Received: 9 February 2022 | Revised: 1 May 2022 | Accepted: 28 May 2022

DOI: 10.1002/col.22809

RESEARCH ARTICLE

COLOR RESEARCH AND APPLICATION WILEY

Images in transformation: The color and its change in a group of Portuguese paintings from the second half of the 16th century

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Funding information
ERIHS.pt, Grant/Award Number: ALT20-03-0145-FEDER-022115 (Program Alentejo2020); Fundação para a Ciência e a Tecnologia, Grant/Award Number: SFRH/BPD/109296/2015; Fundo Social Europeu; Hercules Laboratory Strategic Plan, Grant/Award Number: UIDB/04449/2020

Abstract

Four panel paintings depicting episodes related to the birth of Christ and attributed to the Portuguese mannerist painter Francisco João (doc. 1558–1585) were found to exhibit a muted palette that had no correspondence with the traditionally vivid colors used in the sixteenth century to represent joyful biblical events. Complementing previous research on the disruption and loss of the red glazes in these paintings, the investigation focused on the analysis of materials, painting technique and degradation issues that further affected the original paintings, changing the viewer's perception and understanding of these artworks. The investigation combined the visual examination of the painting surface with microscopic and spectroscopic analysis of the binder and pigments. A conventional palette made of lead white, lead-tin yellow, ochres, vermilion, verdigris, smalt, azurite, carbon black and a red lake made of brazilwood and cochineal was identified. The pigments were bound in an oil-based medium. Chemical and physical alterations detected in paints rich in smalt and verdigris were found to be responsible for color changes affecting significant areas of the compositions. The presence of moisture and the reaction between pigment and binder leading, among other products, to soap and oxalate formation, played a central role in the long-term behavior of the paint film. Understanding the main degradation processes involved and their consequences is crucial when interpreting an artists' color palette and designing the best approach to preserve these paintings.

KEYWORDS

16th century painting, color, degradation, pigments, technique

1 | INTRODUCTION

Four oak panel paintings belonging to a dismembered polyptych attributed on a stylistic basis to Francisco João, the most relevant mannerist painter working in the region of Évora, southern Portugal, between 1558 and 1595, were found to exhibit a muted palette, despite depicting joyful scenes of Christ's life that are usually painted with vivid colors. The main paintings (134 cm × 70 cm) illustrate two episodes related to the birth of Christ: the *Annunciation* and the *Adoration of the Shepherds*. Below them, two predella paintings (44 cm

× 70 cm) portray *Saint John the Evangelist and Saint Amaro* and *Saint Lucia and Saint Bartholomew* (Figure 1). On display in the church of São Miguel de Machede, close to the city of Évora, the panels were removed from their original structure and inserted into new frames. The works under study are part of the largest collection of Portuguese Mannerist altarpieces preserved in the country. Most of them remain unstudied from a material and technical perspective, despite conserving the work of the main national and foreign painters, sculptors and carvers active in the country in the second half of the sixteenth century.[1–5]

The paintings' palette is composed of subdue and neutral colors such as black, grey, white, and ochre, combined with dark red, blue, and a blackish green with a few rare notes of pale yellow that locally brighten the whole (Figure 1). The perception of color is not affected by the thin varnish that coats the surface and whose presence is mostly detected under ultraviolet radiation. The paintings are fairly well preserved, but a disruption and loss of paint is observed in the red glazes (Figure 1). The degradation affecting the red glazes and ochre paints has been previously investigated.[5] In order to further investigate the painter's technique and use of color, the surface of the paintings was inspected under visible and ultraviolet radiation and paint samples were collected and analyzed with microscopic and spectroscopic techniques. Aspects related to materials, technique and degradation of paint films were discussed with the aim of better interpreting and assessing the original and actual color palette of these compositions and advise on the better approach to their safeguard.

2 | EXPERIMENTAL

The colors of the Machede paintings were investigated through surface examination of the paintings and the analysis of paint microsamples that were, in part, embedded in an epoxy resin (*Struers SpeciFix 40*) and polished as cross-sections. A first observation of the cross-sections by 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 Lp425 size), using a Leica DM2500 microscope, provided information concerning the pigments, the pigments' mixtures and the paint stratigraphy.

FIGURE 1 Panels from a dismembered altarpiece attributed to Francisco João (doc. 1558–1595). Church of São Miguel de Machede, Évora, Portugal. © HPM; HERCULES Lab.—U. Évora, Portugal

Digital images were taken with a Leica DFC290HD digital camera.

Scanning electron microscopy coupled with elemental energy dispersive X-rays (SEM–EDX) was used to identify inorganic pigments and extenders and study the morphology of the particles present in paint layers. It was performed on the uncoated cross-sections with a variable pressure scanning electron microscope Hitachi 3700N operated at 20 kV, with a BRUKER Contact 200 EDX detector from Oxford Instruments. Semi-quantitative spot analysis of smalt particles is expressed in weight percentage of oxides normalized to 100%.

Micro Fourier transform infrared spectroscopy (μ-FTIR) was used as a fast method of gathering molecular information helpful in identifying binding media classes, some inorganic compounds, but mostly the degradation products formed as a result of the ageing of the paint. The layers were separated and each one was compressed between two diamond cells and analyzed in transmission mode. The spectra were obtained with a Bruker Tensor 27 spectrometer coupled to an Hyperion 3000 microscope with an MCT detector, controlled by the 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}.

Micro-Raman spectroscopy (μ-RS) was carried out on cross-sections as a complementary technique useful in the distinction between small red particles of minimum and vermilion and between the two types of lead-tin yellow used as a pigment in this period. The analysis was performed on a multiple laser dispersive Raman spectrometer (Renishaw in Via) with a high-power diode laser (Toptica Photonics XTRA) at 785 nm. The instrument was coupled to a Leica DMLM microscope with enclosure using 5× to 100× objectives.

The red lake dyestuffs of organic pigments were analyzed after their mild extraction from the lakes[6] with the HF 2 M in mixture water/organic solvents, 1:1 with High performance liquid chromatography (HPLC) using a Spectra-SYSTEM from ThermoScientific. It consisted of a P1000XR pump, an AS3000 autosampler equipped with a 20 μl 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 μm, 250 × 4.6 mm (Altech, Lokeren, Belgium). The eluents were: (A) MeOH, (B) 5% ACN in water, (C) 0.1% TFA in water; (D) ACN. The flow rate was 1 ml/mn. The elution program was without switching with a typical gradient as follows: 0–15 mn: 90B, 10C; 15–55 mn: 15A, 60B, 10C, 15D; 55–64.5 mn: 45A, 10C, 45D; 64.5–70 mn: 90D, 10C. The temperature at the chromatography laboratory was maintained between 20°C and 22°C by air conditioning.

The optical and electronic microscopy were performed in the HERCULES Laboratory, University of Évora, Portugal. All other analyses: μ-FTIR, μ-RS and HPLC were performed in the IRPA-KIK laboratory, in Brussels, Belgium.

