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USE OF NON-INVASIVE XRF SPECTROSCOPY FOR THE ANALYSIS OF MUDÉJAR POLYCHROME ON THE CHAPEL DOOR IN THE PALACE OF THE DUKES OF ALBA IN SEVILLE

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Abstract

The pigments, execution technique and repainting used on the polychrome wood door of the chapel of the Palace of the Dukes of Alba in Seville (Spain), best known as Palacio de las Dueñas, were studied using portable X-ray fluorescence equipment. This carpentry work is a magnificent example of the Mudéjar art made in Spain in the early 16th century. Portable X-ray fluorescence gave good information on the different components of the polychrome. The following pigments were characterized: red (cinnabar/vermilion, lead oxide, iron oxides, and a mixture of iron oxide and orpiment/realgar), black, white (white lead) and yellow (orpiment/realgar and yellow ochre). Brass was also found in metallic sheets which decorate the door and iron in the bolt which locks it. The pigments were applied with the oil painting technique over a support layer that had been primed with animal glue. This support layer was gypsum in some cases and white lead in others. This study is essential to the polychrome conservation of the studied artwork, and it will help clarify uncertainties in the history and painting of Mudéjar art.

Keywords: portable XRF, pigment, Mudéjar, carpentry, Palacio de las Dueñas

1. Introduction

Mudéjar is a style of Spanish architecture combining Moorish and Christian forms, practiced from the 12th to 17th centuries. *Mudéjar* style is found in many important buildings in the city of Seville. Wood was frequently used in

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important artefacts such as doors, of *Mudéjar* monuments. Several researchers have studied *Mudéjar* art, including artefacts constructed with wood. However, only few papers have been dedicated to the study of the polychrome applied to these wood artefacts.

The Palace of King Peter of Castile, in the Royal *Alcázar* of Seville, is the model that the builders followed to make the *Casa de Pilatos* and the *Palacio de las Dueñas*. The royal house has magnificent tile works, stucco plasterworks and wooden ceilings and roof frameworks, which were imitated in both houses of the family Enríquez de Ribera [1-3].

An important collection in Spain of '*lo blanco*' Spanish carpentry with '*lacería*' decorations is contained in the *Palacio de las Dueñas* which includes wooden coffered ceilings, roof frameworks and doors.

Currently, non-invasive techniques, such as portable X-ray fluorescence/X-ray diffraction and Raman spectroscopy are applied to the study of artworks [4-16]. X-ray fluorescence spectroscopy (XRF) is the most widely used technique for elemental chemical analysis due to a number of favourable analytical characteristics [17-19]. The need to perform in situ non-invasive analysis of art objects, that cannot be easily removed from their location, has led to the development of portable XRF equipment. XRF is recognized as an accurate technique for quantitative analysis. The concentration of one element in a sample is identified as a combination of several factors, such as the measured net peak area within a correcting term that corresponds to the effects of the matrix composition and the calibration constant [20-22].

The aim of this work was the characterization of the pigments that compose the polychrome of the chapel door in the Palace of the Dukes of Alba, using non-invasive XRF. The subjects of this work were as follows: (i) characterization of the painting materials and techniques applied in the *Palacio de las Dueñas* polychrome carpentry; (ii) use of this information to characterize the further polychrome woodwork; (iii) determination of the chromic evolution of the painting materials and (iv) providing conservators with scientific knowledge for restoration.

