Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 173 (2017) 279–291

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Analytical investigation of *Mudéjar* polychrome on the carpentry in the *Casa de Pilatos* palace in Seville using non-destructive XRF and complementary techniques

M.A. Garrote [a,*], M.D. Robador [a], J.L. Perez-Rodriguez [b]

[a] Building Engineering School, University of Seville, Avda Reina Mercedes s/n, 41012 Seville, Spain
[b] Materials Science Institute of Seville (CSIC-University of Seville), Americo Vespucio 49, 41092 Seville, Spain

ARTICLE INFO

Article history:
Received 8 June 2016
Received in revised form 7 September 2016
Accepted 17 September 2016
Available online 20 September 2016

Keywords:
Portable XRF
SEM-EDX
Micro-FTIR and micro-Raman spectroscopy
Optical microscopy
Pigment
Mudéjar carpentry

ABSTRACT

The pigments, execution technique and repainting used on the polychrome wood ceilings and doors in the *Casa de Pilatos* (Seville, Spain) were studied using portable X-ray fluorescence equipment. Cross-sections of small samples were also analysed by optical microscopy, SEM with EDX analysis, micro-Raman and micro-infrared spectroscopy and X-ray diffraction. These carpentry works are magnificent examples 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 SEM-EDX study of the surfaces of small samples gave information on their components and also characterized the compounds that had been deposited or formed by environmental contamination or by the alteration of some pigments. The SEM-EDX study of cross-sections facilitated the characterization of all layers and pigments from the support to the most external layer. The following pigments were characterized: red (cinnabar/vermillion, lead oxide, iron oxides and orpiment/realgar), black (carbon black), white (white lead and titanium barium white), yellow-orange-red-brown (orpiment/realgar and iron oxides), green (chromium oxide), blue (indigo blue and ultramarine blue), and gilding (gold leaf on bole). False gold, bronze and brass were also found. 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.

1. Introduction

Wood was frequently used in important artworks of the *Mudéjar* buildings, such as doors and ceilings. Several researchers have studied the polychrome applied to wood artefacts [1], however, only a few papers have been dedicated to the study of the polychrome applied to the Spanish Moorish wood artworks [2].

A large number of analytical methodologies and tools are available to the characterization of cultural heritage materials. Recently, 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 [3–16]. 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 peak net area within a correcting term that corresponds to the effects of the matrix composition and the calibration constant [17–21]. Energy dispersive spectroscopy coupled to scanning electron microscopy (SEM-EDX) has also been extensively applied to the study of cultural heritage using small samples taken from artworks [22–24]. It is a micro-destructive technique because a small amount of the artwork is collected before performing the experiments. The optical microscopy using both transmitted and reflected light of cross-sections prepared with small samples has been applied to distinguish morphology and characterized components of artworks. SEM-EDX, μ-Raman and μ-Fourier transform infrared (μ-FTIR) spectroscopy study of the layers from cross-sections have attracted the attention of scientists working in the field of art restoration and conservation [8,25–27]. X-ray diffraction (XRD) is considered the best experimental technique for characterizing the crystalline phase of artwork. This technique is also a micro-destructive technique because a small amount of the artwork is collected before performing the experiments [3–16].

The main objective of this work was to apply non-invasive (XRF) and micro-destructive (XRD, SEM-EDX, μ-FTIR and μ-Raman) analytical techniques in the polychrome characterization of the doors, shutters and ceiling in the Casa de Pilatos of Seville. The subjects of this work were as follows: i) characterization of the painting materials and techniques applied in the *Casa de Pilatos* polychrome carpentry; ii) use of

* Corresponding author.
E-mail address: marcoaugn@hotmail.com (M.A. Garrote).

http://dx.doi.org/10.1016/j.saa.2016.09.027
1386-1425/

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.

1.1. The Casa de Pilatos Palace in Seville

The *Casa de Pilatos* palace in Seville is the result of several phases of work over more than one-and-half centuries. This palace is a *Mudéjar* and Renaissance building. Andalusia's Main Governor Pedro Enríquez (c.1435–1492) and his wife Catalina de Ribera (?-1505) began to build their new house in Seville in 1483. The King Peter of Castyle's Palace, in the Royal *Alcázar* of Seville, is the model that the builders followed to make the new Andalusia's Main Governors' house. The work was continued in the 16th century by Fadrique Enríquez de Ribera (1476–1539), their son and the First Marquis of Tarifa, and by Per Afán Enríquez de Ribera (1509–1575), their grandson and the First Duke of Alcalá de los Gazules. Fernando Enríquez de Ribera (1583–1637), Third Duke of Alcalá, finished the building in the early 17th century. The Medinacelis became the owners of the palace after the VII Duke of Medinacelis, Antonio Juan Luis de la Cerda (1607–1671) married Ana Enríquez de Ribera (1613–1645), who inherited the title of V Duchess of Alcalá de los Gazules and the possessions in 1639 from her niece, who died without any descendants. During the 20th century, the palace was the home of the Dukes of Medinaceli. The XVIII Duchess of Medinaceli, Victoria Eugenia Fernández de Córdoba y Fernández de Henestrosa (1917–2013), was the last inhabitant of the palace before dying in 2013 [28].

