






## Article

# Paint, Colour, and Style: The Contribution of Minerals to the Palette of the Descent from the Cross, Attributed to the Portuguese Painter Francisco João (act. 1558–1595)

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**Abstract:** The paint materials and techniques of *The Descent from Cross*, a panel painting attributed to the Portuguese painter Francisco João (act. 1558–1595), were investigated with a combination of visible, ultraviolet, and infrared imaging and an analysis of paint samples with microscopic, spectroscopic, and chromatographic techniques. The colour palette is composed of lead white, lead-tin yellow, minium, vermilion, ochres of different colours, umber, smalt, azurite, verdigris, charcoal black, and a variety of different-coloured red lakes made of brazilwood and cochineal. An oil-based medium was identified. The characterisation of the pigment mixtures, paint build-up, and particular paint handling techniques enabled us to determine their role in the style and formal appearance of this painting and to discuss Portuguese painting practices in the larger context of 16th-century European painting. Mineral and elemental associations or impurities in the blue pigments, as well as degradation issues affecting minium, and smalt paints were reported. In particular, the deterioration of the glass matrix in some of the smalt particles mixed in lead white paint raises special concern.

**Keywords:** minerals; painting; colour; materials; technique; degradation; 16th century; Portugal



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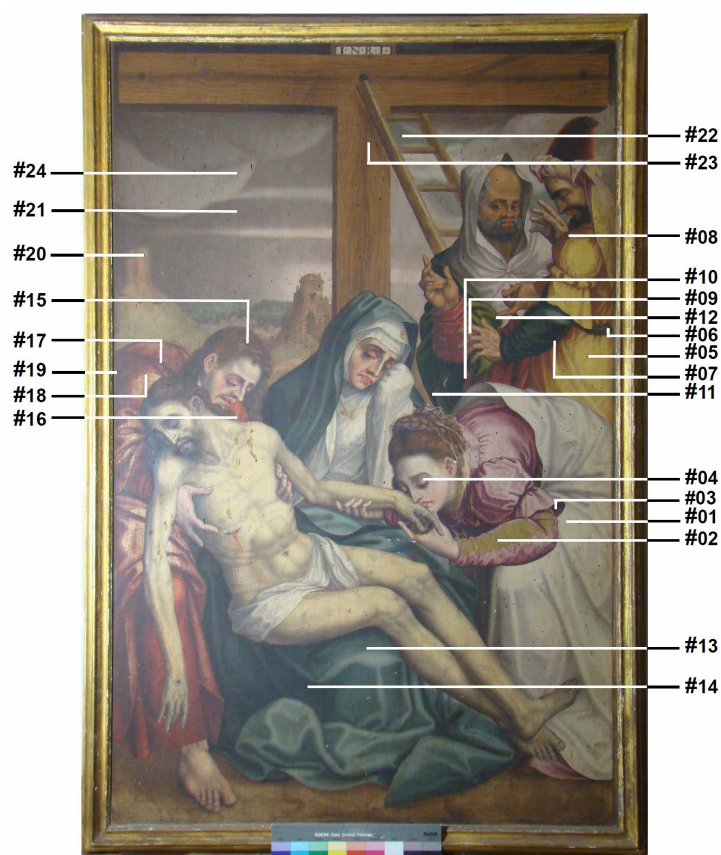
## 1. Introduction

Naturally occurring minerals have been an integral part of painters' palettes and are chosen for their colour, optical properties, handling qualities, availability, and cost. While colour could be a determining factor in their choice for painting, the properties of certain materials in a given binder have also been shown to modify the paint's rheology, drying time, and translucency and to serve as an inorganic substrate for organic dyes in the case of lake pigments. In 16th-century painting practice, colour, and style were largely dependent on the quality and availability of pigments, on the nature and rheology of the binder, and on the technique and expertise of the master in working with both. The analytical characterisation of the materials and the build-up of the paint layers therefore supports any approach to the formal aspects of the final painted image and contributes to a wider understanding of 16th-century Western European painting practice.

In the context of an investigation on mannerist-painted altarpieces in the Alentejo region, this paper examines the materials and techniques responsible for the colour and stylistic appearance of the panel *The Descent from the Cross* (166 cm × 106 cm), attributed, on a stylistic basis, to the workshop of Francisco João, the most renowned painter active in southern Portugal between 1558 and 1595 [1–4]. Dated around 1580, the painting is part of a dismembered altarpiece that was removed from its original structure and transferred

from the church of Graça to the church of São Francisco, which are both located in Évora [5]. This work complements previous research on the use of ground glass in the red glazes of this painting [6].

The painting represents the biblical scene of *The Descent from the Cross*, with the characters gathered in the foreground around the central figure of the Virgin, seated at the feet of the Cross, and holding the dead body of Christ (Figure 1). The scene is set against a pale green background landscape with a stormy light grey sky, which is suitable for the topic depicted. Despite the use of vivid reds and a few deeper greens in some of the garments, the colour palette of blue, green, pink, and yellows has an overall light-valued pastel tonality that recalls the fresco technique, which has a long tradition in southern Portugal, notably in Évora.



**Figure 1.** *The Descent from the Cross*, attrib. Francisco João (doc. 1558–1595), 166 cm × 106 cm, Church of São Francisco, Évora, Portugal. The figure shows the location where the samples (from #01 to #24) were taken.

The investigation was based on the visual inspection of the painting's surface with imaging techniques based on visible, ultraviolet, and infrared radiation and on the analysis of microsamples with microscopic, spectroscopic, and chromatographic techniques. The analytical results were interpreted within the frame of the wider 16th-century European painting practice. Aspects related to paint degradation and their influence on the actual perception of the composition are discussed.

## 2. Experimental Section

The painting was subjected to a detailed and careful inspection of the painting's surface, in situ, with incident and raking light (Vis) and ultraviolet radiation (UV). Digital photographs were made with a Canon Powershot G15 camera. Infrared reflectography (IRR) was obtained with a high-resolution Osiris camera equipped with an InGaAs sensor (900 to 1700 nm).

Twenty-four samples of the main colours were collected in areas adjacent to paint loss. Part of each sample was embedded in an epoxy resin (Struers Specifix 40), polished as a cross-section, and studied with a Leica DM2500 optical microscope. The observations were made in reflection mode under visible (OM-Vis) and ultraviolet radiation (OM-UV). For OM-UV, a bandpass filter BP 340-380 for the excitation radiation, a dichromatic mirror, and a suppression filter LP425 for the fluorescence radiation were used. The images were recorded with a Leica DFC290HD digital camera (Supplementary Material—Table S1).

Subsequently, to characterise the stratigraphy and identify the pigments, fifteen uncoated cross-sections, representative of the main colours, were selected for analysis with scanning electron microscopy (SEM) with energy-dispersive X-ray spectrometry (EDX) on a variable-pressure scanning electron microscope Hitachi 3700N, operated at 40 Pa and 20 kV, with a BRUKER Contact 200 EDX detector. Backscattered electron images (BSE) and EDX maps of major elements were obtained, as well as EDX spectra of single particles, which provided semi-quantitative data.

Micro-Raman spectroscopy ( $\mu$ -RS) was carried out on six cross-sections as a complementary technique for the distinction between small red particles of minimum and vermilion in red and flesh-coloured paints (#04, #08, #09, #10, #16), and for the identification of the type of lead-tin yellow pigment used (#02). A multiple-laser-dispersive Raman spectrometer (Renishaw in Via) with a high-power diode laser (Toptica Photonics XTRA) at 785 nm, coupled with a Leica DMLM microscope with enclosure using 5 $\times$  to 100 $\times$  objectives, was used.

