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Review Article

# Wall paintings studied using Raman spectroscopy: A comparative study between various assays of cross sections and external layers

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## HIGHLIGHTS

- Raman spectroscopy characterisation of the compounds used to produce polychrome wall paintings.
- The reliability of Raman techniques (portable and μ-Raman).
- Effects of the compounds that are formed on or added to the wall paintings in the Raman study.
- Characterisation of the advantages of compounds from cross sections of the wall paintings.

## GRAPHICAL ABSTRACT

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## ABSTRACT

This work describes a comparative study between in situ applications of portable Raman spectroscopy and direct laboratory measurements using micro-Raman spectroscopy on the surface of small samples and of cross sections. The study was performed using wall paintings from different sites of the Alcazar of Seville.

Little information was obtained using a portable Raman spectrometer due to the presence of an acrylic polymer, calcium oxalate, calcite and gypsum that was formed or deposited on the surface. The pigments responsible for different colours, except cinnabar, were not detected by the micro-Raman spectroscopy study of the surface of small samples taken from the wall paintings due to the presence of surface contaminants.

The pigments and plaster were characterised using cross sections. The black colour consisted of carbon black. The red layers were formed by cinnabar and white lead or by iron oxides. The green and white colours were composed of green emerald or atacamite and calcite, respectively. $Pb_3O_4$ has also been characterised. The white layers (plaster) located under the colour layers consisted of calcite, quartz and feldspars. The fresco technique was used to create the wall paintings.

A wall painting located on a gypsum layer was also studied. The Naples yellow in this wall painting was not characterised due to the presence of glue and oils.

This study showed the advantage of studying cross sections to completely characterise the pigments and plaster in the studied wall paintings.



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## Introduction

The Alcazar of Seville is a royal palace in Seville, Spain, originally a Moorish fort. It is the oldest royal palace still in use in Europe. The Alcazar of Seville is a collection of royal palaces spanning different epochs, and its surrounding fortress walls. It is a stunning collection of architecture with Mudejar, Gotic, Renaissance and Baroque influences.

The Alcazar of Seville was begun in 913 during the reign of Abb-Al-Rahman III the first caliph of Andalusia. The Christians period began in 1248. Actually, a few remains still lie from the Islamic Palace. The Gypsum Room in the Gypsum Palace from the reign of Alfonso XI still contains a small arch, attributed to the Almohad period. Alfonso X initiated the first work and ordered the construction of the Gotic Palace. Latter, King Pedro I built the Mudejar Palace, an example of the Andalusian Mudejar style, between 1356 and 1366. Reform were conducted in this Palace at the end of the middle Ages 15th–16th century under the reign of Catholic Kings in the upper story of the Patio de las Doncellas named Peinador de la Reina. Part of this story was also added by Charles V in the style of the Italian Renaissance. El Patio del Crucero, also known as Patio Doña María de Padilla was built in the twelfth century during the Almohade period. It was transformed at the time of Alfonso X the Wise. In 1775 due to damage after the earthquake of Lisbon, its structure arranged in two levels was strengthened.

Wall paintings are located through the Alcazar of Seville, mainly on a gypsum layer, and the colour pigments were applied using glue and oil. Important reforms and restoration of these wall paintings took place at the end of 18th and 19th centuries, respectively [1,2]. However, other wall paintings created using the fresco technique on lime mortars have also been found.

The small arch of the Gypsum Palace attributed to the Amohade period with an original wall painting that was conserved and restored by Prof. Manzano [3]. This arch is considered the oldest preserved wall painting remaining in the Alcazar [4]. This wall painting displays a rich spectrum of colours: white, yellow, red, green and orange. Cross sections from samples were studied by a few authors of this work using EDX and FTIR, and the data were included in a manuscript published in Apuntes del Real Alcazar de Sevilla [5].

Parts of the wall paintings on Mirador de la Reina in the first floor of the Mudejar Palace were created during the reign of the Catholic Kings and were subsequently covered. During recent conservation work under the direction of Prof. Manzano, these wall paintings were found to represent the coats of arms and emblem of the Catholic Kings.

The wall paintings from the Baños de Doña Maria de Padilla were created between 1565 and 1579 by Gonzalo Perez using the fresco technique. These wall paintings are located in a gallery under El Patio del Crucero a building that suffered serious deterioration in the earthquake of 1755. The architect Van der Borch transformed the zone that remained around the part of the building where the paintings were found buried under the new Baroque structures. The paintings have been subjected to successive and meticulous recovery interventions due to the damp microclimate [6,7].

Raman spectroscopy can be used to identify the constituent materials in cultural heritage artefacts because this technique provides information about the characteristic vibration levels of each constituent [8–13]. The usual approach for the micro-Raman technique is to analyse a single spot or only a few selected positions to ultimately identify the material from comparisons with the Raman spectra of reference materials [14–22]. However, Raman spectroscopy alone cannot resolve complex aged paint samples [22,23]. In many cases, the surfaces of cultural heritage artefacts have deteriorated due to natural decay factors (atmospheric pollutants, biological attack, water infiltration, temperature and similar factors). The effects of atmospheric pollutants have received the most attention [24–27]. The dissolution–crystallisation and hydration–dehydration of cultural heritage artefacts results in salt formation on the surface, particularly on wall paintings [28–30]. Biological activity and its consequences on works of art has received special attention. Living organisms, such as lichens, fungi or bacteria, excrete oxalic acid, which is particularly harmful to wall paintings [31,32]. Products, such as acrylic polymers, organic-silicon, lime and gypsum, are frequently used on wall paintings for protection/consolidation. These products are responsible for the heterogeneity of the surface and limit the application of some analytical techniques. Regardless, these products are crucial for preserving cultural heritage.

When wall paintings must be analysed, non-destructive portable instruments are the best option for obtaining information in situ and for maintaining the integrity of the artwork. Micro-Raman instruments have been developed for the in situ analyses of artwork [13]. However, the sensitivity and lateral resolution is frequently not sufficient to obtain information about all layers of