3 | RESULTS AND DISCUSSION

3.1 | Preparatory layers

SEM–EDX and μ-FTIR analysis revealed that the original oak panels were prepared with a single ground layer of *gesso grosso*, mainly composed of anhydrite with small amounts of calcium sulphate dihydrate bound in animal glue.[4] Microscopic analysis of the paint samples under Vis–UV radiation detected a concentration of organic material at the top of the ground (Figure 2). No clear separate intermediate layer was visible under OM or in the SEM back-scattered electron images. This organic-rich surface showed different degrees of penetration into the ground and it was difficult to ascertain its presence in all of the samples collected. It could correspond to an unpigmented sealing layer or else result from the absorption into the ground of the binder of the paint layers above.

3.2 | Paint binder

Infrared spectra identified the paint binder as an aged oil, confirmed by the characteristic ν(C—H) bands at ~2920 and ~2850 cm^{-1}, along with the shifting and broadening of the carbonyl band ν(C═O) band from 1730–40 to ~1712–1703 cm^{-1} due to carboxylic acids formed by triglyceride hydrolysis (Figure 2). In samples containing lead white or lead tin yellow, a shoulder could sometimes be resolved at a lower intensity around ~1736 cm^{-1} and the intensity of the ~1710 cm^{-1} carbonyl band was low when compared to the C—H stretch vibration at ~2920 cm^{-1} (Figure 2). In these samples, lead soaps[7,8] were detected through the presence of a strong ν_{as}COO band centered at ~1520 cm^{-1} or appearing as a doublet at ~1539–1512 cm^{-1} (Figure 2). In medium-rich paints without any lead giving pigment, such as red and green glazes, the ~1736 cm^{-1} band - related to the remaining ester bonds in the binder—is hidden by the intense ~1707 cm^{-1} free fatty acids band - of the same intensity as the C—H stretch vibration at ~2920 cm^{-1} – thus indicating a severe oxidation of the binder of these medium-rich layers and an associated increase in the acidity of the paint[9] (Figure 2). A broad band centered at ~3400 cm^{-1} was found on all samples and, although it might, in the

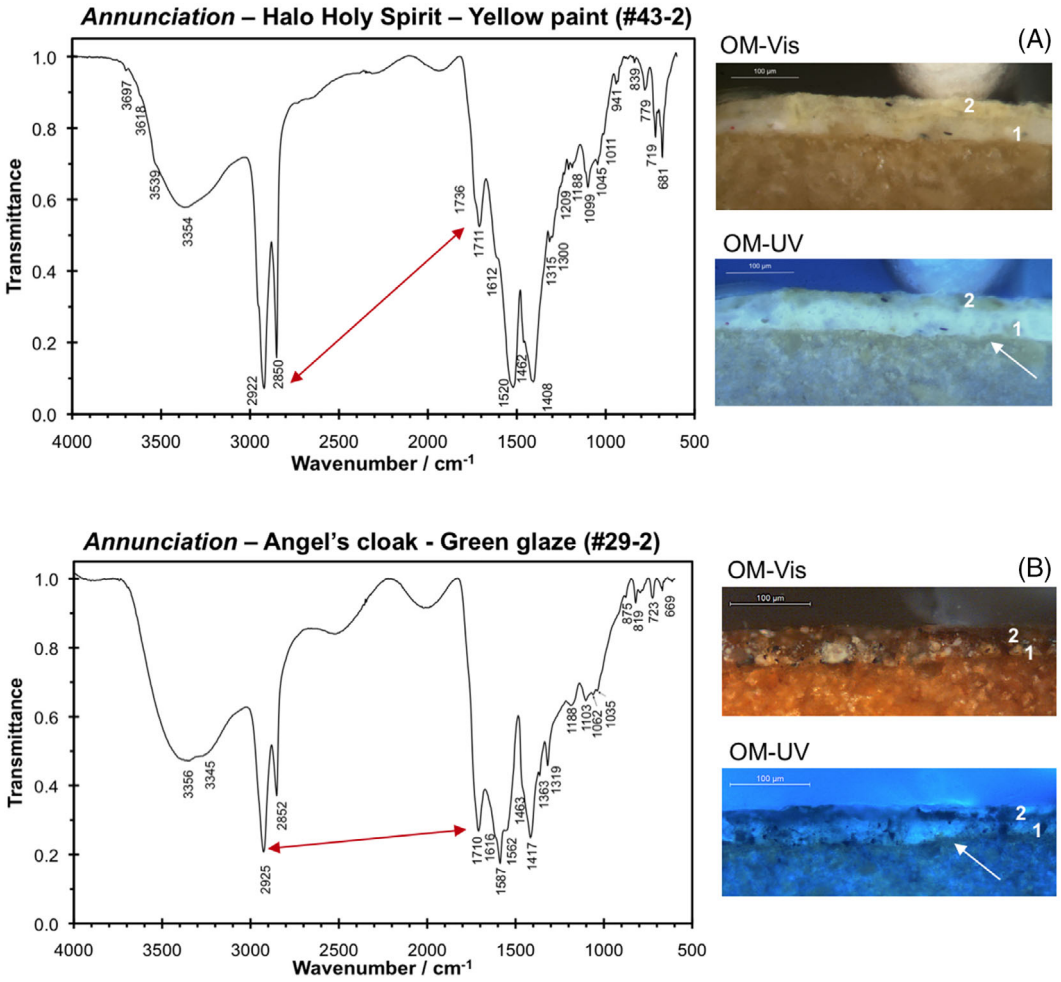

FIGURE 2 Infrared spectra of the uppermost paint layers of samples #43–2 (yellow paint, layer 2) and #29–2 (green glaze, layer 2), and respective cross-sections in the optical microscope under incident light (OM-Vis) and ultraviolet radiation (OM-UV). The red arrow indicates the relative intensity of the ~1710 cm^{-1} free fatty acids' band and the C—H stretch vibration at ~2922 cm^{-1}. (A) Sample #43—*Annunciation*—Yellow of the halo of light of the Holy Spirit. Over the preparatory layers, a first layer of lead white with a little carbon black (1) is covered by a yellow paint made of lead white and lead-tin yellow (2). (B) Sample #29—*Annunciation*—Green of the angel's drapery. Over the preparatory layers, a first greenish paint made of carbon black, lead white, lead-tin yellow and ochre (1) is covered by a brownish verdigris-based glaze (2). The white arrow in the cross-section images (OM-UV) indicates the concentration of organic material. © HPM & JS; IRPA/KIK, Brussels

case of ochre and lake pigments, result from pigment absorptions, in all other cases it could to be assigned to alcohol and/or hydroperoxide vibrations formed during the ageing of oil.[9,10]

HPLC-DAD analysis of one sample from the red glaze of Saint Joseph's cloak detected dehydroabiectic and 7-oxo-dehydroabietic acids, two degradation products of pine resin (*pinacea* sp.).[11] This result indicates that some resin was used as a varnish, original or not, 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[12] and has been analytically found in paintings from this period.[13,14]

3.3 | Pigments

SEM–EDX and μ-FTIR analysis identified lead white and carbon black as the main white and black pigments used to establish the tints and shades of the paints. Infrared spectra of lead white rich paints exhibited the usual carbonate bands at ~1408, 1045, and 681 cm^{-1}, along with a ν(OH) distension at ~3539 cm^{-1} for hydrocerussite ($2PbCO_3 \cdot Pb(OH)_2$) and the characteristic 839 cm^{-1} stretching band for neutral lead carbonate, a component ordinarily found in lead white[15] (Figure 2).