The unmounted parts of thirteen samples were analysed with Fourier transform infrared micro-spectroscopy (FTIR) with the aim of identifying the main class of binder in different colours; the presence of degradation products and inorganic components, especially in the ground layer; and some characteristic pigments in the paints. The choice of samples was limited to the available material, and some paints, notably the green glazes, did not have enough samples to be analysed with this technique. The spectra were obtained using Attenuated Total Reflection, for the separated layers with a Bruker Tensor 27 spectrometer coupled to a Hyperion 3000 microscope with an MCT detector, controlled using the OPUS 7.2 software from Bruker Optik GmbH 2012. Each spectrum was collected in the 4000–600  $\text{cm}^{-1}$  region, using 64 scans and a resolution of 4  $\text{cm}^{-1}$ .

The red lake dyestuffs of organic pigments were analysed in five samples (#03, #10, #16, #17, and #19) after their mild extraction from the lakes [7] with the HF 2M in mixture water/organic solvents, 1:1 with high-performance liquid chromatography (HPLC) using a Spectra-SYSTEM from Thermo Scientific. This device consisted of a P1000XR pump, an AS3000 autosampler equipped with a 20  $\mu\text{L}$  loop, and a UV6000 UV-Vis DAD detector with a range from 200 to 800 nm equipped with a 50 mm detector cell. The analytical column was an Alltima RP C18, 5  $\mu\text{m}$ , 250 mm  $\times$  4.6 mm (Altech, Lokeren, Belgium). The eluents were (A) MeOH, (B) 5% ACN in water, (C) 0.1% TFA in water, and (D) ACN. The flow rate was 1 mL/min. The elution program was carried out without switching with a typical gradient as follows: 0–15 min: 90B, 10C; 15–55 min: 15A, 60B, 10C, 15D; 55–64.5 min: 45A, 10C, 45D; 64.5–70 min: 90D, 10C. The temperature at the chromatography laboratory was maintained between 20  $^{\circ}\text{C}$  and 22  $^{\circ}\text{C}$  using air conditioning.

Analyses via OM, SEM-EDX, and FTIR were performed in the HERCULES laboratory, University of Évora, Portugal, whereas  $\mu$ -RS and HPLC analyses were performed in the IRPA-KIK laboratory in Brussels, Belgium.

### 3. Results and Discussion

#### 3.1. Support and Preparatory System

The *Descent from the Cross* was painted on an oak panel (visual identification of the wood on the back of the panel), prepared with a single white ground layer with a thickness of c. 30  $\mu\text{m}$ , covered by a c. 5  $\mu\text{m}$  thick, medium-rich priming layer, also known as *imprimitura*. The ground layer, analysed with SEM-EDX and FTIR, was found to be made of *gesso grosso*, a coarse material that, in this painting, mainly contained an-

hydrite with small amounts of calcium sulphate dihydrate, bound in animal glue [8] (Supplementary Material—Figure S1). The *imprimitura* was lightly toned with the occasional red particle, identified with SEM-EDX as vermilion (Supplementary Material—Figure S2). Beyond its role in reducing the absorbency of the porous gesso ground, the vermilion-toned *imprimitura* would presumably have imparted an off-white warm tonality to the overall surface to be painted.

A carbon-based dry underdrawing was detected using infrared reflectography, and its black particles were observed, using optical microscopy, to be located over the *imprimitura* (Supplementary Material—Figure S3). An examination of the infrared images revealed a simple contour underdrawing that outlines the main figures and elements of the composition, marking some of the drapery's folds and features of the faces. The underdrawing has a two-dimensional character and was used as a guide in the painting stage.

### 3.2. Binder

Micro-FTIR analysis identified an aged oil as the binding medium. Infrared spectra showed the characteristic  $\nu(\text{C-H})$  bands at 2926–2919 and 2858–2850  $\text{cm}^{-1}$ , together with the ester carbonyl  $\nu(\text{C=O})$  band at  $\sim 1735\text{--}1730\text{ cm}^{-1}$ , with the latter often shifting to  $\sim 1714\text{--}1703\text{ cm}^{-1}$  due to carboxylic acids formed by triglyceride hydrolysis [9,10]. In lead-rich paints, the presence of a strong  $\nu_{\text{as}}\text{COO}$  band centred at  $\sim 1537\text{--}40\text{ cm}^{-1}$  or appearing as a stretch doublet at 1535–1516  $\text{cm}^{-1}$  confirmed that the carboxylic acids have reacted to form lead soaps [9,11,12] (Supplementary Material—Figures S4 and S5). Metal oxalates were detected in all red glazes through the bands at 1317–1315  $\text{cm}^{-1}$  ( $\nu_{\text{a}}(\text{C-O})$ ) and 783–781  $\text{cm}^{-1}$  ( $\delta(\text{O-C=O})$ ). They may be related to the biodegradation of these medium-rich aged layers [13] (Supplementary Material—Figure S6).

HPLC analysis of all red glazes detected dehydroabiatic and 7-oxo-dehydroabiatic acids, two degradation products of pine resin (*Pinacea* sp.) [14]. This type of resin could have been used as a varnish or mixed in the binding medium in order to raise its refractive index and thus increase the transparency and saturation of the glaze, as some historical treatises suggest [15], and has been analytically found in paintings from this period [16,17].

### 3.3. Pigments and Paints

Results regarding the pigments identified in the paints and their mixtures are presented in Table 1.

**Table 1.** Pigments identified and their mixtures.

Colour	Pigment Mixtures		Number of Pigments			Painted Motif	Layer	Sample Number
	Colour Mixture	Pigments	Total	Wh.	C			
Yellow	Y1	Lead–tin yellow + Lead white	2	1	1	Drapery	U U/T	#02 #05
Orange	O1	Lead–tin yellow + Minium + Lead white + Red lake (tr.)	4	1	3	Drapery	U	#06
	O2	Minium + Vermilion	2	0	2	Drapery	U/T	#08
Red	R1	Vermilion + Red lake + Lead white (tr.)	3	1	2	Drapery	U	#09
	R2	Vermilion + Red lake + Lead white (tr) + Vegetable black (tr.)	4	1	3	Drapery	U	#09
	R3	Vermilion + Red lake + Vegetable carbon black	3	0	3	Drapery	U	#10, #16
	R4	Vermilion + Red lake	2	0	2	Drapery	U	#10, #16



Table 1. Cont.

Colour	Pigment Mixtures		Number of Pigments			Painted Motif	Layer	Sample Number
	Colour Mixture	Pigments	Total	Wh.	C			
Pink	Pk1	Lead white + Red lake + Ochre (tr.) + Vegetable carbon black (tr.)	4	1	3	Drapery	U	#19, #17
	Pk2	Lead white + Red lake	2	1	1	Drapery	U T	#03, #17 #03
	Pk3	Red lake	1	0	1	Drapery	T U/T	#09, #10, #16, #17 #19
Purple	P1	Smalt + Azurite + Red lake + Lead white (tr.)	4	1	3	Belt	T	#06
Blue	B1	Azurite + Smalt + Lead white	3	1	2	Drapery, Sky	T	#07, #13, #22, #24
	B2	Lead white + Smalt	2	1	1	Drapery, Sky	U	#07, #13, #22
Green	G1	Lead–tin yellow + Lead white + Verdigris	3	1	2	Drapery	T	#02
	G2	Vegetable carbon black + Lead–tin yellow + Ochre + Lead white (tr.)	4	1	3	Drapery	U	#11
	G3	Vegetable carbon black + Lead–tin yellow + Lead white (tr.)	3	1	2	Drapery	U	#11
	G4	Verdigris	1	0	1	Drapery	T	#11
Flesh	F1	Lead white + Vermilion + Ochre + Umber (tr.) + Red lake (tr.) + Vegetable carbon black (tr.) + Azurite (tr.)	7	1	6	Live flesh	U	#04
	F2	Lead white + Vermilion	2	1	1	Live flesh	T	#04
Brown/ Ochre	Br1	Lead white + Ochre + Vermilion + Red lake (tr.) + Lead–tin yellow (tr.)	5	1	4	Cross	U	#24
	Br2	Lead white + Vegetable carbon black + Vermilion + Yellow lake (tr.)	4	1	3	Cross	T	#24

Note: tr.: Traces, very little amount of pigment; U: Underlayer; T: Top layer; Wh: White; C: Coloured. The information presented in this table is based on the analysis of 16 samples (=39 paint layers). Each pigment mixture corresponds to a paint formulation that was used by the painter in one or more areas (samples) of his composition.

