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Short communication

The use of glass particles and its consequences in late 16th century oil painting: A Portuguese case based on the analytical results and the technical treatises

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ABSTRACT

Colourless glass particles were identified for the first time in Portuguese paintings in two altarpieces attributed to the painter Francisco João, active between 1558 and 1595. They were found in red glazes with conservation problems. The glass was analysed by SEM-EDX and the binder by μ-FTIR. Portuguese 17th century painting treatises, which record earlier practices, were examined providing additional information. The glass particles had a vegetable silica-soda-lime composition, different in the two altarpieces, and a medium to very high alumina content. Although the provenance of the glass could not be determined, the use of local glass is suggested, as archaeological glass of the same period and similar composition has been found in southern Europe, notably Portugal. Furthermore, the glass from one of the altarpieces closely matches the composition of glass found in a painting by the Spaniard Luis de Morales. As a result, it is possible that the painter deliberately added a local glass to his red lakes, as advised in the two Portuguese painting treatises of this period. The exclusive presence of glass in the uppermost medium-rich glazes suggests that it was mainly used for its transparency and assumed siccative role. Although the siccative properties of glass have not been proved, by lowering the oil concentration in the paint, the addition of glass might have indirectly assisted the drying of the glazes. The glass particles were subject to a severe leaching of the alkali, a degradation that might explain the disruption of the glaze layers in these paintings.

1. Introduction and research aim

This paper presents the discovery and characterisation of colourless glass particles in the red glazes of four paintings belonging to two different altarpieces attributed, on stylistic grounds, to the painter Francisco João, active in the Alentejo, southern Portugal, between 1558 and 1595 [1,2]. Although it is known that the addition of ground glass to paints was a widespread practice in European easel painting all through the 15th to the first half of the 17th century [3–16], to our knowledge, this practice had not yet been reported in Portuguese paintings. Consequently, the characterisation of the glass particles and the associated practice is relevant both for the study of these same works and for a deeper characterisation of the European oil painting technique, in particular the different regional practices.

It is recognised that the refinement of European oil painting in the fifteenth and sixteenth centuries owes as much to the nature of the binding medium as to the way its optical, drying and rheological properties were modified by the addition of dryers, extenders and other additives such as glass, although the specific function of this material is still not fully understood [17,18]. Therefore, this study intends to characterise the composition of the glass; to consider the provenance and function of glass particles in the paintings based on the analytical results and on Portuguese historical painting treatises; and to examine the influence of the glass on the state of conservation of the paintings.

Three of the paintings studied belong to the *Calvary Altarpiece* of the Church of São Miguel de Machede, a village on the outskirts of Évora, and the fourth is part of a dismembered altarpiece now displayed in the Church of São Francisco, in Évora's city centre. The paintings are dated 1570–1580. The artistic *corpus* of this painter

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and his workshop, comprising 59 altarpiece panel paintings, was subject to scientific analysis [19] and, for the moment, glass particles were detected exclusively in the above-mentioned altarpieces.

Francisco João lived in the city of Évora, in those days the second cultural centre of the country. This master embodied the Mannerist generation of Portuguese regional painters favoured by the increase of commissions in a Counter-Reformation context and the loss of political independence of Portugal in 1580. He followed a first generation of Flemish artists and well-known Lisbon masters to whom all major national commissions were granted during the first half of the 16th century. Nothing is known about his training but the influence of the Spanish painter Luis de Morales (1512–1586), who also worked in Évora and lived just across the border, is recognized in much of his work [2].

2. Methods

Within the framework of a larger study, the paintings were subjected to a thorough visual inspection of the paint surface *in situ*, under incident and raking light and ultraviolet radiation. Digital photographs were taken with a Sony Cibershot DSC-H9 and a Canon G15 camera.

For the identification of materials and characterisation of techniques, samples of the main colours were collected. The characterisation of glass particles was based on three samples from the altarpiece of Machede and two from the altarpiece of São Francisco.

Part of each sample was embedded in Epofix resin (Struers), polished as a cross-section and studied with optical microscopy (OM) in reflection mode, under visible light (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. Digital images were taken with a Leica digital camera DFC290HD.

Subsequently, the uncoated cross-sections were analysed with scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDX) on a variable pressure scanning electron microscope Hitachi 3700N, operated at 20 kV, with a BRUKER Contact 200 EDX detector. EDX imaging and mapping of major elements gave an accurate characterisation of size, morphology and distribution of the particles present and the semi-quantitative analysis of single particles provided information on elemental composition. The results are expressed in weight per cent of oxides normalised to 100%. In the largest particles, especially where leaching of the alkali components was detected, two measurements were carried out in each particle in order to detect variations in composition.

The unmounted part of the samples was analysed with Fourier transform infrared micro-spectroscopy (μ-FTIR) in order to identify the binder. The layers were separated and each one was compressed between two diamond cells. The spectra were obtained in transmission mode with a Nexus 670 FTIR spectrometer coupled to a Nicolet Continuμm microscope by Thermo Nicolet, in the range between 4000 and 600 cm^{-1}, with a KBr beam splitter and a DMCT detector for MIR measurements. For each sample, 256 scans were recorded with a resolution of 4 cm^{-1}.