The most common lead-tin oxyde type I (Pb_2SnO_4) was identified with SEM–EDX and μ-RS as the main opaque yellow pigment, used in a few garments and in

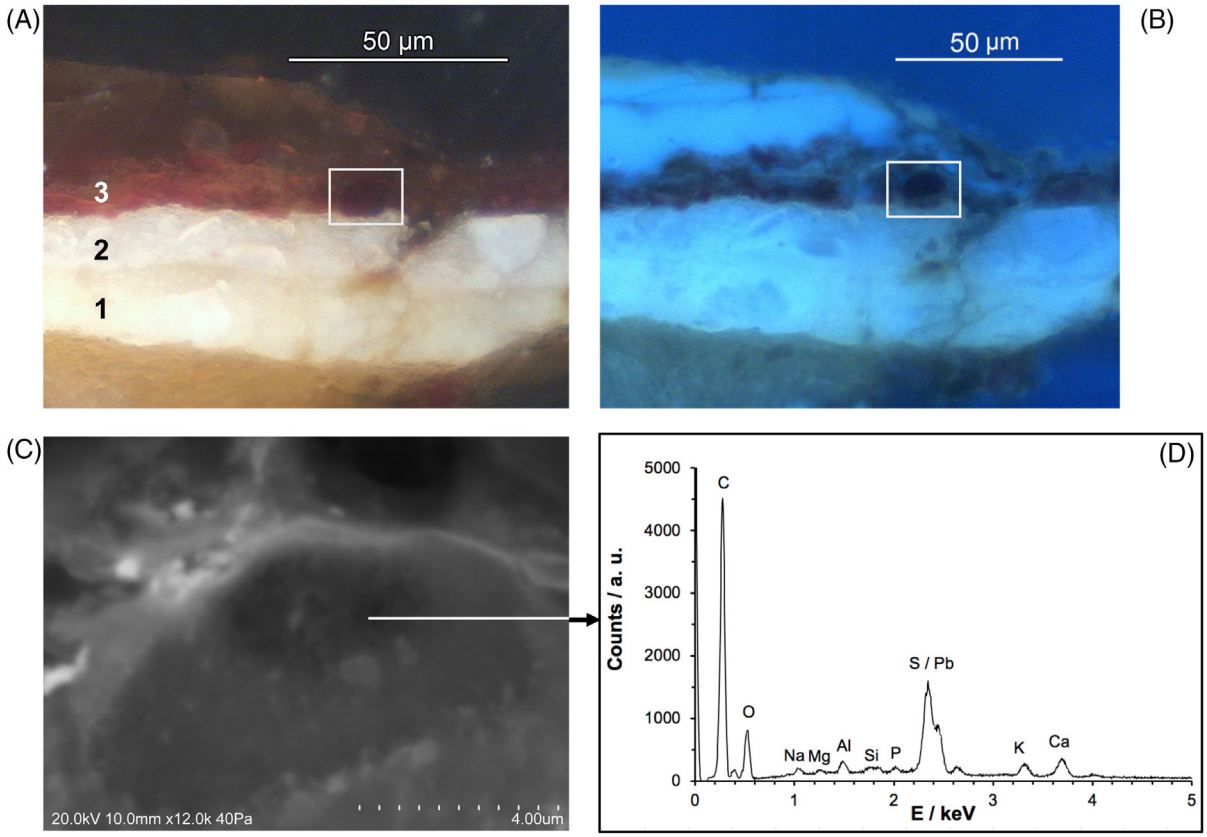

FIGURE 3 Cross-section of sample #23 (Saint Joseph's cloak—*Adoration*), in the optical microscope under incident light (OM-Vis) (A) and ultraviolet radiation (OM-UV) (B), with the location of red lake particle inside a white rectangle; SEM back-scattered electron image of the lake particle (C) located in (A, B) and SEM–EDX spectrum of the lake particle (D). Over the preparatory layers, a first undermodelling of the forms made with a first layer of lead-white and ochre (1), followed by a lead white with a little red lake paint (2), finally covered by a red glaze containing ground glass (3) and by two varnish coatings (fluorescent under UV). © HPM & SV; HERCULES Lab.—U. Évora, Portugal

the light halos opening the heavenly space in the uppermost section of the *Annunciation* and *Adoration*.

Vermillion and red ochre, two opaque red pigments of different brightness, were often mixed together in variable proportions. SEM–EDX elemental analysis detected mercury and sulphur in vermilion and an iron-rich aluminum silicate in the red ochre. A translucent lake pigment exhibiting a violet/crimson hue when viewed under OM-UV was identified in red glazes (Figure 3). HPLC analysis of two samples detected 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 one of the samples, indicating, according to Jo Kirby and colleagues,[16] that weighted silk could have been used as a source of the dyestuff. SEM–EDX semi-quantitative point analysis of lake particles, revealed that they contain mainly carbon and small amounts of calcium and potassium (on average 2.7 wt % Ca and 1.6 wt % K) (Figure 3). This suggests that a calcium compound is present in the lake substrate. Sulphur, silicon, aluminum, sodium, magnesium, phosphorous and chlorine were detected in minor concentrations as well. These are commonly present in red lake substrates and can arise from the scale insect source or from the ingredients and procedures related to red lake manufacturing.[11,16] The identification of two dyestuffs when only one type of red lake was found by OM and SEM–EDX 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 14th to the 17th century.[17] The red lake was found not only in red glazes but in mixtures of red, pink and purple paints. 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.[5]

Two blue pigments, azurite and smalt, were analyzed in separate paint layers and were never mixed together. The mineral azurite, a basic copper carbonate, exhibited