### 3.3.1. Black and White

Vegetable carbon black and lead white were identified using FTIR and SEM-EDX as the main black and white pigments present in the paints. Lead white has a fine grain morphology and, in infrared spectra, was characterised by the presence of carbonate bands at ~1410, 1045, or 1051, and ~683  $\text{cm}^{-1}$ , along with a  $\nu(\text{OH})$  distension at ~3535  $\text{cm}^{-1}$  for hydrocerussite ( $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ) and the characteristic 839  $\text{cm}^{-1}$  stretching band for cerussite, the neutral lead carbonate commonly found in lead white [18] (Supplementary Material—Figures S4 and S5). Except for the red paints and translucent glazes, the opaque lead white pigment was mixed with all pigments, imparting a pastel tonality to the composition (Figure 1).

Charcoal, a vegetable carbon black obtained by charring plant materials, was identified based on its black colour (OM-Vis), its heterogeneous particle size and morphology (OM, SEM-BSE), its high carbon concentration, and the absence of phosphorus, a chemical marker for the alternative ivory or bone black (SEM-EDX) [19] (Supplementary Material—Figure S7). The black pigment was mainly added to the browns, albeit in a small concentration. It was further employed to shade the underpaints for the flesh tones and red or green glazes. Its negligible concentration in the surface paint layers accounts for the painting's clean colour palette (Figure 1).

### 3.3.2. Yellow, Orange, and Brown

Lead–tin yellow was the main yellow pigment identified. Its presence was confirmed through the detection of tin and lead using SEM-EDX in small particles with high atomic weight (SEM-BSE images). A Raman analysis of sample #02 identified the most common Type I variety of this pigment. This opaque, light-toned, yellow pigment was mainly used to model all yellow draperies, lighten the green paints, and, when mixed with red, to make the orange colour. Additionally, lead–tin yellow occurs in low concentration in the mixed ochre and browns of the Cross.

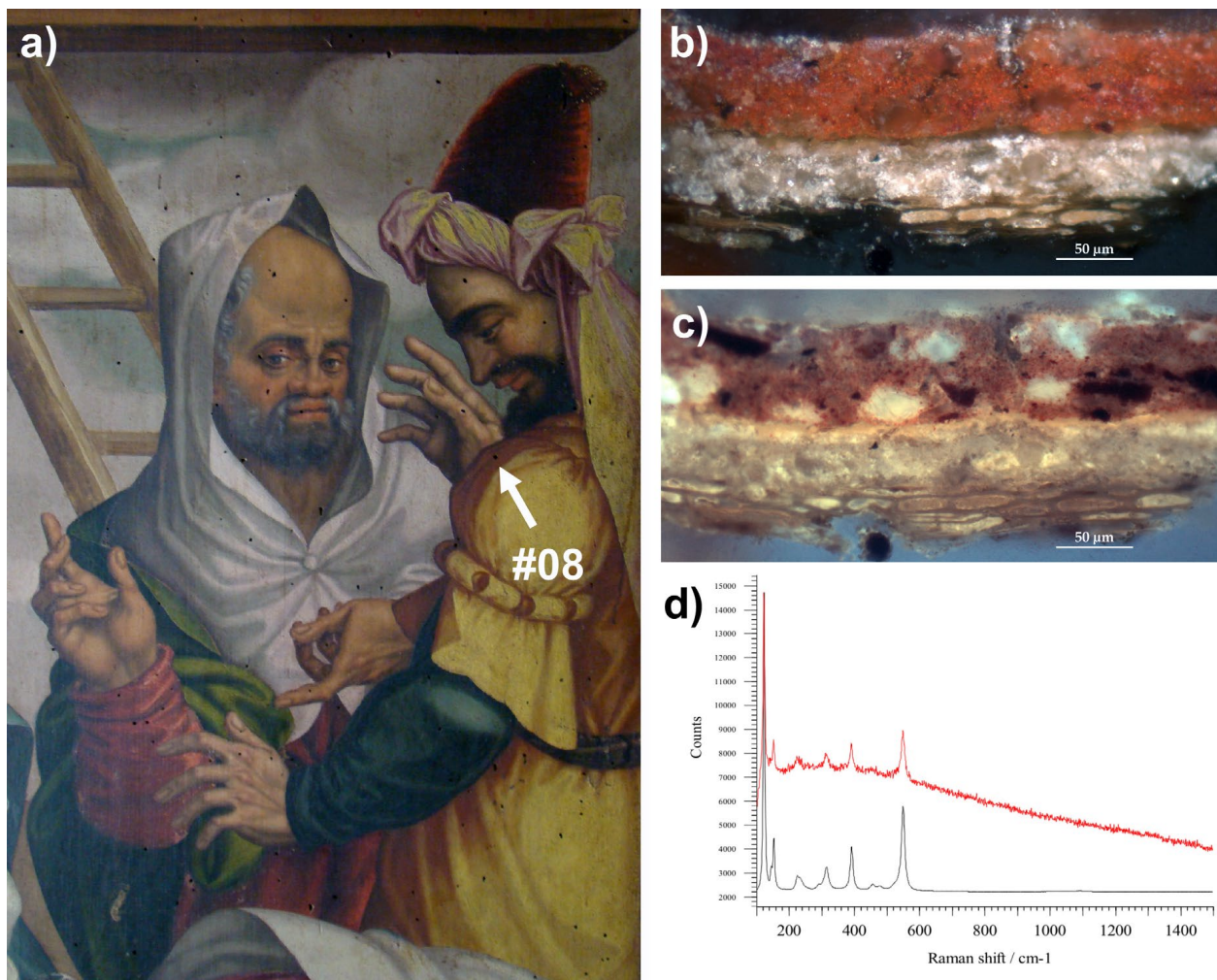
Iron-bearing ochre particles of yellow, brown, and reddish colours were detected through a combined analysis with optical microscopy and SEM-EDX (#04, #11, #17, #19, #24). These three coloured earth pigments were mixed to create the brown paint of the Cross. Brown ochre was further detected in the underlayers of the green glazed draperies, whereas the flesh tones contained mainly yellow and light brown ochres. A single particle of umber, characterised by its high iron and manganese concentrations, was also detected in the underpaint of the flesh tone of St. Magdalene's face (Supplementary Material—Figure S8). The limited sampling may account for this singular detection of a pigment that might have been more broadly used in this painting, presumably together with other ochre pigments.

### 3.3.3. Red

In addition to red ochre, minium, vermilion, and three types of red lake pigments were detected, mainly in the flesh tones and in the orange, red, pink, and purple draperies.

