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Methodology for characterising microlayers in historical plasterwork

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HIGHLIGHTS

- A methodological sequence is proposed for the comprehensive study of plasterwork microlayers.
- Data thus obtained can be conclusive in the decisión-making for restoration interventions.
- Microlayer characterization and dating are useful to confirm chronological hypotheses.
- This case study on plasterwork from the Real Alcázar (Seville, Spain) has confirmed the method's validity.

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ABSTRACT

The study of (micro)layer structure in walls is a fundamental tool for expanding our knowledge of historical buildings and developing suitable proposals for intervention and restoration. In materials such as plasterwork, the (micro)layer sequence can be confusing, resulting in the need for a more detailed analysis in order to accurately determine the materials and interventions carried out on a given decorative element in the past.

This work presents a methodological proposal based on optical microscopy, XRD, micro-XRD, SEM-EDAX, FTIR, and ^{14}C dating to accurately identify the structure and composition of the different types of microlayers comprising the plasterwork. The resulting data are of great use in decision-making for restoration and can be compared with historiographic information in order to confirm hypotheses or clarify gaps in chronological adscription.

1. Introduction

An historic building is the result of a set of actions performed on it over the course of centuries, involving eliminating, adding, replacing fallen elements, and/or restoring elements, which can all leave an imprint behind as sequences of layers and microlayers. A comprehensive analysis of the building must be carried out to compile data from the historical study, study of the materials used, identification of timeframes, detection of pathologies and interventions, and so on.

The analysis examines the visible architectonic surfaces of heritage buildings, comprising a collection of material and historic data that can be an extremely interesting complement to improve our knowledge of the evolution of the walls. It supplies information that can be crucial to a precise understanding of a building's evolutions and the actions on it prior to an intervention, forming part of the archeological, historiographic, and constructive study.

In this work, the concept of a microlayer is established from the standpoint of the minimum capacity for identification and analysis [1]. It refers to each of the preparatory and finishing layers of the decorative coats applied to the wall base with a maximum estimated thickness of one millimetre.

The study of microlayers is a common option in the examination of works of art such as paintings or polychrome sculpture and carpentry [2,3]. However, in architecture it tends to be ignored either to simplify matters or due to ignorance of the available techniques. In the case of historic/archeological walls, the data it provides can be conclusive in the decision-making for restoration interventions or determining the optimal environmental exposure for conservation [4,5]. The various types of supports that may have layers and microlayers include coatings on masonry walls and rammed earth walls, mural paintings, polychrome on wood, and so on.

This work analyses microlayers in the plasterwork of the Real Alcázar of Seville (Spain), which are gypsum-based ornamental coatings. These elements comprise a suitable support for applying these instrument techniques in order to characterise them and develop a specific methodological proposal. In 1987, the Real

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Alcázar of Seville was declared a World Heritage Site by UNESCO. It is an eastern-type palace citadel comprising buildings of different periods and styles subject to restoration interventions over the course of many centuries. As a consequence, the plasterwork has been altered, repositioned, and repaired, with the resulting problems of identifying changes and ascribing a time period.

Some plasterwork studies have taken microphotographs of sections and determined the composition of microlayers to identify pigments in order to confirm their authenticity before restoration work, [6–11]. However, most research has examined the plasterwork as a support to determine its composition [10], looked at historical lime or gypsum mortars [1,13–18], or studied the pathologies and interventions for gypsum finishing coats [19–23]. There are no specific methodologies documented, though, on the study of historic plasterwork microlayers.

2. Review and proposal of analysis method for plasterwork microlayers

The methodology for studying microlayers on building elements is mainly based on optical microscopy, electron microscopy, and X-ray diffraction, with occasional recourse to chemical microanalysis by energy-dispersive X-ray spectroscopy (SEM/EDX and EDXRF).

These techniques all require extraction of a sample from the wall. It should be noted that non-destructive techniques are not possible because they do not supply complete information. A beam on the surface is limited to results on the outer layer or, if there is a certain amount of penetration, the final result still cannot discriminate one microlayer from another. Portable equipment (XRF, XRD, Raman, colorimeter, etc.) can be used to employ auxiliary techniques to obtain additional information. Once the microlayer sequence has been established, it can be used to discriminate and identify pigments [24–26].

Optical microscopy supplies data on layers at the microscopic level and on their thicknesses, allowing an initial examination of the texture and structure of the various undercoats and finishing coats. In some cases, when combined with historiographic data, identifying components microscopically allows the approximate dating of the plasterwork [7].