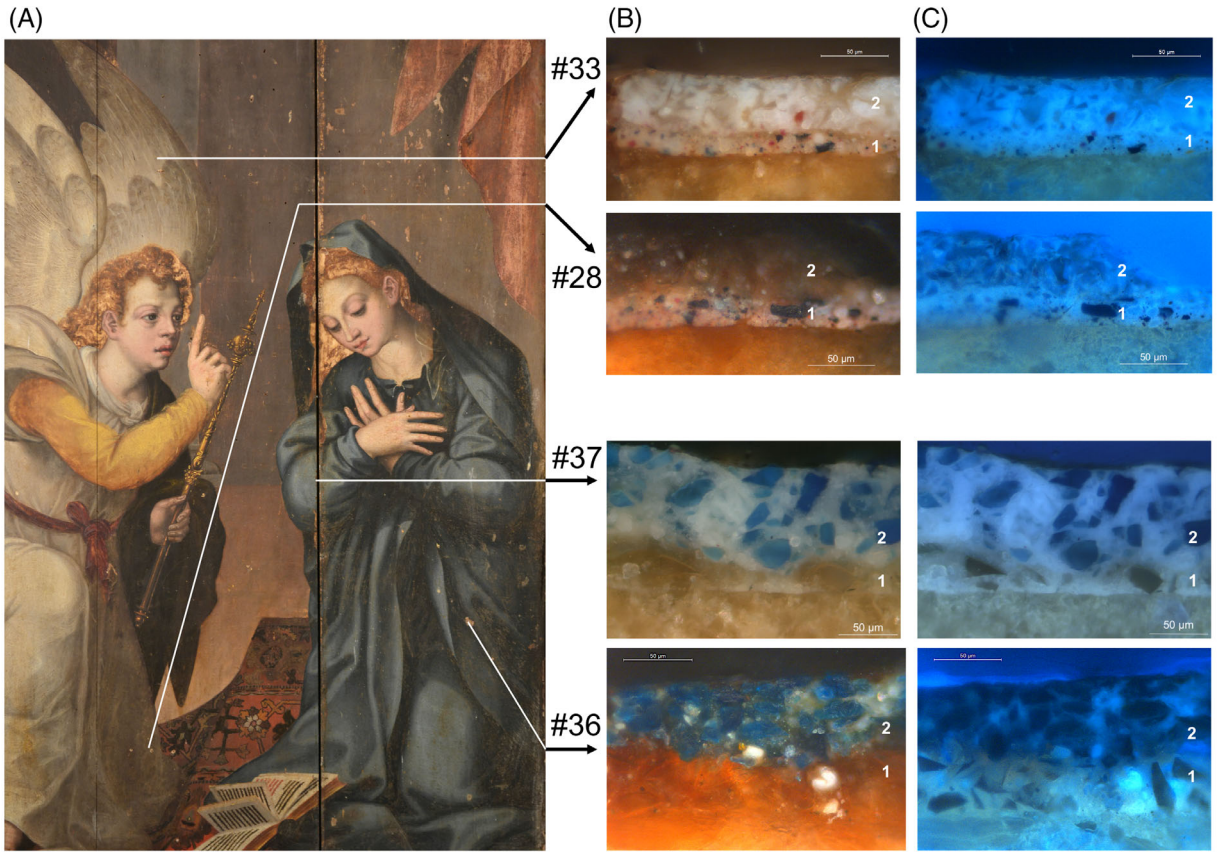

FIGURE 4 Detail of the *Annunciation* (A) with the location of samples with discolored smalt in the wings (#33) and the tunic (#28) of the angel, and under the azurite-based blue garment of the Virgin (samples #37 and #36); cross-sections of the located samples in the optical microscope under incident light (B) and ultraviolet radiation (C). © HPM; HERCULES Lab.—U. Évora, Portugal

easily recognizable broken and coarsely ground blue particles under the optical microscope (Figure 4). SEM–EDX analysis of these particles detected mostly copper and calcium.[18] Furthermore, azurite-rich paints exhibited characteristic infrared spectra with absorption ν(OH) bands around 3427 cm^{-1}; $\nu(CO_3)$ bands at ~1406, ~1092 cm^{-1}; a ν(CO) band at ~955 cm^{-1} and lastly, δ(OCO) bands around 835, 816, 760, and 741 cm^{-1} (spectra not shown). Smalt, a potassium-containing glass coloured blue by cobalt oxide, was found to be completely discolored. In optical microscopy, the smalt particles had the appearance of a translucent yellowish glass with sharp edges and, when used almost pure, they could only be distinguished within the brownish paint matrix when the cross-sections were examined under ultraviolet radiation (Figure 4). EDX elemental analysis revealed that the smalt particles contained silicon and cobalt, but were almost completely depleted of potassium (Table 1). Other elements characteristic of sixteenth century smalt such as aluminum, calcium, sodium, magnesium, iron, nickel and arsenic, were detected by SEM–EDX analysis and derive from the raw materials used in glass manufacture and the cobalt ore.[19–23]

Verdigris was identified by its copper content in elemental EDX analysis and by the detection, in the infrared spectra of green glazes, of copper acetate bands at 1616, 1363, 1062, and 1035 cm^{-1} characteristic of this pigment (Figure 2). Verdigris was the major component of the green glazes where it had largely dissolved, forming the translucent uppermost layer of green draperies. No bands ascribed to the carboxylate of resin acids (~1698 cm^{-1}) characteristic of a true copper resinate, were visible in the infrared spectra.[24,25]

3.4 | Color making and technique

Colors were formulated using straightforward pigment mixtures (Table 2). Generally, one color, mostly originating from a single pigment, such as azurite, smalt, lead-tin yellow, red lake or verdigris, was shaded with black and/or ochre and lightened with lead white. The color red was the only instance when two or three red pigments of different hues and degree of translucency—vermilion, red ochre and red lake—were combined to create different red tonalities. With the same three red pigments

TABLE 1 Composition of the smalt particles in normalized weight percentage of oxides, measured by SEM–EDX

	Smalt particle				Normalized oxyde concentration (wt %)										
Sample	Nbr.	Max. Size (μm)	Spot analyzed		SiO_2	Al_2O_3	CaO	Na_2O	K_2O	MgO	FeO	CoO	As_2O_3	NiO	Cl
#28	Sm01	15 × 5	P1	C	74.7	2.9	5.0	1.1	0.9	1.3	4.2	5.8	2.8	1.0	0.4
	Sm02	20 × 12	P2	C	74.0	2.4	5.1	0.8	0.7	0.0	4.9	6.8	3.9	1.1	0.4
			P3	E	73.1	2.6	4.9	0.9	0.7	0.7	5.1	6.3	4.2	1.0	0.4
	Sm03	15 × 12	P8	C	74.1	2.4	5.5	0.9	0.7	0.9	4.7	6.6	2.8	0.9	0.3
#33	Sm04	15 × 5	P1	C	74.4	3.3	5.8	0.9	0.3	1.0	4.7	5.6	2.5	1.0	0.3
	Sm05	10 × 4	P3	C	72.8	2.9	5.8	1.6	0.6	1.3	4.6	5.9	2.9	1.1	0.5
	Sm06	8 × 5	P5	C	74.8	2.8	5.5	1.3	1.2	0.8	4.1	5.7	2.6	0.9	0.4
#36	Sm07	20 × 15	P3	C	72.5	2.3	7.9	0.6	0.4	0.5	4.5	6.2	3.0	1.8	0.3
	Sm08	12 × 7	P5	C	72.4	2.6	6.5	1.1	0.3	0.8	4.8	6.4	3.1	1.7	0.3
			P6	C	70.8	3.0	6.8	2.1	0.3	1.1	4.7	6.1	2.5	2.1	0.5
	Sm09	10 × 8	P7	E	66.1	3.4	9.9	3.2	0.8	1.5	3.2	3.8	3.1	3.2	1.8
	Sm10	20 × 15	P11	C	68.8	1.2	8.9	0.1	0.2	0.2	6.1	8.2	4.0	2.1	0.2
#44	Sm11	15 × 6	P2	C	74.7	3.1	4.9	1.4	2.3	0.9	3.9	4.9	2.8	0.6	0.5
	Sm12	12 × 6	P3	C	73.9	3.0	5.3	1.8	0.6	1.3	4.4	5.4	3.0	0.8	0.5
	Sm13	10 × 5	P4	C	68.9	1.1	7.6	0.0	1.6	0.2	6.0	8.1	5.0	1.2	0.5
	Sm14	20 × 16	P7	C	74.5	2.7	5.1	1.5	0.8	1.3	3.9	5.2	3.4	1.0	0.6
	Sm15	24 × 20	P8	C	75.2	2.7	3.7	1.2	0.7	1.2	4.3	5.9	3.6	1.0	0.5