3. Results

3.1. Red glazes

Glass particles were detected exclusively in the uppermost red glazes. On the paint surface, these glazes have a deep-red crimson hue and exhibit an opaque and matt appearance caused by their severe lack of cohesion. This phenomenon is particularly serious in the Machede paintings (Fig. 1). The disruption of the glaze layers, evident under the optical microscope, made the analysis of some samples extremely difficult and, on occasions, impossible. Despite their lack of cohesion, the red glazes still preserve some adherence to the underlayers.

The glazed areas are in the draperies and show a traditional build-up with the glaze spread over one or two superimposed opaque undermodelling layers of a light pink or bright red colour. In areas of shadow of the São Francisco painting, the top glaze has been applied over a thick, well-preserved glaze made of red lake to which a minute amount of lead white, but no glass, has been added (Fig. 2, layer 2). EDX analysis of the opaque undermodelling areas in the pink paint revealed the presence of lead white mixed with a red lake and, on occasion a little ochre, while the use of vermillion with a little red lake, and sometimes a little black, is seen in the opaque red underpaint. The lake pigment of these undermodelling layers is rich in aluminium (Al), which is attributed to hydrated alumina used as substrate [20].

The red glazes containing glass are medium-rich and show an irregular thickness that reaches a maximum of 35 μm in the Machede paintings and 15 μm in the São Francisco painting. Besides glass, the glazes mainly consist of small lake particles (5-10 μm) with no apparent fading, that have a deep violet hue under UV (Fig. 3). SEM-EDX analysis showed that the red lakes from those glazes have undefined margins, as if dissolving in the binder, and are not aluminium-rich. Point analysis of larger lake particles in the Machede paintings revealed that they contain mainly carbon and small amounts of calcium and potassium (on average 2.7 and 1.6 wt %, respectively) and under 1 wt % of sulfur (S), silicon (Si), aluminium (Al), sodium (Na), magnesium (Mg), copper (Cu), iron (Fe), phosphorous (P) and chlorine (Cl). This suggests that some Ca compound was used as lake substrate. A Pb compound was also detected in significant amounts in the red lake particles (15–34 wt %) and in the paint matrix (above 12 wt %). Considering the low atomic number of these areas in the SEM images, the lead probably corresponds to mobile lead ions in the paint film that could originate from lead-white based underlayers (Fig. 3), or to a lead siccative added to the oil binder with the aim of improving its drying properties, as described in historical recipes and found in red glazes of 16th century paintings [21,22].

The μ-FTIR spectra of red glazes (Fig. 4) show υ_{as}(Si-O-Si) bands at 1053–1049 cm^{-1} with a shoulder at 1097–1088 cm^{-1} and a smaller υ_s(Si-O-Si) band at 783–781 cm^{-1} that can be ascribed to glass [23,24]. Network modifiers in the glass could be responsible for a small band at ~931–916 cm^{-1} that is sometimes resolved from the stronger υ_{as}(Si-O-Si) band [24].

Infrared spectra of red glazes containing glass sometimes show a band at 1562–1556 cm^{-1} that, together with bands at 1412–1406 cm^{-1} and 1462–1458 cm^{-1}, can be ascribed to metal soap formation, as investigated for the blue pigment smalt, a cobalt-containing potash glass [24] (Fig. 4). A υ_{as}(COO-) doublet at 1541–1518 cm^{-1} characteristic of lead soaps sometimes appears in the same region, suggesting that a mixture of various types of metal carboxylates could be present (spectra not shown) [24,25]. Metal oxalates, prevalent in medium-rich aged glazes and correlated with the biodegradation of these layers, were detected in all red glazes: bands at 1655–1647 cm^{-1} (υ_s(C=O)), 1317–1313 cm^{-1} (υ_a(C-O)) and 781 cm^{-1} (δ(O-C=O)) [26].

Regarding the binder, μ-FTIR analysis identified an aged oil in both sets of paintings, confirmed by the characteristic υ(C-H) bands at ~2920 and ~2850 cm^{-1}, along with a strong carbonyl υ(C=O) band at ~1711–1707 cm^{-1} due to carboxylic acids formed by triglyceride hydrolysis and a δ(C-H) band at ~729 cm^{-1} (Fig. 4). Although the presence of metal soaps (~1540–60 cm^{-1}) and oxalates (~1620–50 cm^{-1}) creates two peaks in the same region of the infrared spectra of, respectively, the amide II and amide I bands, it was nevertheless possible to identify proteins in the red glazes from the Machede paintings thanks to two bands characteristic of

Fig. 1. Details of the disruption of the red glazes in a painting from the altarpiece of Machede (a, b), with the location in (a) of the sample collected and visualized by OM-Vis in (c).

