hall of the Kings in the Alhambra. Furthermore, our results have been collated with information of historic recipes from ancient treatises.

The oldest gilding technology found in the Hall, which probably correspond to the original Nasrid artists, consisted on the very thin gold leaf (1–2 μm). It was fixed directly to the finishing layer of the plasterwork substrate by means of a proteinaceous binder (such as animal glue). The use of animal glue is typical of the traditional technique known as *water gilding* that was based on the use of the gold leaf lying on a primer made of red orange pigments (the so-called bole) and bound by water-based animal glue.[35,36] However, in our case, no bole is present, and in order to attain a good final result, the gypsum layer had to be extremely regular, and therefore, a perfect smoothing of the surface was mandatory.[37,38]

In fact, such smooth finishing is one of the characteristics of the original Nasrid plasterwork.[39] Fissuring and flacking strongly affect the gold leafs; indeed, most of the gold is lost, possibly because of the degradation of the proteinaceous adhesive.

The second gilding technology found in the Hall of the Kings involves a laminated structure formed by a thin gold leaf (1 μm) over a thicker tin foil (10–13 μm). This structure was probably achieved by beating the two metals together because no evidence of any organic adhesive has been found between them. The making and use of this kind of gilded tin is discussed by C. Cennini in Il Libro dell'Arte.[40] This kind of laminated foil was probably used because of its greater thickness and malleability, and according to Tintori,[41] it was even more expensive than gold leaf as stated in a document dated back to 1366. In several samples, this type of gilding is found over the former based only in gold, probably as a result of early redecorations because of the problems of adhesion already affecting the gold leafs.

Two different forms of adhesion of the tin foil to the substrate have been identified in these kinds of laminated structures: animal glue such as in the case of gold leafs and shellac. This reveals the evolution on the gilding technology since shellac introduction in Europe is dated to the 15th century.[42] This natural resin has been reported to be used for particularly porous surfaces, such as gypsum preparations, as an alternative to linseed oil, usually employed in the technique of mordant gilding.[43,44]

Finally, two types of false gilding have also been identified in the Hall and both on the same vault, V7. One is based on tin foil (10–13 μm). which was tinted to look like gold using a varnish based on a mixture of a drying oil and a natural resin. This covering could also play a protective role to prevent metal oxidation; although in spite of it. the tin foil appears blackened because of oxidation to SnO. This false gilding technology can be attributed to a later Christian period since it seems to be similar to the one found in an inscribed table of polychromed carpentry in the *Mexuar* (also in the Alhambra complex and redecorated during Christian ages), although the nature of the organic varnish was not reported.[2] Other examples of such false gold are found in Christian ornaments and altarpieces from 16th to 18th centuries in Andalusia.[5]

The other false gilding is based on bronze foil, and it suffers a severe chemical alteration that provides these areas a greenish appearance because of the formation of copper oxalate. Interestingly, such false gilding has been found only in V7, the one suffering the most serious structural damages, and is probably the result of a different intervention.

Conclusions

The present study highlights the importance of the use of multianalytical approaches in the cultural heritage field. A compromise between minimal impact and obtaining comprehensive information was the guiding principle of all the analytical work. In this way, after the *noninvasive in situ* study with Raman spectroscopy and a well-directed sampling, a sound combination of analytical techniques was employed. SEM-EDX analysis provided the base knowledge of the metal leafs; synchrotron μFTIR spectroscopy was prevalently used to examine the composition of the organic material employed either as adhesive or as varnish, and Raman microspectroscopy (both *in situ* and in laboratory) was the clue technique to provide insight into the different degradation compounds formed.

Furthermore, this work is a diachronic approach that contributes to shed light on the evolution of the gilding materials and technologies applied throughout the history of the Alhambra. Two different technologies of gilding have been found together with the later replacement of gold with imitations, using tin and copper, in one of the vaults. The elucidation of the decay mechanisms of the metals allows the understanding of the appearance of the decorations at present and helps the conservators to preserve them.

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