Note: Spot analyzed: C, centre of particle; E, edge of particle.

mixed in different proportions the painter was thus able to create the bright vivid red of the Virgin's carpet and the dark brick mantle of Saint Amaro (Figure 1, Table 2—R1-R2). The distinct tonalities of the flesh were also formulated with different ratios of the same pigments. As such, the light flesh tones symbolizing the purity of the Holy figures of the angels, saints and the Virgin were obtained with a conventional mixture of lead white and vermilion, to which a little black and/or ochre were often added (Table 2—F1-F3). As for the darker flesh tones of the shepherds, they were based on a lead white and ochre rich paint containing a little black and, sometimes, traces of vermilion (Table 2—F4).

In the underlayers that did not require bright and saturated colors, the painter created the green and purple colors with a light grey paint made of lead white and carbon black, to which he added a little lead-tin yellow, verdigris and ochre for the green and a little red lake for the purple (Figures 4 and 5). This type of mixtures may suggest an economical choice of pigments since the blue pigment often used to make purple and green colors was replaced by a cheap carbon black. However, the optical intention to tone down the undermodelling as part of the painting technique must also be considered.

The technique is fairly simple with most of the samples showing a succession of one or two layers of paint over the preparatory layers. The use of three superimposed layers corresponds to the draperies glazed in red and green. In these cases, the translucent glazes were spread over a local opaque undermodelling of the forms developed in one or two layers (Figures 3 and 5). Green verdigris-based glazes were applied in a single layer over a contrasted underpaint made of a bright lead-tin yellow-rich color for the lights and an black-greenish color for the shadows (Figure 5). The strong contrast between the light and dark areas of the underpaint is a standard painting technique, used to ensure that the shape of the folds would remain visible once the green glaze was applied.[26] Red lake glazes containing translucent ground glass were spread in a single layer over an ochre to pink undermodelling of the draperies, as can be seen in Saint Joseph's mantle and in the curtain behind the Virgin of the *Annunciation* (Figure 3).

Local underpaints were also found beneath the blue mantle of the Virgin, a technique that is commonly found in contemporary paintings of this period, notably Portuguese.[1,3,27] In this case, a smalt-rich paint, to which lead white was added for the lights, created a first modelling of the forms (Figure 4). Over this, the folds were

TABLE 2 Pigment identified and their mixtures

	Pigment mixtures				Number of Pigments		
Color	**Ref.**	**Pigments**	**Painted motif**	**Layer**	**Total**	**Wh.**	**C**
Yellow	**Y1**	Lead-tin yellow + Lead white	Drapery	T	2	1	1
			Halo				
			Sky				
Ochre/Brown	**O1**	Ochre + Lead white	Drapery	U	2	1	1
			Sky				
	O2	Ochre + Lead white + Vermilion (tr.)	Sky	U	3	1	2
	O3	Ochre + Lead white (tr.) + Carbon black (tr.)	Drapery	U	3	1	2
	O4	Ochre + Lead-tin yellow (tr.) + Lead white (tr.) + Carbon black (tr.)	Hair	T	4	1	3
	O5	Ochre + Lead white + Carbon black + Vermilion (tr.)	Sky	U	4	1	3
			Sword	U			
			Drapery	U			
			Floor	T			
Red	**R1**	Vermilion + Red ochre + Red Lake + Lead white (tr.)	Carpet	T	4	1	3
			Lips				
	R2	Vermilion + Red ochre + Red Lake + Lead white (tr.) + Carbon Black (tr.)	Drapery	T	5	1	4
Pink	**Pk1**	Red Lake + Lead white	Wings	T	2	1	1
			Drapery	U			
	Pk2	Red Lake + Powdered colorless glass	Drapery	T	2	-	1
Purple	**P1**	Lead white + Red lake + Carbon black	Drapery	U	3	1	2
			Wings				
	P2	Lead white + Smalt + Red lake (tr.)	Drapery	T	3	1	2
			Wings				
Blue	**B1**	Smalt + Lead white	Sky	T	2	1	1
			Drapery	U			
	B2	Azurite + Lead white	Drapery	T	2	1	1
Green	**G1**	Lead white + Lead-tin yellow + Carbon Black (tr.)	Drapery	U	3	1	2
	G2	Carbon Black + Ochre + Verdigris (tr.) + Lead-tin yellow (tr.) + Lead white (tr.)	Drapery	U	5	1	4
	G3	Verdigris + Calcium carbonate (tr.)	Drapery	T	2	1	1
Grey	**Gr1**	Lead white + Carbon black	Archit.	T	2	1	1
			Halo	U			
	Gr2	Lead white + Carbon black + Ochre	Horse	T	3	1	2
Black	**Bk1**	Carbon black + Ochre	Sword	T	2	0	2
			Drapery				
Flesh	**F1**	Lead white + Vermilion	Light Saints	T/U	2	1	1
	F2	Lead white + Vermilion + Ochre (tr.)	Half tone	T	3	1	2
			Saints				
	F3	Lead white + Vermilion + Ochre (tr.) + Carbon black (tr.)	Half tone	U	4	1	3
			Saints				
	F4	Ochre + Lead white + Vermilion (tr.) + Carbon black (tr.)	Light Shepherds	T	4	1	3

Abbreviations: **C**, coloured; **T**, top layer; **tr.**, traces, very little amount of pigment; **U**, Underlayer; **Wh**, White.

established with a mixture of azurite and lead white, combined in different proportions according to the hues desired (Figure 4). The deep blue of the Virgin's mantle is a result of the use of coarsely ground azurite. Particles showed a wide range of dimensions but many reached a size of 30–35 μm. This produced the thickest paint layer

