



Plasterwork in the Ambassadors Hall (Salón de Embajadores) of the Real Alcázar of Seville (Spain): Graphic reconstruction of polychrome work by layer characterization



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HIGHLIGHTS

- Stratigraphic studies supplied data on polychromy changes in plasterwork.
- Plasterwork polychromies structure have been characterized to define their evolution.
- Graphic analysis and 3D modeling are used for reconstruction from its original state.

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ABSTRACT

This work examines a polychrome plasterwork in one of the most important scalloped arches in the Ambassadors Hall (Salón de Embajadores), which is the most outstanding room in the Mudéjar Palace of the Real Alcázar of Seville (Spain). Characterization by stratigraphy, XFR, XRD, and FTIR studies has supplied data on changes in the composition and colors in this building element. The research is complemented with historical information on the most significant interventions in this hall. Graphic analysis and the modeling of decorative geometric elements in 3D with BIM software were used to simulate its evolution from its original state. The results characterize the base plasterwork and the polychromies constituted by 1–3 microlayers with a thickness between 5 and 300 μm , formed of blue (19.88% Cu-azurite), vermilion (19.00% Pb-massicot and 5.34% Hg-cinnabar), and golden layers (68.93% Au). The colors were obtained through the use of mineral pigments such as azurite, cinnabar-litharge, and gold-leaf, respectively. The rich colors visible in this hall now have varied over time.

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1. Introduction

The Alcázar of Seville corresponds to an oriental type of palace citadel comprising a complex of buildings and palaces of distinct style and periods. Over the centuries, they have become a single complex with very diverse functions. The rooms of the Alcázar have decorative plasterwork from various historical periods, making it quite unique.

The Ambassadors Hall (Salón de Embajadores) is the ancient throne room of the Abadía palace from the Taifa reign of Al-Mutamid in the 11th century. The structures were then restored and decorated by Pedro I of Castile [1] to transform the hall into the true centrepiece of the Mudéjar royal palace from CE (1340–1369)

[1] [2]. Plant motifs in plasterwork cover the corners of the room and the spandrels of the decorative (poly-lobed) arches that frame the keyhole arches separating the adjoining rooms and the rear hall. Above these arches are three tracery windows with geometric elements [3]. The hall's columns and capitels are caliphate-style (Fig. 1).

The Ambassadors Hall was remodeled in the 14th century, with the opening of a doorway to the Patio of the Maidens (Patio de las Doncellas), changing its orientation from facing east (towards Meca) to northeast, although it continued to serve as a throne room for the Spanish monarch. The wall were also covered at the time with tiled panels with knot motifs. It is also worth noting the new wooden dome (or Half Orange) carved in 1427 by Diego Ruiz to substitute the Abbadiate dome.

The Palace's most radical transformation occurred in the 16th century after the wedding of Emperor Charles V. The works developed through the entire century, particularly under the reign of his

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Fig. 1. Plasterwork arch facing west in the Ambassadors Hall.

successor, Emperor Philip II, entailed a more substantive change in the concept of this Palace [4].

Although an obvious conclusion is that all plasterwork was colored to enrich them and provide a wide array of decorative tones, such as in the Ambassadors Hall, some authors claim that certain halls were colored to contrast with others that were left in their original tones [5]. In support of this hypothesis, it should be noted that our characterization has found halls (e.g. the Justice Hall) in the Real Alcázar that were apparently never painted (save for the unlikely event of the perfect elimination of all traces of paint at some point). In addition, the plasterwork loses some of its richness of tone due more to the scant durability of the binders used and weak support rather than to pigment instability. On occasion, color has been obscured or altered by superposed layers during maintenance tasks [6]. Certain halls were even whitewashed in 1813 [7], covering the colors due to the demands of neoclassical taste. Subsequently, these limewashes were removed during the Isabelline period (1843–68) to recover the colors and even hidden plasterwork in some cases [8]. In 1832, the sevillian painter Joaquín Cortés provided an approximate cost for gilding the floral motifs throughout the hall. Work was painstakingly slow in removing the limewash and stopped and started according to the availability of funds. Thus, it was not until 1857 that gilding began. The Romantic period saw growing appreciation for ancient Eastern art. Consequently, restorers from the mid-19th century attempted to unify styles, studying paint remnants before polychroming and carefully observing traces found when chiseling or demolishing [9].

Several studies on the composition and properties of the plasterwork of the Real Alcázar [10,11] expand our general knowledge of Islamic decorative plasterwork. An additional source of information is the plasterworks of the Alhambra of Granada [12], which are very similar to those of Seville [13,14].

In the graphical study of polychromies [15,16], architectonic surveys should be understood as analyses and building surveys that involve all the research that allows an overall perception of the construction material reality [17,18].

2. Objectives

This study examines the polychromies applied on the plasterwork of one of the most important arches in the Ambassadors Hall, in turn the most significant hall in the Mudéjar Palace. The composition and structure of the plasterwork layers have been characterized to define the historical periods for a graphic analysis of their possible evolution (together with historical data on the room) from the original state through interventions over time [19,20].

The specific goal is to accurately define the sequence of micro-layers in the plasterwork and the materials used in their execution, assessing the chromatic changes of this building element, using a graphic program to recreate its original state and effects of interventions over time.

3. Sampling criteria, materials and methodology

The following criteria have been adhered to during sample collection:

- Historic.* Documentation was reviewed to ensure the panel is original (Mudéjar from the 14th century), taking into account the extent and dates of the documented actions on the monument over the centuries (19th, 20th, and 21st centuries). Advice of Real Alcázar curators. Their advice and recommendations were followed to ensure the plasterwork sampled was that for which there was the most certainty on the date of creation.
- Representative sample.* A selection was made of the most characteristic tones overall, considering all variables that could impact the material's characteristics (e.g. construction phase) and those that would affect the conservation status (e.g. orientation, exposure to solar radiation, height above the ground, depth, etc.).
- Minimal impact.* Efforts were made to take the smallest possible samples (while remaining representative) and minimize the visual impact on the panels, extracting using manual techniques.

