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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).

Fig. 1. (A) Patio of the Maidens (Patio de las Doncellas) (PD), (B) Ambassadors Hall (Salón de Embajadores) (SE) and (C) Cenador de la Alcoba (CA).

Table 1
Site, location, labelling, decorative element, and possible construction period of samples.

Sample	Site-location	Decorative element	Possible construction phase and style
PD	Patio of the Maidens (Patio de las Doncellas) (lower inner gallery ajimez)	Plasterwork in ajimez	14th–16th centuries Mudéjar
SE_A	Ambassadors Hall (arch separating hall from roof of Philip II)	Panel plasterwork	14th century Mudéjar
SE_D	Ambassadors Hall (arch separating hall from roof of Philip II)	Panel plasterwork	14th century Mudéjar
CA	Cenador de la Alcoba (south façade)	Frieze plasterwork	14th–16th centuries Mudéjar

Table 2
Proposed methodology in accordance with microlayer characteristics.

	Optical microscopy	SEM-EDAX	XRD[a]	μ-XRD	FTIR	^{14}C[b]
PD	x	–	–	x	–	x
SE_A	x	–	x	–	–	–
CA	x	x	–	–	–	–
SE_D	x	–	–	–	x	–

[a] Samples with organic matter or calcite from lime carbonation.
[b] This technique can be used for microlayers under 50 μm thick.

For a thorough assessment, we selected wall samples with one to several microlayers, polychromed or not. The basic characteristics are given in Table 1.

Sampling was respectful of plasterwork conservation. It was also planned to cover different works in the monument of known historical periods in order to better assess the effectiveness of the microlayer study. The amounts extracted were as small as possible for the analyses and taken to minimize visual impact in the panels. Extraction was by scalpel or box cutter and the zones were recorded with photographs before and after extraction (see Table 2).

4. Instrumental techniques: methodology

The optical microscopy study was performed with a Leica StereoZoom S8 APO microscope coupled to a Leica DC300 camera using the IM50 (Image Manager) software. Images of samples were taken at a magnification of eight. The plasterwork fragments were first embedded in methacrylate resin, cut with a diamond saw, and polished.

The mineralogical analysis of plasterwork layers (when separable) employed a Bruker-AXS D81-A25 diffractometer equipped with a Cu–Kα source (λ = 1.5405 Å), with a Bragg–Bentano θ–θ configuration, a nickel filter, and a LynxEye linear detector using the powder method. Microdiffraction employed a Bruker model D8 Discover diffractometer with a θ–2θ configuration, a Montel system and 1 mm collimator, Vantec 500 area detector, CCD 10X camera and laser, systems allowing focusing and adjustment of the analysis zone and visualisation of the sample to be analysed.

A Jeol JSM 6460-LV microscope was used, equipped with an energy-dispersive X-ray (EDX) microprobe, a beryllium ATW2 window, and specific software (Oxford INCA) for semi-quantitative chemical analyses. SEM images in both secondary electron mode (SE) and in back-scattered electron mode (BSE) were acquired using several gold-coated pieces of sample.

In order to identify the presence and type of organic binders used in the SE_D sample, Fourier-transformed infrared spectroscopy (FTIR) was performed with a Jasco FT/IR4100 equipped with an accessory ATR MiracleTM to measured attenuated total reflection (ATR), which allows a direct measurement of samples without the need for solvents or dissolution media, which can cause blind spots in the spectrum. The spectra were obtained with a resolution of 4 cm^{-1} and recorded between 4000 and 600 cm^{-1}. Organic remains were extracted from samples with acetone using a Sonicator ultrasonic processor for one minute to loosen solid particulates and promote dissolution. They were then centrifuged for 5 min at 13,000 rpm to decant the solid. Most of the acetone was evaporated with an argon current, and the concentrated solution was measured in the ATR.

Finally, ^{14}C dating was carried out with 1 MV accelerator mass spectrometry (AMS). A 50 mg sample of the lime microlayer (calcite from lime carbonation) was first subjected to a gentle acid bath with HCl 0.5 M for a few seconds to eliminate the surface layer. The carbonate is dissolved in H_3PO_4 in a vacuum flask with heat to generate CO_2. The CO_2 is graphitized in the corresponding graphitization line.

