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Italian Influence in a Portuguese Mannerist Painting (Part I): A New Palette with Original Orange and Green Pigments

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ABSTRACT

The palette used by the Portuguese painter Pedro Nunes (1586–1637) in the large panel depicting *The Descent from the Cross* (460 × 304 cm) painted in 1620 for Évora's cathedral was investigated with a combination of the visual inspection of the paint surface and the analysis of the paint layers with microscopic, spectroscopic, and chromatographic techniques. Green earth and an orange artificial arsenic sulphide, two pigments identified for the first time in Portuguese paintings of the sixteenth and seventeenth centuries, were found to be abundantly used in large areas of the composition. The results further reveal the choice of a rich palette also containing lead-white, lead-tin yellow, ochre, vermilion, verdigris, smalt, azurite, vegetable carbon black, and a red lake made of brazilwood and cochineal. All the pigments were bound in an oil-based medium. The introduction of two pigments new to the Portuguese conventional palette is a direct consequence of the painter's training in Rome in the first decade of the seventeenth century.

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Pigments; mannerist; Portuguese; Italian; green earth; artificial arsenic sulphide

Introduction

The magnificent panel painting depicting *The Descent from the Cross* (460 × 304 cm) painted in 1620 by the Portuguese painter Pedro Nunes (1586–1637) is still preserved in its original altarpiece in the Chapel of Esporão, in Évora's Cathedral (Portugal) (Figure 1).

Pedro Nunes was born in Évora in a time of political union with Spain (1580–1640), when the Counter-Reformation spirit and the loss of Lisbon's centrality favoured the development of local painting workshops. He took his first steps in Évora (1601–1606) and later travelled to Rome, where he enrolled in the Academy of Saint Lucas and remained for eight years (1607–1614), notably working for the Cardinal Scipione Borghese (Serrão 1988–1993). Upon his return from Italy, Nunes worked for two years in Cataluña, Spain (1615–1616), before settling definitively in Évora (Serrão 1988–1993). He succeeded a Mannerist generation of local painters, active between 1550 and 1600, whose Italian influence had mainly been apprehended indirectly, through Nordic and Spanish 'Italianized' painters working in the Iberian Peninsula, but also through the work of a few Portuguese painters that were sent to Rome in the 1560s (Serrão 2002).

Information regarding the materials and techniques used by Portuguese Mannerist painters with an Italian experience is almost non-existent (Conde et al. 2010). As a result, from this point of view, Italy's influence in Portuguese painting – dominated up until the 1540s by the Flemish style and painting practice (de Mello, Matos, and Ribeiro 1998; Instituto José de Figueiredo 1999; Mendes 2004; Redol, Seruya, and Pereira 2004; Melo and Cruz 2009; Conde et al. 2010; Serrão and Antunes 2013; Antunes et al. 2016; Melo et al. 2020, 2022) has not yet been assessed.

Considering the scarce available information and the relevance of Pedro Nunes to the Portuguese artistic scene, this investigation aims to understand if, beyond a formal Italian appearance, the training in Rome would encompass material and technical influences as well.

This article focusses on the identification with microscopic, spectroscopic, and chromatographic techniques of the pigments and binder used to make the paints. Technological aspects related to panel construction, preparatory layers, and paint handling will be addressed in a second paper. The analytical results are interpreted within the frame of Portuguese and European painting practice and materials in a transition period between the late sixteenth and the beginning of the seventeenth century.

Experimental

The painting was subject to a thorough visual inspection of the paint surface *in situ*, under incident and

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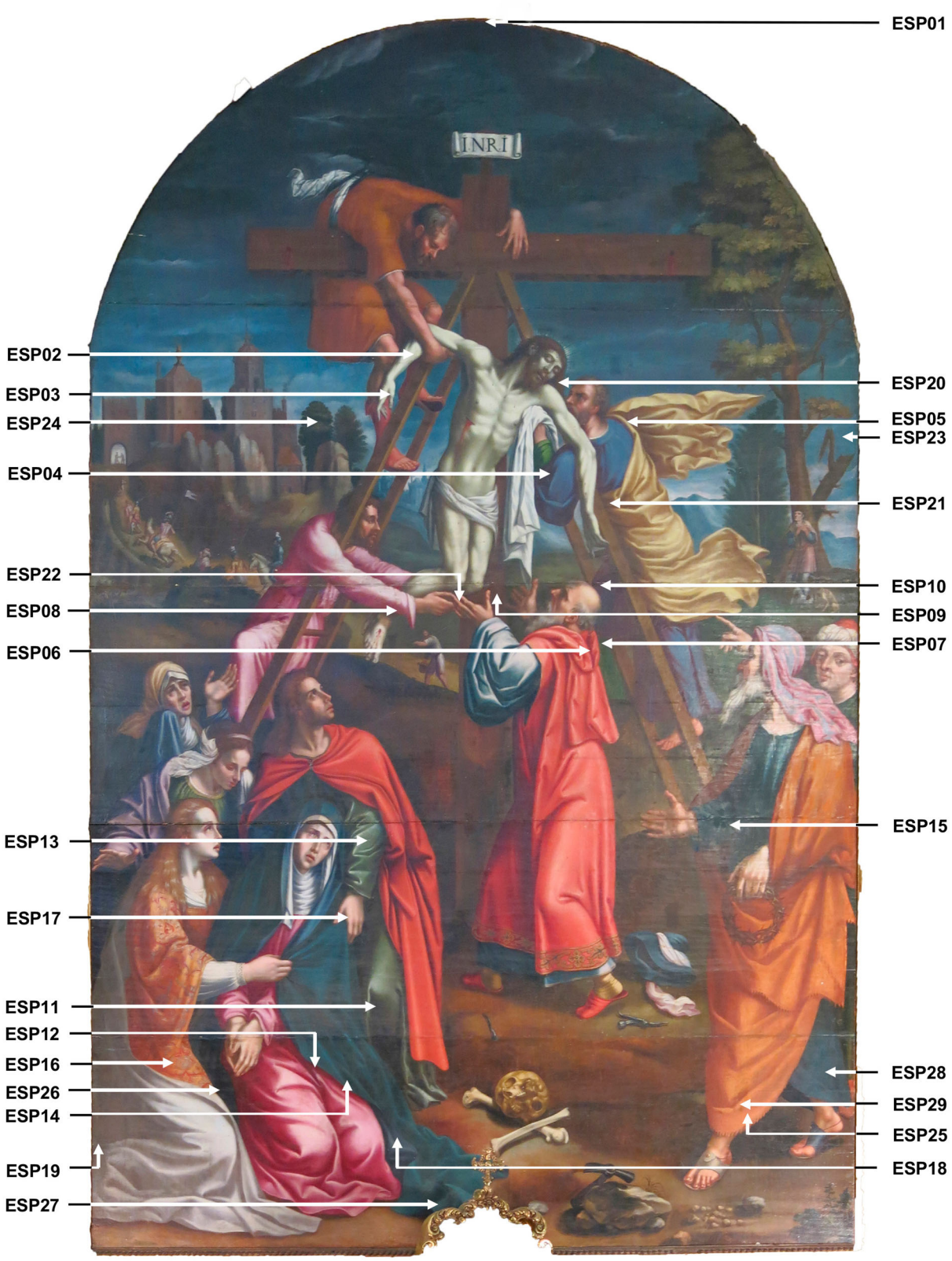

Figure 1. *The Descent from the Cross* by Pedro Nunes, 1620 (460 × 304 cm, oil on panel), Esporão Chapel, Évora Cathedral, Portugal, with location of the 29 samples collected.

raking light. Twenty-nine samples of the main colours were collected in areas adjacent to paint losses or in the margins. Part of each sample was embedded in an epoxy resin (Struers SpeciFix 40), polished as a cross-section, and studied with optical microscopy (OM) in reflection mode, under visible (OM-Vis) and ultraviolet radiation (OM-UV) (excitation filter BP 340–380, dichromatic mirror, and suppression filter of LP 425 size), using a Leica DM2500 microscope. Digital images were taken with a Leica DFC290HD digital camera.

Subsequently, the uncoated cross-sections were further analysed with scanning electron microscopy

(SEM) with energy dispersive X-ray spectrometry (EDX) using a Hitachi 3700N variable pressure scanning electron microscope operated at 20 kV, with a BRUKER Contact 200 EDX detector. The backscattered electron images (BSE) and the EDX maps of major elements gave an accurate characterization of size, morphology, and distribution of the particles present, and the EDX spectra of single particles provided semi-quantitative information on elemental composition. Micro-Raman spectroscopy (μ-RS) was used to identify specific pigments in the paint cross-sections, notably impurities in azurite rich paints. A Horiba XPlora Raman spectrometer equipped with a diode laser of 10.3 mW operating at 785 nm, coupled to an Olympus microscope was used. For the analysis, both diode lasers available in the laboratory equipment, the 638 nm laser HeNe and the 785 nm NIR laser were first tested. Considering the nature of the samples studied and associated fluorescence, the results obtained with the first laser were not considered. The use of the 785 nm laser enabled reducing the fluorescence phenomenon, and consequently, the Raman signal, giving interesting results for the investigation. Raman spectra were acquired in extended mode in the 100–1000 cm^{-1} region. The laser was focused with an Olympus 50× lens, 10% of the laser power on the sample surface (5 s exposure, 5 cycles of accumulation).

The unmounted part of the samples was analysed with Fourier transform infrared micro-spectroscopy (μ-FTIR). The layers were separated and each one was compressed between two diamond cells. The spectra were obtained in transmission mode with a Bruker Tensor 27 spectrometer coupled to an Hyperion 3000 microscope with an MCT detector, controlled by OPUS 7.2 software from Bruker Optik GmbH 2012. Each spectrum was collected in the 4000–600 cm^{-1} region, using 64 scans and a resolution of 4 cm^{-1}.