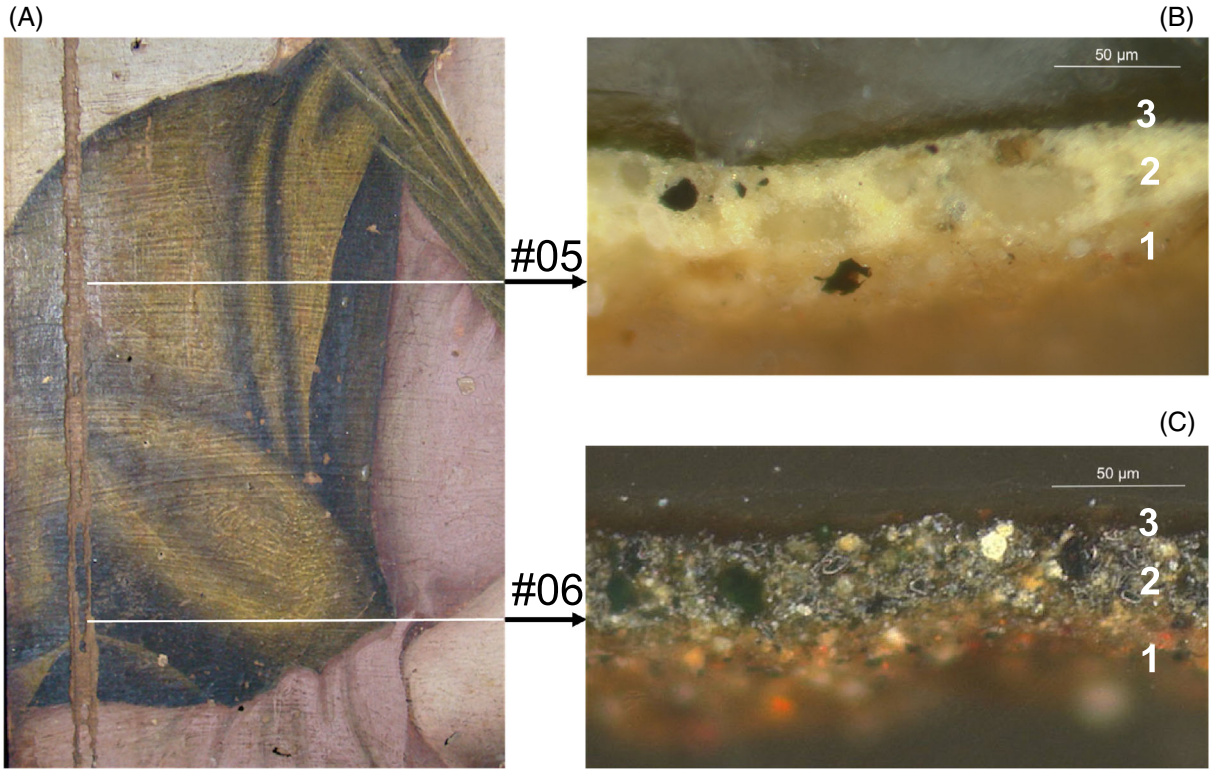

FIGURE 5 Detail of the green cloak of Saint Luzia (A) with the location of the cross-sections of samples #05 (light, B) and #06 (shadow, C) under the optical microscope (OM-Vis). The verdigris-based glaze (3) is applied over a first undermodelling of the forms made with two overlapping paint layers. For the lights (B), a yellow paint made of lead-tin yellow, lead white and a little carbon black (2) is modelled over a first light ochre paint made of lead white, ochre and carbon black (1). For the shadows, a black greenish paint mostly made of carbon black with a little verdigris, lead white and lead-tin yellow (2) is modelled over a first brown paint made of ochre, carbon black and a little vermilion and lead white (1). The preparatory layers are not present in the cross-sections. © HPM; HERCULES Lab.—U. Évora, Portugal

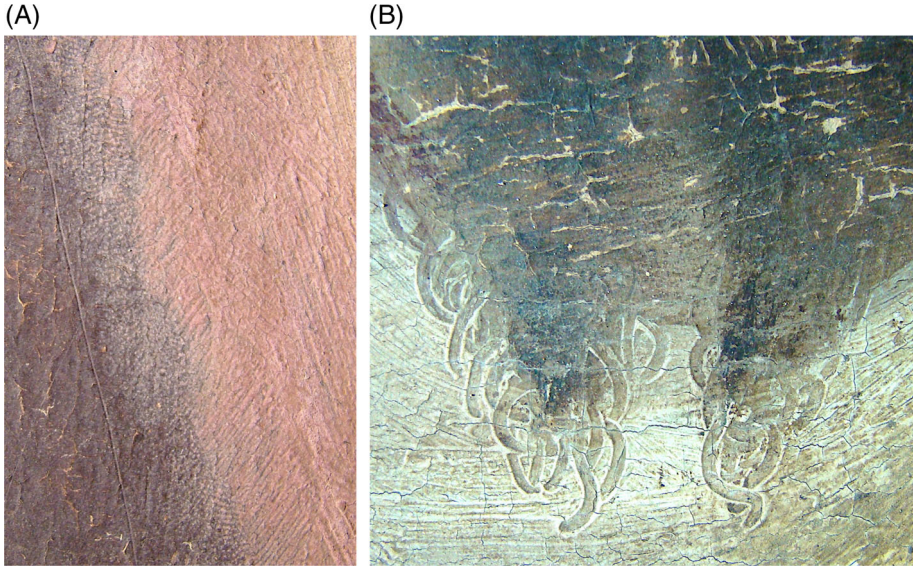

FIGURE 6 Details of the handling of the fresh paint with the fingers to blot the halo of the Holy Spirit (A) and with a pointed instrument such as the tip of the handle of a brush to create the curls in Saint Bartholomew's beard (B). © HPM; HERCULES Lab.—U. Évora, Portugal