Minium, a red lead pigment identified using  $\mu$ -RS analysis (Figure 2), was mixed with vermilion or with lead–tin yellow to create the shades of the yellow draperies. Under optical microscopy, cross-sections of minium-rich paints (#06, #08) revealed the presence of large translucent masses (up to c. 50  $\mu$ m) that exhibited a strong fluorescence when viewed under UV radiation (Figure 2c). These masses probably correspond to aggregations of lead soaps, known as “inclusions”, which are commonly formed as a result of the reaction between the lead-giving pigment and the fatty acids produced during the hydrolysis of the oil binder [11,20–22]. Their abundance in these layers has led to an increased transparency of the paints used to shade yellow draperies, now perceived as ochre, that presumably would have been painted in a more intense vivid orange (Figure 2a). The same aggregations were also found in the lead–tin yellow paints (#02, #05), where their effect on the opacity of the layers is less pronounced due to the presence of lead white.

Vermilion, recognised based on its characteristic opaque, vivid hue when viewed on the paint surface or under the microscope, was identified via the detection of mercury associated with sulphur in elemental EDX analysis. This pigment was very often mixed with a red lake to develop the modelling of the mid-tones and highlights of the red draperies, thus avoiding the admixture of lead white, a pigment that would shift the red colour to a pink hue. Darker areas were shaded with the addition of a little charcoal black at the undermodelling stage.



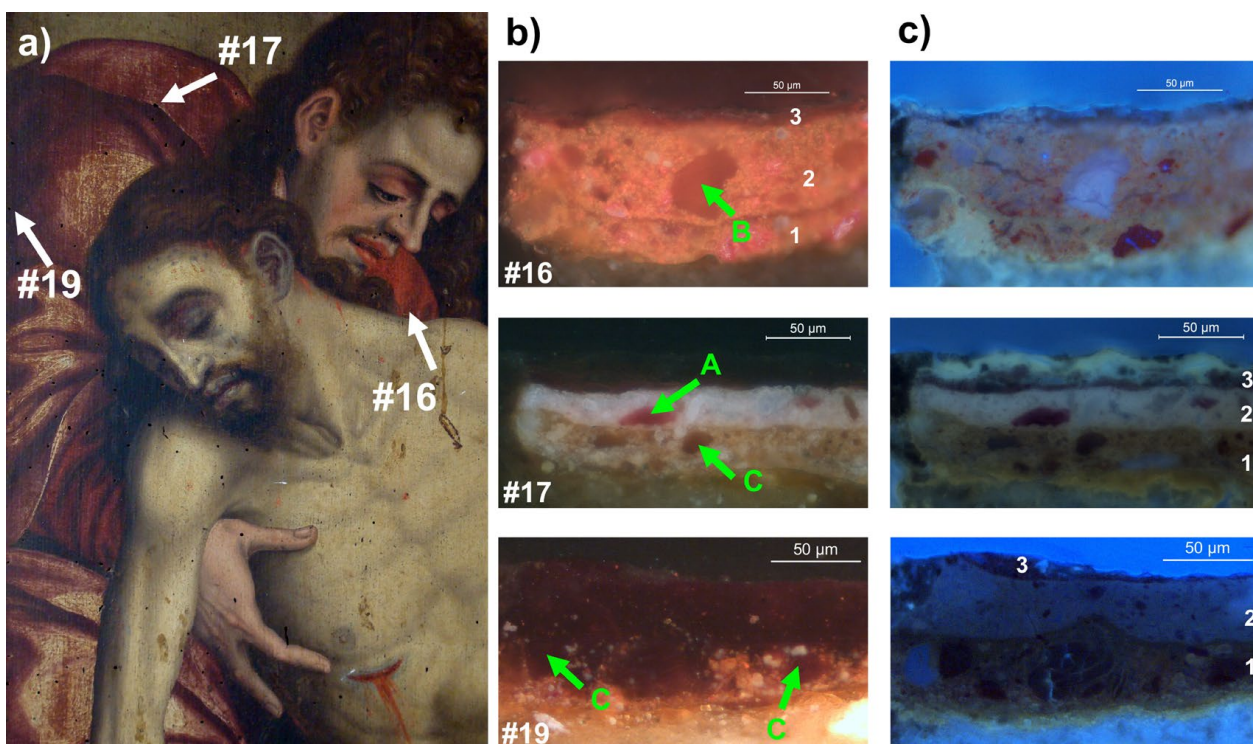
**Figure 2.** Detail of the figures in the background under incident light (a), with the location of sample #08 and the respective cross-sections under OM-Vis (b) and OM-UV (c); Raman spectra (d) of the minium paint from sample #08 (in red) and the minium reference (in black).

Translucent red lake pigments, obtained by precipitating a dye with an inorganic substrate, were used in pure form in the medium-rich glaze layers but also mixed with lead white or with blue pigments in order to formulate the pink and purple colours, respectively. Added in small quantities to red, orange, brown, and flesh-coloured paints, the red lakes broadened the range of hues that were possible to achieve with a standard base paint mixture. As mentioned in the introduction, ground glass was identified in the red glazes, where it could have been added for its optical and assumed siccative properties [6].

Microscopic examination of cross-sections enabled the distinction between at least three different types of red lakes, based on their colour, fluorescence, and morphology (Figure 3). The colour of red lake particles embedded in paint layers is very difficult to ascertain when examining the cross-sections under an optical microscope, as their translucency makes them dependent on the colour and degree of opacity of their surrounding matrix. Despite this interference, some lake particles found in the upper glaze layers and pink paints appear to have a purplish colour (OM-Vis). They have defined edges and elongated shapes and do not exhibit fluorescence under OM-UV (Figure 3, Lake A). Other lake particles, mostly mixed in the vermilion-rich undermodelling of red glazed draperies, mostly consist of rounded particles with non-defined edges and display a white or light pinkish fluorescence when viewed under OM-UV (Figure 3, Lake B). Finally, a third type of lake was exclusively and abundantly used in the ochre pinkish underpaint that serves as the base of the modelling of red and pink glazed draperies. This lake has a wide range of



particle sizes, is usually rounded, and has a burgundy brownish colour and no fluorescence when examined under UV (Figure 3, Lake C).



**Figure 3.** Detail of Saint John holding Christ with the locations of samples #16, #17, and #19 (a); cross-sections of samples located in (a) under OM-Vis (b) and OM-UV (c). The arrows in (b) locate the three types (A, B, C) of red lakes.

An HPLC analysis of five samples from red and pink glazed draperies detected the chromophores carminic acid and brazilein, extracted, respectively, from the scale insect cochineal and the redwood collectively known as “Brazilwood” (*Caesalpinia* spp.). Ellagic acid was detected in sample #19, collected from Saint John’s cloak, indicating, according to Jo Kirby and colleagues [23], that weighted silk could have been used as a source of the dyestuff.