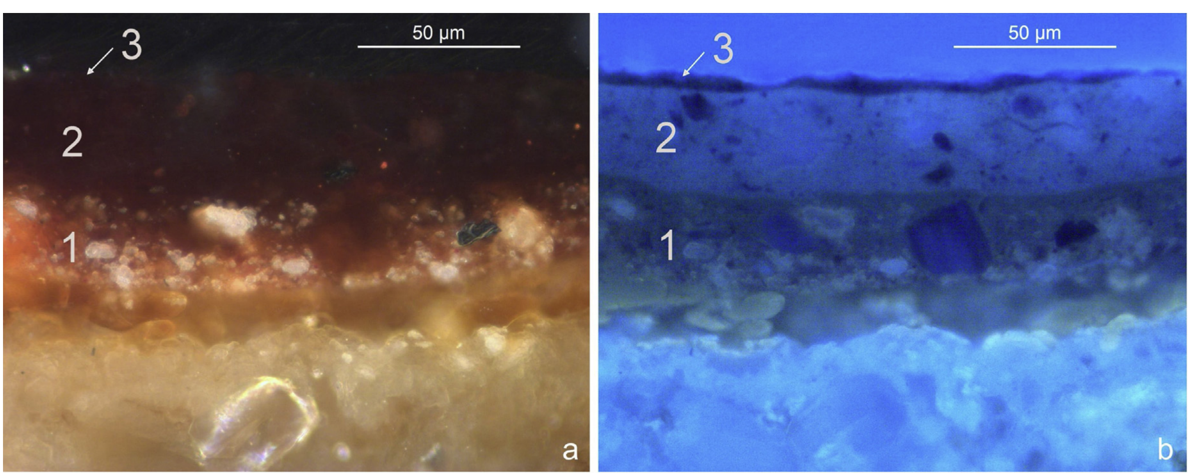

Fig. 2. São Francisco altarpiece - cross-section of sample 157, shadow area. OM under incident light (a) and UV radiation (b). Over the preparatory layers, the paint structure consists of a pink opaque layer (1); a thick aluminium-rich red glaze containing a little lead white (2); and a thin red glaze containing glass (3).

proteins: the υ_{as} (N-H) stretching vibration at 3186–3174 cm^{-1} and the amide II overtone at ~3074–72 cm^{-1} (Fig. 4a). Considering that proteins were not detected in other paints from these works and could reduce the glaze transparency due to an increase in the difference between the refractive index of the binder and the lake/glass, it is most probable that the proteins detected result from previous conservation treatments, justified by the poor state of conservation of the glazes.

Finally, in the case of São Francisco, a small band at ~3224–3217 cm^{-1}, invariably accompanied by a shoulder at ~3145–3138 cm^{-1} is always found (Fig. 4b). According to Arbizzani et al. [27], a ~3220–28 cm^{-1} band can be attributed to the υ(O-H) vibrations of carboxylic acids or secondary alcohols, polar compounds that can be related to the strongly disrupted state of these red glazes.

3.2. Glass particles

The glass particles could only be detected by OM with the help of UV radiation, under which the largest particles are translucent

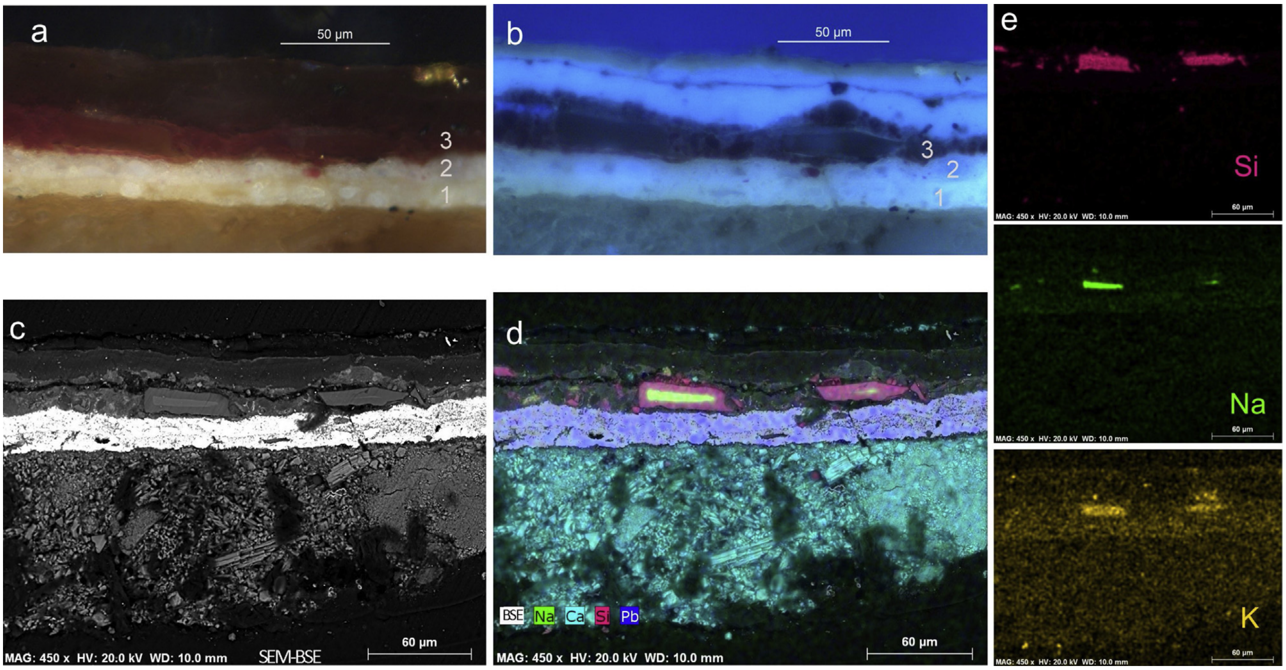

Fig. 3. Machede altarpiece - cross-section of sample 63a, area of light. OM under incident light (a), ultraviolet radiation (b); SEM back-scattered electron image (c); SEM mapping of combined elements (d) and SEM-EDX maps of Si, Na and K (e). Over the preparatory layers, two opaque white (1) and pink (2) undermodelling layers are covered by a red glaze containing glass (3) and two final varnish coatings (fluorescent under UV).

and appear to be colourless or slightly yellowish (Fig. 3). Further details could only be obtained by SEM-EDX, namely their distribution and size (Figs. 2 and 3). According to those results, the paintings had small glass particles, with a diameter under 10 μm, along with large particles of 30 μm and, in one instance, 55 μm. In general, the particles from Machede are larger than those from São Francisco.