1.2. The Mudéjar Ceiling and Doors

Mudéjar is a related style of Spanish architecture from the 12th to 17th century combining Moorish and Christian forms. Wood was used in important artefacts of the *Mudéjar* monuments, such as doors and ceilings. One of the biggest collections of "*lo blanco*" Spanish carpentry with "*lacería*" decorations is contained in the Casa de Pilatos and includes coffered ceilings, "*ataurejado*" wood ceilings and wooden frameworks, doors and shutters.

The *Salón de las Columnas* and its wooden ceiling were built in the years at the end of the 15th century (Fig. 1). The *Salón del Pretorio* doors and shutters were made at the beginning of the 16th century, when this room was built. These consist of the following: a large double door (Fig. 2.a), that closes the doorway to enter from the gallery of the main courtyard; two little doors that lead to the *Galería del Jardín Chico* (Fig. 2.b) and the *Corredor de Zaquizamí* (Fig. 2.c); and three shutters of two leaves each one at the windows to the *Galería del Jardín Chico* (Fig. 2.d) and the others at the window to the main courtyard (Fig. 2.e).

The First Marquis of Tarifa's butler contracted with Andrés de Juara to build the coffered ceiling and the large double door and shutters on the 20th of October 1536. The carpentry work was budgeted at 49.000 maravedís. On the 15th of September 1537 he signed a contract with Diego Fernández and Andrés Martín to paint and gild them as well as other sites in the palace. This painting work was budgeted at 76.000 maravedís [29–30]. The little doors to the *Jardín Chico* gallery and the *Corredor de Zaquizamí* were made as shutters to close the window of the grille, into the *Sala Dorada*. In the 1950s the two shutters leaves were removed to permit the sight of the grille from the room. The two leaves were separated and adapted as two doors, one leaf at the entry to the *Corredor de Zaquizamí* and the other to the *Galería del Jardín Chico*, at the end of the 1970s or at the beginning of the 1980s. The suspected author is Cristóbal Sanchez, who on the 12th of September 1538 contracted the wooden works to the *Sala Dorada* and the *Corredor de Zaquizamí* for 89.000 maravedís. The paint and gilding of the room were made by Alonso Pérez, who signed the contract on 28th of May 1539 for 280.000 maravedís [28].

All doors and shutters have lost most of their original polychrome. Where the polychromy is preserved, the shutters are painted with yellow, red, brown, white and black polychromy, which is very damaged. The carved decorations still have any gilded elements. The little doors are painted with red, brown and black colours. The polygons in these doors have a gold finish [31]. Polychrome remains on the *Salón de las Columnas* ceiling (Fig. 2). It consists of blue, red, ochre, black and white colours, applied in geometrical and foliage patterns.

Angel Barreda, the duke's administrator, expended 430 reals on the 24th of March 1851 to paint the Salón del Pretorio doors and shutters in a green colour, covering their original polychrome and gilding [30]. After this date the doors were repainted in several times with the same colour. González Moreno, secretary of the Duke of Medinaceli and historian, removed this green paint layer in the late 1950s or early 1960s, revealing the original colours. Caustic soda was used like paint stripper [32]. This is the only intervention known on the polychrome of the doors.

2. Experimental

2.1. Materials

The studied doors and ceiling are shown in Figs. 1 and 2, respectively. Sixty-six analyses were made on the different doors, forty-six in situ with the non -invasive system and the other twenty with destructive experiments (see Fig. 2). Nine analyses were made on the ceiling, four

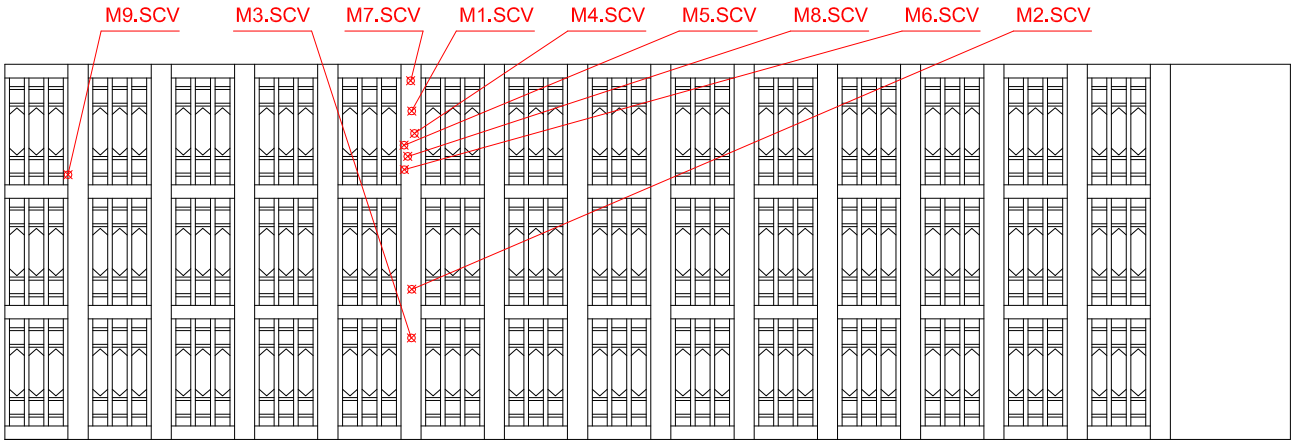

Fig. 1. Ceiling of the *Salón de las Columnas*. Location of the samples taken and their names (letters-number).