Characterization of organic materials in the decoration of ornamental structures in the Alhambra monumental ensemble using gas-chromatography/mass spectrometry (GC/MS)

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ABSTRACT

The identification of the organic material used in the polychrome decorations of Alhambra complex was carried out in this investigation. Samples from motifs painted on different types of supports, namely marble, wood, and gypsum, were studied. In this way, a comparison on the organic materials used in the marble capitals of the columns from different sites (Hall of the Abencerrages, Hall of the Mexuar, The Court of the Myrtles and the Court of the Main Canal), the Nasrid polychrome wooden ceilings of the Hall of the Abencerrages and the gypsum mocarabes in the plaster decorations of the Hall of the Kings was achieved. This is the first wide scientific study regarding the organic materials employed in the execution of the most representative decorative revetments in the Alhambra monument. Despite the small amount of sample and the complex history of interventions in the monument (both documented and not), results obtained with GC-MS show that proteinaceous materials were mainly used as binders in the different supports and periods studied being animal glue identified in almost all cases. Moreover, wax and lipid materials were also found in the samples from the ceilings, probably as restoration materials applied on the surface of the polychromes on wood. These results shed light on the painting techniques in this extraordinary example of Muslim art in its final European stages, thus contributing to provide scientific information about the still little studied medieval Islamic art.

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1. Introduction

The Alhambra monument declared UNESCO World Heritage Site due to its universal beauty and exceptional expression of Moorish and Andalusian culture, was built in Granada (Spain) under the Nasrid dynasty, the last Muslim rulers on the Iberian Peninsula. Originally designed as a military area, throughout the 13th, 14th and 15th centuries, the fortress became a citadel, which houses two main areas: the military area, or Alcazaba, and the medina or court city where the famous Nasrid Palaces are located. Although many modifications took place after the Christian conquer (1492) and the palaces were partially altered to Renaissance tastes, much of the Alhambra retains its original character being the most important vestige of the medieval Hispano-Muslim architecture. Some of the surviving remnants are the rich and expensively polychrome decorations that surprise the visitors all around the monument. The contrast between the simple and austere aspect outside and the rich decoration inside covering every single surface is typical of the Islamic architecture.

Even if the Alhambra complex is probably the most important and visited monument in Spain, most of the dedicated studies have been devoted to the artistic and epigraphic interpretation of the decorations [1,2]. There are few technical investigations about the materials and the execution techniques that however are essential for the understanding of the artistic and material influences and evolution of the Alhambra decorations through the centuries [3–10]. These works are focused on the decoration of typical ornamental structures in the Alhambra like Lacework stucco [5], mocarabes vaults [4,7,8,10], marble capitals [6] and polychrome carpentry [3,9]. These decorative revetments, carved and drawn in the different supports and then decorated with different pictorial layers, are very representative artistic expressions of the medieval Hispano-Muslim architecture. In general, previous studies have been focused on the identification of the pigments employed. Cinnabar,
red lead, natural lapis lazuli and carbon black were encountered in the polychrome decorations. The most recent studies, carried out by our group, have explored the capabilities of portable Raman micro-spectroscopy to perform wider non-invasive investigations in several spaces [4,6,7,9].

In order to complete the information of the decorated revetments in the Alhambra, it is mandatory to investigate the organic materials used in these decorations such as the binders used to fix the pigments. Previous studies on this topic in the Alhambra, and, as a whole in Medieval Islamic art, are scarce and very limited in the number of samples and spaces studied [3,10–14]. The results reported vary depending on the period and the type of support studied, being proteinaceous media, mainly animal glue, egg and tempera grassa the main materials identified. Nevertheless, it is worth mentioning that not all the organic families were investigated in the different works.

The study of the organic material in artworks is however essential to better understand the execution techniques and therefore several researchers have pointed out this topic. Although different analytical approaches have been considered [4,12,15,16], the most used is the coupling of chromatographic techniques with mass spectrometry [17–26]. Considering the small amount of sample that is available when studying artworks, it is particularly interesting the possibility of identifying different families of organic material, lipid, protein, saccharide material, resins, and wax, in the same sample [27]. Regarding the support on which the painting layers are applied, it is worth mentioning that polychrome works painted on marble [28] or gypsum [10,14] have been less studied than wooden ones [3,11,12,15,16,29,30].

Here we present the results of the identification by GC/MS of the organic materials in the polychrome decorations on different ornamental structures in the Alhambra monumental ensemble. Marble capitals of columns from different sites, polychrome wooden ceilings, and mocarabes in the plasterwork decorations of the vaults were investigated.

