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A new insight into the vaults of the kings in the Alhambra (Granada, Spain) by combination of portable XRD and XRF☆

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ABSTRACT

In the Hall of the Kings, along the east side of the Courtyard of Lions in the Alhambra (Granada), the vaulted ceilings are clad in painted leather depicting various Kings or Lords on their seats, the fountain of youth, and a Lady playing chess. These artworks are unique masterpieces because of the unusual medium used (leather) and the presence of human representation in 14th century Muslim art.

The colour palette of the paints used was assessed without taking samples, using a prototype apparatus that simultaneously performs X-ray diffraction (XRD) and X-ray fluorescence (XRF), providing an elemental chemical and mineralogical characterization of the areas studied. The curvature of the vaulted ceiling and the size of device restricted analysis to the flattest parts and the most accessible areas.

The results show that the red hues are made from cinnabar and/or hematite. The flesh colour is a mixture of cinnabar and hydrocerussite, while malachite was used for the greens. Blues were achieved using lazurite and azurite, and the ochre tones using clays. Furthermore, XRD detected the presence of red lead in the red-ochre and orange tones, while gold is present together with tin and iron. Moreover, strontium is associated with the plaster preparation, and a compound made with arsenic and sulphur was observed in the green areas.

1. Introduction

The leather paintings that cover the vaulted ceilings in the Alhambra's Hall of the Kings (Granada) are currently being restored. This restoration work has been commissioned by the Alhambra and the Generalife in Granada in collaboration with the Andalusian Institute of Cultural Heritage (IAPH). The intervention is a broad and comprehensive project, responding to the demands of these unique masterpieces, their current state of conservation, their properties, and their environmental conditions.

The three rooms in the Hall of the Kings are located to the east of the Court of the Lions in the Alhambra. From right to left, we first find the image of a Lady playing chess, second, in the center, the Kings, and third, the Fountain of Youth. Traditionally, these depictions were thought to have been created by painting on leather, but it has now been established that they were made on a mixed medium of leather covering the wooden vaults [1]. Stratigraphic sections show a primer layer of gypsum with animal glue followed by pigments with egg yolk and linseed oil in the latest interventions. Over this surface, some areas have been picked out with gold leaf [2].

Our research centered on the vaulted ceiling of the Hall of the Kings, featuring painted scenes depicting various Lords or Kings on their seats (Fig. 1.a) and the Fountain of Youth (Fig. 1.b). These artworks are masterpieces not only because of the medium used (leather) but also for the presence of human representation in 14th century Muslim buildings [3].

At the beginning of the intervention conducted by the IAPH, the integrity of the three vaulted ceilings was at great risk due to the conditions of their conservation, in particular due to ineffective architectural interventions and restoration attempts since 1618 [2].

In 1855, Rafael Contreras divided the original roof (a single space that spanned the three vaults and provided rainwater drainage) into three separate spaces with double-pitched roofs, channelling rainfall through the new division towards the space between the three vaults. This change in rainfall drainage has caused severe water damage to the vaults leading to bio-deterioration in the wood and leather with consequences for the paintings, which displayed disruptions in their primer and subsequent layers of paint, in the form of peeling and cracks [4].

As a consequence of this intervention in the roof structure, several restorations of the paintings have been undertaken to minimize the effects of water alteration on the paintings. These restorations have mainly focused on treating areas of peeling and scaling paint. For instance,

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Fig. 1. XRD/XRF areas of study in the vaulted ceilings of the Hall of the Kings (Alhambra, Granada). (a) Central vault depicting the Kings, (b) Lateral Vault showing the Fountain of Youth.

new preparation layers were added, the vaults were coated, gaps were patched using different materials, and protective products were applied [5].

The most important restoration of the paintings, carried out in 1960 by Gudiol, involved applying fixing treatments based on waxy compounds (wax-paraffin), bringing about major changes in the nature of the original painting and leading to additional forms of weathering (peeling, stains, gaps) [2].

On account of the weathering conditions of the vaulted ceilings, and the need to evaluate the consequences of damage while minimizing the number of samples taken from the paintings, non-destructive techniques were used to determine the mineralogical composition of the artwork, also providing further knowledge of these masterpieces as well as the general state of conservation prior to new interventions. For this reason, the characterization of paintings was conducted *in situ* using a portable device that combined X-ray diffraction (XRD) and X-ray fluorescence (XRF). The working conditions were challenging due to the shape of the artwork and the accumulation of restoration products such as waxes on the surface.

