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Colours Found During Restoration of the Seville City Hall Facade

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Abstract

Iron oxides, Pb_3O_4 (red lead) with PbO, azurite and calcite were used as pigments in the Seville City hall façade. A gold gild was present in some areas. A black crust caused by environmental contamination was responsible for the black colour. Acrylic resin and other added materials are also responsible for some of the colour changes. The stone was cleaned, reinforced and innovatively consolidated and protected using suitable materials for restoration.

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Keywords: colours; pigments; façade; stone; cleaning; restoration;

1. Introduction

The Seville City Hall is one of the most striking examples of the plateresque architectural style in Andalusia. Diego de Riaño, who had been previously commissioned to design a stone building with a façade for the Major Plaza of Seville, began construction on the building in 1526. Juan Sanchez took over the work following de Riaño's death. The Seville City hall is known for its singularity, trace and proportionality, perfection of its sculptures, wealth, elegance and beauty.

The wall paintings are among the oldest artistic works. During the Renaissance, the finishing techniques for the stucco were refined to create more complex structures. Until recently, wall paintings have been used throughout various architectural periods. The analysis of the paints used in these wall paintings provides valuable information for

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defining the gamut of pigments available both locally and regionally and for understanding the techniques for colour preparation and application over the centuries [1-3]. The surfaces of the ornamental materials on monuments and historic buildings are altered by the interactions between the original materials and environmental pollutants. A layer of contamination from both dry and wet deposits covers the exposed surfaces of buildings. These substances remain on the surfaces for long periods of time and are responsible for the alteration processes that produce black crusts on the exposed surfaces.

The restoration of the Seville City Hall's plateresque façade has proven difficult because of the environmental alterations to the stones and the meticulous details of the stonework. It is a challenge to clean, reinforce and innovatively consolidate and protect the stone with the appropriate materials [4,5].

This work aims to study the colours produced by the original pigments as well as by the additives from environmental contamination and materials used for the restoration of the Seville City Hall façade. The restoration process performed in this work is also described.

2. Materials

A total of 60 samples were collected from the façade and studied in this work. Samples 40, 41, 42 and 52 were collected from the San Fernando sculpture (Fig. 1). Several samples were taken from the protective layers of the façade. Sample 55 was possibly a resin. The restored façade area is shown in Figure 2.

3. Methods

The cross-sections of the samples were observed and photographed using a Nikon OPTIPHOT (mag: 25X, 50X and 100X) optical microscope. X-ray diffraction (XRD) patterns were collected using an X'Pert Pro MPD Panalytical diffractometer with Ni-filtered Cu K_α radiation. An X'Cellerator detector with an angular aperture of 2.18º (2θ) and a step size of 0.016º was used. Elemental chemical analyses of the cross-sections were obtained using a HITACHI S-4800 SEM instrument equipped with a Bruker X-Flash Detector 4010 energy dispersive X-ray (EDX) analyser at an accelerating voltage of 20 kV. The samples were coated with a carbon film prior to SEM analysis. Fourier transform infrared spectroscopy (FTIR) was performed using a Jasco FTIR 6200. An integrated dispersive Horiba Jobin–Yvon Labram Infinity System was used to record the Raman spectra. Simultaneously, TG-DTA measurements (STDQ600, TA Instruments) were performed at a linear heating rate of 10ºC min^{-1} from ambient temperature to 1000 ºC in flowing air.