5. Results

5.1. Optical microscopy

Fig. 2A–D show sections PD, SE_A, SE_D, and CA at a magnification of eighty, revealing the various microlayer structures in each sample. Table 3 gives the main characteristics of the structure: number of microlayers, colour, and range of thicknesses (each microlayer tends to have an uneven thickness).

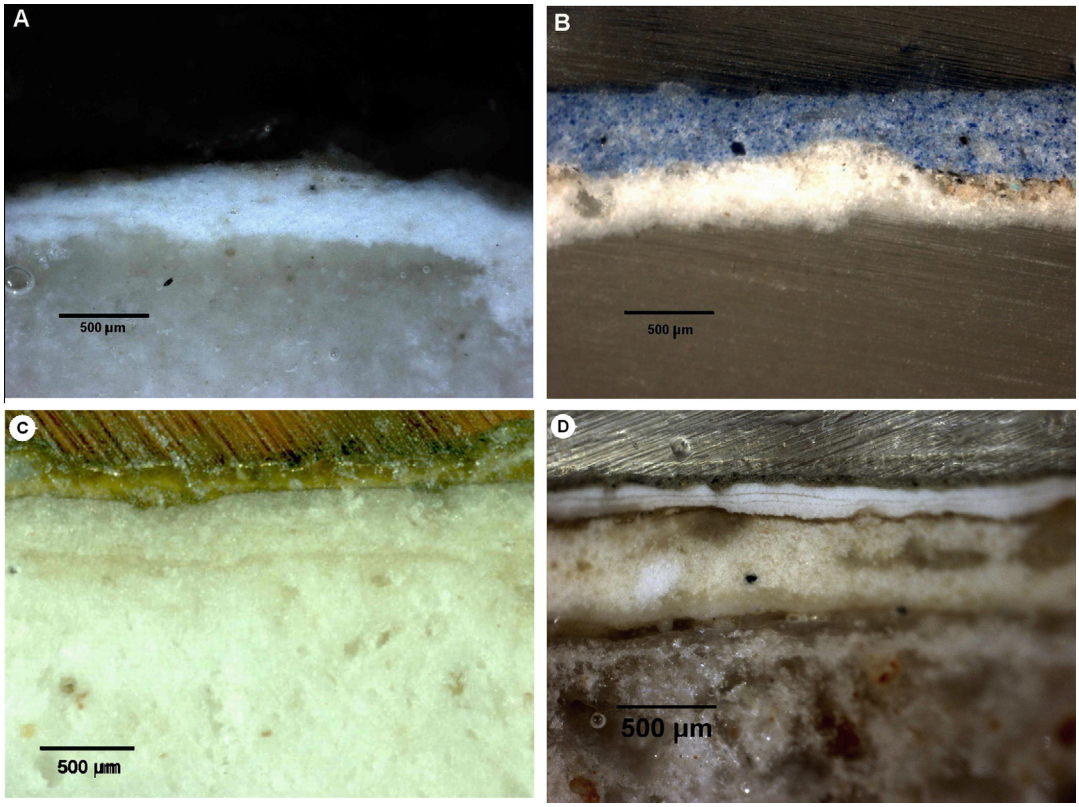

Fig. 2. Image of microlayer structure in PD (A), SE_A (B), SE_D(C), and CA (D) at 80X.

Table 3
Sample structure.

Sample	No. of microlayers/colour	Range of thickness of microlayers (µm)
PD	1/white	100–200
SE_A	1/blue	200–400
SE_D	1/golden	10
	1/yellow	50–100
	1/white	200–300
CA	1/grey	300
	3/white	50–80 each
	1/white	500

5.2. X-ray diffraction

In order to use powdered X-ray diffraction, sample preparation must include the separation of the microlayers from their support and/or individually from the rest of the microlayers to avoid contamination. When it is coloured, it is easier to separate mechanically by eye, as with sample SE_A (Fig. 2A). The XRD mineralogical analysis of the blue microlayer is shown in Fig. 3.

In sample SE_A, the blue colour is due to azurite ($Cu_3(OH)_2(CO_3)_2$) or basic copper carbonate [10,12,37]. Azurite was the most important blue pigment up until the 16th century [38], and was commonly used in Hispano-Moresque painting techniques from the 13th to the 14th centuries. Studies to date indicate that azurite use is also characteristic of the earliest Nazarí art [9]. The major mineral is gypsum (indicating that the binder for this layer was gypsum), with traces of quartz (SiO_2) and mirabilite ($Na_2SO_4{\cdot}10H_2O$).