The glass particles are mainly composed of SiO_2 (58–79 wt %), Na_2O (0.1–17 wt %), Al_2O_3 (2.7–9.1 wt %), MgO (2.5–5 wt %) and CaO (2.8–10 wt %) and have a lower content of K, Fe, Mn, P, S and Ti oxides, and Cl (Tables 1 and 2). A PbO amount of 4–12 wt % was also detected in the glass particles but its concentration is lower than that in the lake particles and the paint matrix, which suggests that Pb is not part of the glass but is likely due to matrix interference. In fact, Pb is not a common component of colourless post-medieval soda-ash glass [28]. Although lead has occasionally been found in soda-ash Islamic glass (notably in southern Spain) and the painter could have reused old glass, the PbO concentration in those glasses is usually higher than 30 wt % and rarely less than 17 wt % [29–31]. Considering the above, Pb was eliminated from the SEM-EDX semi-quantitative analysis of the glass particles.

The discrepancy in Na_2O concentration between the core and the surface of the particles is a consequence of Na leaching from the glass. This is particularly evident in the Machede paintings, where the core of the largest particles shows a higher average atomic number than the surface (Fig. 3). Some K leaching is also noticeable (Tables 1 and 2). The deterioration was confirmed by point analysis and line scans of several particles and further corroborated by the detection of Na and K in the surrounding paint matrix (Fig. 5).

Considering this degradation, the characterisation of the glass relies exclusively on the better preserved areas of the particles, considered as those with a Na_2O content $\geq$ 8 wt % (Tables 1 and 2, in **bold**). In these areas, the presence of Cl and the content of Na_2O (8–17 wt %), MgO (2.9–4.2 wt %), K_2O (2.4–4.5 wt %) and P_2O_5 (0.3–0.9 wt %) are consistent with the use of coastal plant ashes as fluxing agent, thus indicating that all glass particles fall in the vegetable silica-soda-lime type, also known as soda-ash glass [32–34].

The Al_2O_3 and K_2O contents, related respectively to the silica source and the plant ash component, clearly divide the soda-ash glass in two groups that correspond to each set of paintings studied (Fig. 6). In fact, the Al_2O_3 content of 2.7 wt % found in the Machede glass points to the use of a pure silica source such as quartz pebbles or white sand [35], whereas an the Al_2O_3 content above 6 wt % found in the glass of São Francisco is more consistent with the use of an Al-rich sand or a mixture of quartz and an Al-rich feldspar [35]. The contribution of a higher amount of quartz from the river pebbles possibly used as the silica source in the Machede glass, could eventually justify its higher SiO_2 content (Fig. 6a). On the other hand, levels of K_2O below 4.5 wt % such as those found in the better preserved areas of the glass of both sets of paintings, have been assigned to the use of Levantine ashes [32,34]. However, the K_2O content of the glass of São Francisco (average 4.0 wt %) is very close to the frontier of 4.5 wt % established by Cagno for the distinction between K-poor Levantine and K-rich *barilla* ashes [33–35]. No definite conclusion could therefore be drawn concerning the type of ashes used in the manufacture of the São Francisco glass, especially because some K leaching from the glass has occurred and the use of Portuguese ashes could be expected [36]. In fact, historical records from the 15th century show that plant ashes, known (as in Spain) as *barilha*, were being collected in the Algarve, in the south of Portugal, to be used in local glassmaking furnaces [36]. The lime content of the glass particles from both altarpieces, although slightly higher in São Francisco, is between 6 and 9 wt %, a range that is considered as having been naturally introduced by unrefined sodic plant ashes and/or lime-rich sand [35]. The average MgO amount of 3.4 wt % is generally introduced by unrefined plant ashes [32–35]. MnO, known to counteract the colouring effect of iron impurities in the glass batch, is present with a concentration of the same order of magnitude as Fe_2O_3 (below 1 wt %).

In conclusion, SEM-EDX results show that two different sorts of soda-ash glass, each with a consistent composition, were used:

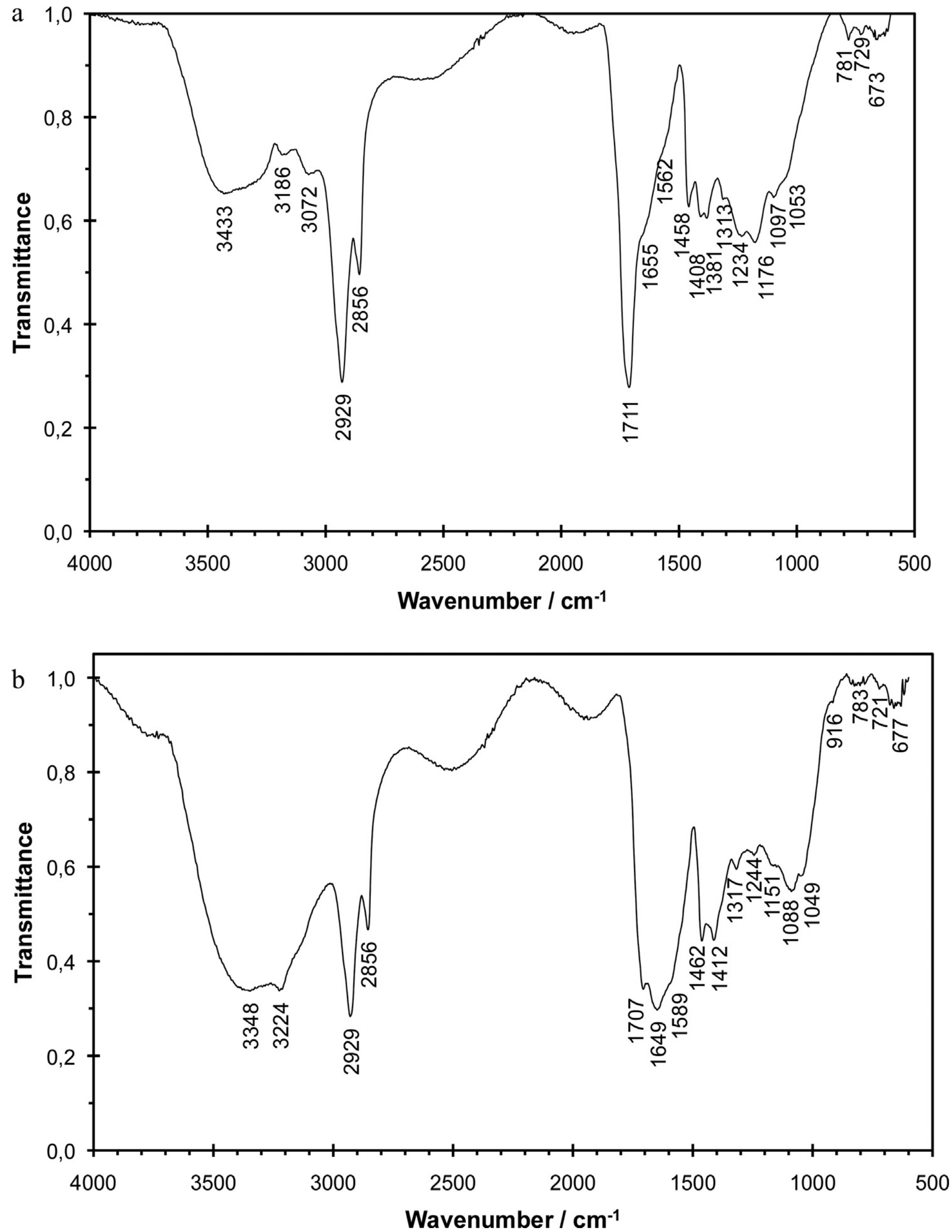

Fig. 4. Infrared spectra of the red glazes containing glass from sample 63 of the Machede (a) altarpiece (a) and sample 157 of the São Francisco altarpiece (b).

- in Machede, a medium alumina soda-ash glass, poor in K_2O, possibly produced with a purified silica source and unrefined Levantine ashes;
- in São Francisco, a very high alumina soda-ash glass, richer in potassium oxide and possibly made from alumina-rich sands.

4. Discussion

4.1. The glass in Portuguese early 17th century historical texts

The use of glass in painting is mentioned in the two contemporary Portuguese treatises known to date: Filipe Nunes, in 1615, advocates the use of glass as drier for red lake, whereas an anonymous monk of the Order of Christ (before 1640), advises this drier for white, blues, ochre and cochineal lake, although both mention other driers for the same purpose and the latter recommends instead the use of verdigris for cochineal (and ochre) [37,38]. Both Portuguese authors explicitly mention that the glass should be burned first. For example, Nunes states: "throw pieces of glass into a fire and leave them there until they are quite red and well burnt" [37]. De Mayerne (1620–46) appears to be, alongside the Portuguese authors, the only author who mentions the detail of calcination as, among several driers, he refers to "*verre crystallin* pulverised until the particles are impalpable, or first calcined and then plunged into cold water, dried and crushed into a very fine powder" and to "*verre de Venise*, either merely ground, either extinguished in water, several times dried and ground" [39]. This relevant information confirms, as stated by Marika Spring [40], that the temperature shock would shatter the glass into pieces that, due to their smaller size, would be easier to grind.

Nunes further instructs that the glass, first ground on the stone (possibly as a dry powder), should only be added to the paint on the palette. For the grinding of the glass he suggests to use the stone still dirty from grinding the lake pigment, so that the glass particles will pick up a little of the red colour from the lake leftovers

Table 1
Composition of the glass particles in the paintings from the altarpiece of São Miguel de Machede, Évora, in normalised oxide weight percentage, measured by SEM-EDX.