The red lake dyestuffs were analysed in two samples (ESP08 and ESP10) using high-performance liquid chromatography coupled to diode-array and mass spectrometry detectors (HPLC-DAD-MS). Extraction of red lake dyestuffs was based on the methodology described by Wouters et al. (Wouters, Grzywacz, and Claro 2011), using 200 μL of a methanol:acetone: water:hydrofluoric acid solution (30:30:40:1, v/v/v/v) to extract the samples during four hours. An LCQ Fleet Thermo Finnigan mass spectrometer, equipped with an electrospray ionization source and an ion trap mass analyser was used. Analytes were detected in full MS negative mode (100–800 m/z, capillary temperature of 300°C, source voltage of 5.0 kV, source current of 100.0 μA and capillary voltage of −3.0 kV). Fragmentation occurred at the source (10.0 V from 0 to 12 min and 30.0 V from 12 to 30 min). A Surveyor Thermo Finnigan HPLC system equipped with an autosampler was used. A reversed-phase Zorbax Eclipse XDB-C_{18} analytical column (Narrow-Bore, particle size of 3.5 μm, 150 × 2.1 mm) was used for the separation of analytes. Temperature was controlled on the column (30°C) and sample tray (24°C). Chromatographic separation was achieved at a 0.2 mL min^{-1} flow rate, with a binary mobile phase (solvent A – 0.1% formic acid in water (v/v), solvent B – acetonitrile). The following gradient programme was used: 0%–63% of B from 0–14 min, 63%–90% of B from 14 to 25 min, 90% of B from 25 to 30 min. The DAD detector was programmed to acquire data from 200 to 800 nm.

Results and discussion

The Descent from the Cross was painted on an oak panel prepared with a calcium sulphate ground and a medium-rich *imprimatura* – *imprimadura*, in Portuguese (Cruz 2006) – lightly toned with ochre. Particular aspects related to the nature and construction of this panel will be presented in a second article on this painting. Pigment mixtures used to make the paints are presented in Table 1, each with a reference that is used in the text whenever necessary.

Black and white

Lead white was identified by its colour (OM), its high average atomic number and fine grain morphology (SEM-BSE images), typical of an artificial pigment, combined with the detection of a high concentration of lead in SEM-EDX mapping and spot analysis. Micro-FTIR analysis of paint layers containing white, showed that this pigment was present as a mixture of hydrocerussite ($2PbCO_3.Pb(OH)_2$) and cerussite ($PbCO_3$). Infrared spectra exhibited the usual carbonate bands at 1401–1398, 1046, and 681 cm^{-1}, along with a ν(OH) distension at ~3539 cm^{-1} for hydrocerussite and the characteristic strong 838 cm^{-1} stretching band for cerussite (Figure 2) (Brooker et al. 1983). Lead white was mixed with pigments of all colours to create the tints used in the modelling of all painted motifs (Table 1).

Vegetable carbon black was the sole black pigment identified by a combination of OM and SEM-EDX. Elongated, irregular, and often angular shaped black particles, with a splintery character when viewed under the optical microscope (Figure 3) were shown by SEM-EDX analysis to be rich in carbon and did not contain phosphorous, a constituent of ivory/bone black pigments (Winter and FitzHugh 2007) (Figure 3). Analysis by μ-RS of some of these black particles detected the D band at 1320 cm^{-1}, known as the 'disorder' band, and the G 'graphite' band at 1603 cm^{-1}, which can both be assigned to an amorphous carbon material (Figure 3) (Tomasini et al. 2012). The presence of a band characteristic of hydroxyapatite, at c. 965 cm^{-1}, although not detected in the μ-RS spectra obtained, usually has a very low intensity that makes it difficult to see (Tomasini et al. 2012). As

Table 1. Pigments identified and their mixtures.

	Pigment mixtures		Number of Pigments					
Colour	Ref.	Pigments	Total	Wh.	C	Painted motif	Layer	Sample Ref.
Yellow	**Y1**	Lead-tin yellow + Lead white	2	1	1	Drapery	**U / T**	**ESP05_C2/C3**
							U	**ESP16_C2**
Orange	**O1**	Lead-tin yellow + Lead white + Vermilion (tr.)	3	1	2	Drapery	**U**	**ESP16_C3**
	O2	Ochre + Lead white + Vermilion (tr.)	3	1	2	Drapery	**U**	**ESP12_C1**
							U	**ESP16_C1**
							U / T	**ESP21_C1**
	O3	Ochre + Lead white	2	1	1	Drapery	**U**	**ESP05_C1**
								ESP08_C1
								ESP25_C1
								ESP29_C1
	O4	Artifical arsenic pigment	1	0	1	Drapery	**T**	**ESP25_C1**
								ESP29_C1
Red	**R1**	Vermilion + Red lake + Lead white	3	1	2	Drapery	**U**	**ESP06_C1/C2**
	R2	Red Lake + Vermilion	2	0	2	Drapery	**U**	**ESP26_C1**
	R3	Vermilion + (possibly) Ochre	2	0	2	Drapery	**T**	**ESP16_C4**
Pink	**Pk1**	Red Lake + Lead white	2	1	1	Drapery	**U**	**ESP04_C1**
							T	**ESP08_C2**
							U	**ESP10_C1**
							U	**ESP12_C2**
							U	**ESP15_C1/C2**
	Pk2	Red Lake	1	0	1	Drapery	**T**	**ESP06_C3**
								ESP12_C3
Purple	**P1**	Smalt + Red Lake (tr.)	2	0	2	Drapery	**U**	**ESP04_C2**
							U	**ESP10_C2**
							T	**ESP19_C2**
	P2	Red Lake + Azurite (tr.)	2	0	1	Drapery	**T**	**ESP04_C3**
								ESP10_C3
	P3	Lead white + Azurite + Red lake + Carbon black (tr.)	4	1	3	Drapery	**U**	**ESP14_C2**
								ESP18_C2
	P4	Lead white + Red lake + Vegetable Carbon black (tr.)	3	1	2	Drapery	**U**	**ESP14_C1**
								ESP18_C1
								ESP26_C2
								ESP27_C1
								ESP28_C1
Blue	**B1**	Azurite + Smalt + Vegetable Carbon black + Red Lake (tr.) + Lead white (tr.)	5	1	4	Sky	**T**	**ESP01_C1**
	B2	Azurite + Lead white	2	1	1	Sky	**T**	**ESP23_C2**
						Drapery	**U / T**	**ESP27_C2/C3**
	B3	Smalt + Lead white	2	1	1	Sky	**U**	**ESP23_C1**
	B4	Azurite + red Lake (tr.)	2	0	2	Drapery	**T**	**ESP18_C3**
								ESP26_C3
	B5	Azurite	1	0	1	Drapery	**T**	**ESP14_C3**
						Drapery		**ESP15_C3**
						Landscape		**ESP24_C2**
						Drapery		**ESP28_C2**
Green	**G1**	Lead white + Green earth	2	1	1	Drapery	**T**	**ESP13_C2**
	G2	Lead white + Green earth + Ochre	3	1	2	Drapery	**U**	**ESP11_C1**
	G3	Lead white + Green earth + Ochre + Carbon black	4	1	3	Drapery	**U**	**ESP13_C1**
	G4	Green earth + Smalt + Ochre	3	0	3	Landscape	**U**	**ESP24_C1**
	G5	Green earth	1	0	1	Drapery	**T**	**ESP11_C2**
	G6	Verdigris + Lead-tin yellow + Ochre + Lead white	4	1	3	Landscape	**T**	**ESP07_C1**
Brown	**Br1**	Brown Ochre + Lead white	2	1	1	Hair	**T**	**ESP20_C2**
	Br2	Brown Ochre + Lead white + Carbon black (tr.)	3	1	2	Hair	**U**	**ESP20_C1**
	Br3	Ochre + Vermilion + Lead white + Carbon black	4	1	3	Cross	**T**	**ESP09_C1**
Grey	**Gr1**	Lead white + Carbon black + ochre (tr.)	3	1	2	Drapery	**U**	**ESP19_C1**
Flesh	**F1**	Lead white + Lead-tin yellow + Ochre + Red lake	4	1	3	Dead flesh, light	**T**	**ESP02_C1**
	F2	Green earth + Ochre + Lead white (tr.) + Lead-tin yellow (tr.) + red lake (tr.)	4	1	3	Dead flesh, shadow	**T**	**ESP03_C2**
	F3	Lead white + Ochre + Red lake	3	1	2	Dead flesh, shadow	**U**	**ESP03_C1**
	F4	Lead white + Vermilion	2	1	1	Live flesh, half-tone	**U**	**ESP22_C1**
								ESP17_C1
	F5	Lead white + Vermilion + Green earth	3	1	2	Live flesh, half-tone	**T**	**ESP22_C2**
								ESP17_C2

Note**: tr.**: Traces, very little amount of pigment; **U**: Underlayer; **T**: Top layer; **Wh**: White; **C**: Coloured. **C1, C2, C3, C4**: Coloured paint layers numbered in ascending order from the surface of the preparatory system to the surface of the painting. The information presented in this table is based on the analysis of 29 samples (= 65 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.

analyses are often hampered by the small size of the black pigments, making it difficult to visualize their particle morphology, the term 'carbon black' is used in this research whenever there is no analytical confirmation of its vegetable origin.

The carbon black pigments were used sparingly and mainly restricted to grey, purple, and greenish underlayers to the azurite-based, smalt-based, or green earth-based mantles of, respectively, the Virgin, Mary Magdalene, and Saint John (Table 1: Gr1, P3, P4, G3).