5.3. Micro-XRD

When the microlayers cannot be easily separated from the support or the other microlayers, or they have a similar colour, it is better to use a technique not requiring sample separation or isolation to avoid contamination, allowing only the selected zone to be analysed. In the case of PD (Fig. 4), micro-XRD was used (Fig. 5).

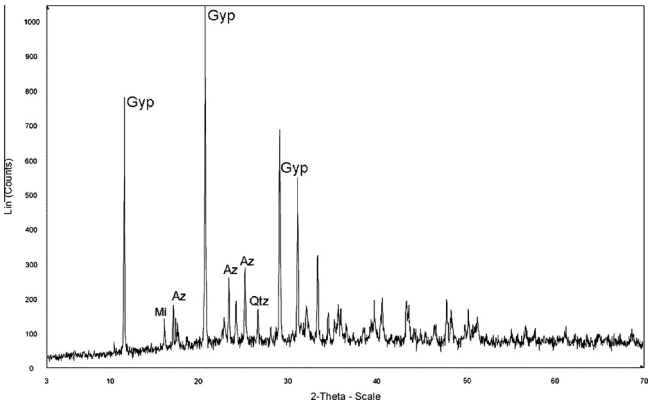

Fig. 3. Diffractogram of sample SE_A. Gyp = gypsum, Az = azurite, Qtz = quartz, and Mi = mirabilite.

The calcite composition of this microlayer clearly indicates a coat of lime paint (limewash) was applied, which turned into calcium carbonate (calcite) once it carbonated in contact with atmospheric CO_2.

5.4. Electron microscopy

Electron microscopy allows observation and spot chemical analysis in very small areas and is a very useful technique in multi-layer samples that are difficult to separate. Below are the chemical compositions of the microlayers in sample CA (Table 4) and a SEM image in SE mode of its structure (Fig. 6).

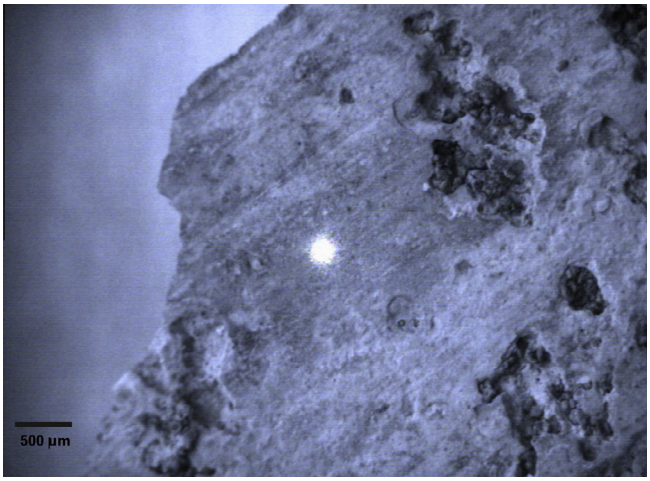

Fig. 4. Image of surface layer of PD, with the focus laser on the X-ray incidence zone.

The results show that, in layer 1 (the outermost layer), the major elements are O, Ca, S, and C, indicating the occurrence of calcite and gypsum minerals, which reveals this layer was a gypsum slurry. The intermediate microlayers (2, 3, and 4) are limewashes based on their major Ca, C, and O contents. Finally, the innermost layer 5 (directly on the plasterwork) also has the major elements Ca, C, and O, which implies it also primarily consists of calcite. However, as it also contains the trace elements Si, Al, Fe, Mg, Na, K, and Ti, it is reasonable to suppose that its contents in impurities (probably silicates) is greater than in the others.

5.5. Infrared spectrography

Both visual observation and optical microscopy (Fig. 2C) show sample SE_D to be goldleaf. Goldleaf was applied on a plasterwork base, which accounts for the occurrence of gypsum and anhydrite in the sample in addition to the gold [39]. Considering the matte surface finish (unburnished), this goldleaf was probably applied using a traditional technique such as mixtion mordant. This technique employs an oil-based adhesive as a primer (yellow layer in Fig. 2B SE_A), which is mixed with drying compounds. When the mordant is tacky, the goldleaf sheets can be applied [40]. Commonly used drying materials are cerussite ($PbCO_3$) and white lead ($2PbCO_3 \cdot Pb(OH)_2$), the presence of which suggests the use of oil-based binders which, together with the plasterwork, could comprise the preparation base for the goldleaf [41].