2. The Palacio de las Dueñas in Seville

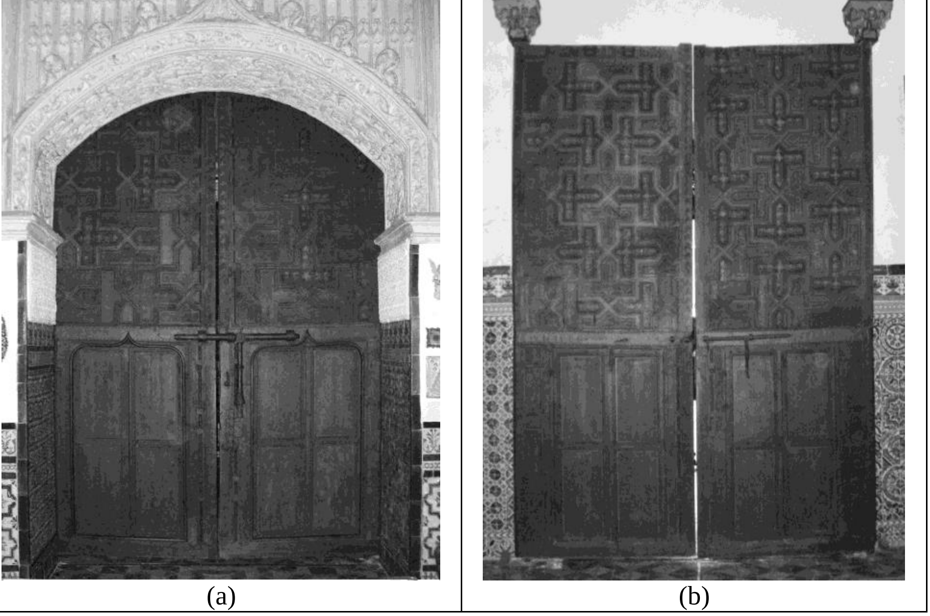
The *Palacio de las Dueñas* in Seville is the result of several phases of work over more than two-and-half centuries. This palace is a *Mudéjar* and Renaissance building. Main Governors of Andalusia Pedro Enríquez (1478-1492) and his wife Catalina de Ribera (†1505) began to build the *Casa de Pilatos*, their new house in Seville, in 1483 [2]. Catalina de Ribera began to build the *Palacio de las Dueñas*, her second house in Seville, in the last decade of the 15th century, after to be widowed. When Catalina de Rivera bought the houses where she began to build the *Palacio de las Dueñas*, she paid to the family Pineda, Lords of Casabermeja and the former owners, 375,000 maravedis. This price was so high because the houses had drinking water supplied by the aqueduct of Carmona. The work was continued in the 16th

century by Fernando Enríquez de Ribera (1477?-1522), their second son and Gentleman Twenty Four of the City Council of Seville, by Inés Portocarrero (†1546) (the widow of Fernando), and by Fernando Enríquez de Ribera II (†1594) (the first-born son of Fernando). Fernando de Silva y Álvarez de Toledo (1714-1776), Twelfth Duke of Alba, finished the building in 1771 with the current main façade [1, 3].

The Dukes of Alba became the owners of the palace after Antonia Enríquez de Ribera (†1623) got married to Fernando Álvarez de Toledo (1595-1667), Sixth Duke of Alba in 1612. During the 20th century, the palace was the home of the Dukes of Alba, and Cayetana Fitz-James Stuart (1926-2014), the Eighteenth Duchess of Alba, was the last inhabitant of the palace before dying in 2014 [1].

2.1. The Mudéjar door in the chapel

The *Mudéjar* houses, which had bought Catalina de Rivera, were transformed in a Renaissance palace from 1515 to 1522, although the construction of the chapel began at the end of the 15th or the beginning of the 16th centuries [1, 3]. This sacred room is covered with a Gothic rib vault and closed with a *Mudéjar* wooden door which is decorated with swastikas and painted arabesques (Figure 1).



(a) (b)

Figure 1. Chapel door: (a) frontal elevation, (b) back elevation.

The woodwork and painting authors of this door are anonymous but the master carpenter in the Alcázar of Seville from 1502 to 1535 was Juan Limpias and before these date Catalina de Rivera had had a slave with the same name. There were also several works in the palace in the year 1571 [1]. The carpenter of the Alcázar of Seville Martín Infante and the bricklayer Master Pedro built the ceiling and roof above the main staircase and renewed several pieces of wood in the palace, perhaps the doors. They both received 213,680 maravedís for those works [1].

The painter Alonso de León was contracted in 1516 to paint a wooden ceiling 'like the Romans'. The painters Alonso de León, Diego Rodríguez Benamad and Sebastián de Alejos (the son of the famous painter Alejo Fernández) also appears named in several documents from 1510 to 1540 [1]. Currently, the large double door of the chapel maintains the entire polychrome on both its external and internal faces, perhaps due to repainting. The polychrome has yellow, red, white and black colours.

3. Materials and methods

The XRF measurements were performed using an Oxford Instruments X-MET7000 hand-held energy dispersive X-ray fluorescence (EDXRF) analyser, equipped with an Oxford Instruments drift (SDD) high-resolution detector; and a 45 kV Rh target X-ray tube (max. 50 μA) with a maximum focal spot size of 2 mm; a Be exit window of 75 μm and a cone angle of 145º; and an automatic 5-position filter changer. The measurement spot size was 9 mm. The analytical range was from Mg to U, and up to 35 elements could be analysed, depending on the calibration.

The energy dispersive system's typical peak overlap and matrix effects did not allow for straightforward elemental quantification because the peak intensity for a given element was not directly proportional to its concentration. Instead, the intensity was also a function of the concentration of other elements present in the sample [23]. Therefore, quantification was based on standard analyses of an equivalent elemental matrix measured under the same conditions. Quantitative analyses were performed using the fundamental parameter method [24] and the software associated with the equipment. The fundamental parameter evaluation procedure was calibrated and set up to analyse 14 certified pure metals, from Si (lightest element) to Pb (heaviest element), which were used as reference materials to compose the internal software library of elemental sensitivities. The results of the analyses were expressed in weight percentages (wt%). These results must only be considered as approximations.