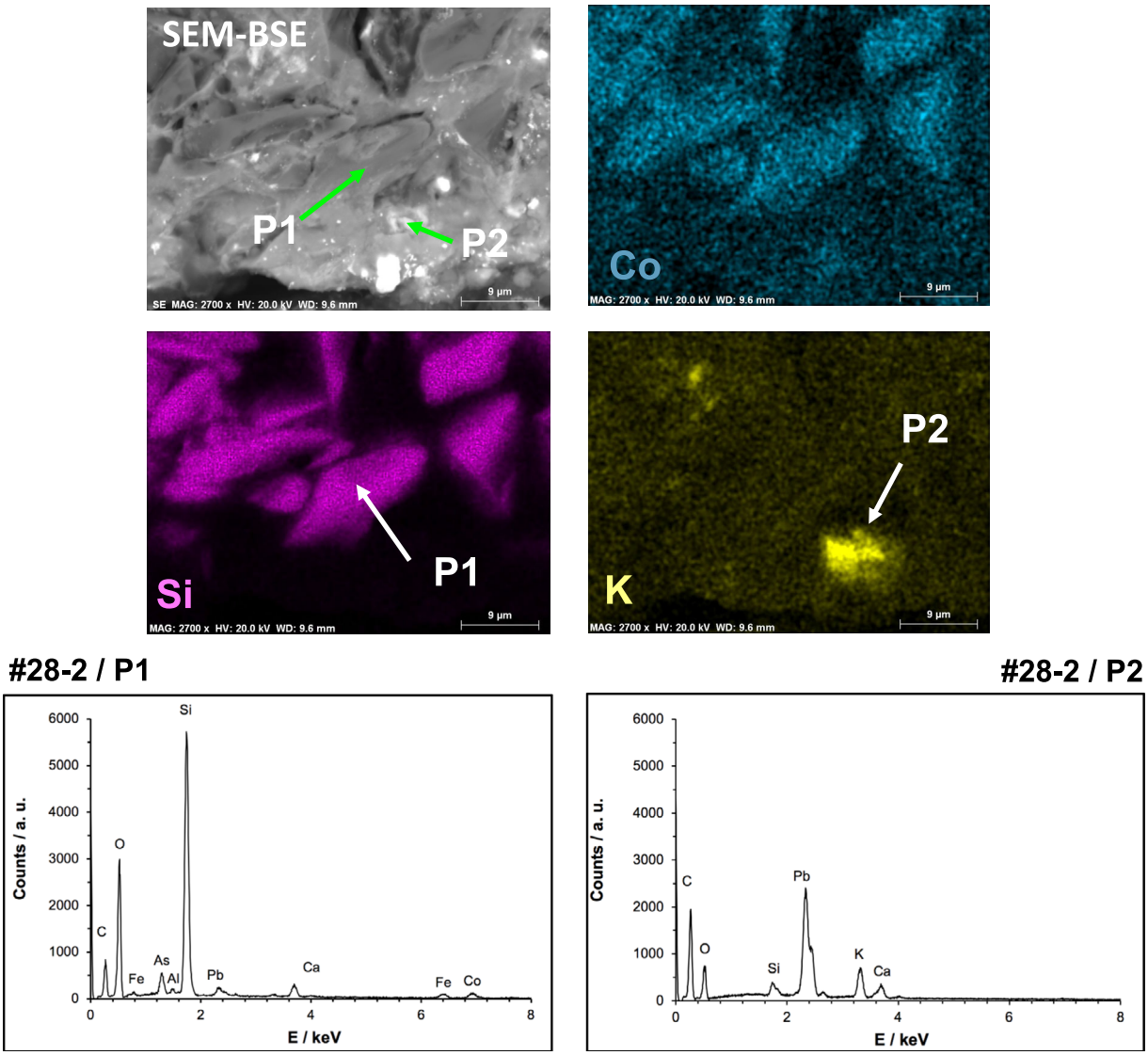

FIGURE 7 Smalt-rich uppermost layer of sample #28 corresponding to an area of shadow from the tunic of the angel of the *Annunciation* (cfr. Figure 4). SEM back-scattered electron image; SEM–EDX maps of Co, Si, K with location of particles P1 and P2; SEM–EDX spectra of smalt particle #28-P1 and of K-rich area #28-P2. © HPM & SV; HERCULES Lab.—U. Évora, Portugal

of the main paintings and the last one to be applied, as it slightly overlaps all adjoining motives in both the *Annunciation* and the *Adoration*.

The painter created color not only through pigment mixtures and paint build-up but with a palpable handling of the paint when it was still fresh. Evidence of this approach can be found in the halo of the Holy Spirit, whose yellow pinkish paint was blotted with the fingers all around the margins, with the aim of suggesting a smoky and ethereal cloud of light (Figure 6). Moreover, a pointed hard instrument such as the handle of a brush was used to open the fresh paint and thus create the curls of Saint Bartholomew's beard, in a simplified and decorative technique (Figure 6).

3.5 | Color change

3.5.1 | Smalt

The complete discoloration of the smalt used in blue and purple areas caused a dramatic change in the color balance of these paintings. The discoloration particularly affected the now "white" angel of the *Annunciation*, whose tunic and wings were made of a basic mixture of smalt and red lake, to which lead white was added in the lights (Figure 4). The presumably blue to purplish nuances of color have been completely lost. Likewise, the originally blue background sky from both predella paintings, made of a mixture of lead white and smalt, is now perceived as a dull light grey (Figure 1). In the smalt

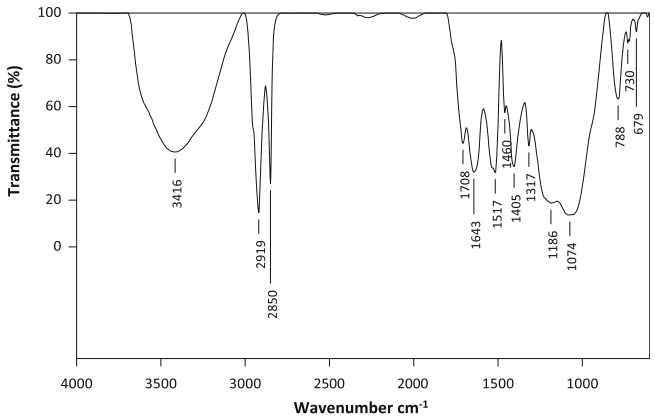

FIGURE 8 Infrared spectrum of the smalt-rich uppermost layer of sample #28 corresponding to an area of shadow from the tunic of the angel of the *Annunciation* (cfr. Figures 4, 7). © HPM & JS; IRPA/KIK, Brussels

containing underpaint of the blue mantles of both Virgins, the thickness of the azurite-based uppermost paint seems to have limited the effect of the smalt discoloration on the surface color (Figure 4).

Despite larger dimensions (c. 20–25 μm), most of the smalt particles were under 15 μm in size. The CoO content between 3.8 and 8.2 wt % indicates, according to Marika Spring,[28] that the pigment would originally have had a strong blue color. However, in this case, the fine grinding of the pigment would likely have slightly reduced the intensity of the color from the beginning.

Smalt particles exhibited an identical average atomic number in the SEM-BSE images. Spot analysis in several points of the same particle revealed that the K_2O concentration, with an average of 0.8 wt %, was constant across each particle (Figure 7). SEM–EDX mapping detected leached potassium concentrated in some areas of the paint matrix around the smalt particles (Figure 7). Elemental semi-quantitative analysis of these areas, in addition to potassium (av. 8.6 wt % K), detected mainly sulphur (av. 5.9 wt % S) (Figure 7). The compound could not be identified, but the atomic ratio between K, S, and Ca in one of the two points analyzed, suggests that it may be syngenite [$K_2Ca(SO_4)_2{\cdot}H_2O$], a salt characteristic of glass deterioration.[23,29]

The leaching of the potassium from the glass particles has led to the formation of potassium soaps, whose presence was confirmed by μ-FTIR analysis (Figure 8). Since the smalt samples also contained lead-white, not only potassium soaps were detected, through a resolved shoulder at 1460 cm^{-1} from the strong 1406 cm^{-1} carbonate band, as the 1539–1516 cm^{-1} doublet indicates the formation of both potassium and lead soaps[23] (Figure 8).