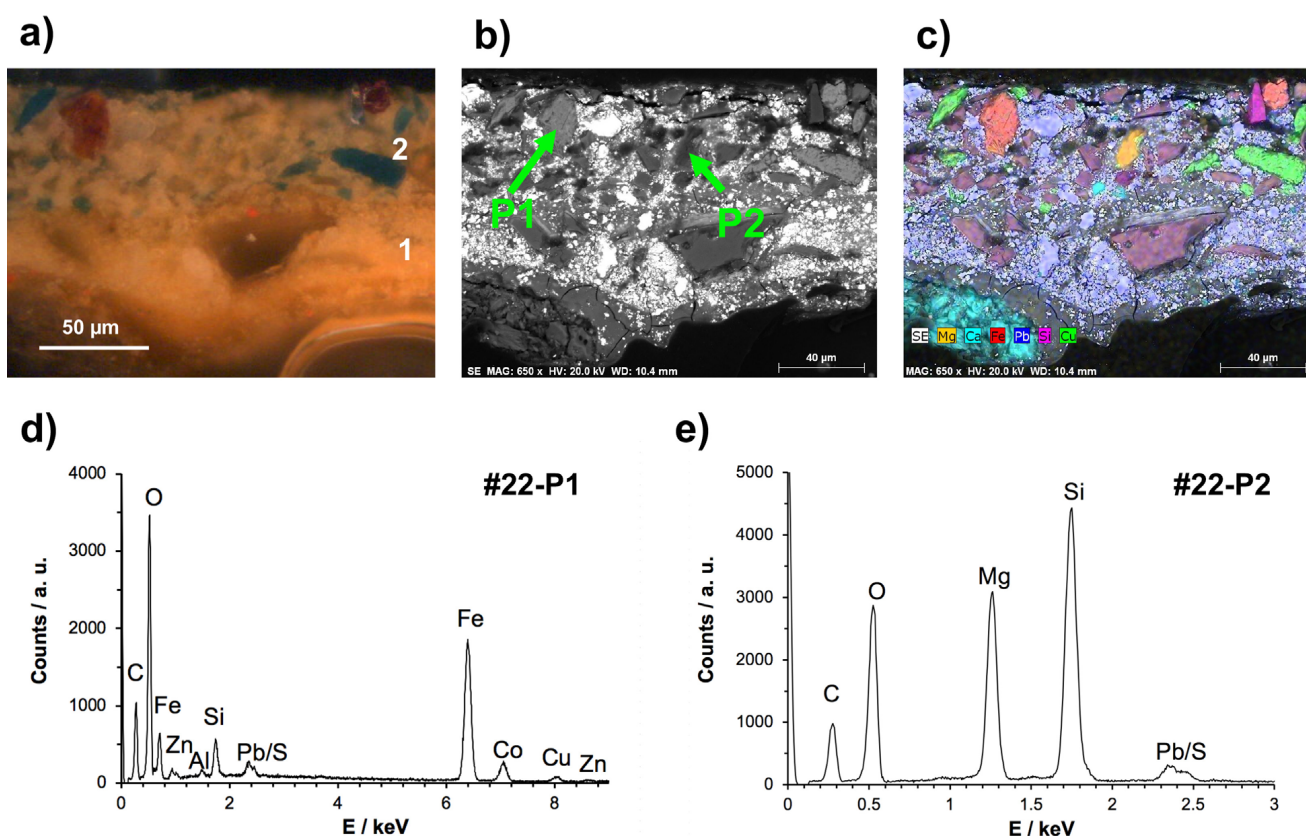
Dyestuff analysis is performed on whole paint layers, making it challenging to relate these three types of red lakes to their dyestuff(s). Since the most common manufacturing procedure of red lake pigments from the 14th to the 17th century involved the indirect extraction of the dyestuffs, not from the raw materials but from dyed textile clippings, a mixture of dyestuffs could be expected in the final product [24]. In fact, the association of cochineal and brazilwood in the same lake pigment was found in many mannerist paintings produced in the region of Évora [4,25]. This subject, with further results, will be addressed in depth elsewhere.

### 3.3.4. Blue

Smalt and azurite were the two blue pigments identified through OM, SEM-EDX, and FTIR. Smalt was used alone in the underlayers and combined with azurite in the upper blue and purple paint layers (Figure 4). Particles of azurite, a basic copper carbonate, were rich in Cu (SEM-EDX) and exhibited an irregular size and angular appearance, which are typical of a crushed mineral [26]. In a sample from the sky area, EDX elemental analysis of two large red-brown particles (OM-Vis) detected a significant concentration of iron and a minor amount of zinc (Figure 4a,b,d). Although the blue paint contained lead white and smalt and these particles could correspond to an added ochre pigment, identical particles have been linked to impurities of the azurite pigment in paintings with

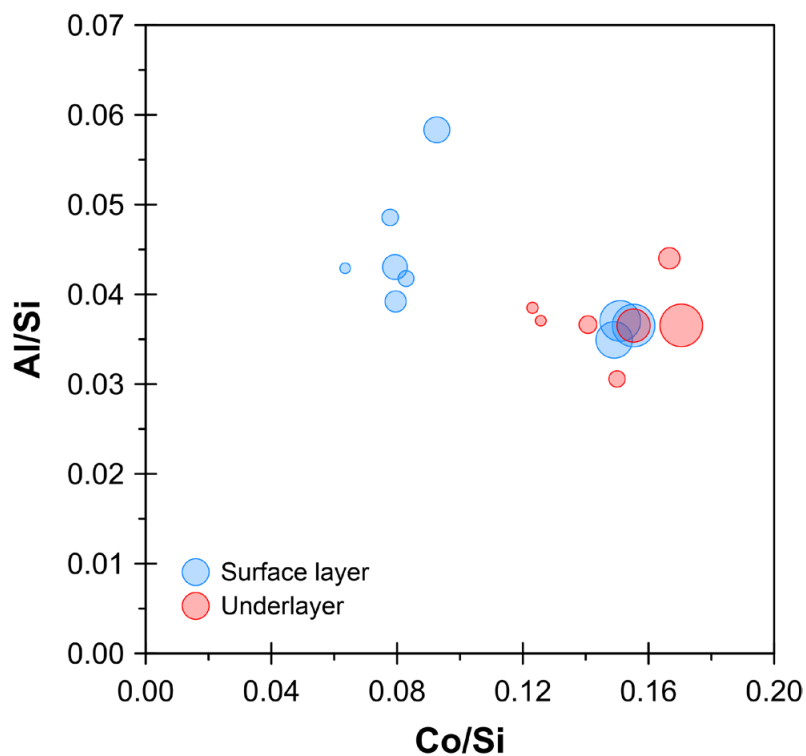


no admixture of smalt [25,27]. Similarly, EDX mapping also spotted a magnesium-rich particle with a translucent appearance under the microscope (Figure 4a,c,e) that has a strong correspondence to similar particles consistently found in azurite-rich paints from mannerist paintings produced in the Alentejo region [6,25]. This pattern may be related to the same provenance of the pigment, maybe from the Aljustrel mine, which is located in the region, with documented activity in the production and commercialisation of azurite pigment in the 16th century [28].

