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Original article

Gildings from Andalusia: Materials used in different types of artworks along centuries

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ABSTRACT

The majority of the studied artworks were altarpieces, sculptures and/or wood-based works from different periods. Non-traditional gilding techniques have been first described in this paper, such as those that employ materials as oil in the gilding on bole, glue and bole with lead white in mordant gilding, vermilion in the preparation layers; and brass gilding or those with aluminium, lead chromate, mica or corla trying to imitate the golden hue in restoration or repaint processes. For the determination of the composition of the different gilded layers, spectroscopic techniques, such as FTIR and micro-Raman, and SEM-EDX elemental chemical analyses were successfully used.

1. Introduction

Gilding techniques are based on the use of gold and/or gold alloys. Gold has been employed since ancient times for its golden shine, resistance to corrosion and uncommon [1,2]. From a face-centred cubic structure, gold forms a continuous solid solution with silver and copper, both with the same crystallographic structure as gold [3]. However, silver has been found to be particularly susceptible to decay [2,4], and its presence in gold gives pale-coloured alloys [1]. In some studies, silver leaf covered with resins, or tin or brass powders have been used as substitutes for gold [2,4,5]. Tin is considered better than silver because it does not degrade with time [2]. There are scarce documents about the use of brass to make gildings [2,4,6]. Gold leaf thicknesses are approximately 1 μm or less, while tin cannot be reduced to less than 10–20 μm [1,4], and brass leaves have been found to be 10 μm thick [6].

There were two main ways of performing gildings, named water gilding on bole and oil-based mordant gilding [2,4,6–8]. Water gilding on bole uses the most refined clay available, normally red bole, polished to a fine finish, or lead oxides [2,4]. A mixture of siccative oil and lead-based compounds is usually employed for oil-based mordant gilding [4,6,9].

Infrared and Raman spectroscopies provide information about the characteristic vibration levels of the constituent materials of cultural heritage artefacts [10–13]. The compositions obtained by IR and/or Raman are complemented in this manuscript by other experimental techniques such as XRD and SEM-EDX.

Although all periods have been favourable for the creation of gilded artworks in Andalusia, the majority of artefacts dealt with in this paper belong to the Renaissance and Baroque periods. Previously, only partial studies have been carried out on gilded artworks belonging to the Andalusian heritage from these times [2,7], so this is the first paper that encompasses and classifies a great number of artworks in which different gilding techniques and materials were used.

Research aims: It is the intent to carry out the most complete scientific study of gilding artworks belonging to the Andalusian school, which is highly important from an historical and artistic point of view, and to compare them with the methodology, and materials used in other sites.

2. Materials and methods

Artefacts dated between the 15th to the 18th centuries have been majority studied in this manuscript. Altarpieces are unique

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elements of the world's cultural heritage because of not only their morphology and artistic value but also their social, economic and cultural implications [14,15]. Wall paintings from primarily the 18th century were also extensively studied in this paper.

We classified the gildings' samples depending on the metals forming part of them and/or the composition of the preparation layers upon which the metallic leaves were laid. Fig. 1 shows some of the artworks that were studied in the paper, including altarpieces, sculptures, wooden-based artefacts and wall paintings. Cross-sections were prepared from samples collected from the artworks [16,17]. The cross-sections were morphologically studied using a stereo microscope Nikon Hoptihot with 25×, 50×, 100× and 200× objectives (Fig. 2 and Figs. S1–S3). Fig. 2b and Fig. S1top correspond to cross-sections from samples containing gypsum-bole-Au (Table S1). Fig. 2a and Fig. S1bottom show samples that contained gypsum-bole-Au-estofado and repaints (Table 1). In Fig. 2c and Fig. S2top, calcite or gypsum was used as a ground, and Au was laid directly on it (Table S2). In Fig. 2d–h and Fig. S2middle, lead white—with or without other compounds—and gold are found (Table 2). Fig. 2i and Fig. S2bottom show samples with Ag (Table S3). Fig. S3top depicts samples with double gilding containing Au-Au (Table S4). Fig. 2j and Fig. S3middle show samples with Cu-Zn alloys (Table S5). Fig. S3bottom presents samples with other gildings (Table S6). In addition, we used two scanning electron microscopes, JEOL JSM 4500 and HITACHI S-4800, both equipped with energy-dispersive X-ray analysers (EDX) to determine the composition of the samples. The cross-sections were coated with gold/carbon films. Micro-FTIR absorbance measurements were performed using a Nicolet 510 apparatus (Source: Globar, Detector: DTGS). Micro-Raman experiments were performed using integrated dispersive Horiba Jovin Yvon LabRam equipment, with two laser sources at 532 nm and at 785 nm, and a CCD detector.

When possible, collected samples were ground and studied by XRD and FTIR in transmission mode. The crystalline phases were determined by XRD using a Siemens diffractometer, model Kristalloflex D-5000, with Cu-Kα radiation, a diffracted-beam graphite monochromator and a scintillation detector. For FTIR transmission assays, samples were ground and prepared in KBr pellets (5 mg of sample in 100 mg of KBr).

3. Results and discussion

3.1. Gold used as gilding

3.1.1. Water gilding on bole (with or without estofado)

3.1.1.1. Ground layer. Gypsum and, in some cases, animal glue were detected as forming part of the ground layer. The thickness of the layer was of 150 μm in the case of the sample T1-SPB10 (Table 1, Fig. 2a), and similar thicknesses were observed for all the samples (Table 1, Table S1, Fig. S1). S, Ca, C and O were detected by EDX.