Researchers have shown that the leaching of potassium from the smalt particles is responsible for the discoloration of the pigment as it generates an increase in the coordination of the cobalt ion from tetrahedral to octahedral, leading to the loss of the blue colour.[30–32] In these paintings, the leaching of the potassium from the glass particles was promoted by the acidity of the binder and the uncontrolled environmental conditions of the church, usually closed and subject to fluctuating relative humidity levels. Water, in the form of atmospheric moisture, is known to promote the leaching of potassium ions from the silicate network and the development of microorganisms responsible for oxalate formation.[7,29,33–35] Calcium oxalates were in fact present in these deteriorated layers, as can be seen from the infrared absorption bands at 1643 cm^{-1} ($\nu_{as}COO$), 1317 cm^{-1} (ν_sCOO), and 788 cm^{-1} (δOCO) (Figure 8). Other deterioration products such as potassium sulphates that appear to have been formed, namely syngenite (see above), are highly hygroscopic and would have further contributed to the degradation of the smalt-rich paints.[29]

3.5.2 | Green glazes

Green glazes were thinly applied (3–10 μm). Cross sections examined under the microscope revealed the browning of the surface and, on occasions, of the whole glaze (Figure 5). This degradation particularly affected the drapery hold by the angel of the *Annunciation*, converting it into an almost black mass with no perceptible folds (Figure 1). SEM–EDX elemental analysis of green glazes detected, beyond copper, a little calcium. The green glazes showed no distinct particles under OM and in the BSE images, suggesting that an interaction of the verdigris with the binder had taken place.[36] Evidence of the reaction of the copper from the pigment verdigris with free fatty acids in the binder was confirmed by μ-FTIR analysis and is part of the expected drying process of the paint (Figure 2). Infrared spectra showed the presence of copper (II) carboxylate complexes indicated by the characteristic bands at 1587 cm^{-1} ($\nu_{as}COO$), close to the 1616 cm^{-1} absorption for copper acetate, together with the absorption at 669 cm^{-1} for copper (II) linoleate[8,36] (Figure 2). The CH_2 deformation vibration band at 1463 cm^{-1} typical of copper carboxylates appeared as a shoulder in the strong carbonate absorption band at 1417 cm^{-1}. The latter masked the copper carboxylate ν_sCOO band at ~1411 cm^{-1} and, together with the (δOCO) bending vibration at 875 cm^{-1}, indicated the presence of some form of calcium carbonate, as detected in SEM–EDX. It is possible that the calcium compound corresponds to the substrate of a yellow lake possibly added to the glaze.

Infrared spectra of the green glazes further revealed the presence of copper oxalates, confirmed by the ν_sCOO doublet at 1319 cm^{-1} and 1363 cm^{-1} and the δOCO

absorption band at 819 cm^{-1} (Figure 2).[37] The ν_{as}COO band at ~1660 cm^{-1}, typical of copper oxalates, was masked by the copper acetate and carboxylate bands absorbing in the same spectral region (Figure 2). Oxalates, usually prevalent in medium-rich aged glazes and correlated with the biodegradation of these layers, are promoted by the reactivity of the copper from the pigment with the acidity of the binder, confirmed in the infrared spectra by the high intensity of the free fatty acids 1710 cm^{-1} band relative to the ester band[35–37] (Figure 2).

The presence of oxalates and the reaction between the lipid binder and the verdigris are a sign of the chemical alteration of these translucent layers. The alteration of green copper glazes has been investigated but the mechanism that causes the browning of these layers is not yet fully clear.[24,38]

4 | CONCLUSION

The colors of the paintings from the Machede altarpiece were created with common pigments for sixteenth century practice, namely lead white, lead-tin yellow, ochres, vermilion, verdigris, smalt, azurite, carbon black, and a red lake made of brazilwood and cochineal. Simple pigment mixtures, lighted with lead-white and shaded with black and/or ochre, were used to build volume and shape. Glazing red and green draperies and the use of local undermodelling under the blue draperies are characteristic of the painter's traditional working methods.

Building on previous investigation on the disruption of the paintings' red glazes, the degradation of paints rich in smalt and verdigris has had a dramatic and irreversible impact in the overall appearance of these compositions. Beyond the presumed original blue color of the skies of the predela panels, the pigment deterioration has especially affected the central figure of the angel in the *Annunciation*. Although it is impossible to accurately determine the original color of the paints, where an almost "black and white" angel is now observed, a much more nuanced and brilliant blue, pink and purplish tunic and wings would have richly combined with a saturated and vivid green cape lying over the angel's left arm. These vibrant and diverse colors would have framed the central yellow raising arm of the angel, imparting him a celestial glorious status that is now obscured.

Aspects related to the nature of the materials used, to paint formulation and build-up, and to the uncontrolled environmental conditions where the paintings have been kept for more than four centuries, are responsible for these alterations. The moisture and the interaction between pigment and binder, leading to soap and oxalate formation seems to play a central role in the complex, and not yet fully understood, processes involved in the deterioration of these multi-layered painting systems. Understanding the main processes involved in the transformation and their consequences is crucial when interpreting an artists' color palette and designing the conservation protocols that are better suited for the preservation of these works. For the moment, their safeguard appears to be directly dependent on stabilizing the atmospheric conditions inside the church, but the original brighter color palette is forever lost.

AUTHOR CONTRIBUTION

HPM conceived the study, collected the samples, mounted the cross-sections and analysed them under optical microscopy. JS performed and interpreted HPLC analysis of the dyestuffs. HPM performed the μ-RS and μ-FTIR analysis and interpreted the results with the collaboration of JS, AJC and AMC. SV performed the SEM-EDX anlysis and, together with HPM and AJC, interpreted the results. HPM wrote the manuscript that was reviewed and accepted by all authors.

ACKNOWLEDGMENTS

The authors wish to acknowledge Father Eduardo Pereira da Silva and the Diocese of Évora for granting access to the altarpiece and Yigit Helvaci for his collaboration in the fieldwork.

FUNDING INFORMATION

This work was supported by the Fundação para a Ciência e Tecnologia (FCT), Portugal [Grant SFRH/BPD/109296/2015], Fundo Social Europeu, ERIHS.pt [ALT20-03-0145-FEDER-022115 (Program Alentejo2020)] and HERCULES Strategic Plan [UIDB/04449/2020 e UIDP/04449/2020].

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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How to cite this article: Pinheiro de Melo H, Cruz AJ, Sanyova J, Valadas S, Cardoso AM, Candeias A. Images in transformation: The color and its change in a group of Portuguese paintings from the second half of the 16th century. *Color Res Appl*. 2022;47(6):1358-1371. doi:10.1002/col.22809