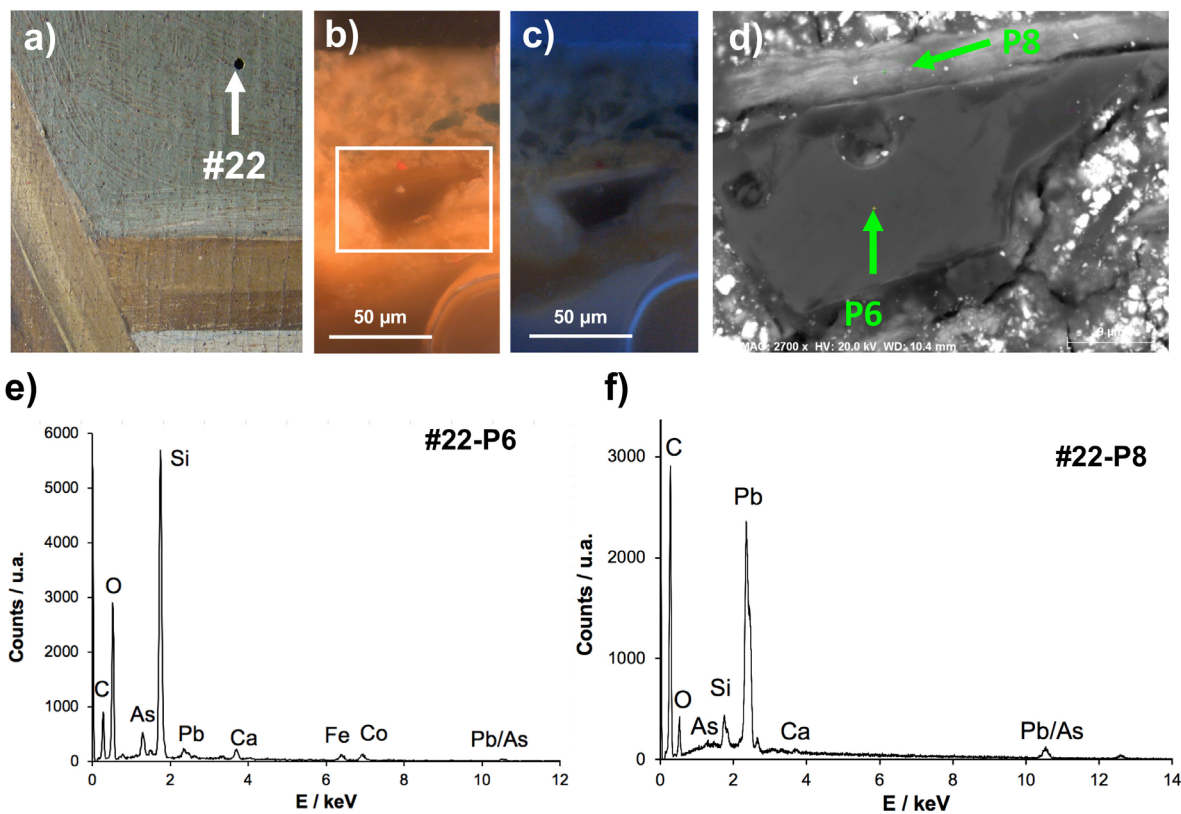


**Figure 4.** Cross-section of sample #22 corresponding to the area of the sky under OM-Vis (a) and the respective SEM-BSE image (b); combined map of elements (c) with magnesium (yellow), calcium (turquoise blue), iron (red), lead (deep blue), silicon (pink), and copper (green); and EDX spectra of points P1 (d) and P2 (e), located in (b).

Smalt, a potassium-containing glass coloured blue by cobalt oxide, was recognised under OM-Vis and OM-UV as entirely discoloured translucent yellowish particles with sharp edges, characteristic of a broken glass. The pigment was coarsely ground, with its particles often reaching a size of 25, 30, and 50  $\mu\text{m}$ . Beyond silicon and cobalt, arsenic and nickel, which are elements associated with the cobalt ore, were detected through EDX elemental analysis [29–35] (Figures 5 and 6). Other minor elements characteristic of 16th-century smalt, such as aluminium, calcium, and iron, as well as traces of sodium, magnesium, and manganese, were detected through SEM-EDX analysis and are derived from the cobalt ore and the raw materials used in glass manufacturing [29–35]. Spot analyses performed on smalt particles using SEM-EDX suggest the use of two batches of the pigment: one characterised by a lower Co/Si ratio, found only in particles of the surface layer, mixed with azurite; the other, with a higher Co/Si ratio, used essentially in the layer without azurite, although particles of it were also detected in the layer with azurite. The Al/Si, Fe/Si, and As/Co ratios, although to a more limited extent, also contribute to the distinction of the two batches (Figure 5).

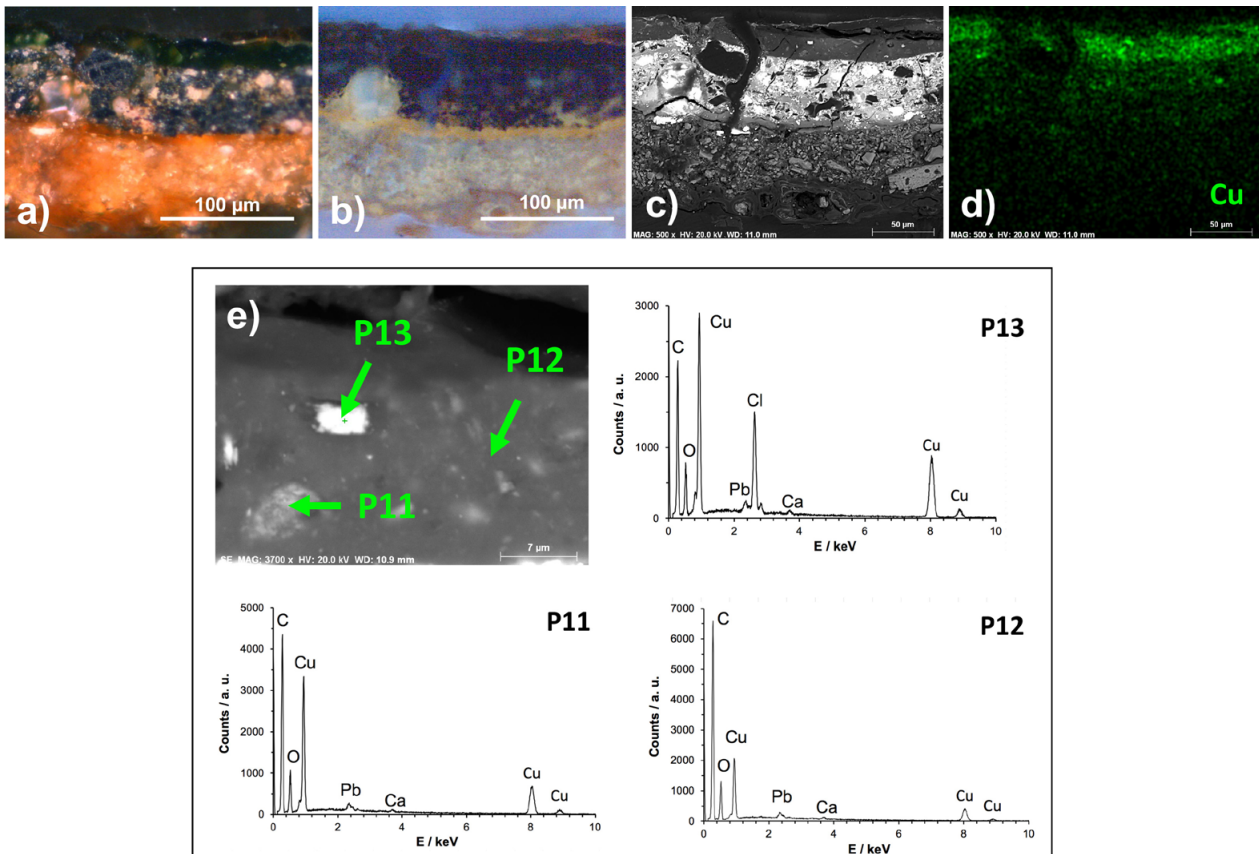


**Figure 5.** Co/Si, Al/Si, and Fe/Si ratios in small particles according to SEM-EDX analysis. The Fe/Si value is expressed by the size of the mark.



**Figure 6.** Detail of the sky under incident light (a), with the location of sample #22; detail of the cross-section of sample #22 under OM-Vis (b) and OM-UV (c); SEM-BSE image of small particle located in (b); and SEM-EDX spectra of points P6 (e) and P8 (f), located in (d).

Smalt particles were almost entirely depleted of potassium (Figures 6 and 7) as a result of the leaching of this element to the paint matrix, a phenomenon responsible for the pigment's loss of colour [36–38]. The reaction of the leached potassium alkali with the acidic oil binder led to the formation of potassium soaps, whose presence was confirmed via FTIR analysis (Supplementary Material—Figure S9). In the infrared spectrum of a deep blue paint layer made from the mixture of smalt, azurite, and lead white, a well-resolved shoulder at  $1462\text{ cm}^{-1}$  in the strong  $1406\text{ cm}^{-1}$  carbonate band, along with a  $1535\text{--}1516\text{ cm}^{-1}$  doublet, indicated the formation of both potassium and lead soaps [32] (Supplementary Material—Figure S9).