Sample	Particle				Normalised oxyde concentration (wt %)												
	Nr.	Size (μm)	Spot analysed		SEM density	SiO_2	CaO	Al_2O_3	Na_2O	K_2O	MgO	MnO	Fe_2O_3	P_2O_5	SO_3	TiO_2	Cl
63a	**G1**	**15 × 55**	**P9**	**C**	**H**	**65.4**	**6.2**	**2.7**	**15.5**	**2.4**	**3.2**	**0.6**	**0.6**	**0.6**	**1.1**	**0.3**	**1.3**
			P10	D	M	75.6	6.5	3.6	2.3	2.0	4.4	0.5	0.8	1.0	1.4	0.4	1.5
			P11	**C**	**H**	**67.0**	**6.3**	**2.8**	**13.5**	**2.5**	**3.3**	**0.6**	**0.7**	**0.4**	**1.2**	**0.3**	**1.2**
			P13	D	M	76.9	6.6	3.4	1.8	1.5	4.4	0.6	0.7	0.9	1.4	0.4	1.4
	G2	2-4 × 10	P14	C	M	77.4	7.2	3.4	1.1	0.9	4.2	0.5	0.8	1.0	1.8	0.5	1.4
	G3	11 × 43	P15	C	H	73.6	6.8	3.4	4.2	2.8	4.0	0.5	0.6	0.7	1.4	0.4	1.4
			P16	D	M	76.9	6.7	3.4	1.5	1.7	4.3	0.5	0.8	0.8	1.5	0.3	1.5
81	G4	3.5 × 8.5	P4	C	M	76.5	6.8	4.0	1.6	0.4	4.3	0.5	0.8	1.5	2.2	0.4	1.0
	G5	5 × 20	P2	C	M	78.7	6.4	3.6	1.9	2.0	3.8	0.4	0.6	0.7	0.3	0.3	1.4
81a	**G6**	**8 × 20**	**P1**	**C**	**M**	**71.6**	**7.9**	**2.7**	**8.0**	**2.5**	**2.9**	**0.7**	**0.9**	**0.3**	**1.5**	**0.2**	**0.8**
			P2	E	M	77.0	8.1	3.0	0.8	1.5	3.7	0.6	0.8	0.9	1.8	0.4	1.3
	G7	12 × 14	P5	C	M	79.0	7.0	3.4	0.9	0.6	3.9	0.6	0.8	0.6	1.9	0.4	1.0
			P6	E	M	78.2	8.7	3.0	0.2	0.8	2.8	0.6	1.0	0.4	2.5	0.6	1.0
	G8	11 × 16	P7	C	M	74.4	6.8	4.6	2.1	2.2	4.3	0.5	0.8	0.9	1.5	0.5	1.5
			P8	C	M	78.4	6.3	3.6	1.5	0.9	4.4	0.6	0.7	0.7	1.3	0.4	1.2
	G9	2.5 × 9	P10	C	M	77.5	7.3	3.5	1.2	0.6	3.9	0.8	1.1	0.7	1.7	0.6	1.2
			P11	E	M	77.0	7.4	3.7	1.2	0.6	4.0	0.6	0.9	0.9	1.6	0.7	1.3
	G10	6 × 13	P16	C	M	76.8	6.8	3.7	1.5	0.7	4.4	0.7	0.9	1.1	1.6	0.4	1.2
	G11	6 × 9	P17	E	M	77.4	7.5	3.6	0.9	1.5	3.8	0.6	0.9	0.8	1.2	0.5	1.4
			P18	C	M	76.0	6.8	4.0	1.8	1.1	4.6	0.6	0.8	1.1	1.4	0.5	1.4
	G12	4 × 10	P19	C	M	78.1	7.0	3.7	1.3	0.7	4.4	0.5	0.7	0.7	1.3	0.5	1.1
			P20	C	M	75.6	6.0	4.3	2.4	0.9	5.0	0.5	0.8	1.4	1.5	0.5	1.1
113	G13	5 × 9	P13	C	M	76.3	9.2	2.7	0.1	0.8	2.8	0.8	1.1	0.5	4.1	0.4	1.1
	G14	2.6 × 22	P11	C	M	74.1	6.9	4.0	1.5	0.6	4.6	0.4	0.8	1.8	3.5	0.4	1.2
			P16	C	M	73.3	7.8	4.1	1.3	0.6	4.2	0.6	0.9	1.4	4.4	0.4	1.1
	G15	2.4 × 7	P14	C	M	75.5	8.8	3.1	0.2	1.0	3.0	0.7	1.0	0.9	4.4	0.4	1.0
	G16	2.6 × 7	P15	C	M	75.7	8.6	3.1	0.5	0.5	3.4	0.6	1.0	1.1	4.0	0.5	1.1

Spot analysed: C: centre of particle; D: degraded area; E: edge of particle.
SEM density: M: Medium density; H: Higher density.
Particles with a relatively high Na_2O content are presented in bold.
Samples 63a and 81a correspond to samples 63 and 81 repolished and reanalysed.
Sample 113 has higher levels of sulfur (S) due to the interference of the vermilion-rich underlayer.

Table 2
Composition of the glass particles in the painting from the altarpiece of São Francisco, Évora, in normalised oxide weight percentage, measured by SEM-EDX.