Based on these criteria, we extracted and documented a plasterwork sample from the Ambassadors Hall (GAH) and three fragments of polychromies corresponding to the three colors observed (vermilion (PV), blue (PB), and gilding (PG)), taken from the scallops of the arch framing the keyhole arches separating the Ambassadors Hall from the Ceiling Hall of Felipe II (Fig. 2).

For the gypsum stucco works, the major and minor chemical components of the plaster were analyzed by X-ray fluorescence (XRF) using an Axios Panalytical spectrometer. The mineralogical composition was established by X-ray diffraction (XRD) using a Bruker-AXS D8, and the XRD patterns were obtained using the powder technique, at an angle of 2θ , a range of 3° – 70° , and a 0.03° step scan with a 1 s step.

The polychromies structure was observed by means of an S8 APO LEICA optical microscope, with LEICA DC300 video capture and IM50 software (Image Manager) v.1.20.model. The layer sections were prepared by impregnation with methacrylate resin at low pressure, then cut using a diamond blade, and finally ground. The structure and microlayer thickness were examined with a scanning electron microscopy. A Jeol JSM 6460-LV microscope was used, equipped with an energy-dispersive X-ray (EDX) microprobe, a beryllium window ATW2 and specific software (Oxford INCA) for point semiquantitative chemical analyses [21,22]. SEM images in secondary electron mode (SE) and in back-scattered electron mode (BSE) were acquired using several gold-plated pieces of sample. The mineralogical composition of pigments was studied in different zones of blue and vermilion polychromies and gilding by X-ray powder diffraction (XRD) using a Bruker-AXS D8 Advance diffractometer; the patterns were obtained by using the powder technique after using a scalpel to separate 50–100 mg of sample. In order to identify the presence and type of organic binders used in the polychromies Fourier-transform infrared spectroscopy (FTIR) was performed with a Jasco FT/IR4100 equipped with an accessory ATR Miracle™ to measure attenuated total reflection (ATR), which allows a direct measurement of samples without the need for solvents or dissolution media, which could cause blind spots in the spectrum. The spectra were obtained with a

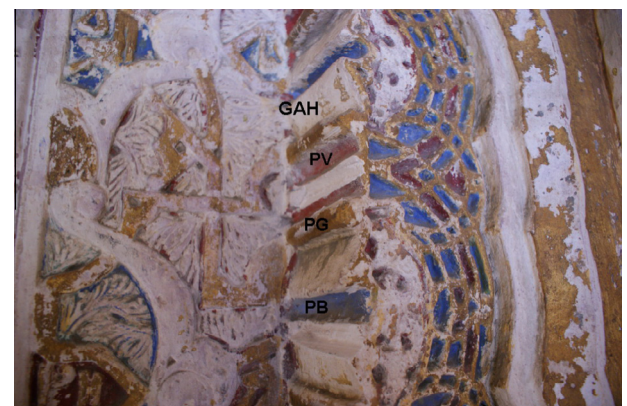


Fig. 2. Location of sample sites in western arch of the Ambassadors Hall. Note: GAH is gypsum stucco work, PV vermilion polychromy, PG gilding, and PB blue polychromy.

resolution of 4 cm^{-1} and recorded between 4000 cm^{-1} and 600 cm^{-1} . In the PG sample, organic remains were extracted with acetone using a Sonicator ultrasonic processor for one minute to loosen solid particles 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.

Once the study on the polychrome work in the arch scallop is completed, the work needs to be visualized. To do so, a succession of images have been created based on the chromatic series obtained that reveal the arch scallop's evolution for the period studied. To do so, a succession of images have been created based on the chromatic series obtained that reveal the arch scallop's evolution for the period studied.

The first step was to survey the architectural detail as a basis to portray the data from the study. Conventional procedures for this type of work (photogrammetry or 3D laser scanning) have millimetric accuracy, which exceeds the aims and scope of this part of our study. Therefore, we opted for a so-called traditional survey comprising in-situ sketching and measuring of the elements and their subsequent virtual treatment and modeling. Although it lacks the accuracy of the other procedures mentioned above, it is more than sufficient for providing a good visualization.

From data collection, the study zone was virtually reconstructed by modeling the geometric elements in three dimensions with graphical software as visualization tool, following the sequence of figures in the real model. Below, the geometric model is a montage in a photograph, adapting the visibility characteristics of the model to those of the reference photograph and subsequently assigning the textures to the geometric models taken directly from the photographs of the architectural reference point. Finally, a rendered photograph of the whole is obtained.

4. Gypsum plasterwork characterization

4.1. Chemical analysis

The chemical composition of plasterwork GAH is shown in Table 1. The results show a composition with enriched SO_3 , CaO, and LOI, which are associated with the gypsum contents ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The values obtained are close to those of a pure reference plaster (if all the contents analyzed in SO_3 were attributable to hydrated gypsum, the purity would be 88.25%). The presence of Sr may be due to the mineral celestine (SrSO_4) or to traces of heavy metals such as Cu and Pb in remnants of the polychrome pigments.

4.2. Mineralogical analysis

Sample GAH mainly comprises hydrated gypsum deriving from the rehydration of the semi-hydrated plaster with the batching water used in preparing the slurry; minor sulfated phases identified are anhydrite (CaSO_4) and kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), in addition to trace amounts of quartz (SiO_2) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) (Table 2, Fig. 3). Anhydrite can be artificially obtained by heating the dihydrate above $200\text{ }^\circ\text{C}$ [22], although it also exists as a natural mineral associated with gypsum as do kieserite and dolomite. Quartz can occur either as an impurity in the raw material or as an aggregate incorporated into the slurry mixture, although in this case the latter is less likely as the concentrations are very low [23].