4. Results and Discussion

The petrographic study of the stone showed the presence of a fine-grained carbonate rock composed primarily of bioclasts and fine sand. The XRD samples were used for semi-quantitative analyses. The concentrations of calcite and quartz in the stone were 85-90% and 5-10%, respectively. Conventional optical microscopy was utilized to examine the cross-sections of the wall paintings found in this monument. A selection of the micrographs is shown in Fig. 3. The surface of Sample 40 (cross-section shown in Fig. 3a) is a red-brown colour and the interior is a yellowish colour. The chemical analysis of a red particle by EDX showed the presence of Pb as well as a small percentage of Cl (spectrum an in Fig. 4), suggesting the presence of a lead compound. The micro-Raman spectroscopy of red-coloured surface showed peaks for red lead, Pb_3O_4 (118 (vs), 379 (w), and 545 (s)), and PbO (147, 287 and 339 cm^{-1}). The black zones in this pigment layer are attributed to PbO_2 produced by oxidation of the Pb_3O_4. This red-brown layer (spectrum an in Fig. 4) is deposited on a yellow layer composed of gypsum and calcite (spectra b and c in Fig. 4 b, c). Sample 41 (cross-section shown in Fig. 3b) contains a gypsum substrate (spectrum e in Fig. 4) onto which gold gilding was applied (spectrum d in Fig. 4). The FTIR spectra showed absorption bands for the gypsum at 1161 cm^{-1} and for the animal glue at 1615 cm^{-1}. Therefore, the substrate was prepared by mixing the gypsum with the animal glue. The surface of sample 42 (cross-section shown in Fig. 3c) is blue and the interior is a yellowish colour. The EDX analysis of the blue surface showed Pb, Cu and Cl (spectrum a in Fig. 5), suggesting the presence of a copper chloride hydroxide. However, the analysis of a blue particle showed only the presence of Cu and O (spectrum b in Fig. 5). The FTIR analysis confirmed the presence of a carbonate suggesting that an azurite pigment was used.

Fig. 1. San Fernando sculpture.

Fig. 2 Restored façade.

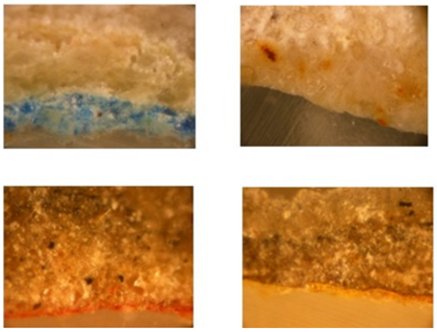

Fig. 3. Optical micrographs of the cross-sections of: a) sample 40, b) sample 41, c) sample 42, d) sample 52.

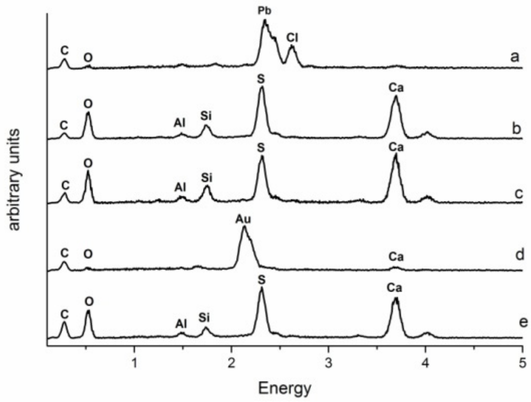

Fig. 4. EDX analysis of cross-sections of samples 40-41.

The Cl may be associated with the Pb as it is in sample 40. Our analyses indicate that, at one time, the wall paintings may have covered the entire surface of the façade. Sample 52 was collected from such a wall painting. The surface of sample 52 (cross-section shown in Fig. 3d) is a compact, yellowish layer with red particles and the interior is white. The yellow layer is composed of Ca and O (spectra c and d in Fig. 5) or calcite. The red particles contain Ca and Fe (spectrum e in Fig. 5). Therefore, the surface layer contains calcite with iron oxides as pigments. Pigments from other samples (samples 33, 34, 47 and 60) studied also content of iron oxides.

A black crust was also found in some zones of the façade. Mass spectroscopy of this black crust indicated the presence of alkanes produced by petrol combustion. Other organic compounds, including isoprene hydrocarbons, fatty acids, amides and polycyclic aromatic hydrocarbons, were also present. These organic compounds have also been found on other monuments in Seville [6-8]. XRD of the black crust samples revealed high gypsum content with smaller amounts of calcite and quartz. This analysis also identified the presence of Fe, Al, Ti, Cr, V and Pb, all of which are catalysts for gypsum formation in the presence of SO_2.

