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Revealing Juan de Oviedo y de la Bandera's Artworks: The Case of the Polychrome of a Stone-Carved Sculpture from the Madre de Dios Convent Façade in Seville

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Abstract: The entrance of the Madre de Dios convent in Seville was carved in stone by Juan de Oviedo y de la Bandera, an important sculptor who made great artistic productions, highlighting his carvings in wood and stone. Several studies have been carried out on the carvings in wood, but no interest has been paid by experts to the carving pieces in stone. In this work, this polychrome made on stone around 1590 was studied for the first time. Micro-samples were taken and studied using micro-analytical techniques (optical microscopy, SEM-EDX, colourimetry, XRD, FTIR, and Raman spectroscopy). The pigments (smalt, atacamite, malachite, copper resinate, cinnabar, red earth, yellow ochre, carbon, and bone black) and the consolidation product (acrylic resin, very possibly Paraloid B72) were characterized. The experimental study indicated that the polychrome was applied on a layer of white lead (cerussite and hydrocerussite) that was laid on the substrate stone, constituted by calcarenite. This study also includes a comprehensive discussion on the use of these materials and techniques in other artworks within Seville's cultural heritage.

Keywords: pigments; stone; sculpture; mineralogy; Sevillian artworks

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1. Introduction

The Madre de Dios Convent in Seville began to be built in the middle of the 16th century. The Church of the Convent was finished in 1572, under the direction of the architects Juan de Simancas and Pedro Díaz de Palacios. The entrance of the church was located on the left wall and was carved in stone (Figure 1a). In the central niche, there were reliefs of the Virgin of the Rosary with the Child giving a rosary to the founder of the order, Santo Domingo de Guzmán (Figure 1b). In the attic of the entrance, the Eternal Father was sculpted (Figure 1b) and the royal coat of arms of Castile in the lintel flanked by the shields of the Dominican order was also sculpted (Figure 1c). These ornamental works were sculpted by Juan de Oviedo y de la Bandera around 1590 [1,2].

Juan de Oviedo y de la Bandera, el Mozo (Seville, 1565–San Salvador de Bahía, 1625), was the son of the carver Juan de Oviedo Hernández and the pupil of his uncle, Juan Bautista Vázquez, el Viejo. Thus, he was linked to the most illustrious sculptors' family of the Sevillian school of the early Renaissance. In 1586, at the age of 21, he obtained a master's degree in sculpture, Roman carving, and architecture. In the first decade of his practice, his activity was linked to the family's sculptures and the production of altarpieces. However, the young Juan de Oviedo y de la Bandera entered the new professional role of the modern architect. He had great success in his social and professional life, carrying out numerous religious and civil commissions [3–6]. A company formed between the Sevillian

sculptors Juan de Oviedo y de la Bandera and Juan Martínez Montañés, established in 1596 until 1602. This relationship helped Juan de Oviedo y de la Bandera to incorporate in his works the expertise of an exceptional artist, from whom he received his valuable teaching [7]. The contact with the Duke of Alcalá and the Count–Duke of Olivares was enough for him to be promoted to the military engineer of the crown of Spain. At the age of 60, he was appointed as the major military engineer of the Navy of Philip IV. He died in the vanguard of the siege that gave victory to the Spanish Empire in the recovery of San Salvador de Bahía from the Dutch [3–6].

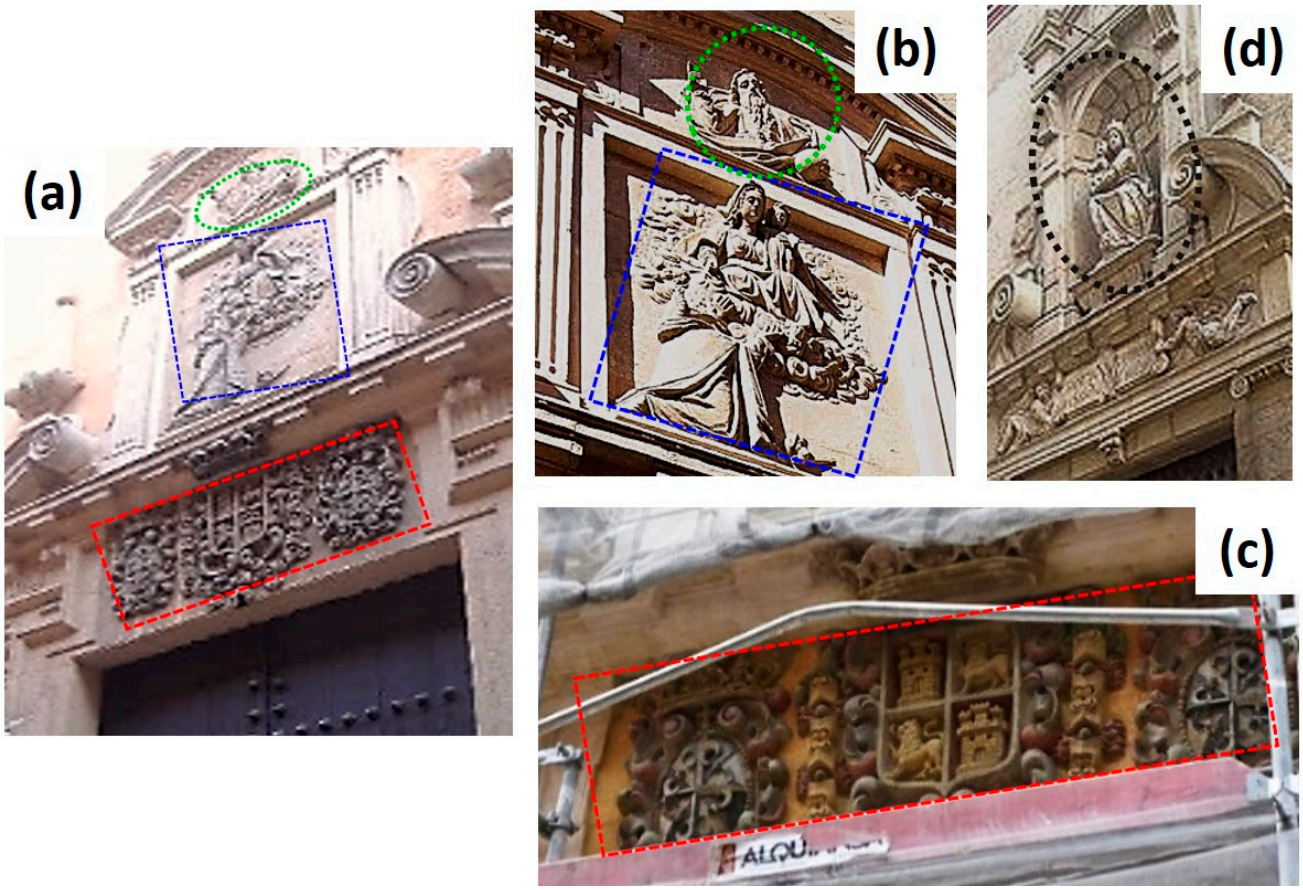


Figure 1. Photos of: (**a**–**c**) Madre de Dios convent façade (in blue square: Virgin of the Rosary and Santo Domingo Guzmán; in red square: royal coat of arms of Castile flanked by the shields of the Dominican order; in green circle: the Eternal Father) and (**d**) Santa Maria de Jesus Convent façade (in black circle: Virgin and Child).