In SE_D sample, the goldleaf layer and the underlying yellow preparation (Fig. 2C) were separated from the base layer of plaster. The SE_D IR spectrum for the extraction with acetone is shown in Fig. 7. The main bands are at 2925.48 and 2855.1 cm^{-1}, corresponding to the asymmetric and symmetric stretch C–H aliphatic ν_{CH}, 2360.44 and 2341.16 cm^{-1} corresponding to the asymmetric and symmetric stretch of atmospheric CO_2 ν_{CO2}, 1620.5 cm^{-1} corresponding to the C=C stretch, 1703.8 cm^{-1} corresponding to the carbonyl stretch $\nu_{C=O}$, 1457.92 cm^{-1} to the asymmetric bend δ_{CH2}, 1363.43 cm^{-1} to the symmetric bend δ_{CH3}, 1231.33 and 1171.54 cm^{-1} to the C–O stretch ν_{C-O}, and finally 669.18 cm^{-1} to the C–H out-of-the-plane bend $\delta_{oop\ C-H}$. These results are compatible with the afore-described technique and can be ascribed to polymerized linseed oil used as a binding agent, which was accelerated by incorporating drying chemical compounds.

The use of cerussite was confirmed by X-ray diffraction and the presence of lead was confirmed by the chemical microanalysis carried out by SEM. This compound catalyses the polymerization of the linseed oil in the primer layer [41], which is consistent with the minimal identification of the C=C group in the spectrum, which disappears with the formation of C–O groups, which have a very intense band (1171.54 cm^{-1}). Therefore, infrared spectrography is ideal for characterising the organic compounds in the paint base and, in combination with other techniques, to determine the decorative techniques employed in the plasterwork based on the nature of the microlayers.

5.6. Carbon 14 dating

Carbon-14 dating was used on the lime microlayer of sample PD (Fig. 2A). This technique can be used here because it is a single layer (applied once) of a calcium hydroxide paint that has absorbed environmental CO_2 (containing ^{14}C) during its carbonation (see Fig. 8 and Table 5). It is worth noting that the age ranges (each with a different probability) are intrinsic to ^{14}C dating due to the fact that ^{14}C amounts in the atmosphere have varied over time.

The original plasterwork in the Patio of the Maidens (Patio de las Doncellas) is from the 14th century. With the arrival of the Austrians, the palace was remodelled to bring it into line with the aesthetic tastes of the 16th and 17th centuries. During the

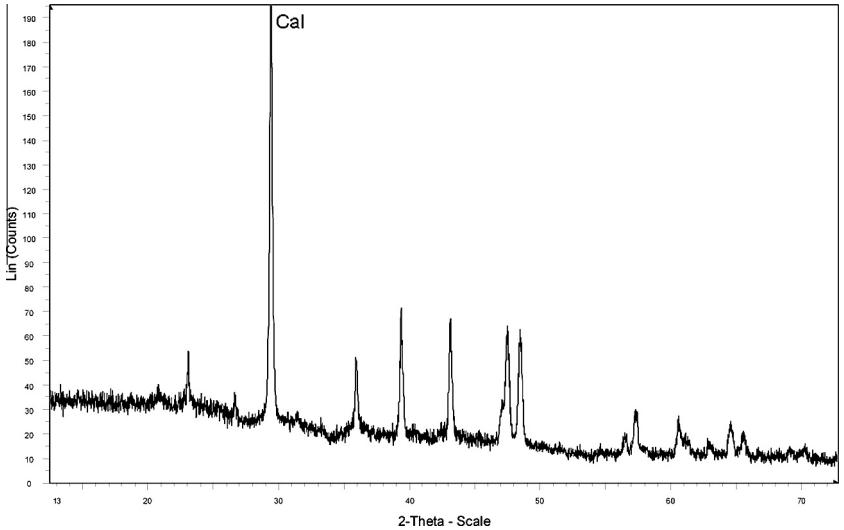

Fig. 5. Diffractogram of sample PD. Cal = calcite.

Table 4
Chemical composition of CA microlayers determined by SEM-EDAX in accessible areas.