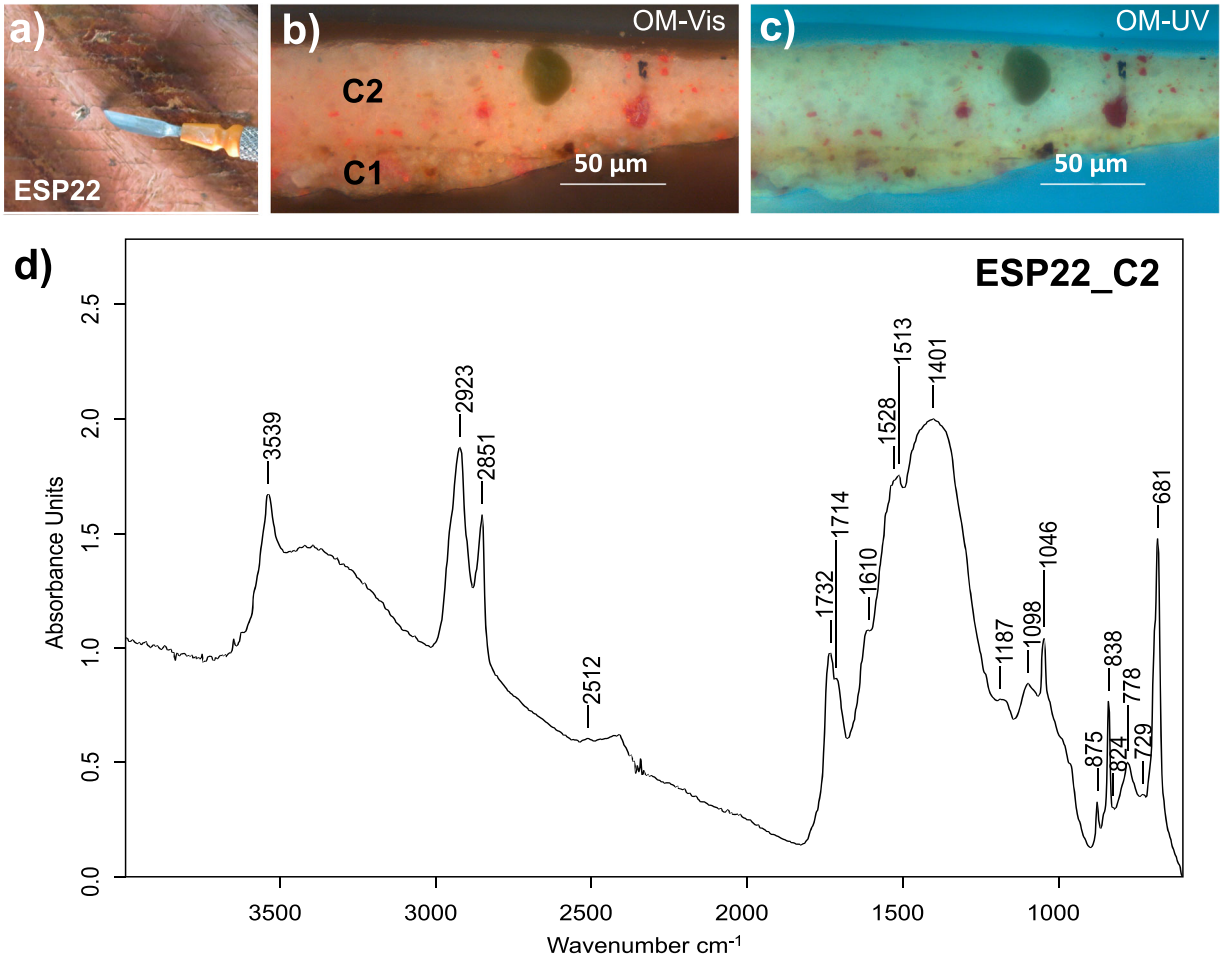

Figure 2. Lead white rich paint (flesh tone). Location of sample ESP22 (a) corresponding to the light tone of the hand of Saint Peter and respective cross-section under OM-Vis (b) and OM-UV (c); µ-FTIR spectrum (d) of the lead white rich flesh paint C2 located in (b) (see Table 1, pigment mixture F5).

A small amount of black was nevertheless mixed in the surface blue paint layers that create the stormy areas of the sky and in some brown paints (Table 1: B1, Br2, Br3).

Yellow

As yellow pigments, Pedro Nunes used the opaque and light coloured lead-tin yellow as well as ochre. Lead-tin yellow, identified by SEM-EDX analysis due to the presence of lead and tin, was abundantly used, not only for the yellow of the mantles or the brocade decorations, but also in some flesh tones and, in combination with red pigments, to create the orange colour (Table 1, O1). Ochres of various shades were rich in iron (Fe) and sometimes contained titanium, an impurity found in ochres, notably from Portuguese paintings and ores (Gil et al. 2007; Melo 2012).

Orange

Besides the mixture of lead-tin yellow and vermilion to make an orange colour, *The Descent from the Cross* exhibits a large-scale application of an orange pigment with spherulic particles visible under OM (Figure 4a,b). EDX elemental analysis reveals these particles to be rich in arsenic and sulfur and to have a diameter between 3 and 15 µm (Figure 4c,e,f). Many of the particles have a round shape that is typical of amorphous arsenic sulphide particles obtained by sublimation (Grundmann et al. 2007; Grundmann and Richter 2012). This pigment was used by the painter to make the tunic of the apostle bending over the Cross and the more than two meters-high figure standing to the right of the scene (Figure 1). Its detailed characterization, based on analytical results and documentary sources of the time is the subject of a recent publication (Cruz et al. 2002). Although arsenic sulphide pigments such as orpiment and realgar have been found in a few Portuguese artworks from the sixteenth and seventeenth centuries (Ledesma, García, and García 2000; Muralha, Miguel, and Melo 2012; Barata et al. 2013; Sousa 2016), this is the first documented occurrence of an artificial arsenic sulphide pigment in a Portuguese painting.

Red

Two red pigments were identified. One, with a vivid red hue, was characterized with SEM-EDX by the

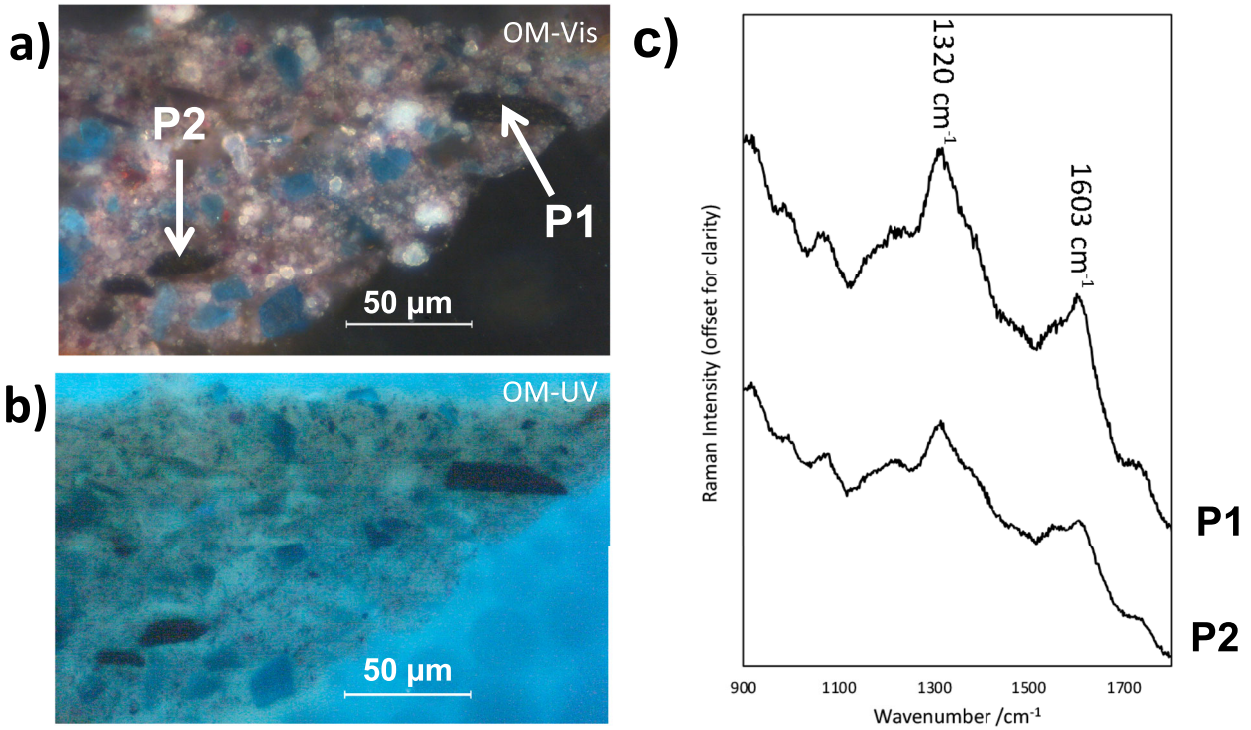

Figure 3. Carbon black. Cross-section of sample ESP01 under OM-Vis (a) and OM-UV (b) and Raman spectra of black particles P1 and P2 located in (a).

presence of mercury and sulphur and by its large broken particles (up to 45 µm) (Figure 5). This pigment could either correspond to natural cinnabar or to its synthetic equivalent, vermilion, produced at the time by the dry-process method. Both varieties are very difficult to distinguish (Eastaugh and Walsh 2004). However, the non-detection of associated minerals by EDX imaging, elemental mapping, and semi-