Juan de Oviedo y de la Bandera made great artistic productions, highlighting his carvings in wood and stone. His outstanding wood carvings included the Christ of the Mercy (1591) in San Juan del Puerto (Huelva, Spain) for the Monastery of Carmen; the Virgin and Child of the disappeared altarpiece of the Chapel of Our Lady of the Rosary of the Parish of the Incarnation in Constantina (Seville, Spain); Santa María del Buen Aire, belonging to the disappeared altarpiece of the hospital of the University of Mareantes in Triana (Seville, Spain); and the San Francisco of the Franciscan Convent of Cazalla de la Sierra (Seville, Spain) [3–6]. His great artistic production was carried out by playing with the richness of the classicist language and developing his artistic lexicon. A detailed description of his works can be found in [3]. The stone carvings also stood out: the high relief with the Virgin of the Rosary, the Child, and Santo Domingo de Guzmán on the doorway of the Church of the Madre de Dios Convent (Figure 1a–c) and the Virgin and Child of the Santa María de Jesús Convent of Seville around 1590 (Figure 1d). For the sculptures made in stone of the façade of the Madre de Dios Convent, he would very

possibly have applied the teachings of his uncle, Juan Bautista Vázquez, el Viejo, who made the reliefs in stone of the City Hall of Seville, whose polychrome was studied by the authors of this work [8,9].

Very few scientific studies of the artworks realized by Juan de Oviedo y de la Bandera have been carried out. The image of Santa María del Buen Aire has been well studied [10]. However, this sculpture made in wood was transformed by Duque Cornejo in 1725, and none of the original polychrome was preserved [10]. No scientific studies have been carried out on the sculptures made on rock by Juan de Oviedo y de la Bandera.

This is why the façade of the Madre de Dios Convent (Figure 1a–c) was selected for this study. The polychrome of the reliefs and lintel has been preserved, including the red incarnation of the lips of the Virgin and some of the face, and an important part in the coats of arms of Castile and the Dominicans of the lintel. This polychrome was restored in the restoration works of the façade in 2021, recovering its past splendour [11].

The application of analytical methods to polychrome enables a more detailed and accurate knowledge of the site's physicochemical features and provides data on their qualitative and quantitative characteristics. A physicochemical analysis provides useful information for defining the variety of pigments available on local and regional scales, and for understanding the techniques of colour preparation and application [8,9,12–14]. Minerals are the main components of cultural heritage polychrome. In the last few decades, mineralogical methods and techniques have been applied in analysing the polychrome of different artworks [12–14]. Compounds such as smalt [15–17], atacamite [18–20], malachite [8,9,21,22], verdigris [23], cinnabar and vermilion [9,16,17,19,22,23], earth pigments [15–21,23], goethite [17,20,21,23], bone black [19,24], and carbon black [9,16,19,20] have been found in Sevillian artworks from different epochs. However, the full potential of mineralogy science methodologies has not been explored for the polychrome of the stone sculptures created by Juan de Oviedo y de la Bandera.

The analysis of the different components used in the ornamental work of the entrance of the Madre de Dios Convent in Seville not only provided information on the technology used by this excellent sculptor, but also provided insight into what materials were used in Seville to make these ornamental works in the late sixteenth and early seventeenth centuries. The characterization of this polychrome was undoubtedly important in understanding the history of the work of art and in the resolution of problems related to conservation, restoration, dating, and author attribution.

2. Materials and Methods

Figure 2 shows the zones on the façade in which the samples (10) were taken for the study. A microgram amount of powder and solid fragments was collected.

The micromorphology and chemical elemental analyses of the different samples were studied using optical microscopy (Nikon Optiphot microscope with a Nikon Coolpix 4500 camera) (Nikon, Tokyo, Japan) and scanning electron microscopy (Hitachi S-4000 SEM microscope) (Hitachi, Tokyo, Japan) coupled with an energy-dispersive X-ray analyser (EDX Bruker XFlash 4010) (Bruker, Karlsruhe, Germany) at an accelerating voltage of 20 kV and a 10 μA beam current. The samples (dimensions of ca. 1.5 × 1.5 × 2.0 mm) were detached by hand without polishing and then covered by a 16 nm thin layer of molecular gold using the Emitech K550 sputter coater equipment (Richmond Scientific, Lancashire, Great Britain). EDX quantitative analyses were performed by using the theoretical inner pattern and the ZAF correction method. The live time, which is the effective measurement time in EDX, was set to 100 s. For a quantitative X-ray microanalysis of the specimens, several corrections were necessary, since various factors were different for the specimen and the standard, such as the backscattering and the stopping power, which depend on Z (atomic number), A (the X-ray absorption), and F (the fluorescence) [25].

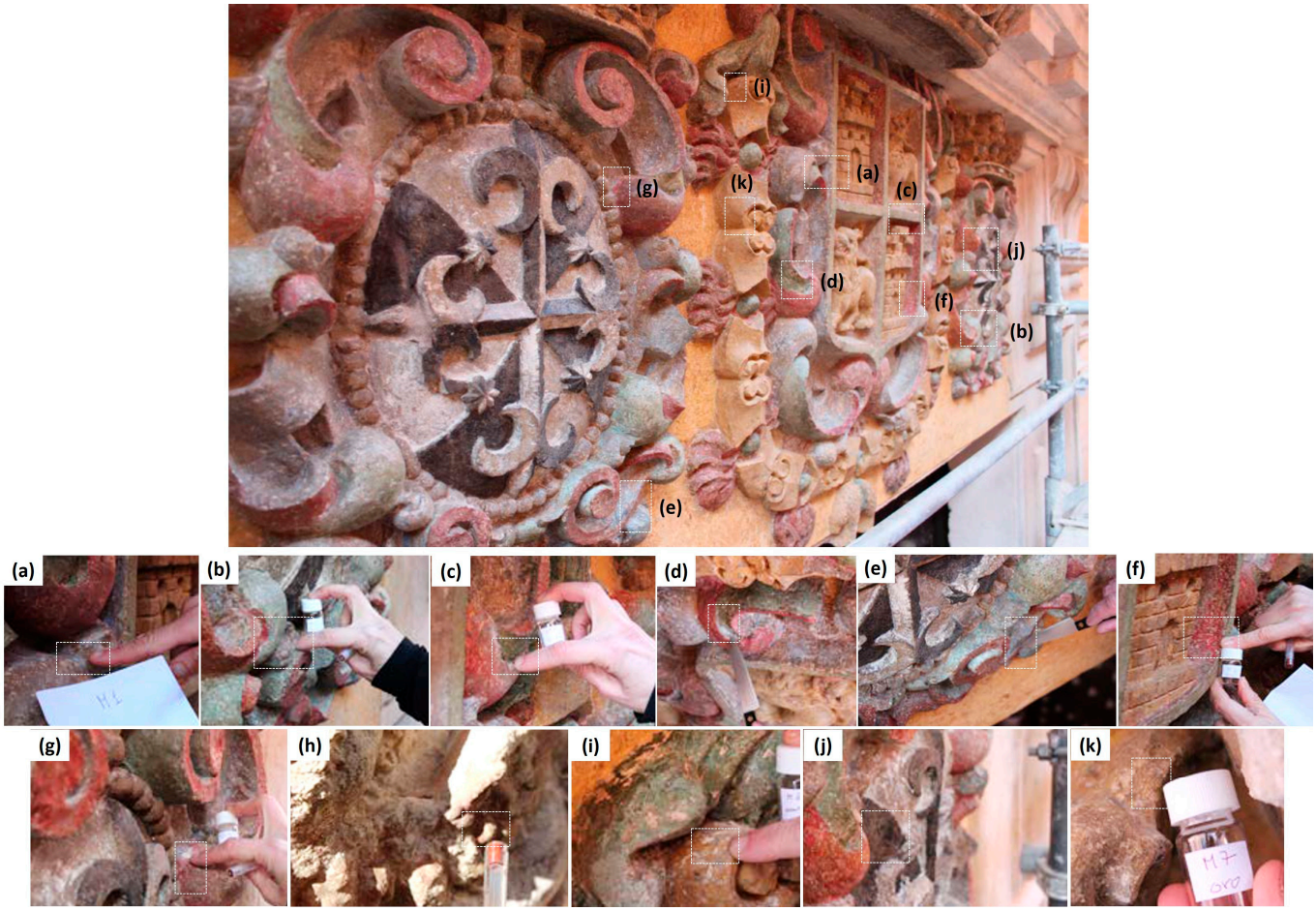


Figure 2. Photos of sampling zones within the façade of the Madre de Dios Convent (in white square): (**a**) sample 1, blue colour; (**b**) sample 4, green colour; (**c**) sample 5, green colour; (**d**) sample 10, green colour; (**e**) sample 9, turquoise colour; (**f**) sample 2, red colour; (**g**) sample 3, red colour; (**h**) sample 11, red-brown colour; (**i**) sample 6, yellow colour; (**j**) sample 8, black colour; and (**k**) sample 7, golden colour.