The DTA/TG/DTG curves shown in Fig. 6 for the black crust indicate a high mass loss (16.5%) and an endothermic reaction attributed to the vaporization of water bound primarily in gypsum that occurs between 100 and 200 ºC. The evolution of the organic compounds between 200 and 600 ºC with a maximum exothermic reaction between 325 and 410 ºC is of particular interest. The total mass loss associated with the organic compounds is between 5 and 7.5%. Another endothermic peak, with a mass loss of 3.5%, appears between 600 and 725 ºC and corresponds to decomposition of carbonates.

The FTIR analysis of several samples indicated the presence of an acrylic resin covering the façade. This resin was most likely used during a previous restoration of the Seville City Hall and is responsible for some of the colour changes in the façade.

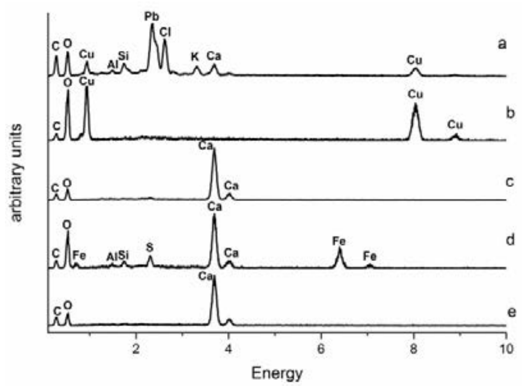

Fig. 5. EDX analysis of cross-sections of samples 42-52.

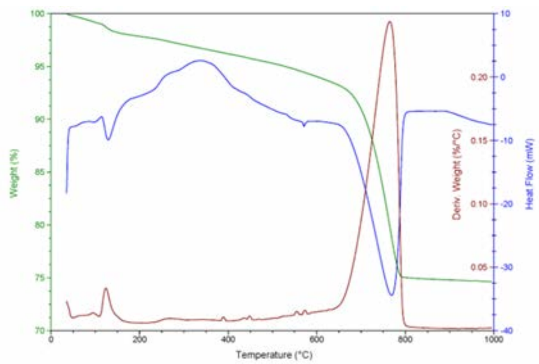

Fig. 6. ATD/TG/DTG curves for black crust.

The stones were cleaned using water and natural soap so as not to damage them. After the stones were cleaned, they were consolidated and protected by stable, well-studied, mineral materials that were compatible with the stone. The degraded joint mortar was removed and filled with Cumen lime mortar in a technically controlled process.
The deteriorated stone was replaced by stones similar to the original stones. The missing carved stones were adhered using a lime and sand mortar with a composition similar to that of the original stones. The façade was coated with a thin layer of fine, lime mortar coloured to match the stone.

5. Conclusions

The stones in the Seville City Hall façade comprise fine-grained carbonate rock composed of bio clasts and fine sand. The rock contains 85-90% calcite and 5-10% quartz. Wall paintings have been recovered in discarded materials from the restoration work in the Seville City Hall. The red-brown layer contains Pb_3O_4 (red lead), PbO and PbO_2. This red-brown layer is deposited onto a yellow layer containing gypsum and calcite. Gilding was applied over the gypsum layer. The blue colour contains azurite and albayalde (lead basic carbonate). Yellow layers containing calcite with iron oxide pigments were present throughout the façade. A black crust produced by environmental contamination was also found in some zones of the façade. An acrylic resin applied during a previous restoration also contributed to the yellowish colour of the stones.

The stones were cleaned using water and a natural soap. The stone was consolidated and protected by stable, mineral materials compatible with the stone. The degraded joint mortar was removed and filled with lime mortar. The deteriorated stones were replaced by stones similar to the original stones. The missing carved stones were adhered using a technically controlled lime mortar. The façade was coated with a thin layer of fine, lime mortar coloured to match the stone.

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