	C	Si	S	O	Cl	Ca	Fe	Al	Mg	K	Na	Ti	Total
ML-1	11.51	1.01	11.86	57.08	–	18.00	0.26	0.29	–	–	–	–	99.72
ML-2	16.02	–	0.56	54.79	0.42	28.21	–	–	–	–	–	–	99.58
ML-3	15.19	0.22	0.25	53.29	0.52	30.52	–	–	–	–	–	–	99.47
ML-4	14.85	0.20	–	52.52	0.50	31.85	–	–	–	0.08	–	–	99.42
ML-5	17.79	1.98	–	58.44	0.40	19.53	0.37	0.54	0.25	0.26	0.31	0.12	98.11

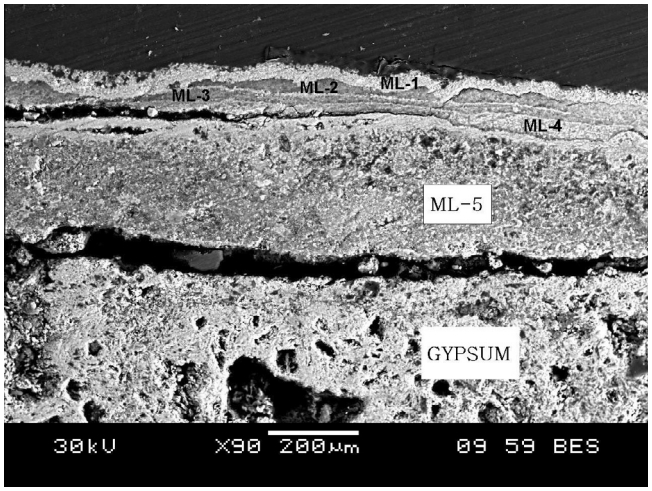

Fig. 6. SE-SEM micrograph of section of CA with microlayers 1–5.

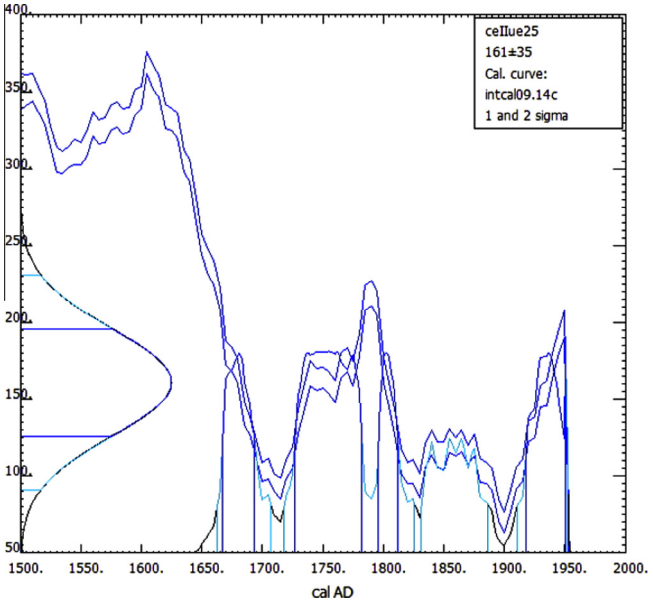

Fig. 8. Radiocarbon age versus calibrated age.

18th century, the damage caused by the Lisbon earthquake of 1755 and the fire of 1762 was repaired. Interventions carried out in the 19th century are confusing and even contradictory [42], with significant changes under the direction of architect Rafael Contreras [43]. In 1813 most of the plasterwork was washed with marmorino veneziano (a limewash mixed with ground marble and pigment) [44], rendering the stucco and polychrome work invisible, in accordance with neoclassical taste [45]. Subsequently, though, in the Isabelline period (1843-68), parts of the limewashes were removed to uncover the hidden plasterwork.