**Figure 7.** Cross-section of sample #11 corresponding to a green drapery, under OM-Vis (a), and OM-UV (b); respective SEM-BSE image (c) and elemental mapping for copper (d); SEM-BSE image of green glaze from sample #11 with the locations of points P11, P12, P13, and the respective EDX spectra (e).

In layers where the smalt was combined with lead white, some of the smalt particles exhibited lead-enriched rims or, in some instances, an accumulation of lead in the shape of a larger band along one of the pigment's margins (Figure 6). This band was mainly composed of lead and was depleted of the potassium expected to be found in the crusts formed on the surface of potash glass [32,39]. The observed deterioration of the smalt particles can be correlated with historical window or vessel glass degradation, where, in extreme cases, the surface of the material becomes a hydrated silica gel, and heavy metals from the environment, notably lead, can migrate into the crust [32,39]. Further research is needed to understand the reasons behind the severe degradation affecting these smalt particles located in the underlayers that have less contact with the environment and mixed with lead white, a pigment known to have a protective effect on smalt [32,37].

### 3.3.5. Green

The deep saturated green translucent glaze of draperies had a quenching effect on the fluorescence when examined under OM-UV. With a low atomic weight (SEM-BSE), which is typical of an organic material, the analysed green glaze was rich in copper (EDX mapping) (Figure 7). Specks with the appearance of a pigment partially dissolved in its binder, showing indefinite edges, variable shapes and sizes, and a medium atomic weight (SEM-BSE), were distributed throughout this layer (Figure 7e). The EDX point analysis revealed that they mainly contained copper in a higher concentration than the surrounding paint matrix (Figure 7e). The optical characteristics of this layer, the absence of distinctive pigment particles, and the non-detection of metallic elements other than copper indicate the use of verdigris, the most common green pigment in Western painting from the 13th to the 17th century [40].

Verdigris is a mixture of copper salts resulting from the corrosion of copper and its alloys [40,41]. Its composition depends on the starting copper metal and the manufacturing process and is therefore variable [40–44]. In the green glaze of this painting, an EDX analysis of two very small particles (1–2 µm) with a high atomic weight (SEM-BSE) detected, in addition to copper, a high concentration of chlorine (Figure 7e). Although the possibility of copper chlorides forming from the reaction of the copper pigments with the environment cannot be excluded, in easel painting, as is the case here, it is more likely that the copper chlorides originated from the verdigris-production procedure [41–44].

### 3.4. Technique and Style

The painting technique is based upon a sharp contour of the forms, coloured inside with smooth gradations of paint and thinly spread over the surface, without any brush-stroke imprints (Figures 1 and 2a). In this regard, this composition is the paradigm of the primacy of *disegno* (form) over *colore* (colour), which is typical of the Roman Mannerist School that strongly influenced contemporary Portuguese painting practice [2]. Colour gradation is achieved by adding lead white to the medium tones and highlights and by using more saturated paint mixtures in the shades. With the black pigment mostly circumscribed to underlayers, the areas of shadow correspond to the most saturated hues, a situation that has no correspondence with reality and a technical choice that is responsible for the decorative, anecdotal appearance of the composition. Except for the floor, painted with a single layer, the figures and background are modelled with two superimposed paint layers, covered with a final translucent glaze in the areas corresponding to red, pink, and green draperies.

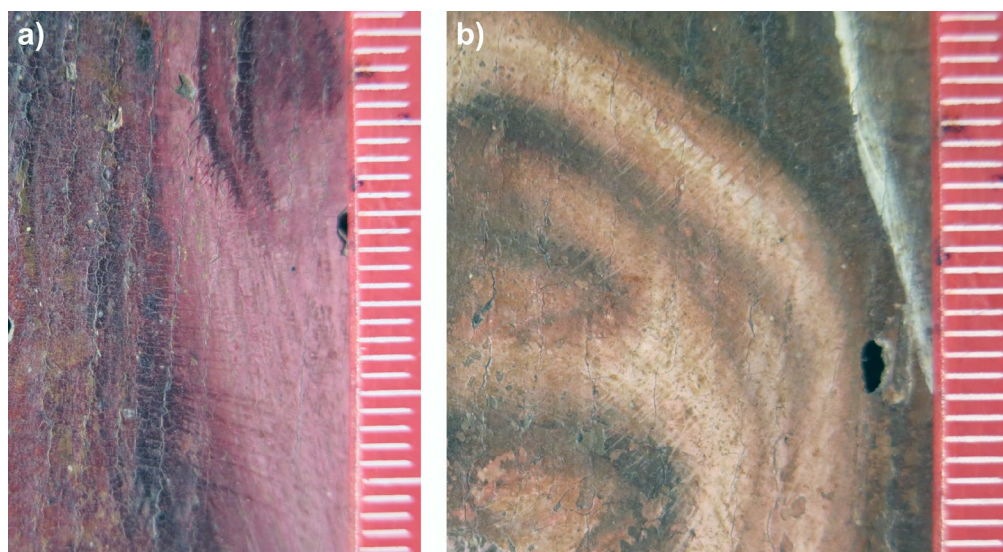
The assortment of red pigments, mixed in a variety of combinations in the majority of paints (Table 1), suggests they were a useful ingredient in colour formulation. The use of red glazes evenly laid on top of a red or pink undermodelling of the folds further broadened this diversity of hues (Figure 3). Two superimposed opaque bright red paints, mostly containing variable amounts of vermilion, and red lake were used in the undermodelling of red draperies (Table 1, R1, R2, R3, R4; Figure 3, #16). In the pink glazed garments, the painter established a first modelling of the folds with an opaque ochre-pinkish layer, mainly containing lead white, red lake, and a little ochre and charcoal black (Table 1, Pk1; Figure 3, #17, #19). Over this base, and prior to the final glaze, the painter developed the highlights with an opaque light pink layer (lead white and red lake) and the deep shadows with a 20 µm thick deep red glaze, which is rich in organic binder and red lake. A similar technique was used for the green glazes, applied over a contrasting undermodelling of the forms, achieved with an opaque yellow paint for the lights and a black-rich underlayer in the shadows (Table 1, G2, G3).

In the blue areas of the sky and draperies, a single underlayer consisting of lead white and smalt, in different concentrations according to the hues desired, was used underneath a final azurite–smalt-containing paint. A similar option was made for the purple–greyish areas of the sky, in this case modelled by adding a little red lake to the upper azurite–smalt-based paint and using an opaque grey paint as the foundation. This two-step build-up of