5. Polychromy characterization. Results and discussion

5.1. Layers

After preparing the layers sections of polychromy samples for the three colors observed (vermillion (PV), blue (PB), and gilding (PG)), they were observed by optical microscopy. Fig. 3 shows

Table 1
Chemical composition of major, minor, and trace elements of GAH.

Sample	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	MgO %	CaO %	Na_2O %	K_2O %	SrO %	P_2O_5 %	SO_3 %	LOI %	TOTAL %
GAH	2.68	0.64	0.30	0.86	29.73	0.02	0.18	0.28	0.00	41.04	22.55	97.98
Pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	–	–	–	–	32.57	–	–	–	–	46.50	20.93	100

Table 2
Mineralogical composition of GAH.

Mineral	Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Anhydrite CaSO_4	Kieserite $\text{MgSO}_4 \cdot \text{H}_2\text{O}$	Dolomite $\text{CaMg}(\text{CO}_3)_2$	Quartz SiO_2
GAH	++++	+	+	+	+

++++ Very abundant +++ Abundant ++ Medium + traces – Not detected

the images ($80\times$) of the sections, and Table 3 gives the number of layers and their thicknesses.

As the study shows, the arch bands that are currently vermillion were previously blue, with a preparatory layer between the two. The bands currently blue have always been that color. Finally, the golden bands were applied over a yellow layer that had in turn been applied on a base white layer.

5.2. Mineralogical composition

Fig. 4 gives the diffractograms of the colored microlayers. The vermillion layer (Fig. 4a) comprises gypsum, cinnabar, massicot, and quartz. Cinnabar (HgS) and massicot (PbO) were commonly ground and used to produce vermillion [6,24]. The usual provenance for cinnabar used in Andalusia is the Almadén site (Ciudad Real, Spain). However, it is also possible synthetic vermillion was used (obtained by sublimating sulfur and mercury), which was a widely used method known since ancient times and described by Pliny [25]. The presence of gypsum may be due to its use as a binder for pigments or to contamination from the underlying layer during extraction [26,27].

In addition to gypsum, layer PB (Fig. 4b) contains the mineral azurite ($\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$). Azurite was the most common blue pigment up to the 17th century [28], commonly used in Hispano-Moresque painting techniques in the 13th and 14th centuries. Studies to date seem to indicate that azurite was more usual in the earliest Nasrid art [15].

As with the plasterwork from the façade of the Palace of King Pedro I, the pigments usually have no preparatory interlayers, with the main color changes being the superposition of vermillion over blue [4]. In the Ambassadors Hall plasterwork, this change is noted only occasionally.

In the PG (Fig. 4c), the gold derives from the use of gold-leaf for decorating the plasterwork in the Ambassadors Hall (Figs. 1 and 2). Gold-leaf was applied on a plasterwork base, which accounts for the occurrence of gypsum and anhydrite in the sample in addition to the gold. Cerussite is a mineral consisting of lead carbonate (PbCO_3), and its use as a secant suggests the use of oil-based binders which, together with the plasterwork, could comprise the preparation of the gold-leaf [4]. The data show that the gilt was applied on mixture, a procedure that entails fixing the gold-leaf on a prepared layer called mordant or mixture [29]. The mordant consists of a mixture of linseed oil with compounds of lead and manganese oxides. In addition to making the mixture visible, these products aid in rapidly drying the oil.

5.3. Scanning electron microscopy

Fig. 5 shows two images in BAH mode (backscattered electron) of layer PV (Fig. 5a) and layer PG (Fig. 5b) and another two images

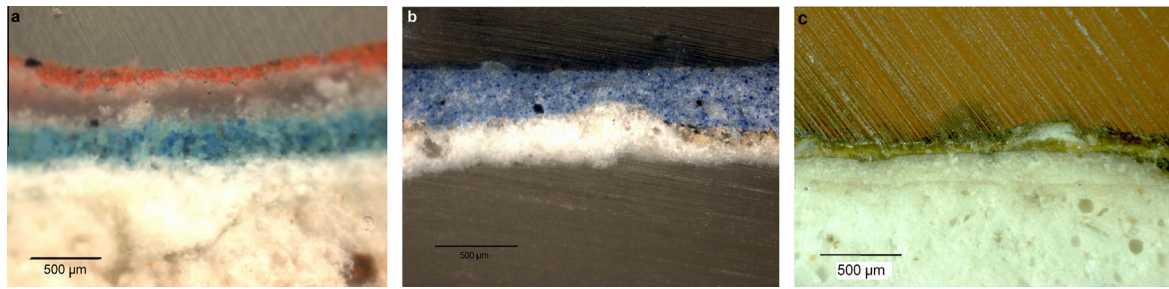


Fig. 3. (a) Layer PV, (b) layer PB, and (c) layer PG.

Table 3

Number and thicknesses of layers PV, PB, and PG.

Sample	Number of layers	Thickness of layers in micra
PV	1 layer of vermilion paint	5
	1 intermediate transparent layer	150–300
	1 layer of blue paint	100–200
PB	1 layer of blue paint	20
PG	1 layer of gilding	1
	1 layer of yellow paint	100
	1 layer of white paint	200–250

in SEI mode (secondary electron imaging) of the azurite (Fig. 5c) and massicot (Fig. 5d) pigments. Table 4 gives the chemical composition of the three PV layers and the two PG layers.

Energy-dispersive X-ray (EDX) microprobe analysis of the vermilion layer confirms the presence of the elements Hg, Pb, S, O and Si as constituents of the minerals previously identified by XRD. The carbon detected may derive from the organic compound used in applying the color or from the methacrylate resin used to prepare the samples. In the blue layer of PV, there is Cu, C, and O from the azurite, S and Ca from the gypsum, and other minor elements such as Si, Cl, Fe, and K. The transparent layer separating the vermilion and blue layers in the PR stratigraphy contains S, Ca, and O from the gypsum and anhydrite detected by XRD. It also shows some Cu and Pb (probably contamination from the underlying layer) in addition to silica and trace impurities.