A Konica Minolta CM-2300d spectrophotometer (Konica, Tokyo, Japan) was used for the colourimetric analyses. A D65 light was the source. The measurements were carried out in triplicate, providing values of L* (lightness, 100, to darkness, 0), a* (reddish, positive, or greenish, negative values), and b* (yellowish, positive, or bluish, negative values). The measurements of colour allowed us to check some of the hues and relate them to the chemical composition.

X-ray powder diffraction was carried out on a PANalytical X'Pert Pro MPD diffractometer (Malvern Panalytic, Malvern, United Kingdom), using Cu Kα radiation (λ = 1.54 Å) at 45 kV and 40 mA. The detector was a PIXcel solid state one. The sample holder was a standard +0.5 mm insert, with a composition based on steel + aluminium, a 25 mm diameter, a 0.5 mm depth, and a required sample volume of 245 mm^3. This study allowed for the chemical and mineralogical characterization of the sample components, which were properly ground in an agate mortar. A milligram amount of the samples was measured.

Spectroscopic studies were carried out by employing two types of equipment: The Fourier-transform infrared (FTIR) study was performed using a Jasco FTIR 6200 (Jasco, Hachioji, Tokyo) with an ATR accessory. To record the Raman spectra, an integrated dispersive Horiba Jobin Yvon LabRam was employed [15].

3. Results and Discussion

3.1. Consolidation Products

The SEM observations of the samples clearly showed the presence of coatings or external films and how these penetrated the artwork (see Figure S1a–c). The EDX measurements of this continuous layer showed a carbon-rich material. The observation of the samples in the scanning electron microscopy displayed the continuous destruction of this material produced by the energy of the electron beam of the microscope.

The FTIR analysis confirmed that these films were constituted by acrylic resin (Figure S1d), very possibly Paraloid B72. The absorption bands of the experimental spectrum matched with those of the standard: stretching bands were observed of C=O at ca. 1730 cm^{-1}, C–O–C at ca. 1150 cm^{-1}, and other signals [26,27].

The term resin indicates a range of natural and synthetic organic compounds employed as consolidating, adhesive, and varnish agents [26]. There are natural resins, produced from insects and plants, and synthetic resins, usually purer than natural ones [26,28]. Some studies [26–28] on the application of resins over cultural heritage artefacts are present in the literature. The best product was the one that allowed the cohesion of the pictorial films and adhesion between the colour layers and the stone substrate [28]. Acrylic resin has been widely applied as a consolidant. Normand et al. (2020) [29] provided insight into the performance of nanolime, ethyl silicate, and acrylic resin for the consolidation of wall paintings. Acrylic resin showed the best results at the mid-term [29].

In this work, the presence of the consolidation products within the samples affected the study performed using some of the experimental techniques, making the characterization of the polychrome difficult. Also, the presence of the acrylic resin hindered the identification of the possible paint binders, i.e., linseed oil or similar substances.

3.2. Study of the Polychrome and Preparatory Layers

3.2.1. Blue Colour

Sample 1 (Figure 3a) showed a blue external layer on another of an ochre colour, and finally, at the bottom, a rock material of a white colour appeared. The colourimetric study of sample 1 presented the following values: L* = 51.66 ± 3.93, a* = −6.83 ± 1.59, and b* = −12.61 ± 2.32, which is characteristic of blue zones (negative b* values) (Table S1). The punctual chemical elemental analysis on the blue colour layer of this sample, performed using an EDX analyser, indicated the presence of silicon (Si) in a high percentage, in addition to the detection of potassium (K), arsenic (As), cobalt (Co), iron (Fe), aluminium (Al), and nickel (Ni) (Table 1 and Figure S2a). Although there were inconvenient overlaps in the emission peaks of the elements, such as in Pb/As, Pb/Bi, and As/Mg, that could have affected the EDX results, the determination was accurately obtained thanks to the differentiation based on spectral deconvolution, where respective characteristic line ratios aid in distinguishing between the different elements. The chemical composition of sample 1 was the following (in % *w*/*w*): SiO_2 = 76.40; K_2O = 9.80; As_2O_3 = 3.65; CoO = 3.52; Fe_2O_3 = 3.32; Al_2O_3 = 0.90; NiO = 0.75; Bi_2O_3 = 0.70; and Na_2O = 0.20. Other chemical analyses carried out on the other zones of sample 1 showed a similar composition to the previous zone (Table 1 and Figure S2b), with the appearance of lead (Pb), which was attributed to the underlayer material. The chemical analyses of the white colour at the bottom were constituted by calcium (Ca) in a very high percentage, accompanied by a small percentage of lead (Pb), silicon (Si), and potassium (K), which were attributed to the stone material support, contaminated by small percentages of the pigment blue layer and/or the layer between the external blue and the support (Table 1 and Figure S2c). A band at 462 cm^{-1} (Figure 4a) was observed in the Raman spectrum obtained on the blue external layer, and it was assigned to the cobalt-containing silicate glass compound (smalt pigment). The XRD study of the total powder sample (Figure 5a) showed the presence of calcite ($CaCO_3$, PDF 05-0586; signals at 2Θ = 29.4°, 39.4°, 43.1°, 47.4°, and 48.5°), assigned to the rock material support (calcarenite); hydrocerussite ($Pb_3(CO_3)_2(OH)_2$, PDF 13-0131; signals at 2Θ = 27.1°, 34.2°, and 40.4°); and cerussite ($PbCO_3$, PDF 47-1734; signals at

2Θ = 20.1°, 24.8°, 25.4°, and 36.0°) appearing in the intermediate layer on the rock material. The presence of smalt was not determined using XRD because it is a glass-based material and does not show X-ray diffraction signals. The colour we observed over the course of this study may have been different from the initial colour due to degradation processes. During all the time that has passed since this polychrome was carried out, the potassium was possibly leached upon smalt degradation. The depletion of potassium ions created a deficiency in charge, which was compensated for with the ions around cobalt. This fact was responsible for some changes in the colour, as described in the literature [30,31].