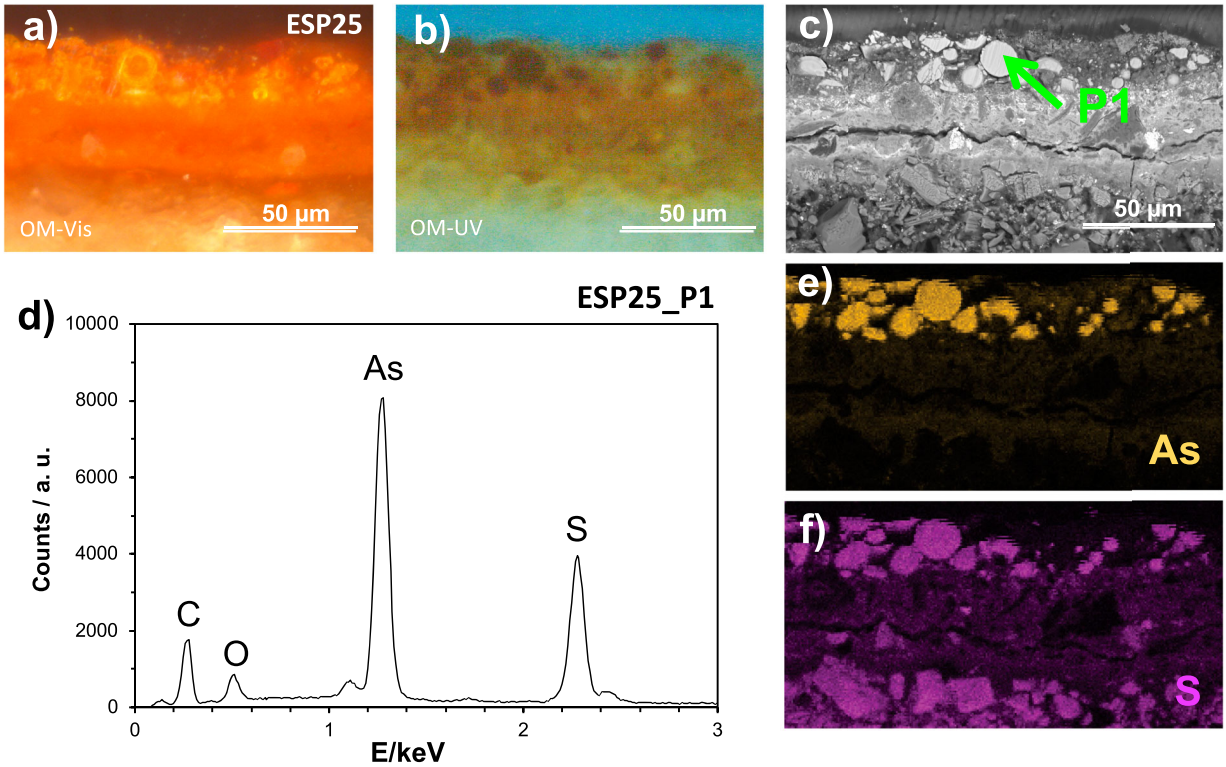

Figure 4. Orange artificial arsenic sulphide paint. Cross-section of sample ESP25 under OM-Vis (a) and OM-UV (b); SEM backscattered electron image (c); SEM-EDX spectrum of P1 (d) located in (c); and SEM-EDX maps of As (e) and S (f). Over the preparatory layers, an ochre rich underlayer is covered by an orange artificial arsenic sulphide paint.

quantitative point analysis, suggests that the artificial dry-process type vermilion was used (Moreno and Thomas 2008; Miguel et al. 2014; Nöller 2015; Franquelo and Perez-Rodriguez 2016). On this issue, Filipe Nunes, in his 1615 treatise on the art of painting states that the red pigment '*vermelhão*' commonly used in Portugal is made artificially with sulfur, mercury, and fire (Ventura [1615] 1982).

The other red pigment is a red lake that exhibits a deep red translucent colour (OM-Vis) and a purple tonality when observed under OM-UV (Figure 5a,b). HPLC analysis of two samples detected the chromophores carminic acid and brazilein, extracted, respectively, from the scale insect cochineal and the redwood collectively known as 'Brazilwood' (*Caesalpinia* spp.) (Table 2). The presence of urolithin C, a marker for brazilwood, further confirms the presence of this dyestuff (Peggie et al. 2018). HPLC-DAD-MS analysis did not detect minor components of the Polish or Armenian cochineal. Considering the date of Nunes' painting, American cochineal was most probably used (Kirby, Spring, and Higgitt 2005). The association of cochineal and brazilwood in the same lake pigment was found in many mannerist paintings produced in the region of Évora (Melo 2012). This can be explained by the indirect extraction of the dyestuff from textile shearings containing different dyestuffs, a common manufacturing procedure of red lake pigments from the fourteenth to the seventeenth century (Kirby 1987). In fact, in the textile dyeing industry, brazilwood was often added to other red dyestuffs with the aim of emulating the colour of more expensive draperies (Kirby and White 1996, 68). The addition of raspings of brazilwood and gum arabic to the dyestuff extracted from scrapings of scarlet cloth, a recipe for 'common lake' found in the 1635 *Brussels Manuscript* by Pierre Le Brun, could otherwise explain the association of these two dyestuffs (Merrifield [1849] 1999). SEM-EDX point analysis of the red lake substrate detected mainly carbon and aluminium (2–15 wt %), together with some calcium (0.6–5.0 wt %), sulfur (1.0–2.6 wt %) and sometimes, trace amounts (<1.5 wt%) of potassium, copper, iron, magnesium, sodium, phosphorous, or chlorine (Figure 5). These results suggest the use of the common amorphous hydrated alumina as the dyestuff substrate (Kirby, Spring, and Higgitt 2005). Minor elements as those found in the red lake substrates can originate from the scale insect source or from recipe materials and procedures used in the manufacturing of the red lake (Kirby, Spring, and Higgitt 2005; Sanyova 2008).

Vermilion, with a little red lake and lead white, was used to create the bright opaque red robes of two of the central figures in the composition (Figure 1). Its admixture in small quantities to different yellow pigments (lead-tin yellow or yellow ochre) broadened the orange hues of the robes of Magdalen and the apostle holding Christ to the right of the Cross (Table 1: O1, O2). From the red pigments analysed, vermilion was added in small amounts to impart a pink tonality to the flesh tints of living figures whereas the red lake was preferred for the dead body of Christ. To make the pink and purple colours, the painter resorted to the red lake pigment added, respectively, to lead white or to azurite and smalt-based paints (Table 1). Finally, the red lake was also used as a translucent glaze applied locally over opaque undermodelling layers in order to deepen certain areas of shadow in the red, pink, and purple garments. Traces of azurite were sometimes added to specific red glazes with the aim of shifting their hue towards a purple tinge without strongly affecting the translucency of the glaze (Table 1: P2).

Blue

Azurite and smalt were used for the blue and purple colours and smalt was further used in some of the green paints as well (Table 1). As a basic copper carbonate, azurite had a characteristic infrared spectrum with absorption ν(OH) bands around 3427 cm^{-1}; ν(CO_3) bands at 1407, 1092 cm^{-1}; a ν(CO) band at 958 cm^{-1}, and lastly, δ(OCO) bands at 838, 812, 771, and 748 cm^{-1} (Figure 6). Azurite had a wide particle size range with a majority of particles measuring 15–25 µm and larger ones reaching 35–45 µm.

The pure azurite paints showed a green tinge (OM-Vis) and light green particles, possibly consisting of malachite, a mineral commonly associated with azurite (Rutherford, Gettens, and Fitzhugh 1993), were visible under the optical microscope. Impurities of an orange, deep red, and sometimes almost black colour (OM-Vis) were also detected (Figure 7). SEM-EDX semi-quantitative analysis revealed they were rich in iron (Figure 7c–e) and thus probably correspond to iron-bearing oxides or hydroxides originating in the azurite ore, as frequently found in azurite paints (Aru, Burgio, and Rumsey 2014; Smieska et al. 2017). The analysis of these particles by µ-RS only gave clear results for the deep-red to blackish particles identified as hematite (alpha-Fe_2O_3), based on their characteristic Raman bands at 230 cm^{-1} (assigned to the A1g modes) and at 248, 299, and 410 cm^{-1} assigned to the Eg modes (Chamritski and Burns 2005) (Figure 8). In addition, SEM-EDX revealed that the azurite also incorporated occasional aluminium silicates rich in magnesium and containing a little iron (Figure 7f–h). Under optical microscopy, these appeared as very small particles with an indefinite colour, apparently translucent with an ochre tinge, but it was difficult to make a definite assessment of this parameter (Figure 7b). With the available analytical methods it was not possible to identify these magnesium-rich particles. Except for the case of azurite paints from Portuguese