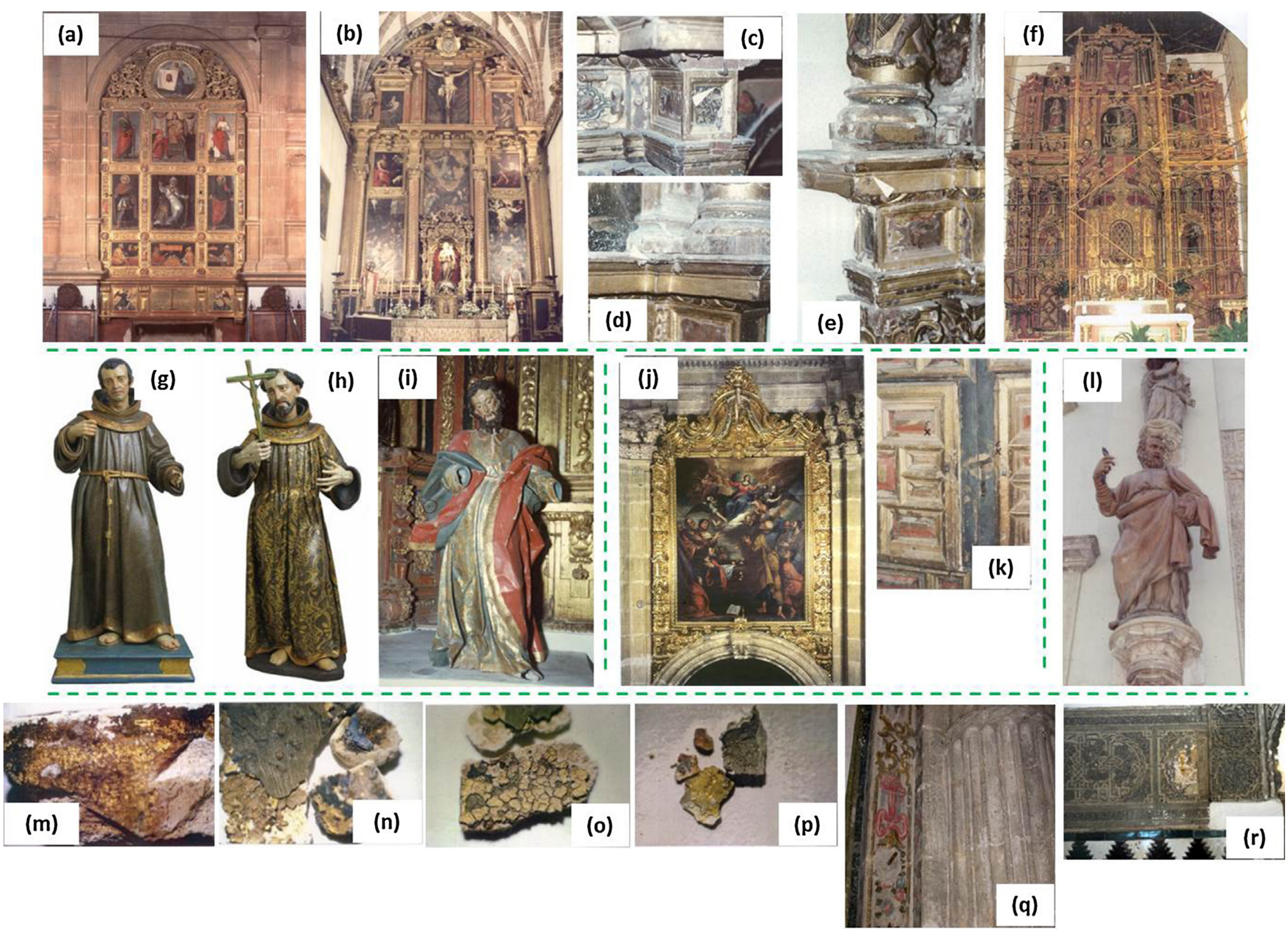

Fig. 1. ALTARPIECES: a: Altarpiece of San Pedro de Osma, Jaen Cathedral (sample 4); b: Major Altarpiece, Church of Santa Maria de la Oliva, Lebrija, Seville (sample 5); c–e: Altarpiece of San Juan Bautista, Church of Santiago, Montilla, Cordoba (samples 8, 8-2 and 8-1); f: Major Altarpiece, Cañar Church, Granada (sample 1). SCULPTURES: g: San Pascual Bailon, Medina Sidonia, Cadiz (sample SPB-); h: San Francisco de Asis, Medina Sidonia, Cadiz (sample SFA-); i: Santo Tomas Apostol, Granada (sample 1). POLYCHROME ON WOOD: j: Wooden framework, Apse of Guadix Cathedral, Granada (sample 62); k: Polychrome on wood (Camerin), Church of Benecid, Almeria (sample 74). POLYCHROME ON CERAMICS: l: Sculpture on ceramics (Saint Peter) in Pardon Portico, Seville Cathedral (sample 61). WALL PAINTINGS: m–p: Monastery of La Cartuja, Sevilla (samples 71-1, 71-5, 71-7 and 71-9); q: El Salvador Church (sample IS-1S); r: Seville Alcazar (sample 70-3).

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