The gold layer (underlain by a yellow layer, then a white layer, then plaster) shows Au as the major mineral, with minor Ag and Pb. The yellow layer has C and O as major elements and Si, Fe, and Al as minor elements, suggesting an organic composition.

The white layer applied beneath the yellow layer and above the base plaster shows a very similar composition to that of the plaster, typical of a hydrated gypsum, with the plasterwork having more impurities than the white layer. The data again confirm it is a mixture of gold-leaf.

5.4. Fourier-transform infrared spectroscopy

Several absorption bands were related to different compounds in agreement with reference data in the literature [30,31] (Fig. 6).

5.4.1. PV-vermilion microlayer

The infrared spectrum of the analyzed sample was clearly useful to identify gypsum (dihydrate calcium sulfate), which shows absorption bands at 1110, 670, and 597 cm^{-1} , characteristic of the sulfate group (vibration modes of sulfur–oxygen bonds). In particular, bands over 3000 cm^{-1} (3524 and 3398 cm^{-1}) are related to water incorporated in the gypsum structure (O–H stretch vibrations), apart from other wavenumbers of absorption maxima (1683 and 1619 cm^{-1}), likely due to vibrations resulting from the water bonds. Low proportions of calcite relative to gypsum may explain the weak absorption band at 1396 characteristic of the carbonate group. Massicot and cinnabar have their strongest absorption bands below 505 and 400 cm^{-1} respectively, which makes to observe in mid-IR spectroscopy.

FTIR results seem to indicate that the sample contains no organic compounds.

5.4.2. PV-white microlayer

The infrared spectrum allows reveals calcite absorption bands at 1416, 873, and 712 cm^{-1} , characteristic of the carbonate group. Gypsum shows absorption bands at 1110, 670, and 597 cm^{-1} , characteristic of the sulfate group (vibration modes of sulfur–oxygen bonds). In particular, bands over 3000 cm^{-1} (3524 and 3398 cm^{-1}) are related to water incorporated in the gypsum structure (O–H stretch vibrations), apart from other wavenumbers of absorption maxima (1681 and 1618 cm^{-1}), likely due to vibrations resulting from the water bonds. FTIR results seem to indicate that the sample contains no organic compounds.

5.4.3. PB

The infrared spectrum reveals gypsum with absorption bands at 1111, 669, and 595 cm^{-1} , characteristic of the sulfate group. In

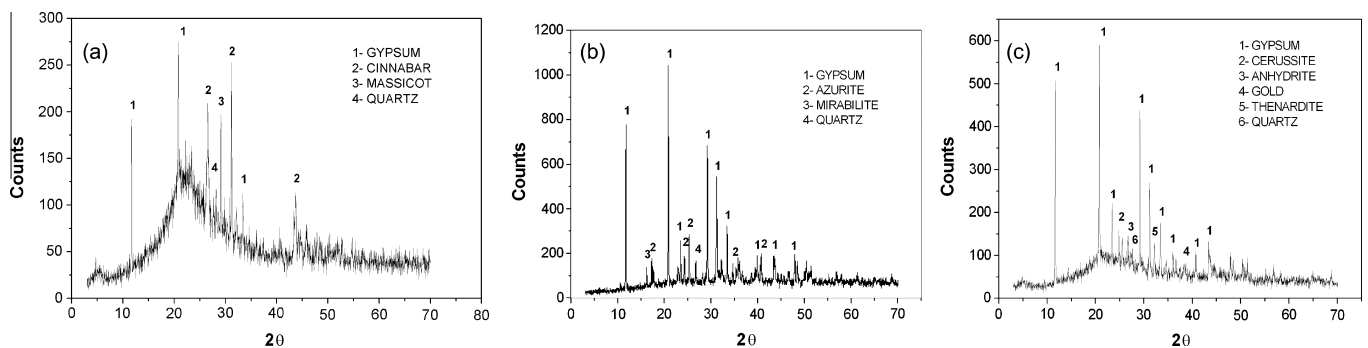


Fig. 4. (a) XRD diffractogram of PV, (b) XRD diffractogram of PB, and (c) XRD diffractogram of PG.

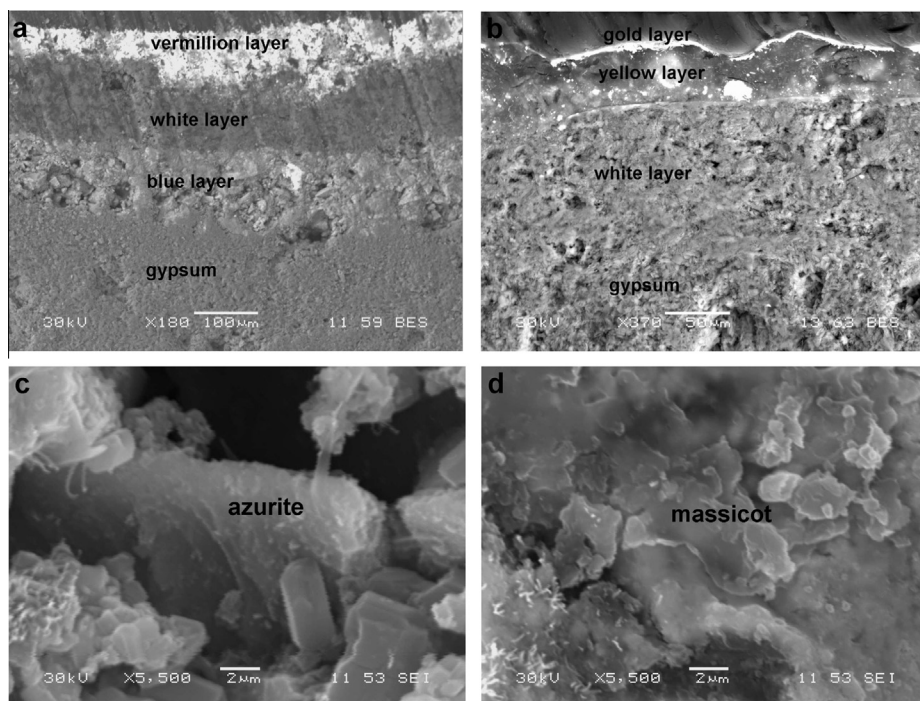


Fig. 5. (a) SEM image in BSE mode of PV, (b) SEM image in BSE mode of PG, (c) SEM image in SE mode of azurite crystal in PB, and (d) SEM image in SE mode of litharge crystal in vermilion layer of PV.