4. Results and discussion

For XRF, the depth of analysis depends on the nature of the elements assayed and on the energy of the fluorescing X-ray used for their detection (e.g., for Pb-L, E = 9.2 to 15.8 keV or for Pb-M, E = 2.3 to 2.6 keV). In this work, qualitative and approximately quantitative analysis of the external zone of the polychrome carpentry was carried out by XRF (Figure 2). In addition to the pigment layer, the analysed elements were also found to compose other layers of the polychrome. Multi-layer easel paintings have been quantitatively analysed by XRF by several authors, who did not obtain accurate quantitative information when using this technique [5, 21]. These two drawbacks suggested that quantitative results obtained using this technique must only be considered as approximations.

The chemical composition based on XRF is shown in Table 1.

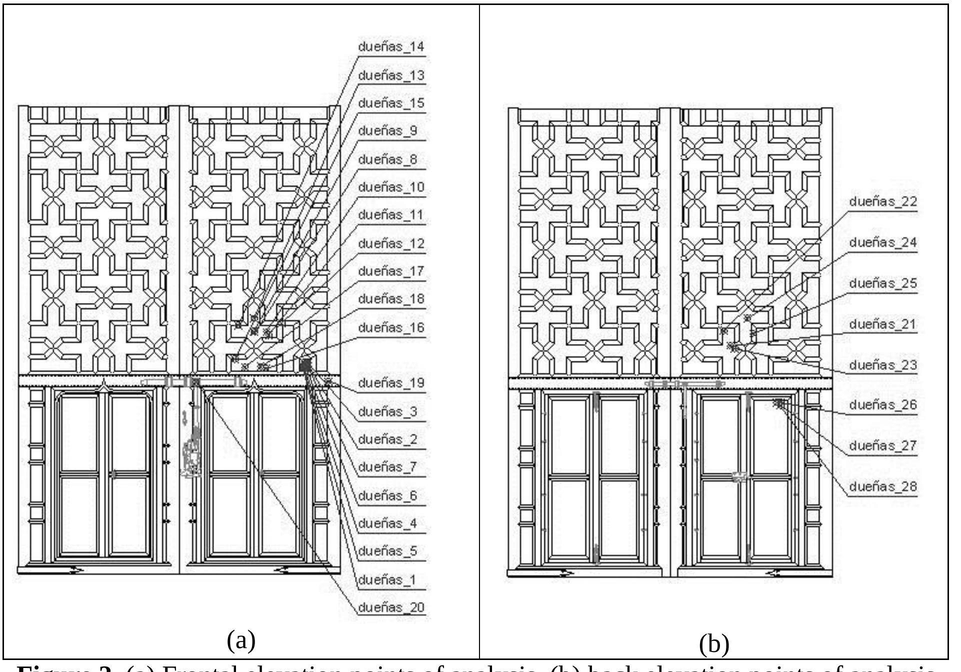


Figure 2. (a) Frontal elevation points of analysis, (b) back elevation points of analysis.

4.1. Red pigments

The portable XRF system revealed four types of red pigments. Hg and S, characteristic of cinnabar/vermilion, were detected in the analyses dueñas_3, dueñas_7, dueñas_11, and dueñas_22. Artists have been using mercury sulphide since antiquity [25, 26]. Cinnabar, a natural pigment extracted from mining, and vermilion, a synthetic pigment, have been used since ancient times; however, XRF cannot distinguish between the natural and synthetic variants [16]. The Romans referred to cinnabar/vermilion as minium, which was one of their most valuable pigments [27]. Theophrastus asserted, 200 years before Vitruvius, that the cinnabar used by the Romans had Spanish origin and their mines were located in Sisapo (Almaden at the present time) [8, 28]. Cinnabar has been found in Roman wall paintings found in Seville excavations [29]. High amounts of Pb were also found in the red areas containing Hg. The presence of Pb suggests that the cinnabar/vermilion may have been mixed with read lead to obtain the pigment. In a point (dueñas_16), only Pb was detected suggesting the presence of red lead without vermilion.