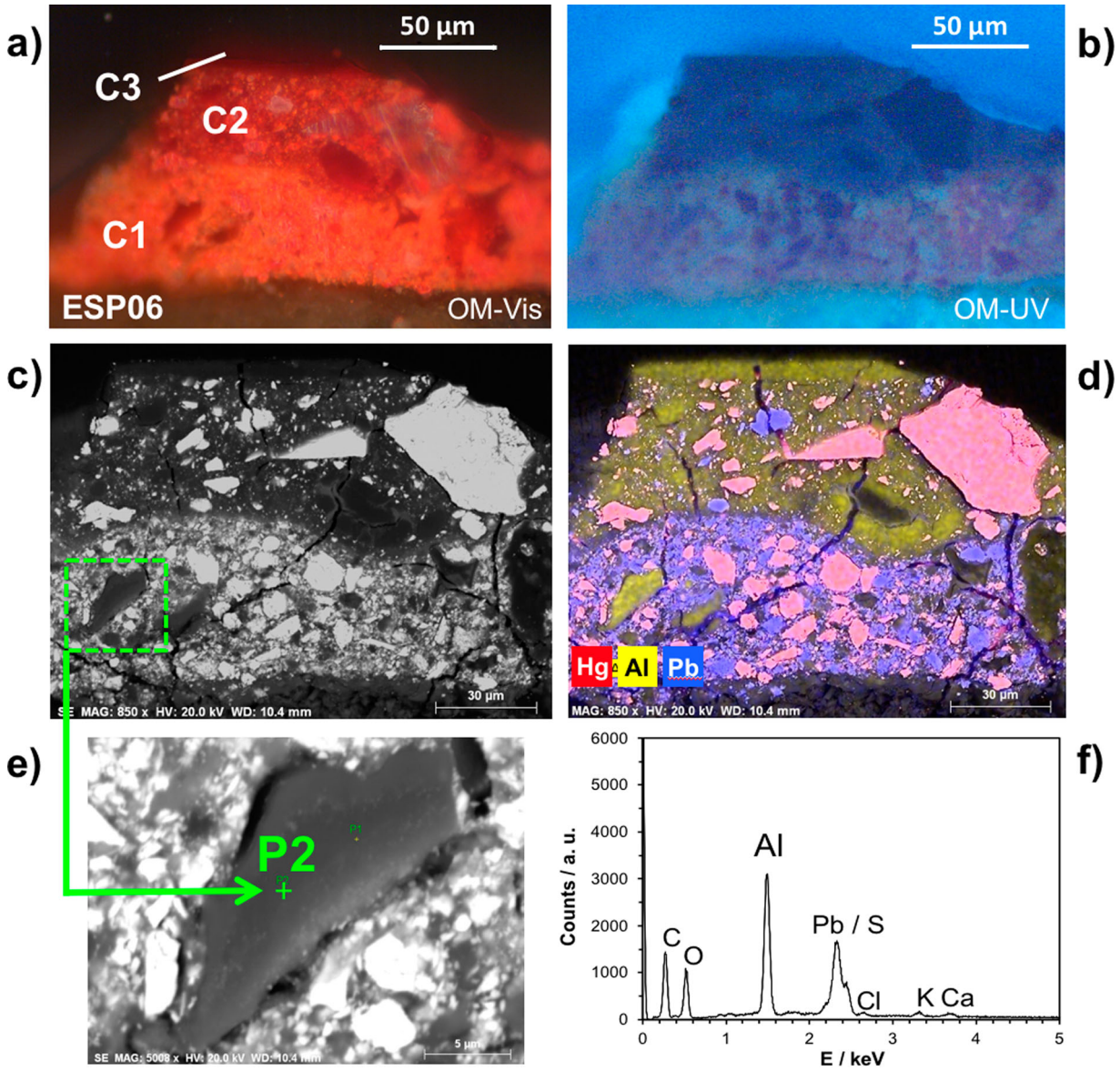

Figure 5. Red pigments. Cross-section of sample ESP06 corresponding to the red mantle of the apostle at the centre of the composition, under OM-Vis (a) and OM-UV (b); SEM back-scattered electron image (c); SEM-EDX mapping of combined elements: Hg (red); Al (yellow), Pb (blue); SEM back-scattered image of a red lake particle P2 (e) located in (c) and respective SEM-EDX spectrum (f). Over the preparatory layers, two opaque red layers containing vermilion, red lake and lead white in different relative proportions (C1, C2), are covered by a red glaze rich in Al (C3)(d, yellow).

paintings produced in Évora around 1590 (Melo 2012), to our knowledge, no magnesium rich mineral of this type as, for the moment, been found in the literature concerning historical azurite (Aru, Burgio, and Rumsey 2014; Valadas 2016). Although further research and the analysis of a larger group of works from this region is needed, the presence of this associated mineral may point to a common source of the azurite used by some southern Portuguese painters in the end of the sixteenth, beginning of the seventeenth century. Possibly the situation may be related to the use of the pigment obtained in the mines of Aljustrel, southern Portugal, for which there is documentary evidence in 1521 (Viterbo 1903).

Table 2. HPLC-DAD-MS results of red lake analysis (values in bold represent the molecular ions).

Retention time (min.)	DAD data (nm)	MS data (*m/z*)	Identification
15.75	238, 276, 491	**491**, 447, 357, 327	Carminic acid
17.01	242, 276, 444	**283**, 239	Brasilein
17.44	250, 310, 350	**243**, 187, 169	Urolithin C

Smalt particles in a size range of 5–30 µm were easily identified by OM due to their broken, fractured and glassy appearance (Figure 9). SEM-EDX analysis detected Si, Co, K, As, Fe, Al, and Ni, elements typical of the sixteenth century smalt pigment (Table 3) (Gratuze et al. 1996; Stege 2004; Spring, Higgitt, and Saunders 2005). Some particles still preserved a pale blue colour, but the large majority was totally discoloured (OM). For this reason, Magdalene's mantle

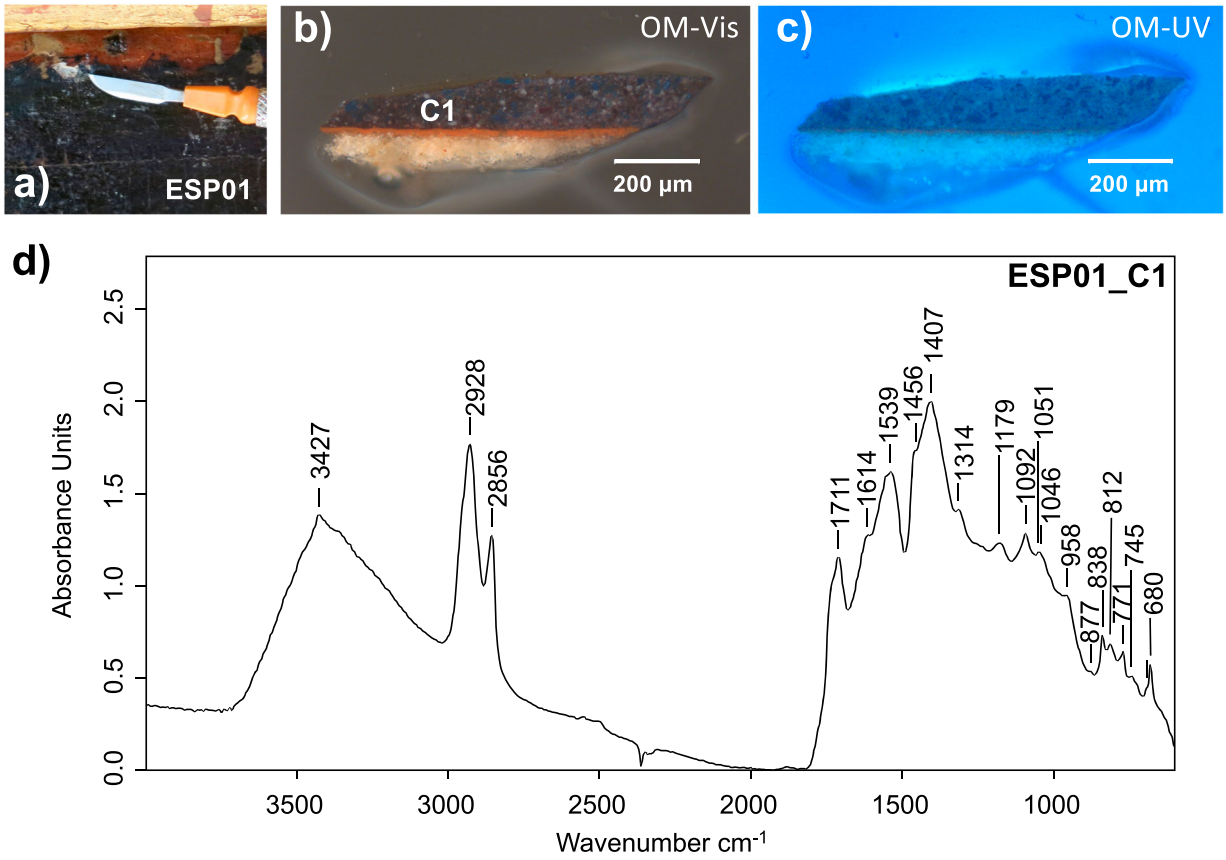

Figure 6. Location of sample ESP01 (a) corresponding to the deep blue of the sky and respective cross-section under OM-Vis (b) and OM-UV (c); infrared spectrum (d) of the azurite rich paint C1 located in (b) (see Table 1, pigment mixture B1).

painted with smalt and a little red lake, now appears grey (Figure 1, Table 1: P1). Smalt discolouration is associated with the leaching of the potassium from the pigment (Robinet et al. 2011, 2013), a phenomenon that was detected in the largest particles of this painting. In fact, smalt particles had a quite constant CoO content between 2.5 and 5.3 wt %, whereas their K_2O concentration varied between 3.1 and 21.3 wt % (Table 3). EDX point analysis and line scans of large smalt particles confirmed this deterioration since the core of the particles had a higher concentration of potassium oxide than the rim (Figure 9c,d). Furthermore, evidence of potassium soap formation caused by the reaction of smalt with the binding medium is visible in the µ-FTIR spectra of smalt-rich paints due to the presence of an absorption band at 1560–1558 cm^{-1} (Figure 10) (Spring, Higgitt, and Saunders 2005).

Azurite and smalt were used on their own, in separate paint layers, but also as a mixture in the dark areas of the sky, creating a deep blue with a colder cast than the azurite-based paints. Smalt was widely combined with other pigments besides azurite, such as green earth, red lake, or lead white, but with the exception of Magdalene's mantle mentioned above, it was restricted to underlayers of green, purple, or azurite-based blue colours (Table 1). As for azurite, it was used almost pure in the blue greenish-blue mantles of the figures, but also mixed with lead white or red lake to create, respectively, the light blue and purple paints used in top and intermediate layers. Furthermore, with the addition of a little red lake to azurite-based paints, Nunes was able to counteract the greenish tinge of the azurite when used in strong concentrations and to diversify the blue hues of the draperies and the sky (Table 1: B1, B4). This resourceful technique reveals Nunes' deep knowledge of the optical properties of the pigments.