Sample	Particle				Normalised oxyde concentration (wt %)												
	Nr.	Size (μm)	Spot analysed		SEM density	SiO_2	CaO	Al_2O_3	Na_2O	K_2O	MgO	MnO	Fe_2O_3	P_2O_5	SO_3	TiO_2	Cl
155	**G17**	**12 × 30**	**P1**	**C**	**M**	**58.3**	**7.9**	**6.0**	**16.7**	**4.0**	**3.6**	**0.6**	**0.8**	**0.7**	**0.2**	**0.3**	**0.9**
	G18	6 × 12	P2	C	M	73.3	4.0	8.8	3.0	2.1	3.7	0.4	1.0	1.3	1.2	0.6	0.6
155a	G19	2 × 10	P5	C	M	71.8	6.2	8.3	2.2	2.3	4.4	0.7	1.1	0.9	0.7	0.7	0.8
			P6	E	M	76.0	2.8	9.1	2.2	1.1	4.3	0.4	1.2	1.2	0.7	0.6	0.5
	G20	**2 × 7**	**P8**	**C**	**M**	**64.3**	**7.9**	**6.9**	**9.0**	**3.8**	**3.8**	**0.6**	**1.0**	**0.7**	**0.3**	**0.6**	**1.0**
157	**G21**	**10 × 20**	**P1**	**C**	**M**	**58.8**	**9.0**	**5.9**	**14.7**	**4.5**	**3.2**	**0.5**	**1.1**	**0.3**	**0.6**	**0.5**	**1.0**
			P2	E	M	68.5	10.0	6.3	3.8	3.9	2.5	0.8	1.5	0.2	0.8	0.8	1.0
	G22	**7 × 30**	**P27**	**C**	**M**	**58.2**	**8.0**	**6.5**	**15.5**	**4.0**	**3.7**	**0.6**	**0.9**	**0.5**	**0.6**	**0.6**	**1.0**
			P28	**C**	**M**	**62.9**	**8.2**	**6.8**	**10.3**	**4.1**	**3.8**	**0.7**	**1.0**	**0.4**	**0.5**	**0.5**	**1.0**
	G23	**2.7 × 6**	**P30**	**C**	**M**	**62.4**	**6.4**	**7.5**	**11.8**	**3.3**	**4.2**	**0.6**	**0.9**	**0.9**	**0.7**	**0.4**	**0.8**

Spot analysed: C: centre of particle; E: edge of particle.
SEM density: M: Medium density; H: Higher density.
Particles with a relatively high Na_2O content are presented in bold.
Sample 155a corresponds to sample 155 repolished and reanalysed.
The amount of Al_2O_3 in sample 157 could be slightly inflated due to interference from the aluminium-rich underlayer. This is not the case for sample 155, where the glaze lies over a lead-white paint containing only a very small amount of Al-rich red lake. Since the values are similar, we consider them both valid for discussion.

[37]. Likewise, the anonymous monk warns that the glass should be mixed with the paint only on the palette and never ground directly with the paint on the stone, "so that the paint can be kept fresh for later use" [38]. Thus, both authors believe in the siccative role of glass. Interestingly, the opposite advice is given by the Spanish painter Palomino, a century later (1714–24): when referring to driers that may be used on the palette, he mentions the use of glass prepared in oil like any other colour, kept like other colours in little pouches, ready to use when needed [37]. Although historical texts are sometimes contradictory in relation to technical details, notably whether the glass should be ground directly with oil or mixed with paint only in the palette, it is nevertheless evident that Portuguese authors were quite informed on this subject, which suggests that the use of glass as a drier may have been a well-known practice in Portugal at the time.

4.2. The glass particles in the Portuguese context

The soda-ash-based silica-soda-lime glass of the Machede and São Francisco altarpieces conforms with the published analytical data of glass objects found in Portuguese territory, dated between the 14th and the 17th century. These show the general use of soda-ash glass, in line with the Mediterranean glassmaking tradition and the presence of genuine imported Venetian glass in the country [41,42]. An exception is stained glass dating from the first half of the 16th century, thought to be produced in the Monastery of Batalha,