Table 1. Chemical composition based on measured by the portable XRF system (%)

Analysis	Descr.	K	Ca	Fe	Cu	Zn	As	Sn	Ba	Hg	Tl	Pb
dueñas_1	Yellow	1.20	8.88	1.07	0.01		2.64			0.06	0.05	13.9
dueñas_2	Yellow	0.88	13.7	4.29	0.01	0.02	5.71			0.06	0.02	1.24
dueñas_3	Red	0.88	7.47	0.62		0.02	1.63			6.36	0.04	8.21
dueñas_5	White	0.86	7.54	0.56	0.01					0.06	0.07	23.7
dueñas_6	Yellow	0.67	13.1	4.53	0.01	0.02	5.67			0.05		1.20
dueñas_7	Red	0.83	9.94	0.77	0.01	0.01	2.80			3.93		6.16
dueñas_8	Yellow	1.03	4.90	0.46	0.01			0.24		0.71	0.11	32.6
dueñas_9	Yellow	0.62	4.55	0.48	0.01			0.15		1.01	0.09	33.9
dueñas_1	White	0.61	6.07	0.69	0.01		1.24	0.10		0.09	0.13	30.8
dueñas_1	Red		14.1	2.59	0.01	0.01	3.38			1.03	0.02	4.14
dueñas_1	White		13.4	1.58	0.01	0.01	1.99			0.17	0.02	1.51
dueñas_1	White	0.72	7.33	0.61			1.87			0.04	0.06	14.3
dueñas_1	Yellow		16.0	1.04		0.01	1.99			0.33	0.03	3.85
dueñas_1	Red		1.91	0.95		0.01	0.15				0.01	1.90
dueñas_1	Sheet	0.74	2.13	22.3	28.7	11.2		0.04	0.17			0.93
dueñas_2	Bolt		2.00	63.4	0.05	0.01		0.04				0.09
dueñas_2	Yellow		15.8	1.65		0.01	4.39			0.05		0.48
dueñas_2	Red	0.73	5.51	0.55		0.01	3.76			7.00	0.03	10.8
dueñas_2	Black		5.08	0.26		0.01						0.02

Relatively high concentrations of Fe and As mixed with Hg and S were detected in another point of analysis (dueñas_11). The As was attributed to the presence of realgar. These analyses suggest that cinnabar/vermilion and red lead are the original pigment. Only in the analysis carried out in dueñas_11 appeared an addition of realgar and red ochre which were attributed to repainting. Natural iron oxides, usually mixed with clay minerals (kaolinites, illites, smectites, etc.), were widely used as pigments [30]. Red ochre was one of the first pigments used in ancient paintings [31, 32] and by Roman artists [32-34]. Both natural and artificial ochres, obtained by the calcination of yellow ochre, were used [27].

4.2. Yellow pigments

Three types of yellow pigments were revealed by the portable XRF system. The points containing high amounts of As and S (dueñas_1, dueñas_2, dueñas_6, dueñas_14, dueñas_21) are made of orpiment, probably mixed with yellow ochre, due the presence of Fe.

High amounts of Pb, found with As, S and Fe in most points of analysis (dueñas_1, dueñas_2, dueñas_6, dueñas_14), and alone in two points (dueñas_8, dueñas_9), were attributed to repainting or addition of massicot.

4.3. Black pigments

Chemical elements responsible for black colour cannot be observed by XRF. This technique does not usually detect C or P (which are normally responsible for black colour) due to the low energy of the radiation, absorption by the Be window and the strong absorption of X-rays by the air (2.5 cm) between the analyser and the XRF detector (dueñas_26).

4.4. White pigments

High amounts of Pb were found in the white layers (dueñas_5, dueñas_10, dueñas_13), suggesting the presence of white lead (basic lead carbonate). In another analysed white layer (dueñas_12), high concentration of Ca was found, suggesting that this layer was made with gypsum (calcium sulphate dihydrate) and was used as support for all pigments applied on the wood.

4.5. Brass and iron

The door is decorated with metallic elements: sheets and several bolts. The XRF analysis on the sheets showed high amounts of Cu, Zn and Fe (dueñas_19). The presence of Cu and Zn reveals the use of brass sheets. The analysis carried out on the biggest bolt (dueñas_20) showed that it was highly pure Fe.

5. Conclusions

The non-invasive XRF technique provided useful information for the characterization of components in the external layer of the carpentry polychrome. The experimental techniques revealed four types of red pigments, cinnabar/vermilion, red lead, iron oxides and realgar, in the door paint. Cinnabar/vermilion appeared together with red lead pigment in most of the analysed areas. Cinnabar/vermilion was also found with realgar and red ochre. One analysis showed the presence of only red lead. A mixture of orpiment and yellow ochre was used to produce yellow colour. Massicot was probably also used as a yellow pigment.

Carbon black or bone char could have been used as a black pigment. Two pigments were used in white paints: white lead and gypsum. Both materials were also used as pigment support. Metallic sheets were made with brass, alloyed with a large amount of iron. The bolt was made with silicates and iron oxides.

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