2. Materials and methods

To characterize the mineralogical pigments, a portable XRD/ XRF device was used. This equipment is capable of performing crystalline phase identification and elemental chemical analysis simultaneously on a single area. This portable XRD/XRF system was developed by the Centre de Recherche et de Restauration des Musées de France (Louvre Palace, Paris), with the support of European projects EU-ARTECH (EU FP6 RII3-CT-2004-506171) [6] and MOLAB CHARISMA (EU FP7–228330) [7]. As this equipment was designed to study various kinds of artworks, in particular canvas paintings [8–10], it was a challenge applying it to this medium and a vaulted ceiling from the top of scaffolding.

To provide a brief explanation of how it functions, X-rays are produced by a Cu anode source. The beam impinges the artwork at a nominal angle of 10° from the surface where it irradiates an area of 3×3 mm^2. XRD is obtained from the Cu-Kα line (8.05 keV). XRF analysis is performed with a silicon drift detector (energy resolution of 150 eV at 6 keV) that identifies fluorescence lines between 2 and 30 keV.

Because of the Cu source, XRF spectra always include the Cu-Kα line and no Cu-Kβ which is absorbed by the Ni filter on the source window [8–10]. The presence of Cu in the object can be revealed by the presence of the Cu-Kβ line or by carrying out a specific XRF measurement with an Al 750 μm thick filter that eliminates the Cu line from the source [8].

With these conditions, the analyzed depth of materials is directly related to the penetration of X-rays, corresponding in the case of XRD to a 20 μm thick layer of matter for light elements (Al, Si, K,. . .) and 5 μm for heavy elements (Pb, Hg, Sn,. . .). In the case of XRF, penetration depends on the energy of the fluorescence line, which can be less than 1 μm at 2 keV for Pb-M and as high as 50 μm at 25 keV for Sn-K [10].

A layer of organic matter that is 100 μm thick does not significantly absorb X-rays above 5 keV [9]. Therefore, the presence of wax layers should not be a problem in this study. The challenge in this case is to position the XRF-XRD equipment on a concave surface and to maintain its alignment when it is located on scaffolding that moves under the weight of the operators. Nevertheless, the possibilities of the prototype meant it could be adapted to the conditions and cope with such difficulties. It also proved to be a valuable experience to improve the equipment.

The concave surface and the geometrical constraints meant that the XRD–XRF system had to target greater distances than it does when analyzing flat objects such as canvas [9,10]. This has no effect on the collection of diffracted beams, but it does mean that the XRF detector is no longer situated in an optimized position, with possible XRF intensity loss at low energy levels (below about 5 keV). Bearing this in mind, qualitative interpretation of XRF spectra is still useful, particularly when interpreting XRD diagrams. For XRD, the main difficulty is caused by the instability of the scaffolding, making it necessary to determine the center of the diffraction pattern for each measurement. This can be done by trial and error because the artwork generally includes known minerals (quartz, cerussite, hydrocerussite, etc.) that can be identified in the diagrams at the expense of additional work for the operators.

When studying the section of vaulted ceiling depicting the Kings, eleven points were analyzed using XRD–XRF (Fig. 1.a), whereas fourteen points were analyzed using XRD–XRF (Fig. 1.b) for the Fountain of Youth. In both cases, evaluating the colour compositions of the paints and the mineralogical phase of the pigments beneath the weathering agents were the main aims of the research. The points were selected depending on the palette, the restorations, the curvature of the vaults, and the experimental conditions, which meant that only accessible parts of the vaults could be selected.

3. Results

Table 1 summarizes the results of the chemical and mineralogical analysis performed on the vaulted ceiling depicting the Kings. On-site XRF spectra detected the presence of Ca, S, Fe, Hg, Cr, K, Cu, Co, Au, Si, As, Ba, Pb, Sn, Zn, and Sr. Most of these elements were also confirmed by taking sample and analyzing them with SEM-EDX [11]. However, Al, Na, and Mg could not be detected using such non-destructive techniques and under on-site XRF conditions, as their emission lines