Green

Beyond the standard use of verdigris, the main green pigment of European oil painting from the fifteenth to the seventeenth centuries (Kühn 1993), Nunes abundantly favoured the use of green earth in his painting. The intensity and abundance of this pigment is striking as it is absent from Portuguese earlier and contemporary painting production. The green earth was visible as large green to brownish translucent particles (20–50 µm) under optical microscopy (Figure 11a,b). SEM-EDX semi-quantitative analysis revealed, besides silicon (14 wt %) and aluminium (2.4 wt %), mainly iron (8.8 wt %), potassium (4.2 wt %), and magnesium (2.3 wt%) (Figure 11d–m). Although the distinction between celadonite and glauconite, the major components of green earths, is problematic due to the similarity of their chemical

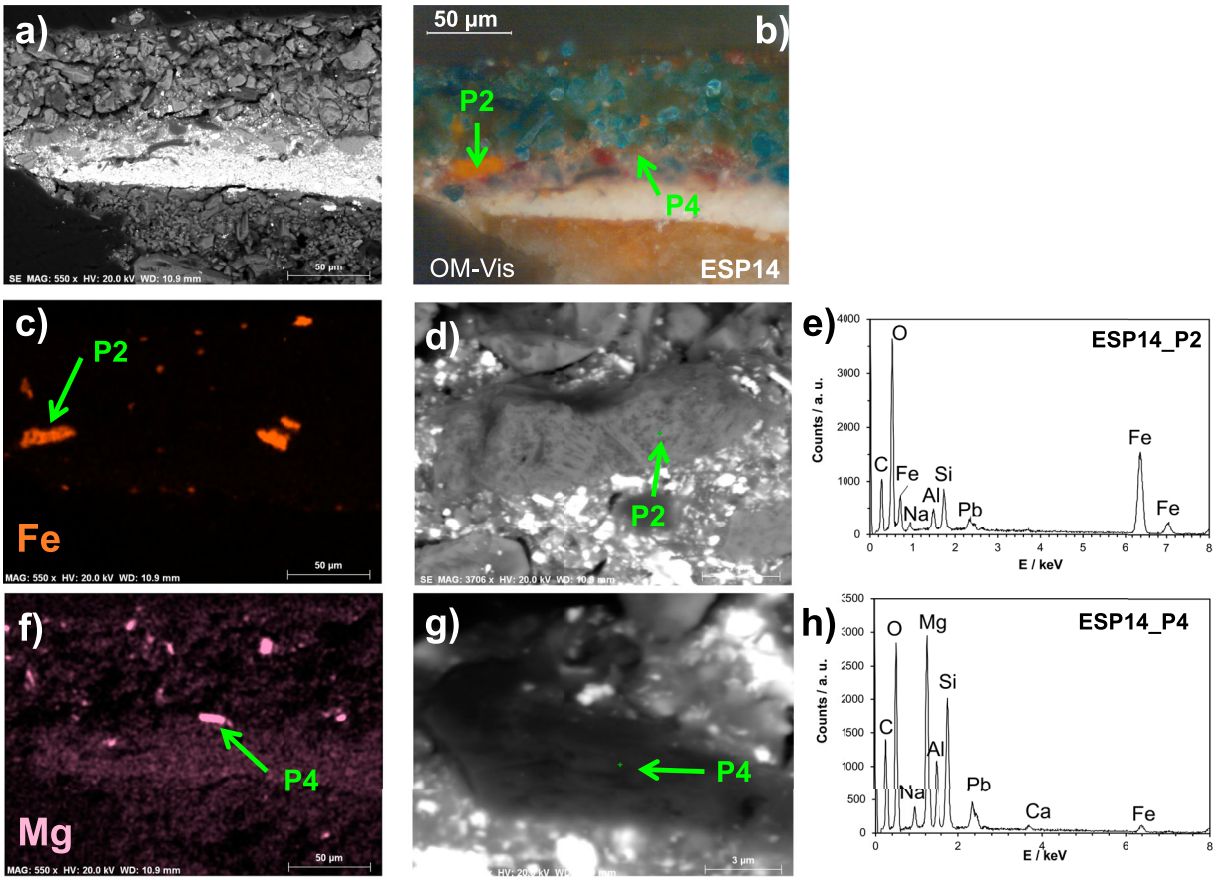

Figure 7. Impurities in the azurite paints. Cross-section of sample ESP14 corresponding to the Virgin's blue cloak, as a SEM back-scattered electron image (a) and under OM-Vis (b); SEM-BSE map of Fe (c) and Mg (f); SEM back-scattered electron images of particles P2 (d) and P4 (g) located in (b, c, f); and respective SEM-EDX spectra (e, h).

composition and structure (Hradil et al. 2011; Perez-Rodriguez et al. 2015), the obtained infrared spectra suggests that celadonite is the main constituent of the green earth used in this painting. In fact, the region of hydroxyl stretching frequencies in the infrared spectra show three narrow bands, well resolved, at 3601, 3557, and 3533 cm^{-1}, with a profile and intensity that are characteristic of celadonite (Figure 1c) (Grissom 1986; Odin 1988). A band at 1626 cm^{-1} is present and can be attributed to water inside the silicate layers (Moretto, Orsega, and Mazzocchin 2011). Bands at 1076 and 984 cm^{-1} can be assigned to the absorptions in the Si-O stretching region of the green earth pigment. Finally, δ(OH) bands of green earth were detected at 839, 800, 747, and 679 cm^{-1} (Moretto, Orsega, and Mazzocchin 2011).

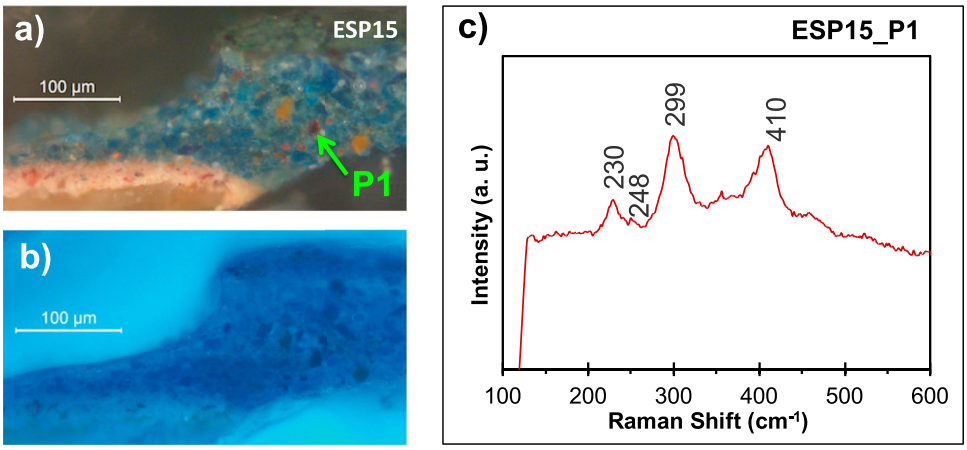

Figure 8. Azurite associated materials. Cross-section of sample ESP15 corresponding to the blue tunic of the apostle standing to the right of the composition, under OM-Vis (a) and OM-UV (b); Raman spectrum of reddish particle P1 (c) located in (a). Over the preparatory layers, a pink undermodelling layer containing lead white and red lake is covered by two layers of almost pure azurite. The top green layer corresponds to an overpaint.

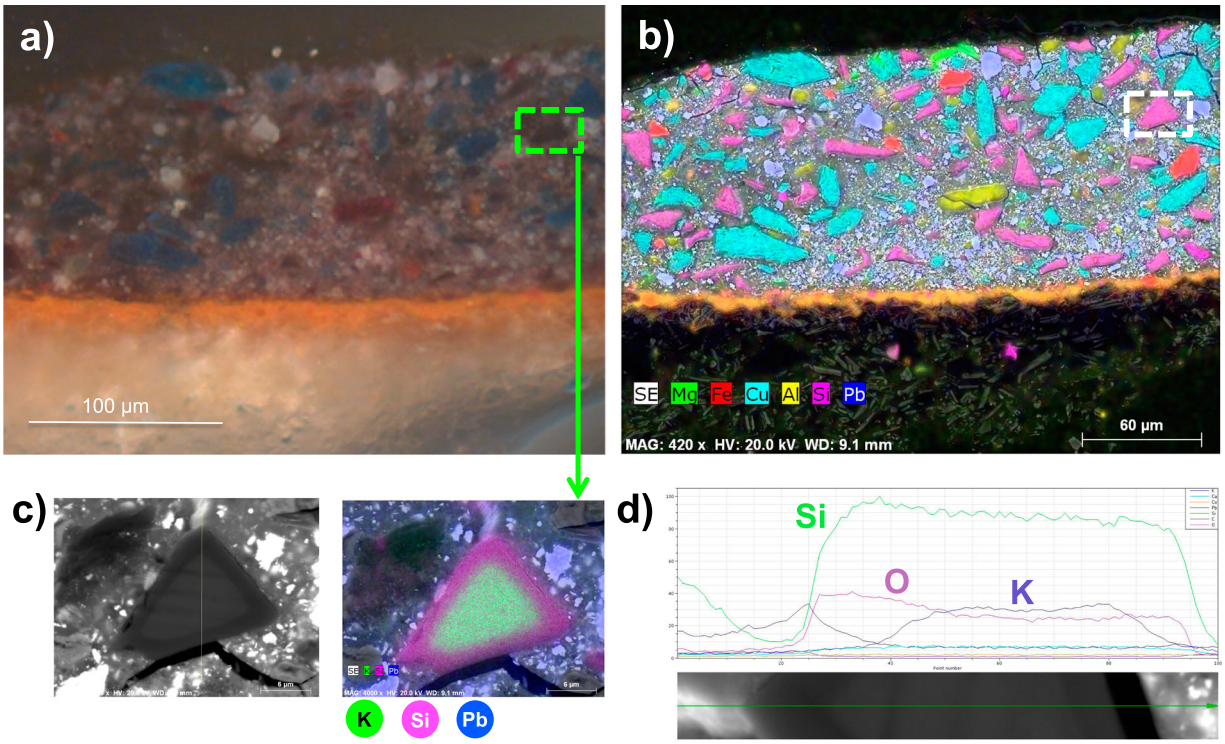

Figure 9. Blue pigments. Cross-section under OM-Vis of sample ESP01, corresponding to the deep blue area of the sky (Table 1, pigment mixture B1) (a); SEM-EDX mapping of combined elements: Mg (green), Fe (red), Cu (light blue), Al (yellow), Si (pink), Pb (deep blue) (b); SEM back-scattered electron image and SEM-EDX mapping of combined elements: K (green), Si (pink), Pb (blue) of smalt particle (c) located in (a, b); line scan analysis of smalt particle (d). The orange thin layer over the ground in (a) corresponds to the bolus applied to the altarpiece structure (sample taken in the margin between panel and altarpiece).