Table 4
Semiquantitative chemical analysis by EDX of PV, PB, and PG.

Element	PV (Fig. 5a)			PG (Fig. 5b)	
	Blue layer Weight%	White layer Weight%	Vermillion layer Weight%	Gold layer Weight%	Yellow layer Weight%
C	17.06	19.09	17.63	–	25.74
Al	0.36	–	0.18	–	0.50
Si	1.01	0.14	0.35	–	0.73
S	1.77	6.63	2.86	–	–
Cl	1.16	–	–	–	–
K	0.14	–	0.22	–	–
Ag	–	–	–	2.44	–
Ca	2.22	8.24	0.50	5.45	–
Au	–	–	–	68.93	–
Fe	0.20	–	–	–	0.44
Cu	19.88	0.90	–	–	–
Pb	0.58	0.50	19.00	11.54	2.44
Hg	–	–	5.34	–	–
O	55.62	64.50	53.92	11.64	70.15
Totals	100.00	100.00	100.00	100.00	100.00

particular, bands over 3000 cm^{-1} (3519 and 3400 cm^{-1}) are related to water incorporated in the gypsum structure (O–H stretch vibrations), apart from other wavenumbers of absorption maxima (1686 and 1620 cm^{-1}), likely due to vibrations resulting from the water bonds. The azurite absorption band at 3309 cm^{-1} has been assigned as the O–H stretching mode. For the carbonate group, bands are observed at 1406 cm^{-1} (C–O stretching modes) and 995 and 816 cm^{-1} . FTIR results seem to indicate that the sample contains no organic compounds.

5.4.4. PG

The infrared spectrum reveals gypsum, which shows absorption bands at 1110 , 672 , and 604 cm^{-1} , characteristic of the sulfate group. In particular, bands over 3000 cm^{-1} (strong at 3399 cm^{-1}) are related to water incorporated in the gypsum structure (O–H stretch vibrations), apart from other wavenumbers of absorption

maxima (1638 cm^{-1}), likely due to vibrations resulting from the water bonds. Absorption bands at 1320 cm^{-1} (C–O stretch vibrations) and 778 cm^{-1} characteristic of the carbonate group can be associated to cerussite. FTIR results seem to indicate that the sample contains aliphatic organic compounds associated to absorption bands at 2924 , 2853 , 1458 , and 1364 cm^{-1} .

5.4.5. PG extracted with acetone

In order to concentrate the organic remains observed in PG, this sample was extracted with acetone, later evaporated, and the concentrated solution measured in the ATR. FTIR results show 2925 and 2855 cm^{-1} bands (asymmetric and symmetric νCH_2 stretching), a strong band at 1703 cm^{-1} ($\nu\text{C}=\text{O}$ stretching), weak bands at 1620 cm^{-1} ($\nu\text{C}=\text{C}$ stretching), 1457 , and 1363 cm^{-1} (asymmetrical $\delta\text{CH}_3, \text{CH}_2$ and symmetrical δCH_3 bending), 1231 cm^{-1} ($\nu\text{OC}-\text{OH}$ stretching), 1171 cm^{-1} ($\nu\text{C}-\text{O}$ stretching), and 669 cm^{-1} (cis $\delta\text{C}-\text{H}$ out of the plane). This infrared spectrum may be quite similar to the one obtained after linseed oil polymerization after being exposed to the air [32].

5.5. Overall characterization

The vermilion PV sample has a blue underlying layer as the original colored layer. This layer comprises gypsum (as a binder) colored with azurite. Over this original layer is a white layer of lime and gypsum; given its quality and texture, it was likely applied to improve the application of vermilion by preventing color mixing between the vermilion and the blue. The current top layer (vermilion) also has gypsum as a binder and inorganic pigments (massicot and cinnabar in this case). No organic compounds have been detected, as verified by the FTIR analyses, which has contributed to the stability of the colored layers as they have not undergone changes from the oxidation or degradation of organic compounds.

Sample PB is an original layer (similar to the blue layer identified in PV) that has not been repainted nor covered by other layers. This is deduced from the evenness of the interface between the plasterwork and the blue layer. If any previous layer had been