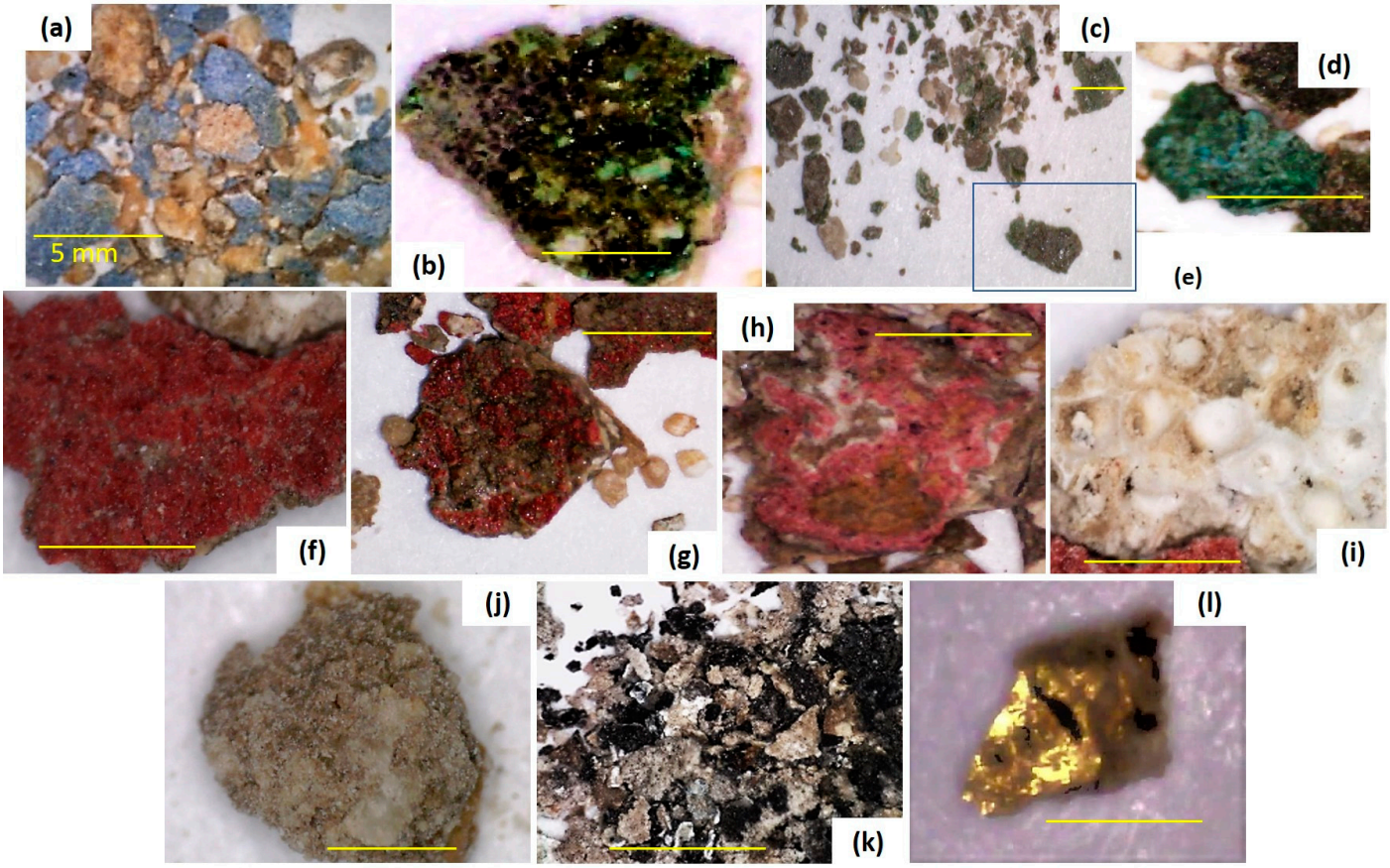


Figure 3. Micrographs corresponding to the different samples studied in this work: (**a**) blue sample 1; (**b**) green sample 10; (**c**) green sample 4; (**d**) green sample 5; (**e**) turquoise sample 9; (**f**) red sample 3; (**g**) red sample 2; (**h**) red sample 11; (**i**) support of the red sample 3; (**j**) yellow sample 6; (**k**) black sample 8; and (**l**) golden sample 7.

Table 1. Elemental chemical analyses of the samples.

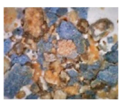
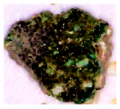
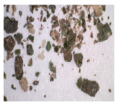
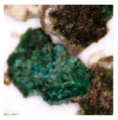
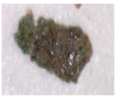
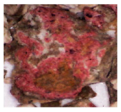
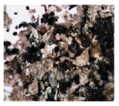
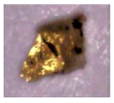
Colour	Sample	Micrographs	General/Punctual and Zones	Composition	Figures
Blue	1		Punctual zone 1	Si, K, As, Co, Fe, Al, Ni	S2a
			Punctual zone 2	Si, Pb, K, Ca, As, Fe, Co, Al, Ni	S2b
			General preparatory layers	Ca, Pb, Si, K	S2c

Table 1. *Cont.*

Colour	Sample	Micrographs	General/Punctual and Zones	Composition	Figures
Green	10		General	Ca, Pb, Si, Cu, Cl, Fe, Al, Na	S3a
			Punctual zone 1	Cu, Cl, Pb, Ca	S3b
			General preparatory layers	Ca, Pb, Al, Si	S3c
	4		Punctual zone 1	Si, K, Fe, Co, As	S3d
			Punctual zone 2	Cu, Cl, Pb	S3e
			Punctual zone 3	Cu, Pb	S3f
	5		Punctual zone 1	C, Cu, Pb	S3g
			Punctual zone 2	Cu, Cl, Pb, Ca	S3h
			General preparatory layer	Pb	S3i
			Stone support	Ca	S3j
Turquoise	9		General surface	Ti, C	S4a
			General preparatory layers	Ca, S, Ti	S4b
			Punctual zone 1	Fe, Mn, Ca, Si	S4c
			General	Ca, S, Pb, Fe, Ti, Mn, Si	S4d
Red	3		Punctual zone 1	Hg, S	S5a
			General	Hg, S, Si, Al, Na, K, Fe, Pb, Ca	S5b
	11		Punctual zone 1	Pb, Si, Fe, Mn, Ca, Al	S5c
			Punctual zone 2	Fe, Mn, Pb, Si, Al	S5d
Yellow	6		General	Ca, Pb, Si, Fe	S6a
Black	8		General preparatory layers	Ca, Pb	S6b
			Punctual zone 1	P, Ca, Si, C	S6c
Golden	7		General surface	Au, Ca, Pb, Si, Al, Fe	S6d

The obtained data agreed with the presence of smalt, a glass-based pigment with a blue colour. Smalt is a potassium silicate glass coloured by cobalt ions. The blue pigment smalt was commonly used by Sevillian artists between the 16th and 18th centuries [15–17]. The chemical composition found in this sample was similar to that of the blue pigments used in several artworks by painters in Seville from the 17th century, such as Murillo, Zurbaran, Mohedano, Bocanegra, etc. These painters very frequently used smalt for blue colour, and they only used the expensive lapis lazuli mineral for some special details [16,17]. The smalt found in this artwork also contained other elements, such as arsenic (As), iron (Fe), and nickel (Ni), which could be associated with cobalt ore. Historic documentary sources show that several grades were sold that varied in their colour intensity as a consequence of differences in both the particle size and the cobalt content [30]. The presence of arsenic in the sample could be associated with the presence of mineral sources such as erythrite ($Co_3(AsO_4)_2 \cdot 8H_2O$) or cobaltite ((Co,Fe)AsS) [16,17,31]. Smalt was also widely used in Sevillian ceramics [15]. These glasses are heterogeneous vitreous compounds prepared

from a frit made of river sand, potassium-rich wine dregs, and pigments containing metallic oxides. This pigment has also been used frequently in wall paintings in aqueous media and lime, and, with the addition of white lead, to prevent degradation processes [30,31], in a similar way to that employed in this artwork.