Nunes used the two green pigments, verdigris and green earth, separately in different hues of the landscape and the draperies of the figures. To make the tints, lead white is added to green earth-based paints, but lead-tin yellow is preferred for the verdigris-based paints. Green earth was further mixed with smalt in the trees of the background (Table 1: G4). Lastly, green earth was directly mixed with the flesh tints in variable amounts according to the hues desired, both in the cool tones of the dead Christ and the vivid pinks of live figures as well (Figures 2 and 12).

Green earth is associated with Italian tempera painting, where it served as the base of the *verdaccio* layer in flesh tones (Grissom 1986). Mostly forgotten in the oil painting technique of the fifteenth and sixteenth centuries, this pigment was however occasionally found in small amounts in the flesh tints of works by Italian painters such as Michelangelo (1475–1564) (Dunkerton 1994), Veronese (1528–1588) (Penny, Roy, and Spring 1996), or Tintoretto (1518–1594) (Plesters 1980). In the seventeenth century, however, green earth can no longer be considered an 'Italian' pigment since it was gradually reintroduced in the painter's palette

Table 3. Composition of the smalt particles in normalized weight percentage of oxides, measured by SEM-EDX.

	Smalt Particle				Normalized oxide concentration (wt %)							
Sample	Nr.	Max. Size (µm)		Spot analysed	SiO_2	K_2O	CaO	Al_2O_3	FeO	CoO	As_2O_3	NiO
ESP01	**Sm1**	**20 × 14**	**P1**	**C**	62.8	19.2	4.3	3.9	3.4	3.3	0.7	2.3
			P2	**C**	60.8	21.3	4.2	3.6	3.1	3.1	1.5	2.4
			P3	**E**	71.1	9.0	4.9	4.4	3.4	3.7	0.8	2.7
			P4	**E**	69.8	12.1	4.9	4.0	3.7	3.0	1.2	1.4
	Sm2	**10 × 6**	**P10**	**C**	78.3	3.1	3.9	4.2	4.0	3.4	1.8	1.3
ESP10	**Sm3**	**20 × 5**	**P6**	**C**	65.6	14.8	5.7	4.0	3.7	3.2	1.5	1.4
			P7	**E**	65.1	8.8	8.7	2.5	5.4	4.5	2.8	2.2
	Sm4	**12 × 8**	**P8**	**C**	69.9	13.1	5.3	4.1	3.0	2.5	1.0	1.2
			P9	**E**	75.7	3.5	6.1	5.9	3.5	2.8	1.3	1.3
ESP19	**Sm5**	**20 × 7**	**P3**	**C**	75.3	5.2	4.9	4.1	3.8	3.5	1.6	1.6
			P4	**E**	68.2	4.8	6.7	2.8	4.8	4.1	6.8	1.7
	Sm6	**25 × 15**	**P5**	**C**	63.6	13.8	5.8	2.1	5.2	4.4	3.3	1.7
			P6	**E**	66.0	7.4	6.9	2.2	6.1	5.3	3.1	2.8
ESP24	**Sm7**	**24 × 12**	**P5**	**C**	67.4	15.2	3.9	3.7	4.0	3.1	1.4	1.3
			P6	**E**	71.0	7.1	6.3	4.0	4.6	3.4	2.0	1.6

Note: Spot analysed: **C** = centre of particle; **E** = edge of particle.

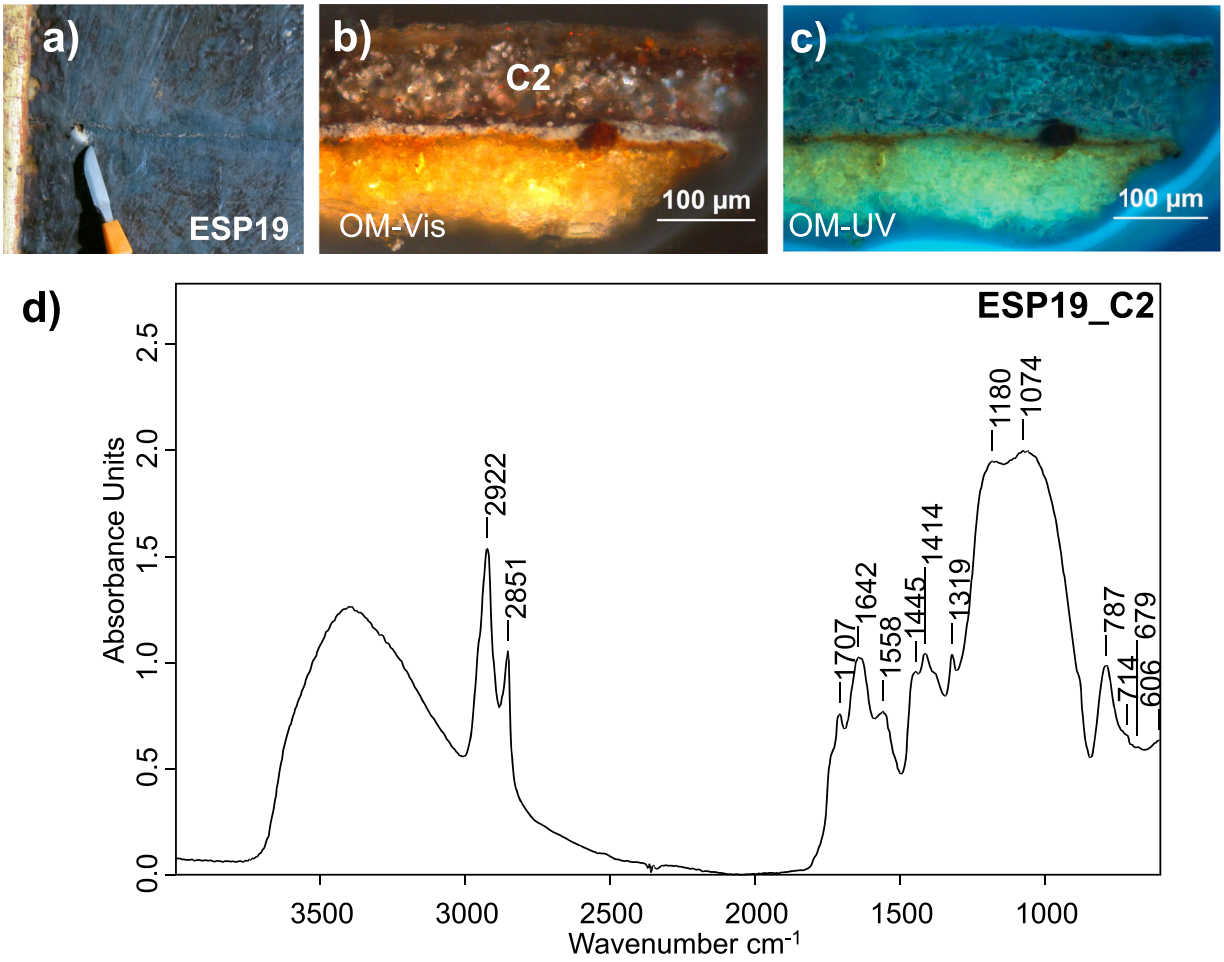

Figure 10. Smalt-rich paints. Location of sample ESP19 (a) corresponding to Magdalen's mantle and respective cross-section under OM-Vis (b) and OM-UV (c); infrared spectrum (d) of the smalt rich paint C2 located in (b) (see Table 1, pigment mixture P1).

and is found in works by painters all over Europe (Dunkerton, Foister, and Penny 1999). According to Dunkerton, Foister, and Penny (1999), its less vivid hue when compared to verdigris would be better suited for landscape painting and the new artistic Baroque style.

Flesh tones

Although only four flesh areas were sampled, looking at the painting surface, the distinctive tints of Christ's body in relation to all major figures, clearly indicates that that the painter used two different pigment mixtures depending on the liveliness of the flesh depicted (Figure 1).

From the samples analysed, the difference is not dependent on the use of green earth, a pigment found in both types of flesh, but on the choice of red and yellow pigments. Beyond the standard use of lead white, Christ's dead body was painted with a red lake and ochres of various shades, whereas vermilion, a brighter red pigment, was preferred to create the pink colours of live flesh (Table 1). Furthermore, lead-tin yellow was used exclusively to tone down the brightness of lead white in the paint mixture formulated to depict the body of Christ and was absent from the live flesh areas sampled (Figure 11, Table 1: F1, F2). It is possible that a comparable choice of paint formulation was followed for all flesh tones, especially concerning the use of the green earth pigment, whose colour is perceived when observing the paint surface in the mid-tones and shadows of the flesh tones of all figures (See Part 2, Figure 12).