2. Experimental

2.1. Samples

Eighteen micro-samples from several locations were studied. Fig. 1 shows a typical example of the three types of decorative revetments considered. A total of eight samples were taken from marble capitals of different halls and courts representative of different periods: the Hall of the Abencerrages (Muhammad V 1362–1391), The Court of the Myrtles (Yusuf I 1333–1354), The Hall of the Mexuar (Isma’il I 1314–1325) in the Nasrid Palaces and The Court of the Main Canal (Muhammad III 1302–1309) in the Generalife (Table 1a). Five samples were taken from the polychrome mocarabes in the plasterwork decorations of the vaults in the Hall of the Kings (Table 1b) while five samples were taken from the wooden ceiling in the Hall of the Abencerrages (Table 1c). Samples of paintings on wood and plasterwork are from the period of Muhammad V (1362–1391). Complete information about the different locations and supports is given in Table SM1.

Samples were preliminarily observed under a microscope in order to study the sample build-up. Due to the tiny size of the samples available (100 μg – 1 mg) and in some cases their hardness, sub-sampling of the different paint layers was rarely possible. However, it was possible to obtain two or three subsamples by mechanical separation under the microscope from six of the samples analyzed: ABJ4, PMC1-2M, BM1-Y20, Z5V, 28V, and Z5R. Sub-samples are briefly described in the respective tables (Tables 1a, 1b, and 1c) where the images from the microscope are also provided.

2.2. Materials

All the solvents were Baker HPLC grade and were used without any further purification. Trifluoroacetic acid (99% purity) and anhydrous pyridine were from Fluka (Milan, Italy). Ethenethiol (ETS; 99.5%), dimethylformamide (DMF), N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with and without 1% trimethylchlorosilane, N-tetrabutyl-dimethylsilyl-N-ninethyltrifluoroacetamide (MTBSTFA) with 1% trimethylchlorosilane, and triethylamine and hexamethyldisilazane (HMDS, 99.9%) were purchased from Sigma-Aldrich (Milan, Italy).

The following solutions were prepared by weighing pure substances (purchased from Sigma-Aldrich) and were used as standards: (i) solution of fatty and dicarboxylic acids in acetone, containing lauric acid (0.24 mg/g), suberic acid (0.27 mg/g of Su), azelaic acid (0.28 mg/g of A), myristic acid (0.25 mg/g of My), sebacic acid (0.3 mg/g of Se), palmitic acid (0.25 mg/g of P), oleic acid (0.51 mg/g of O), stearic acid (0.51 mg/g of S); (ii) monosaccharides and uronic acids solution in bidistilled water containing D- (+)-galactose (0.1 mg/g), L-(-)-fucose (0.1 mg/g), L-(-)-arabinose (0.1 mg/g), L-(-)-xylose (0.1 mg/g), L-(-)-manno-nose (0.1 mg/g), D- (+)-xylose (0.1 mg/g), D- (+)-glucose (0.1 mg/g), D-glucuronic acid (0.1 mg/g), D-galacturonic acid (0.1 mg/g) monohydrate. The standard of amino acid in an acid solution, 0.1 M HCl, was purchased from Sigma-Aldrich and contained 12.5 μmol/mL of proline (Pro) and hydroxyproline (Hyp) and 2.5 μmol/mL of aspartic acid (Asp), glutamic acid (Glu), alanine (Ala), arginine, cysteine, phenylalanine (Phe), glycine (Gly), hydroxyslysine, isoleucine (Ile), histidine, leucine (Leu), lysine (Lys), methionine (Met), proline (Pro), serine (Ser), tyrosine (Tyr), threonine, and valine (Val). The standard solutions were stored at 4 °C.

N,O-Bis(trimethylsilyl) trifluoroacetamide ≥99%, N,O-Bis (trimethylsilyl) trifluoroacetamide with trimethylchloro-silane, N-tetra-Butyldimethylsilyl-N-methyl-trifluoroacetamide with 1% tert-butylmethyldichlorosilane ≥95% were employed for derivatization purposes and purchased from Sigma Aldrich. Norleucine solution in bi-distilled water (Sigma-Aldrich; purity 99%, 75.27 μg/g, tridecanoic acid

Fig. 1. Types of decorative revetments under study in the Alhambra monument. (A) Marble capital of the Hall of the Abencerrages, (B) plasterwork mocarabes of the Hall of the kings and (C) wooden ceiling of the Hall of the Abencerrages.
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