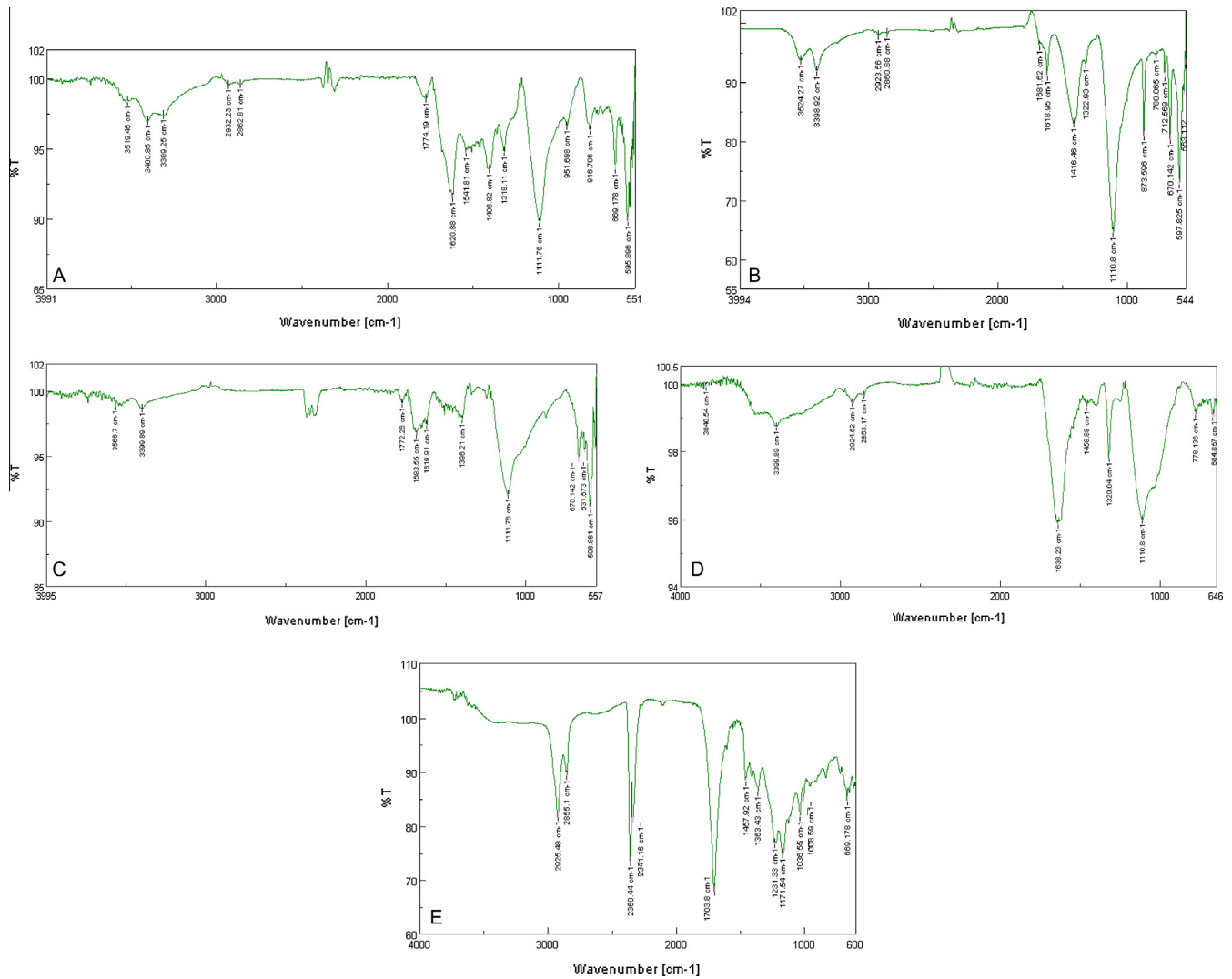


Fig. 6. Infrared spectrum: (A) PV-blue, (B) PV-white, (C) PV-vermilion, (D) PG, and (E) PG acetone extracted.

scraped down, the base plaster would be uneven. As with sample PR, its exclusively mineral composition has allowed perfect color conservation.

Finally, in the gold layer (sample PG), there are three superposed layers. The lowermost is a white layer consisting solely of gypsum, identified as a preparatory layer to reduce the porosity of the base plaster for a better adhesion of the gold-leaf. On top of this initial preparatory layer is a second preparatory layer for the gold-leaf. It comprises polymerized linseed oil and cerussite, whose function (as mentioned above) is to aid the drying process. The final layer is the gold-leaf, making a spectacular effect in the room's entry arch. The FITR analysis reveals organic compounds in the intermediate layer, which are clearly defined in the new spectrum when the sample is treated with acetone. In this case, any degradation by oxidation that the linseed oil might have undergone has not caused any aesthetic problems since it is an intermediate preparatory layer. The final gold-leaf layer is completely stable, having undergone only a natural loss of shine typical of these types of decorations.

6. Graphic reconstruction of arch scallop

This study shows the evolution over time of the polychrome plaster in the arch's scallop in the western wall of the Ambassadors Hall. Modeling of the original geometry with parameterized 3D

solids provides a virtual reconstruction of the analyzed elements. The subsequent application of color found in the characterization recreates the state of these forms in different periods. The subsequent montage of the modeled and colored form in a photograph-type image of the arch's scallop (with the correct positioning and lighting) virtually recreates the whole element. Three periods and possible applications have been differentiated in the polychromies of the elements and their sequence of application: (a) original state, 14th and 15th centuries; (b) intermediate states, 16–17th century and 19th century; (c) current state, 21st century.

6.1. Original state, 14th and 15th centuries

The polychrome stratigraphy shown in Fig. 3 yields a color scale (R/G/B) for the tones applied to the 3D solids, with blue (33/77/107), white (221/204/187), and to represent the golden tone, we chose a color simulating gold since it is not a true RGB color. There are two possible original options (Fig. 7), although the right-hand one is more likely since blue and gold were the colors of divinity and royalty.

Fig. 7 gives the two possible combinations of colors the decorative scallop of the arch could have had in the 14th and 15th centuries (period of construction), considering the gold as having been applied originally or not. Both options have blue as the base color in the composition of the semicircular concave forms,

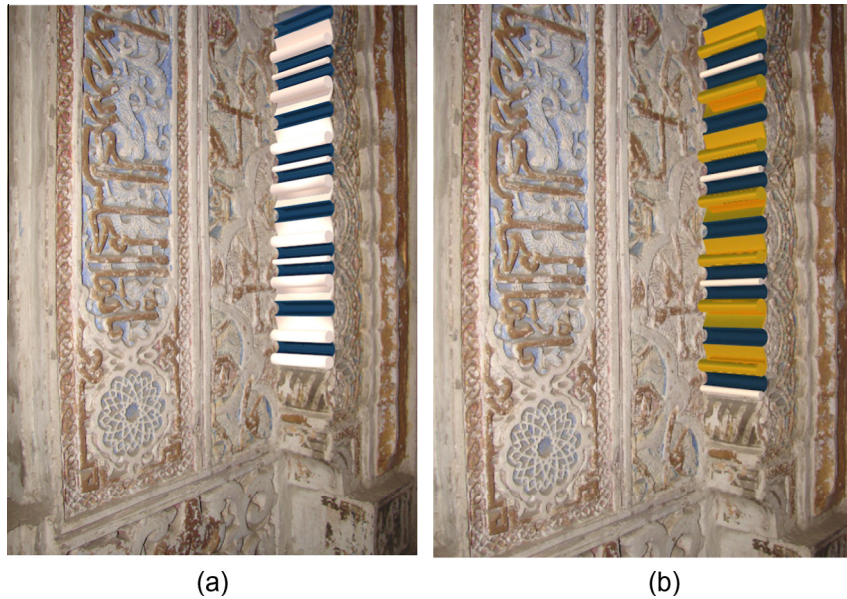


Fig. 7. Options one and two for original state in the 14th (a) and 15th centuries (b).