Binder

Through µ-FTIR, an aged oil was identified as the binding medium, confirmed by the characteristic ν (C–H) bands at 2928–2920 and 2856–2850 cm^{-1}, together with a carbonyl ν(C = O) band at 1714–1701 cm^{-1} due to carboxylic acids formed by triglyceride hydrolysis (Figures 2, 6, 10, 11) (van der Weerd *et al.* 2005; Mazzeo et al. 2008). The usual ester carbonyl band at 1744 cm^{-1} due to the triglyceride oil constituents was absent from red glazes, a fact that is indicative of the pronounced aging of the binder in these medium-rich layers. However, in the case of lead-rich paints, it appeared at 1737–32 cm^{-1} with a stronger intensity than the acid carbonyl band (Figure 2). In these lead-rich paints, the asymmetric stretch doublet assigned to lead fatty acid soap formation

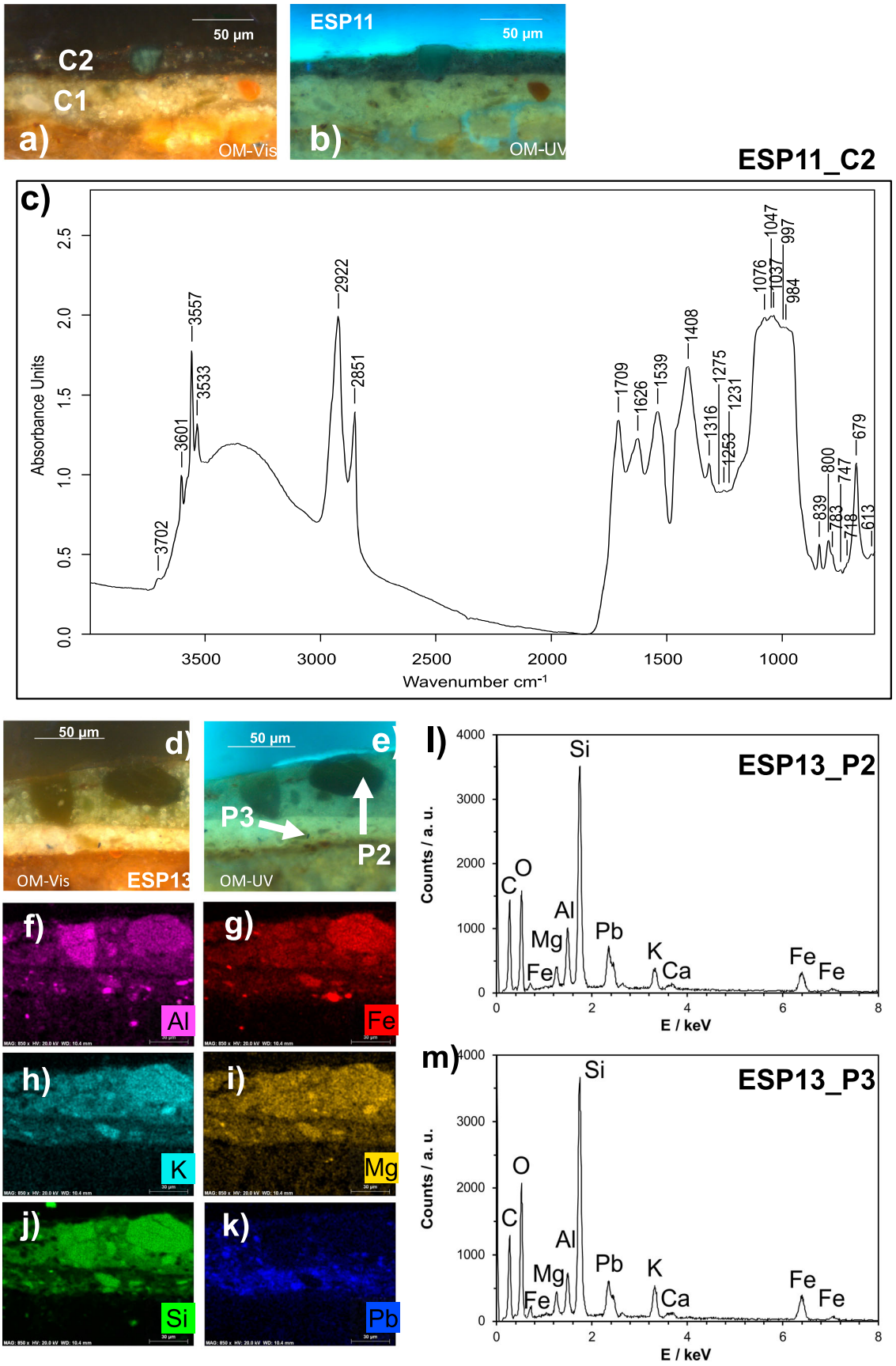

Figure 11. Green earth based paints. Cross-section of sample ESP11 corresponding to the green tunic (shadow) of St. John, under OM-Vis (a) and OM-UV (b); μ-FTIR spectrum (c) of the green paint C2 located in (a) (see Table 1, pigment mixture G5); cross-section of sample ESP13 corresponding to the green tunic (mid-tone) of St. John, under OM-Vis (d) and OM-UV (e); SEM-EDX maps of the elements Al (f), Fe (g), K (h), Mg (i), Si (j), Pb (k); and SEM-EDX spectra of particle P2 (l) and particle P3 (m) both located in (e).

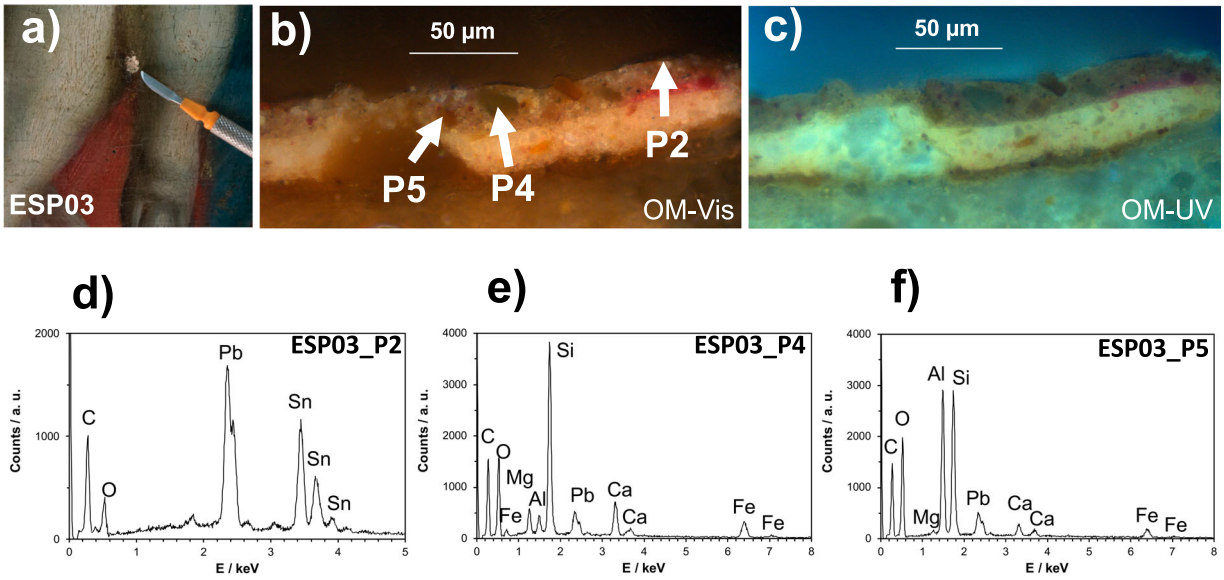

Figure 12. Flesh paint, shadow. Location of sample ESP03 (a) corresponding to a shadow area of Christ's hand and respective cross-section under OM-Vis (b) and OM-UV (c); SEM-EDX spectra of particles P2 (d), P4 (e) and P5 (f) located in (b) (see Table 1, pigment mixture F2).

was visible at 1528–1513 cm^{-1}, thus confirming that the carboxylic acids reacted to form lead soaps (Figure 2) (Higgitt, Spring, and Saunders 2003; Robinet and Corbeil 2003; van der Weerd *et al*. 2005). Metal oxalates, prevalent in medium-rich aged glazes, were especially detected in all red glazes, but also in smalt rich and green earth rich layers, through bands at 1655–1642 cm^{-1} [ν_s(C = O)], 1319–1313 cm^{-1} [ν_a(C–O)] and 787–783 cm^{-1} [δ(O–C = O)] (Higgitt and White 2005) (Figures 10 and 11).

Conclusion

Pedro Nunes creates his colours with a wide variety of pigments, namely lead-white, lead-tin yellow, ochre, an orange artificial arsenic sulphide, vermilion, verdigris, green earth, smalt, azurite, vegetable carbon black, and a red lake made of brazilwood and cochineal. His colour mixtures are extremely varied and the use of a black pigment was mostly limited to underlayers, a technical choice that justifies the brightness of his composition. Changes in saturation and value were mostly created by an adjustment in the relative concentration of each pigment in the mixture or, for the lights, by the admixture of white and, in some instances, lead-tin yellow. The experienced formulation of translucent and opaque pigment mixtures enables the painter to broaden the hues of his colour palette. Moreover, through the ingenious addition of a little red lake to the azurite paints, he counteracts the greenish tonality of this blue pigment.

The identification of green earth and an orange artificial arsenic sulphide, two unusual pigments not previously found in Portuguese painting of this period, clearly singles out this painting from Portuguese practice. While green earth and arsenic pigments have a strong connotation to Italy – the first widely used in Italian Medieval tempera painting and the second favoured by the sixteenth century Venetian School, both pigments were employed in the seventeenth century by Italian and Northern painters alike. However, the use of green earth in flesh tones and not only in the landscape, along with the extensive use of the artificial arsenic pigment in large passages of the composition testify to Filipe Nunes' direct contact with the Italian pictorial practice and tradition.

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