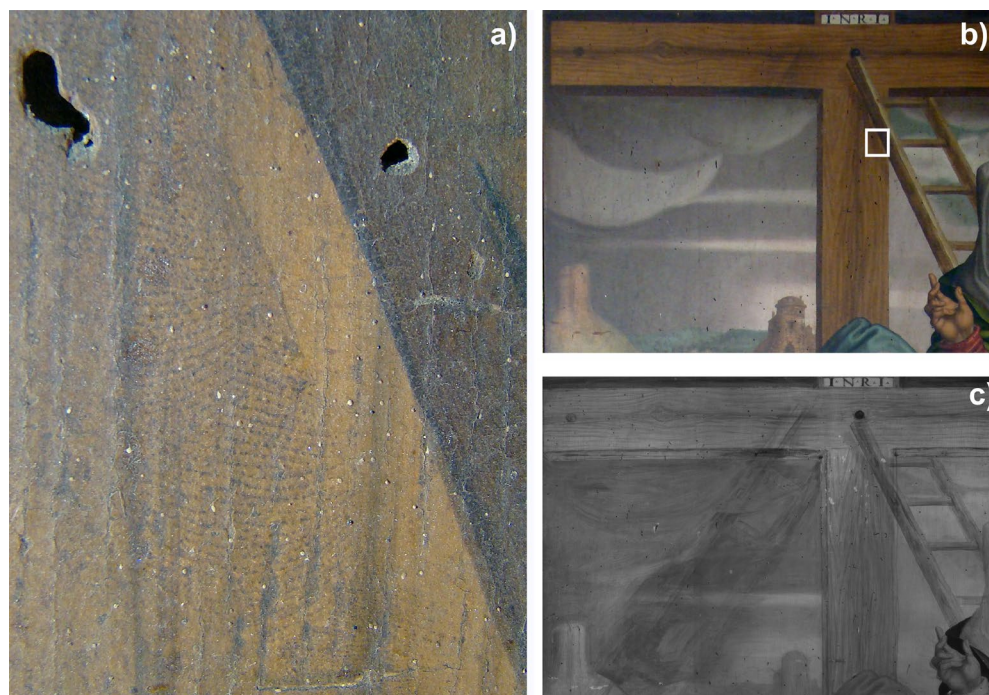
blue areas, where the more expensive blue pigment, in this case, azurite, is reserved for the upper paint layers, reflects a traditional 16th-century practice [16] that is consistently found in Portuguese paintings [4,25,45–48]. This option not only reveals an economical use of materials, but it also reflects the most efficient technique in retaining the purity and hue of the strongest blue pigments without muting them with the addition of a black pigment. In this painting, the addition of smalt to the azurite paint, in addition to being cost-effective, since smalt is cheaper than azurite [30,31], could also have been a deliberate technical choice by the painter in order to counteract the greenish tinge of the azurite pigment. This combination is notably praised by Francisco Pacheco in his 1649 treatise, where, for the darkest shadows in blues, he warns against the use of black and instead advises the use of pure blue (azurite) or the addition of a “little good, fine smalt of a pretty colour” [49] (p. 73). Today, the complete discolouration of the smalt pigment impairs the original colour balance of the painter’s work.

Material evidence of the use of a dry soft brush gently sweeping the surface of applied wet paint, in order to promote a subtle blending between light and shade, was found in the flesh tones and in the blue and pink garments of the figures (Figure 8). This particular blending technique, in part responsible for the continuous soft gradation of colours observed in this painting, is described in an anonymous treatise written c. 1640 that advises [50] (p. 270), “After the panel is painted, and the colours put in place, as stated, and blended, I use a new brush to blend the paints one over the others, and cleaning [the brush] on the back of my hand, making it precious (. . .)”. This immediate handling of fresh paint, favoured by the slow drying time of the oil-based medium, is further noticed in the imprints of the fingers used to blot the brown paint of the shadow of the ladder over the Cross (Figure 9a), a technique found in other paintings attributed to this master [4].



**Figure 8.** Details of the pink tunic of Mary Magdalene (a) and her left ear (b), where visible marks of the passage of a soft brush over the fresh paint are visible.

Despite a controlled execution, a significant change, evident in raking light and under IRR, was made at the painting stage, with the ladder leading to the Cross painted on the left side of the composition, behind the figure of Saint John, and later covered by the sky (Figure 9b,c).



**Figure 9.** Detail of the shadow of the ladder (a) located with a white rectangle in (b), with the imprint of the fingers used to blot the brown paint, and details of the painting under visible radiation (b) and IRR (c).

#### 4. Conclusions

The investigation of the materials and techniques used in *The Descent from the Cross*, attributed to the Portuguese mannerist painter Francisco João, revealed a rich palette containing lead white, lead–tin yellow, minium, vermilion, ochres of different colours, umber, smalt, azurite, verdigris, charcoal black, and red lakes made of brazilwood and cochineal. The variety of red and blue pigments analysed, notably the use of at least three different-coloured red lake pigments, and the combination of azurite and smalt reveal a search for a broad range of hues that would enrich the colourful pastel-toned composition. The soft transition of shades and tints within well-defined contour outlines, together with the absence of brush marks on an extremely smooth surface—in part resulting from the use of a dry brush to blend the thickest paints while these were still wet—defines the painter’s technique and illustrates the formal influence of Roman Mannerism in this artwork. The severe degradation of the smalt pigment, apparently affecting the silica structure of the glass, is restricted to lead-white-rich underlayers. Although apparently not strongly influencing the colour perception of the composition, this degradation requires further research in order to minimise the predicted future deterioration of these paint layers.

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/min13091182/s1>: Figure S1: FTIR spectrum of the ground layer of sample #13: sulfates (3537–3400, 1161, 1113, 1016, 673, 615  $\text{cm}^{-1}$ ), oxalates (1317, 779  $\text{cm}^{-1}$ ), proteins (3078, 1651, 1550, 1450  $\text{cm}^{-1}$ ), lipids (2925, 2852, 1711  $\text{cm}^{-1}$ ). Figure S2: Detail of the area of the sky with location of sample #22 (a); cross-section of sample #22 under OM-Vis (b); cross-section of sample #22 under OM-UV (c); SEM-BSE image of detail from (b,c) (d); and SEM-EDX spectrum of P12 (e). Figure S3: Details under IRR (a,c) and, under visible radiation (b,d). Figure S4: Detail of the drapery in Saint Magdalene’s arm with location of sample #02 (a); cross-section of sample #02 under OM-Vis (b); cross-section of sample #02 under OM-UV (c); and FTIR spectrum of yellow layer marked in (b) with an arrow (d). SEM-BSE image of detail of cross-section from sample #02 with location with an arrow of the particle P1 analysed (e); and respective SEM-EDX spectrum (f). Figure S5: Detail of the tunic of Saint Magdalene with location of sample #03 (a); cross-section of sample #03 under OM-Vis (b); cross-section of sample #03 under OM-UV (c); and FTIR spectrum of

pink-ochre paint marked in b) with an arrow (d). SEM-BSE image of detail of cross-section of sample #03 (e); same detail under OM-Vis (f) and under OM-UV (g); SEM-EDX maps of Al (h), C (i), and Pb (j). Figure S6: Detail of the cloak of Saint John with location of sample #19 (a); cross-section of sample #19 under OM-Vis (b); cross-section of sample #19 under OM-UV (c); and FTIR spectrum of the red glaze marked in c) with an arrow (d). SEM-BSE image of detail of cross-section of sample #19 (e); same detail under OM-Vis (f) and under OM-UV (g); SEM-EDS maps of Al (h), C (i), and Pb (j). Figure S7: Cross-section of sample #11, corresponding to a green drapery, under OM-Vis (a); cross-section of sample #11 under SEM-BSE (b); SEM-EDX spectrum of charcoal particle (c) viewed in the SEM-BSE image (d). Figure S8: Detail of cross-section of sample #04, corresponding to the flesh of Saint Magdalene's face, under OM-Vis (a); detail of cross-section of sample #04 under OM-UV (b); SEM-BSE image of cross section of sample #04 with the location of the detail shown in (a,b) (c); SEM-EDX spectrum of umber particle (d) viewed in the SEM-BSE image (e). Figure S9: Detail of a blue drapery with location of sample #07 (a); cross section of sample #07 under OM-Vis (b); cross section of sample #07 under OM-UV (c); and FTIR spectrum of blue paint marked in b) with an arrow (d). SEM-BSE image of detail, marked in b), of cross-section of sample #07 (e); SEM-EDS maps of Cu (f), Si (g), and Pb (h). Table S1. List of samples collected and analytical methods performed.

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