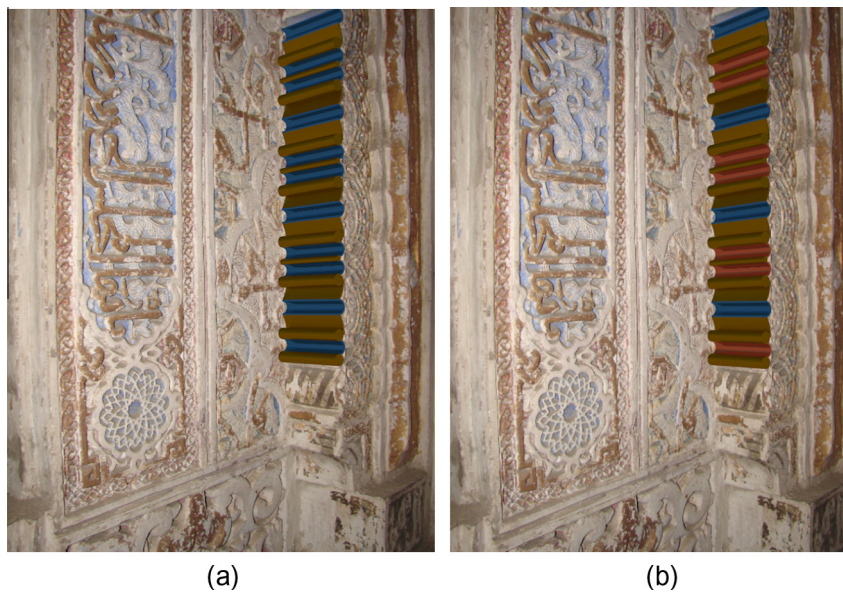


Fig. 8. (a) Intermediate state in 16th and 17th centuries and (b) intermediate state in 19th century.

combined with white in the case of Fig. 7a. In the second option, it is quite possible that gold-leaf was used for the larger scrolls and concave forms and white for the small scrolls, as in Fig. 7b.

6.2. Intermediate state in the 16th–17th centuries for the vermilion and 19th century for the gold

Starting with the polychrome stratigraphy in Fig. 3, we have determined two possible combinations, in this case defining blue (33/77/107), white (221/204/187), gold (231/174/24), and vermilion (156/69/41) (see Fig. 8).

Fig. 8 shows the two possible color combinations for the scalloped arch in the 16th–17th centuries and the 19th century. The most likely application is vermilion in the 16th–17th centuries and re-application of gold-leaf in the 19th century. The gold-leaf

is maintained in the 19th century as the base color of the composition in the semicircular concave forms, together with the small white scrolls, combined in the first with blue for the rest of the concave cylindrical figures and with white for the rest of the elements (Fig. 8a). It is quite possible that gold-leaf was used for the larger scrolls and concave forms and white for the small scrolls, as in Fig. 8b.

6.3. Current state recreated without deterioration

For this case, the color samples were taken directly from the actual photograph of the arch scallop (Fig. 2), which shows the final version of this polychromy. In this case, the colors are blue (24/52/74), white (255/255/222), gold (206/142/16), and vermilion (181/81/49).



Fig. 9. Current state idealized reconstruction of the polychromies with no deterioration.

It is not easy to imagine the state of the restored arch given the deterioration of certain motifs in the scallop and the dirt deposited over the colors. The Fig. 9 shows an idealized reconstruction of the polychromies found, with no deterioration.

7. Conclusions

The results obtained lead to the following conclusions:

- XRF, XRD, and FTIR techniques and stratigraphic analysis have been used to characterize the base plasterwork of the Ambassadors Hall of the Real Alcázar of Seville and its polychrome work. Its chromatic richness, comprising blue, vermilion, and gold layers, was obtained with the mineral pigments azurite and cinnabar-litharge bound with gypsum and with gold-leaf applied with mixtion, respectively.
- The stratigraphic study has revealed that the colors currently visible in the decorative elements have not been the same throughout the history of this room. These changes are compared with the historic data on the most significant interventions carried out in the hall. These data have been complemented with a graphic analysis and 3D modeling of the decorative geometric elements to graphically recreate the different stages in the polychromy evolution.
- It is apparent that stratigraphic characterization using instrument techniques combined with graphic representation comprise a suitable methodology to analyze the evolution of polychrome decorative elements, providing valuable information to complement historiography data.