Unfortunately, in these cases, the time range provided by ^{14}C dating is very large, covering from 1663 to 1953 (290 years). The problem derives from the shape of the calibration curve, which spikes and drops many times in this period. Consequently, when the radiocarbon date is plotted with the curve, they intersect at many points and therefore provide several possible age ranges. This drawback occurs in all samples with a radiocarbon age of approximately just under 200 years BP. Fluctuations in that period were caused by changes in the magnetic field of both the Sun and Earth, with the increase in CO_2 during the Industrial Revolution

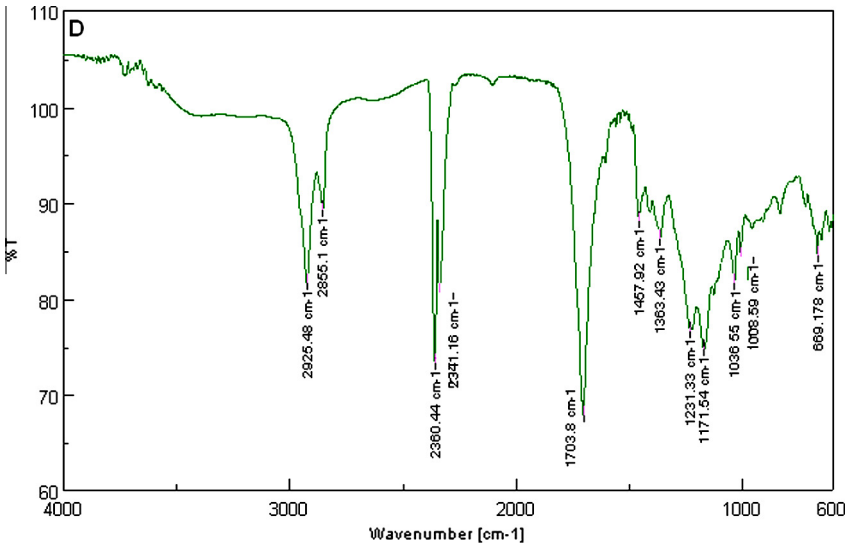

Fig. 7. FTIR spectrum of microlayer SE_D after acetone extraction.

Table 5
Results of ^{14}C dating of sample PD.

Conventional radiocarbon age:160 ± 35 BP pM (% about of radiocarbon[a]): 98.02 ± 0.42 % $\delta^{13}C$ ($^{12/13}C/^{14}C$ ratio): −23.44 ± 1.40‰	
Calibration 2σ (95% probability): [Start:End] Relative area	Probability of chronological assignment (percentage)
[cal AD 1663: cal AD 1707]	17.6953
[cal AD 1719: cal AD 1827]	48.4344
[cal AD 1832: cal AD 1887]	15.1685
[cal AD 1911: cal AD 1953[a]]	18.702

[a] To express the amount of radiocarbon, 100% is taken as a reference for the year 1950.

contributing to the distortion. Similar intervals occur in other historical periods as well [46].

Despite the aforementioned high dispersal, the data in the highest-probability interval are in the period of applying the marmolino veneziano to the Mudéjar Palace of Pedro I.

6. Conclusions

- The proposal presented herein allows a methodological sequence for characterising microlayers in plasterwork in terms of their number, colour, and the organic or inorganic nature of its components. Based on the specific characteristics of the finishing of each plasterwork, a specific methodological proposal can be established in accordance with the criteria described.
- Characterising and analysing a plasterwork's microlayers provides very concrete, accurate data for decision-making for restoration work. A correct knowledge of the instrument techniques and the information they offer allows greater certainty in identifying the stratigraphic phases and functions, decorative techniques used, and application methods. This knowledge allows those in charge of the maintenance, conservation, and restoration of plasterwork to have at their hands sufficient data to optimise interventions.
- Data obtained through an accurate identification of the microlayer structure and composition can be contrasted with the historiographic data in order to confirm hypotheses or clarify gaps in chronological adscription. Given that the uncertainty associated with dating techniques can be complemented and corrected with compositional information (e.g. type of pigment and period of common use), the historical periods corresponding to different elements and construction phases can be correlated.
- Applying the proposed methodology to the samples from the Real Alcázar of Seville (Spain) has allowed a complete characterization of the structure of its microlayers. Sample PD is a 100–200 μm limewash applied in the 18th century or early 19th century according to ^{14}C dating. SE_A is a 200–400 μm polychrome with azurite as a pigment and bound with gypsum. Sample SE_D has three layers (white, yellow, and golden) comprising a total thickness of 400 μm. First is a base layer of plaster, then a primer layer of linseed oil and lead carbonate (cerussite), followed by a finishing layer of goldleaf. This sequence is a classic goldleaf technique termed mixtion mordant.

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