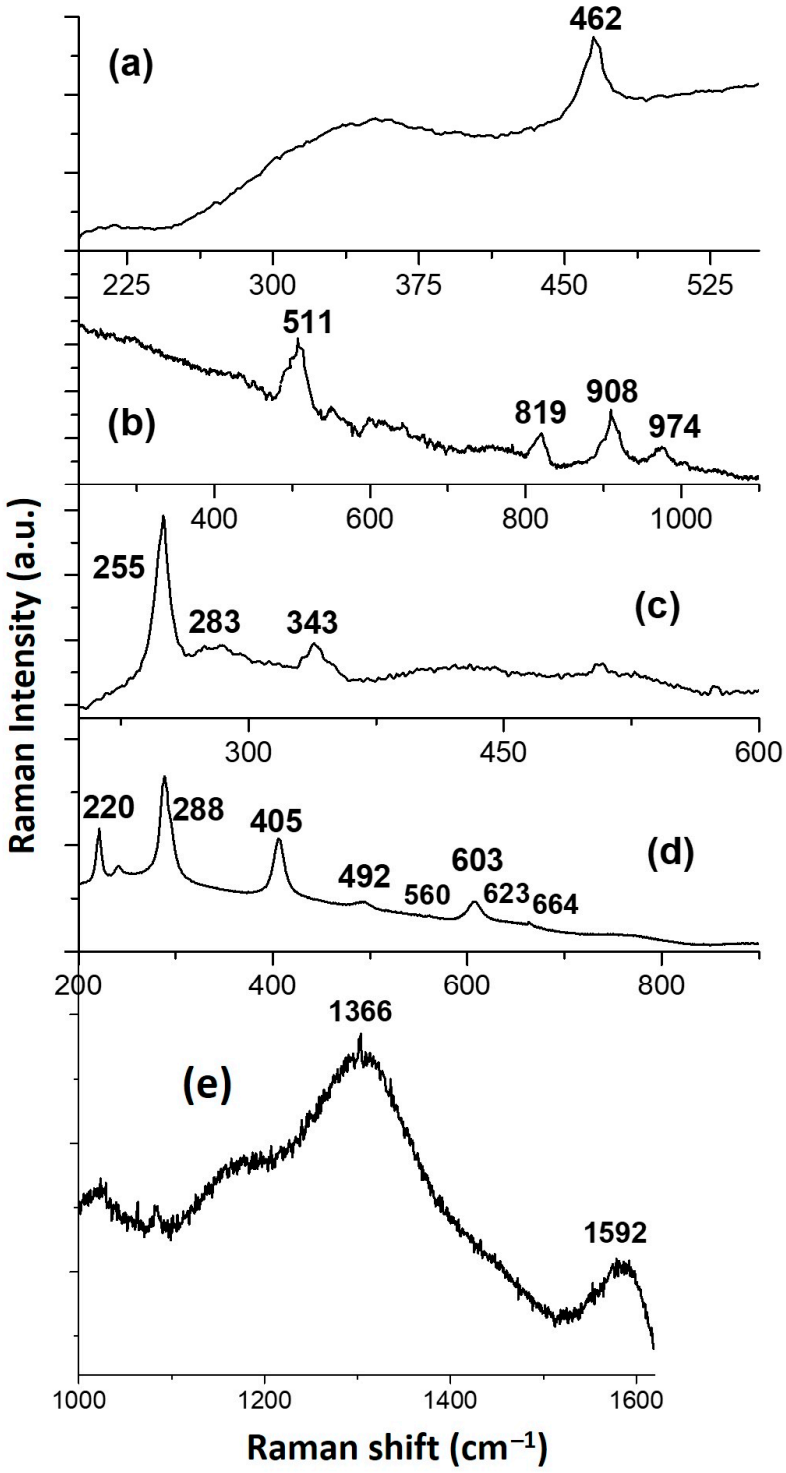


Figure 4. Raman spectra of the following samples: (**a**) blue 1; (**b**) green 10; (**c**) red 3; (**d**) red 11; and (**e**) black 8.

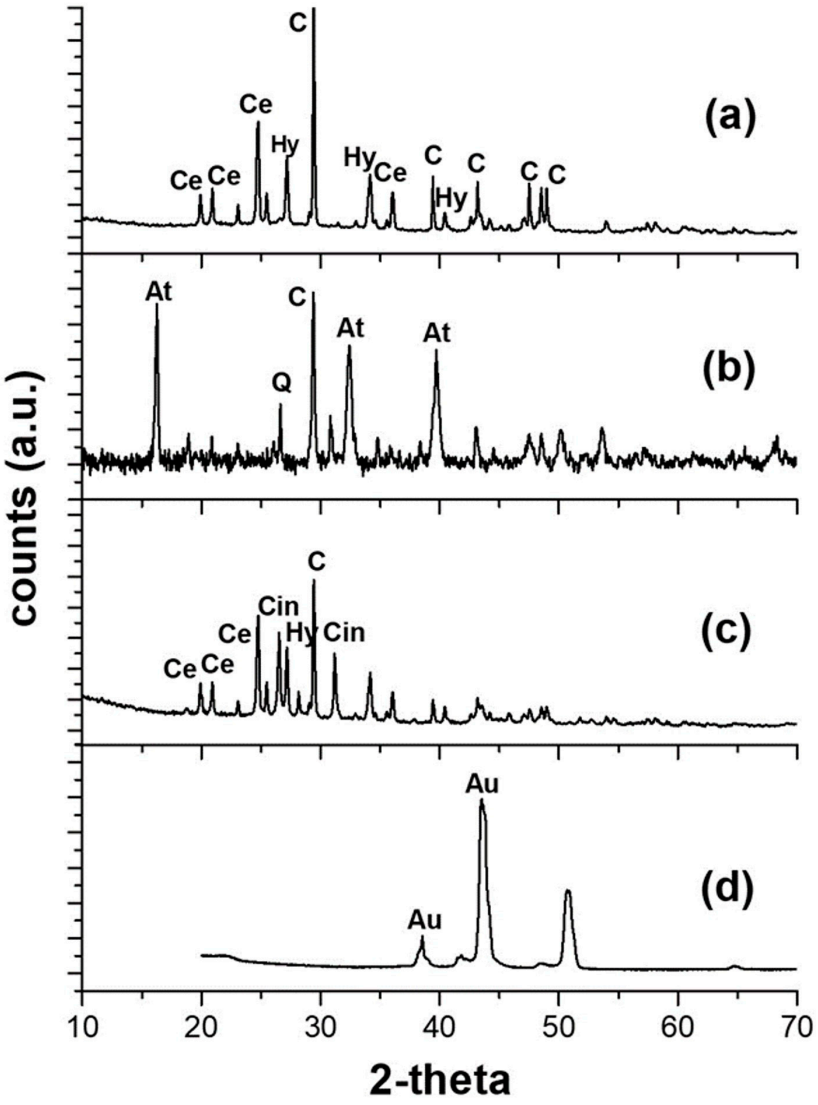


Figure 5. XRD diffractograms of the following samples: (**a**) blue 1; (**b**) green 10; (**c**) red 3; and (**d**) golden 7 [C = calcite, Hy = hydrocerussite, Ce = cerussite, At = atacamite, Q = quartz, Cin = cinnabar, and Au = gold].

3.2.2. Green Colour

Three different hues were observed when studying the three green colour samples (10, 4, and 5) (Figure 3b–d). The colourimetric values were the following for sample 10: L* = 35.27 ± 1.53, a* = −17.16 ± 0.63, and b* = 17.12 ± 1.51. In the case of samples 4 and 5, the colourimetric values ranged from 26.22 (sample 5) to 30.05 (sample 4) for L*, from −12.07 (sample 5) to −0.82 (sample 4) for a*, and from 2.79 (sample 5) to 11.85 (sample 4) for b*. Sample 10 showed colourimetric values characteristic of greenish-yellow, with lower values of a* and higher values of b* (Table S1). The chemical composition of the three green samples was different. The underlayer composition was based on lead compounds, similar to the blue samples.