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References

- [1] J. Guerrero Lovillo, Los maestros yeseros sevillanos del siglo XVI, *Archivo español de arte*, 28, 109, 1955.
- [2] O. López Cruz, A. García Bueno, V. Medina Florez, The evolution of the colour in the eaves of the façade of the palace of the king Pedro I, *Royal Palace of Seville. Contribution of the study of materials to the identification of the conservation works undertaken throughout its history*, *Arqueología de la Arquitectura* 8 (2011) 163–178.
- [3] J. Morales Alfredo, J.C. Hernández Nuñez, *El Real Alcázar de Sevilla*, Scala Publishers Ltd. (1st ed.), Imp. En España por Fournier A. Gráficas, S.A., London, 1999.
- [4] A. Almagro, A. García Bueno, O. López Cruz, V. Medina Florez, Restoration of the façade of the Palace of Peter Ist. Second phase. Right wing, *Apuntes del Alcázar* 11 (2010) 9–35.
- [5] R. Cómez Ramos, *El Alcázar del Rey Don Pedro*, Diputación Provincial de Sevilla, Sevilla, 77–88, 1996.
- [6] M. Doerner, *The Materials of the Artist and their Use in Painting* (6th ed.), First Harvest, Orlando, 53, 1984.
- [7] R. Ford, *Manual para viajeros por Andalucía y lectores en casa*, Ediciones Turner, Madrid, 1980.
- [8] I. Baceiredo Rodríguez, M.J. López Madroñero, Restoration of the Almohad hollow in the patio del yeso, *Apuntes del Alcázar* 4 (2003) 76–95.
- [9] M.R. Chávez González, *El Alcázar de Sevilla en el siglo XIX*, Patronato del Real Alcázar, Sevilla, 2004.
- [10] F.J. Blasco López, F.J. Alejandre, Characterization of Islamic tradition plasterwork Real Alcazar of Seville, Ed. Océ, Sevilla, 1–62, 2010.
- [11] F.J. Blasco López, F.J. Alejandre, The plasterwork of the Courtyard of the Sun of the Real Alcázar de Sevilla: characterization test and chronology, *Inf de la Const.* 65 (530) (2013) 175–182.
- [12] F.J. Blasco López, F.J. Alejandre, Porosity and surface hardness as indicators of the state of conservation of Mudéjar plasterwork in the Real Alcázar in Seville, *J. Cult. Herit.* 14 (2) (2012) 169–173.
- [13] M.D. Mérida Álvarez, Construcción y restauración del Real Alcázar de Sevilla en el periodo isabelino (1843–1868), *Actas 2nd Cong Nac de Historia de la Construcción vol II 2000*, Sevilla, 683–88.
- [14] R.F. Rubio Domene, *Yeserías de la Alhambra: Técnica y Conservación* (Tesis doctoral), Granada, 2002.
- [15] A. García Bueno, V. Medina Florez, A. González Segura, La Policromía de los fragmentos de yeso almacenados en los depósitos del Museo de la Alhambra, in: 16th Int Meet Heritage Conservation, Univ Politécnica Valencia, 1601–1613, 2006.
- [16] V.H. López Borges, L. Burgio, R.J.H. Clark, Documentación y autenticación de yeserías nazaries a través del tratamiento de conservación y el análisis científico. GE-IIC conference “Investigación en conservación y restauración” 2005, Barcelona, 109–117.
- [17] A. Almagro, Planimetry of the Alcázar of Seville. Loggia, *Arquitectura y Restauración* 14–15 (2002) 156–161.
- [18] A. Almagro, A. Almagro-Vidal, La expresión gráfica en el análisis del Patrimonio: El patio del Crucero del Alcázar de Sevilla, *Actas del IX Cong Int Expresión Gráfica Arquitecta* 2002, La Coruña, 517–522.
- [19] R. Angulo Fornos, Setting-up a graphical basis for an information and management system of architectural heritage: House Hylas, *Arqueología de la Arquitectura* 9 (2012) 11–25.
- [20] L. Gómez Robles, M.V. Quirosa García, New computer graphics technologies as knowledge tool in the field of the Historic heritage: some Spanish experiences, *E-rph: Rev. Elect. Patrimonio Histórico* 4 (2009) 150–174.
- [21] A. Sever Škapin, P. Ropret, P. Bukovec, Determination of pigments in colour layers on walls of some selected historical buildings using optical and scanning electron microscopy, *Mater. Charact.* 58 (11) (2007) 1138–1147.
- [22] J. Weber, W. Prochaska, N. Zimmermann, Microscopic techniques to study Roman renders and mural paintings from various sites, *Mater. Charact.* 60 (7) (2009) 586–593.
- [23] L. Villanueva Domínguez, A. García Santos, *Manual del Yeso*, Asociación Técnica y Empresarial del Yeso ATEDY-DOSSAT 2000, Madrid, 2001.
- [24] A. Pedrola, *Materiales, procedimientos y técnicas pictóricas* (3rd ed), Ariel, S.A., Barcelona, 2004.
- [25] J.M. Medianero Hernández, *Aportaciones documentales sobre la técnica de la pintura Hispalense a fines de la Edad Media*, vol. 6, Laboratorio de Arte, 1993. 69.
- [26] A. Duran, M.C. Jimenez de Haro, J.L. Perez-Rodriguez, M.L. Franquelo, L.K. Herrera, A. Justo, Determination of pigments and binders in Pompeian wall paintings using synchrotron radiation-high-resolution X-Ray powder diffraction and conventional spectroscopy-chromatography, *Archaeometry* 52 (2) (2009) 286–307.
- [27] L. Bertolini, M. Carsana, M. Gastaldi, F. Lollini, E. Redaelli, Binder characterisation of mortars used at different ages in the San Lorenzo church in Milan, *Mater. Charact.* 80 (2013) 9–20.

- [28] M. Matteini, A. Moles, *La Química en la restauración (La Chimica nel restauro. I materiali dell'arte pittorica)*, Nardini ed., San Sebastián, 110–113, 1989.
- [29] R. Mayer. *The Artist's Handbook of Materials and Techniques*, (5th ed.) Tursen, Hermann Blume 1991, Barcelona, 752, 1993.
- [30] G.C. Jones, B. Jackson, *Infrared Transmission Spectra of Carbonate Minerals*, Chapman & Hall, London, 1993.
- [31] H. Kühn, *Artist's Pigments, A Handbook of their History and Characteristics II A*, in: Roy (Ed.), Oxford University Press, London, 1993.
- [32] A. Groza, A. Surmeian, M. Ganciu, I.I. Popescu, *Infrared spectral investigation of the linseed oil polymerization in a corona discharge in air at atmospheric pressure*, *Europhys. Lett.* 68 (5) (2004) 652–657.