Petrographic microscopy of polished thin sections using polarised light can be a useful complementary technique to discriminate the nature of very similar layers (e.g. gypsum and lime) as they can present distinct properties under crossed nicols. The microstructure, texture, and mineralogy of each mineral can also studied by examining the optical properties of each mineral [3].

Microscopic chemical analysis may be necessary in those cases in which the data from the mineralogical analysis are insufficient and the chemical compositions and elements must be identified in order to reproduce the material.

In the case of pigmented or polychrome microlayers, chemical analysis may identify chemical elements (usually heavy metals) that allow us to set criteria regarding the painting materials used and their temporal relations.

The mineralogical analysis identifies the crystalline phases in the microlayers, which derive primarily from the gypsum and lime (as binders), aggregates, pigments, and impurities. Current equipment provides high-quality diffractograms from samples on the order of tens of milligrams, but it is first necessary to mechanically separate the existing microlayers with a scalpel and a magnifying glass or optical microscope in order to pinpoint their composition. This difficulty in identifying the mineralogy of each microlayer requires complementary techniques such as X-ray microdiffraction, which can determine the mineral composition of a small area or section of sample. One can use especially designed polycapillary X-ray optics with spot sizes of 50–200 μm in a commercially available microdiffractometer [27].

Electron microscopy analysis provides a better approximation to the microlayer structure, revealing its evolution over time, influence of conservation conditions, and interventions carried out [28,29]. It can also identify crystalline and vitreous formations, internal and external alterations [30], and the microstructure of the layer system and its internal adhesion.

On occasion, complementary XRD techniques may be necessary, such as micro-Raman spectroscopy, which is more accurate in identifying mineral phases [12]. Raman spectroscopy can identify pigments by resolving sample zones with distinct chemical compositions by analysing changes in the frequency of scattered light [7,31,32].

Layers painted with organic substances are analysed by Fourier transform infrared spectroscopy (FTIR) [13]. This technique supplies sufficient data to identify molecular bonds and functional groups (not recognisable by other means) of compounds commonly used in preparation layers such as adhesives, consolidants, binders, varnishes, and colourants. The use of natural proteins, waxes, natural resins, bituminous material, and drying oils were common in the making of stucco, lime slurries, or binders in preparing painting or varnishes for pigments used in polychrome works [33,34]. Identifying these types of microlayer components can lead us to hypotheses on the painting techniques used and even on their chronology as the use of many pigments is characteristic of certain time periods.

Infrared spectroscopy can be performed with different devices depending on the sample's macroscopic characteristics. FTIR spectroscopy is appropriate when 10-mg samples can be mechanically separated into different layers or when material can be extracted with organic solvents. When such separations are not possible, FTIR microscopy is more suitable. In this case, if the sample has a smooth, well-defined surface, reflection microscopy can be used. If the samples are very uneven or very small, they can be embedded in resin and polished for infrared study, with a minimum thickness of 10 μm [35].

Although some might have doubts about including dating techniques within microlayer characterization, it must be recalled that they provide data on the differentiating characteristic of age or period of manufacture, and therefore it is important to use these complementary techniques. Analytical instrument techniques currently available for dating are based on different fundamentals and require different components in the plasterwork microlayers.

Carbon 14 dating is not usually applied for plasterwork despite the very interesting data it can provide to complement historiographic or archeological data. It is even more useful for microlayers as it allows the chronological estimate of possible phases of execution and intervention by differentiating each layer. ^{14}C dating, based on the law of exponential decay or disintegration of the ^{14}C isotope, detects the amount present in various substances in order to assess the age of the elements made with them. It can determine ages of up to 50,000 years and is particularly useful in dating elements from organic matter, which, in the case of plasterwork, mainly includes plant fibres used for reinforcement, lime nodules, or carbon remains from the firing process [36]. Calcium carbonate samples deriving from lime carbonation can be studied in order to date microlayers (mainly marmolino veneziano and limewash).

3. Materials and sampling

The proposed methodology was tested on four traditional Islamic plasterworks from the Real Alcázar of Seville from well-known rooms in the palace complex: the Patio of the Maidens (Patio de las Doncellas) (PD) (Fig. 1A), the Ambassadors Hall (Salón de Embajadores) (SE) (Fig. 1B), and the Cenador de la Alcoba (CA) (Fig. 1C).