Sample 10

The general chemical analyses performed on this sample using EDX showed the presence of high percentages of calcium (Ca) and lead (Pb). Other elements such as silicon (Si), copper (Cu), chlorine (Cl), iron (Fe), aluminium (Al), and sodium (Na) were also present (Table 1 and Figure S3a). The punctual chemical analyses on some of the green particles performed using the EDX analyser (Table 1 and Figure S3b) indicated the major

presence of copper (Cu) and chlorine (Cl), suggesting the presence of atacamite. EDX mapping of the green particles showed a composition based on copper (Cu), chlorine (Cl) (both elements matched in the central area), and lead (Pb) (Figure 6), which were respectively attributed to the composition of the green colour and the support on which the pigment was laid. The chemical analyses of the stone indicated a predominance of calcium (Ca), which is consistent with a calcarenite composition (Table 1 and Figure S3c), and also lead (Pb), aluminium (Al), and silicon (Si), possibly from the layer on the rock support. The X-ray diffraction analyses of the green colour (Figure 5b) indicated the presence of atacamite ($Cu_2Cl(OH)_3$, PDF 25-0269; signals at 2Θ = 16.2°, 32.4°, and 39.5°), calcite ($CaCO_3$, PDF 05-0586; signals at 2Θ = 29.4°, 39.4°, 43.1°, 47.4°, and 48.5°), and quartz (SiO_2, PDF 33-1161; signals at 2Θ = 27.4° and 21.0°). The analysis using Raman spectroscopy confirmed the presence of atacamite due to their bands at 511, 819, 908, and 974 cm^{-1} [19] (Figure 4b).

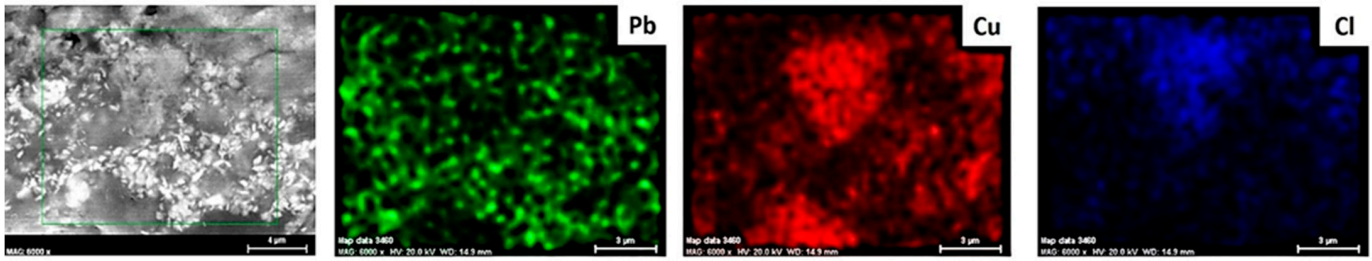


Figure 6. EDX mapping of sample green 10.

As a green pigment, atacamite has been detected in some artworks from Seville [18–20]. Basic copper chlorine (atacamite) has been detected in some wall paintings within the Real Alcazar: those of the Cenador del Leon close to the Pabellón de Carlos V [18], Mirador de la Reina, and Baños de Doña Maria de Padilla [19]. The green colour of the wall paintings from the Monastery of San Isidoro del Campo was due to the presence of the mineral atacamite [20]. In cultural heritage artifacts, there is no agreement on whether atacamite was used intentionally as a pigment or if was produced through the degradation processes of copper-based pigments. Atacamite may be synthesized using various methods. The copper halide mineral, with the chemical formula $Cu_2Cl(OH)_3$, is found in northern Chile, Peru, Bolivia, and Mexico, and was used in South America as a green pigment [32]. In Europe, atacamite is a rare mineral. Therefore, it was a long time before all the pigment compendia included atacamite among the green pigments. The last decades have shown that atacamite can be found in Swedish European medieval paintings [32].

Sample 4

This sample (Figure 3c) consisted of a mixture of three different pigments. In this sample, the consolidation product was also detected (described in Section 3.1), which made it difficult to characterize the different components of the polychrome. Only the punctual chemical analyses performed using EDX facilitated the characterization of the different pigments. Similar to some of the previously studied samples, sample 4 showed a high percentage of carbon (C), attributed to the presence of the consolidating products. The punctual chemical analyses showed the presence of a high percentage of silicon (Si) (Table 1 and Figure S3d). In addition, elements such as potassium (K), iron (Fe), cobalt (Co), and arsenic (As) were also present and were attributed to the presence of smalt, similarly to sample 1. The punctual chemical analyses of other zones showed particles constituted by copper (Cu) and chlorine (Cl) (Table 1 and Figure S3e), and other punctual analyses showed the presence of only copper (Cu) (Table 1 and Figure S3f). These results confirmed the presence of two other components based on chlorine (Cl) and copper (Cu) (suggesting the presence of atacamite) and others only constituted by copper (Cu) (very possibly due to the presence of malachite). The EDX analyses agreed with a mixture of three pigments of green and blue colours. Under this coloured layer appeared other layers constituted by lead (Pb). The XRD analyses clearly showed the presence of cerussite, hydrocerussite,

and calcite, which were attributed to the preparatory layer of the pigments and the rock material. Malachite, smalt, and atacamite were not detected, possibly due to their low content in the sample.

The malachite pigment has been employed in Sevillian artworks, mainly in the wall paintings from City Hall made on rock support [8,9]; Real Alcazar, in Patio de las Doncellas [21]; and the Palace of King Pedro I [22]. The malachite pigment is prepared from the basic copper carbonate mineral ($CuCO_3 \cdot Cu(OH)_2$) through careful selection, grinding, and sieving. The use of malachite in artworks runs closely parallel to that of azurite. Malachite was widely employed in Europe until the 19th century, when artificial green pigments supplanted it.

Sample 5

The elemental chemical analysis of sample 5 (Figure 3d), performed using the EDX analyser, showed a high percentage of carbon (C). The punctual chemical analyses showed a high percentage of carbon (C) and copper (Cu) (Table 1 and Figure S3g), which were associated with the analyses and could have been due to the presence of an artificial organic copper pigment, possibly copper resinate. The other punctual chemical analyses also detected copper (Cu) and chlorine (Cl) (Table 1 and Figure S3h), which were attributed to atacamite. These chemical analyses agreed with a mixture of pigments: organic green copper pigment and atacamite. Analyses of the underlayer showed high percentages of lead (Pb) (Table 1 and Figure S3i). The stone support, similar to the other studied samples, was constituted by calcium (Ca) (Table 1 and Figure S3j).

Copper resinate is formed by dissolving copper acetate, Verdigris, or other copper-based pigments in resinous solutions, such as balsam or Venice turpentine. Verdigris ($Cu(C_2H_3O_2)_2 \cdot 2Cu(OH)_2$) is copper dibasic acetate, prepared by exposing copper to the vapours of fermenting vinegar. Verdigris has been mentioned as a component of various artworks from Seville [23] (Carmelitas Saints portraits from Descalzos Church in Ecija), although there have been problems with its unambiguous identification.

3.2.3. Turquoise Colour

Sample 9 was located at the bottom of the stone carving and showed a grey colour (Figures 2e and 3e). The colour was affected by the treatment applied during the conservation processes. The measurements of the colour showed values of L* = 28.44 $\pm$ 1.14, a* = 0.26 $\pm$ 0.22, and b* = 7.10 $\pm$ 0.39 (Table S1). In addition to the observation of the consolidation product using SEM (see Figure S1), the EDX analyses (Table 1 and Figure S4a) showed the presence of titanium (Ti) (the relative intensities of the energy peaks and the number of peaks agreed with the presence of titanium, K_α(Ti) = 4.5 keV, K_β(Ti) = 4.9 keV, and not of barium, L_α(Ba) = 4.5 keV, L_β(Ba) = 4.8 keV, L_γ(Ba) = 5.5 keV), accompanied by a high percentage of carbon (C). The punctual chemical analyses showed the presence of a high percentage of calcium (Ca), possibly from the stone support material, and sulphur (S) (Table 1 and Figure S4b). In the other punctual chemical analyses (in the polychrome), a high percentage of iron (Fe) and silicon (Si) were found, with a small percentage of manganese (Mn) and calcium (Ca) (Table 1 and Figure S4c). Figure S4d depicts the EDX spectrum corresponding to the general analysis of sample 9. The spectrum showed the presence of calcium (Ca), sulphur (S), lead (Pb), iron (Fe), titanium (Ti), manganese (Mn), and silicon (Si). The semiquantitative analysis of sample 9 resulted in the following (in % *w*/*w*): CaO = 49.37; PbO = 27.83; SO_3 = 15.57; Fe_2O_3 = 3.28; SiO_2 = 2.25; MnO = 0.37; and TiO_2 = 0.28.

The presence of gypsum ($CaSO_4 \cdot 2H_2O$, PDF 33-1161; signals by XRD at 2Θ = 11.7°, 20.8°, 23.4°, 29.2°, and 31.2° were present in the sample) due to the presence of sulphur and titanium (Ti), together with the consolidation agent, represented important differences with respect to the previous samples. The localization of this sample, at the bottom, may be critical for detecting higher degrees of contamination and alteration or perhaps an ancient restoration process, which could explain the presence of gypsum. There are two

different explanations for the presence of titanium. One is the presence of titanium white pigment (TiO_2), as has been detected in the other scientific study performed on a Juan de Oviedo y de la Bandera wood sculpture, that of the Virgen del Buen Aire (sample E36Q10) [10]. Otherwise, TiO_2 nanoparticles may have been used to develop photocatalyst films to induce self-cleaning properties together with the consolidating products, as recently mentioned [33], although the addition of TiO_2 could have affected the physical properties of the supports.

3.2.4. Red Colour

Three different hues were observed when studying the three red colour samples (3, 2, and 11) (Figure 3f–h). Samples 3 (Figure 3f) and 2 (Figure 3g) corresponded to red and sample 11 (Figure 3h) corresponded to a brown-orange hue. Comparatively, the colourimetric values of samples 3, 2, and 11 showed numeric data from 25.92 (sample 3) to 38.29 (sample 11) in L*. A higher brightness was observed for sample 11. Low values of a* and b* were collected from samples 3 (average a* and b* values of 6.62 and 6.46) and 2 (average a* and b* values of 2.65 and 6.59) (Table S1), perhaps due to the presence of higher amounts of carbon in these samples. The underlayers below these red samples showed a composition based on lead (Pb), similar to the samples previously studied with blue, green, and turquoise colours.

Samples 3 and 2

Figure 3i shows the red-coloured layer on the Pb-based preparatory layer and the rock material, which was clearly distinguished by its whitish colour. The XRD diffractogram of sample 3 (Figure 5c) showed the presence of cinnabar (HgS, PDF 42-1408; peaks at $2\Theta = 26.5^\circ$, 28.2°, and 31.2°), cerussite, hydrocerussite, and calcite. The EDX punctual chemical analyses of sample 3 showed the presence of mercury (Hg) and sulphur (S) (Table 1 and Figure S5a), which are characteristic of cinnabar or vermilion pigment. Both are names assigned to a single chemical composition (HgS) of different origins, with the first being natural and the second being synthetic. In addition, the general EDX analyses of this sample (Table 1 and Figure S5b) showed the presence of silicon (Si), aluminium (Al), sodium (Na), potassium (K), and iron (Fe), which were attributed to minerals that accompanied the cinnabar mineral. A high percentage of lead (Pb) also appeared, which was attributed to the underlayer, and calcium (Ca) appeared from the original rock support. The mapping analysis of these samples carried out using EDX showed the presence of particles constituted by mercury (Hg), lead (Pb), and calcium (Ca) (Figure 7). The semiquantitative estimation of the composition showed the following values (in % w/w): PbO = 37,88; HgO = 23,45; SO_3 = 22,91; CaO = 10,36; K_2O = 9.38; SiO_2 = 3.90; and Fe_2O_3 = 0.36, according to the data described previously. The Raman spectroscopy analysis confirmed the presence of cinnabar, thanks to the signals at 255, 283, and 343 cm^{-1} [16,20] (Figure 4c). Very similar results were observed for sample 2.

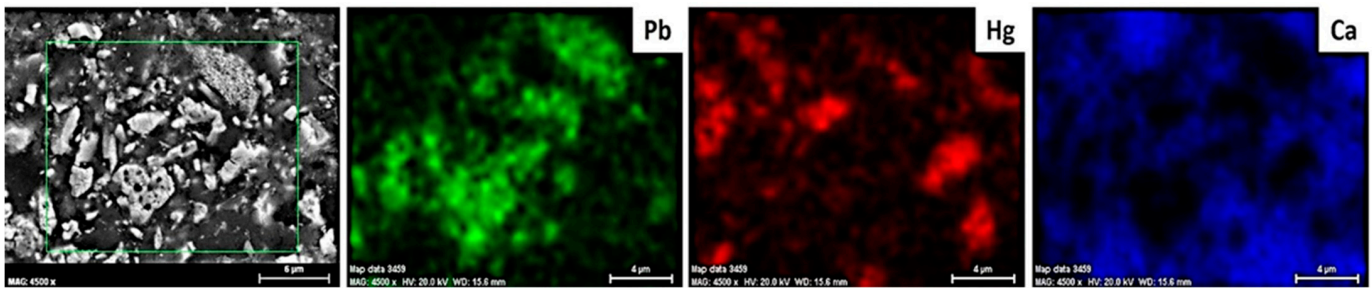


Figure 7. EDX mapping of red sample 3.

Cinnabar commonly occurs in veins and small impregnations associated with volcanic activity and hot spring action. It is found in association with other minerals such as quartz,

pyrite, and calcite [16,23]. Vermilion is artificially obtained through dry or wet methods. The dry method was used by ancient Chinese and Dutch alchemists by combining mercury and molten sulphur, which were heated into retorts, producing red mercury sulphide. For the wet method, both mercury and sulphide were ground together in water and caustic potash was added to complete the transformation. In samples 3 and 2, the detection of other components (based on silicon, potassium, etc.) using EDX, together with the heterogeneity of the particle sizes (Figure 7), seems to indicate the natural origin of the red pigment. Vermilion has been found in various rock artworks, such as those from the Seville City Hall decoration [9]. Cinnabar and vermilion have been employed in different epochs and artworks from Seville: wall paintings from the Real Alcazar [19,22,23], easel paintings [16,17,23], etc. Vermilion was also detected in the Virgen del Buen Aire sculpture (sample E36Q6) [10].

Sample 11

The elemental analysis of sample 11, performed using the EDX analyser, indicated the presence of silicon (Si), lead (Pb), iron (Fe), manganese (Mn), calcium (Ca), and aluminium (Al) (Table 1 and Figure S5c). Other punctual chemical analyses clearly showed the presence of iron (Fe) and manganese (Mn) (Table 1 and Figure S5d), which were responsible for the colour. The Micro-Raman spectroscopy of the sample showed peaks at 220, 288, 405, 492, and 603 cm^{-1}, which were attributed to red earth (hematite or Mars red and clay minerals) [23], as well as some manganese oxides with signals at 560 and 623 cm^{-1} (manganite, MnO(OH)) and 664 cm^{-1} (pyrolusite, MnO_2) [34] (Figure 4d). The pigments responsible for the brownish colouration of sample 11 were red earth pigments (Fe_2O_3 + silicoaluminates) together with possibly sienna earth pigments (Fe_2O_3 + Mn oxides + silicoaluminates).

Earth pigments include mixtures of clays and metal oxides, ochres, siennas, and umbers, and they usually show a high stability. The hematite mineral (α-Fe_2O_3) has been frequently applied to obtain a red colour in artworks. Spanish red earth contains more than 85 wt% iron oxide and 15% silicoaluminates [35]. Like ochre, sienna is hydrated ferric oxide with silicoaluminates; sienna normally contains 50%–70% iron oxide, silicoaluminates, and manganese dioxide (0.6%–1.5%). Earth pigments have been employed since prehistoric times. In Seville, they were employed in all the epochs [15–21,23]. Also, earth pigments were detected in samples E36Q1, E36Q3, E36Q4, E36Q5, E36Q6, E36Q7, E36Q8, E36Q9, and E36Q10 from the Virgen del Buen Aire sculpture [10].

3.2.5. Yellow Colour

Figure 3j shows images of sample 6, with a yellowish colour. The colourimetric values were L* = 36.21 ± 3.55, a* = 2.83 ± 0.57, and b* = 17.95 ± 2.72, which are characteristic of yellowish tones (Table S1). The elemental chemical analysis of the sample, performed using the EDX analyser (Table 1 and Figure S6a), indicated the presence of high percentages of calcium (Ca) and lead (Pb), which were attributed to the support underlayer of the pigment (assigned to the lead-based compounds and white lead) and the stone sculpture (assigned to calcium-based compounds and biocalcarenite). Silicium (Si), aluminium (Al), and iron (Fe) were also present in high percentages (Table 1 and Figure S6a), suggesting the presence of a yellow ochre pigment (constituted by α-FeOOH, clay minerals, and quartz).

Red and yellow pigments are generally associated with iron oxides or, specifically, hematite (α-Fe_2O_3) and goethite (α-FeOOH). Goethite has been largely detected in Seville artworks [17,20,21,23].

3.2.6. Black Colour

The sample numbered 8 clearly exhibited a black colour and the underlying whitish preparatory layers (Figure 3k). The elemental chemical analyses of the sample (Table 1 and Figure S6b) indicated the presence of calcium (Ca) and lead (Pb), which were attributed to the preparatory layer (cerussite and hydrocerussite) of the pigment layers and the

rock under the polychrome (constituted by calcite). A high percentage of carbon (C) was found in the black colour. Additionally, phosphor (P), calcium (Ca), and silicon (Si) were detected and assigned to the presence of calcium phosphate (Table 1 and Figure S6c). These data confirmed the possible presence of both carbon black and bone black. The Raman spectroscopy analysis confirmed the presence of carbon black pigment, thanks to the presence of wide bands at 1366 and 1592 cm^{-1} (Figure 4e) [19]. The values of a* were the lowest of all the measured samples, ranging from 1.28 to −1.75, close to the achromatic zone (Table S1).

Bone black, or animal black, is made by charring animal bones, and carbon black, or lamp black, is made by charring natural gas, oil, wood, and other organic materials [35]. Bone black is blue-black and denser than carbon black. Carbon is a very stable pigment in acid and alkalis and is only destroyed by burning at very high temperatures [35]. Bone black [19,24] and carbon black [9,16,19,20] have been found in Sevillian artworks. Bone black was also detected in sample E36Q3 from the Virgen del Buen Aire [10].

3.2.7. Golden Sample

Figure 3l shows the golden sample, 7. The image clearly shows a golden layer deposited on a white layer. The general microanalysis reported from the EDX in Table 1 and Figure S6d showed the presence of gold (Au), calcium (Ca), and lead (Pb). In addition, silicon (Si), aluminium (Al), and iron (Fe) appeared. The XRD diffractogram of the superficial layer indicated the presence of gold (Au, PDF 04-0784; peaks at $2\Theta = 38.2^{\circ}$ and 44.4°) (Figure 5d). The semiquantitative chemical analysis of the preparatory layer of the gold foil displayed the following percentages (in % w/w): CaO = 51.37, PbO = 31.57, SO_3 = 10.37, SiO_2 = 2.92, Fe_2O_3 = 2.39, and Al_2O_3 = 0.93. The XRD analysis confirmed the presence of cerussite, hydrocerussite, and calcite as the main components of the preparatory layer.

Gilding is the technique of applying a thin sheet of gold on a firm support. For the application of gold foil on external surfaces, the "mordant" gilding technique was generally used. It employed an adhesive or water. Usually, this technique was used for a wood support, which was covered by a layer of gypsum. On it, red bole was laid, polished into a fine finish, and allowed to dry. The surface was then wetted with water and gold leaf was put on it immediately. This gilding technique was applied to the polychromed wood sculpture of Virgen del Buen Aire [10]. In the samples studied for this article, this method was not the method employed by Juan de Oviedo y de la Bandera. For the gilding of the polychromed stone sculpture, the sculptor used a technique applied by his master, Juan Bautista Vázquez, who made the gilding on stone of the Meeting Room in Seville City Hall [9,36]. Juan Bautista Vázquez, in a similar way to Juan de Oviedo y de la Bandera, used a layer based on cerussite and hydrocerussite on the stone, which served as a preparing layer of the gilding layer. These compounds have been detected in other Sevillian gildings: wall paintings of the Monastery of La Cartuja and polychromed ceramics from Pardon Portico of the Seville Cathedral [36,37].

4. Conclusions

The substrate used to manufacture the entrance of the Madre de Dios Convent was calcarenite stone, whose composition was based on calcite. On this support was deposited a layer of white lead constituted by cerussite and hydrocerussite, which was employed as support for the pigment layers. The employment of these materials indicates a different technique than the usual technique employed in sculptures, which was carried out with pigments laid on a gypsum layer and animal glue. Conservation treatments with acrylic resin (very possibly Paraloid B72) were used to adhere the superficially raised paint material to the rock during the recent restoration carried out in the Convent.

Regarding the composition of the polychrome made by Juan de Oviedo y de la Bandera, the blue colour was made using smalt, a glass-based pigment formed by potassium silicates and cobalt ions. Several pigments were used to obtain the green colours: one of them with only atacamite; another with a mixture of smalt, atacamite, and malachite; and the third

green hue was obtained with a mixture of an organic pigment (possibly copper resinate) and atacamite. The pigment used to obtain the red colour was cinnabar. The ochre-brown and yellow colours were obtained using red earth (hematite or Mars red and clay minerals) and yellow ochre (goethite, clay minerals, and quartz), respectively. The pigments used to obtain the black colours were carbon black and bone black, composed of carbon and calcium phosphate. The presence of consolidation products and mixtures of pigments did impair the characterization of the materials forming the artwork. The pigments detected in the entrance of the Madre de Dios Convent matched with those used in Seville in the 16–17th centuries. Also, some of them were detected in the Virgen del Aire sculpture, made on wood by Juan de Oviedo y de la Bandera in a similar period.

For gilding purposes, a layer of white lead was detected beneath the gold foil. Similar results were found in polychromed stones and ceramics from the Seville City Hall and the Seville Cathedral, made in a close epoch.

The investigation performed facilitated the restoration processes of the polychrome of the façade of the Madre de Dios Convent and also provides very valuable artistic and historical information about Juan de Oviedo y de la Bandera, one of the most prolific artists in the Baroque period in Seville.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min14030225/s1. Figure S1. SEM micrographs showing the consolidating products on polychrome: (a) sample 2; (b) sample 4; (c) sample 5. IR spectrum corresponding to the consolidation product (d). Figure S2. EDX spectra of the blue sample: (a) 1, punctual zone 1; (b) 1, punctual zone 2; (c) 1, general support layers. Figure S3. EDX spectra of the green samples: (a) 10, general; (b) 10, punctual zone 1; (c) 10, general support layers; (d) 4, punctual zone 1; (e) 4, punctual zone 2; (f) 4, punctual zone 3; (g) 5, punctual zone 1; (h) 5, punctual zone 2; (i) 5, general support layer; (j) 5, stone support. Figure S4. EDX spectra of the turquoise sample: (a) 9, general surface; (b) 9, general support layers; (c) 9, punctual zone 1; (d) 9, general. Figure S5. EDX spectra of the red samples: (a) 3, punctual zone 1; (b) 3, general; (c) 11, punctual zone 1; (d) 11, punctual zone 2. Figure S6. EDX spectra of the yellow, black and golden samples: (a) yellow 6, general; (b) black 8, general support layers; (c) black 8, punctual zone 1; (d) golden 7, general surface. Table S1. Colourimetric values of the samples.

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