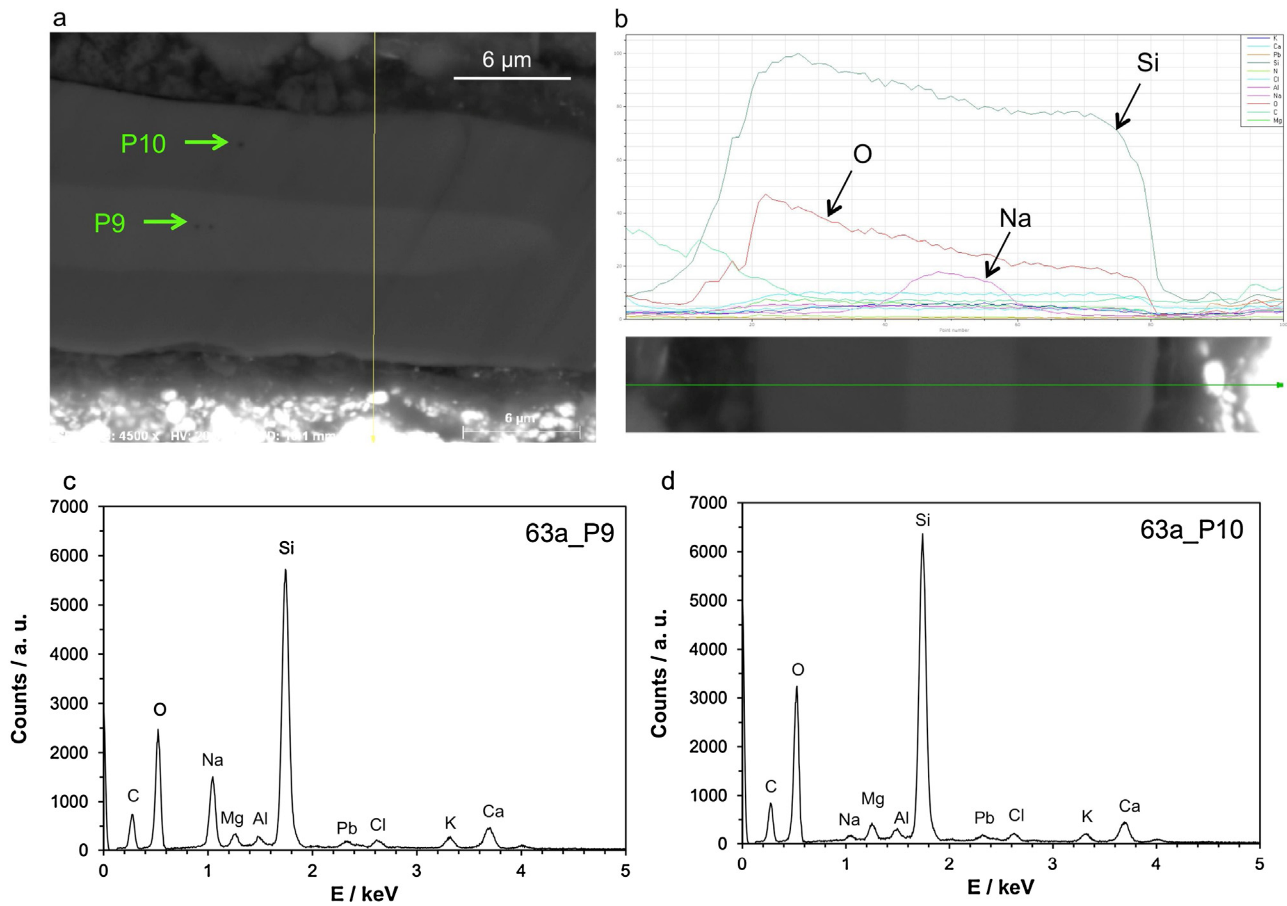

Fig. 5. Glass particle from a painting of the Machede altarpiece in SEM-BSE with the location of the line scan analysis and the two points analysed by SEM-EDX (a); line scan analysis (b); P9 (c) and P10 (d) SEM-EDX spectra.

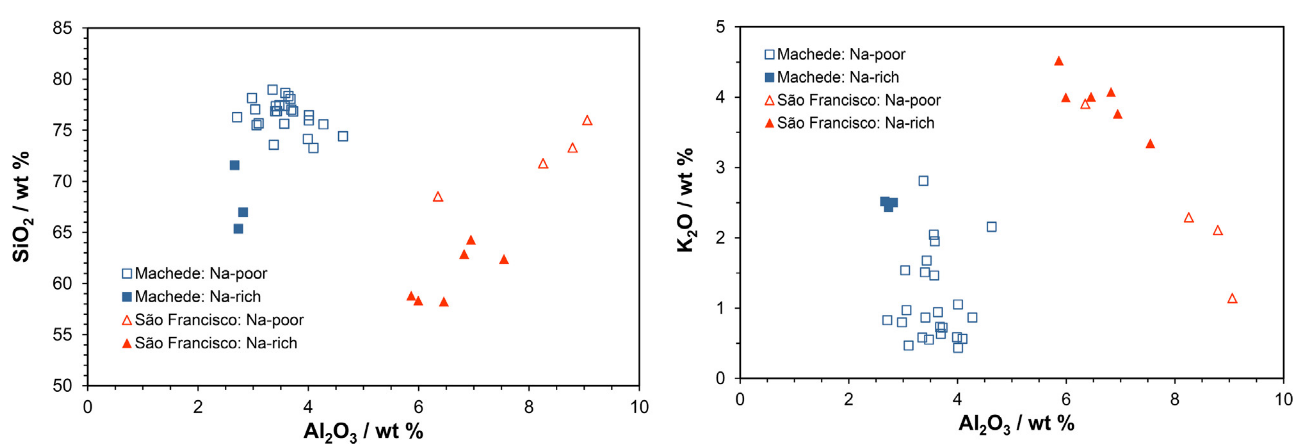

Fig. 6. Binary plots of SiO_2 *vs* Al_2O_3 (a) and K_2O *vs* Al_2O_3 (b) for the glass particles of both altarpieces analysed with SEM-EDX.

which is of the mixed-alkali type [43], typical of northern Europe glass production.

The Al_2O_3 content, exceeding 2 wt %, excludes any Venetian provenance for the glass of both altarpieces [42]. Glass with a similar composition to the glass of these altarpieces has been found in glass fragments dated from the 14th–17th century excavated in several areas of Portugal, notably in Beja, a city located only 80 km from Évora (Table 3) and also in some Italian and Spanish glass from the same period [32–35,44,45]. However, the very high concentration of Al_2O_3 in the glass from São Francisco is quite particular and was only found in a few glass fragments excavated in Portugal (Table 3) and Italy (Tuscany and Liguria) [32,35].

Considering the scarce available analytical data on 14th–16th century glass production in the Iberian Peninsula and the fact that no Portuguese glass furnace from this period has so far been examined in archaeological excavations, the conclusions concerning the provenance of the glass are limited. It can nevertheless be stated that the glasses used in both altarpieces, despite their differences, especially concerning their Al_2O_3 and K_2O content, are of the type most commonly found in southern Europe, notably Portugal.

Table 3
Chemical composition of the glass particles (only areas with $Na_2O \geq 8$ wt %) from the red glazes of the Machede and São Francisco paintings in comparison with glass of the same period found in Portugal (separated in different categories according to Al_2O_3 content).

Location	Category (Al_2O_3 wt %)	Date (century)	*n*	Concentration (wt %)											
				SiO_2	CaO	Al_2O_3	Na_2O	K_2O	MgO	MnO	Fe_2O_3	P_2O_5	SO_3	TiO_2	Cl
Machede	**[2-3[**	**16th**	**3**	**68.0**	**6.8**	**2.7**	**12.4**	**2.5**	**3.2**	**0.6**	**0.7**	**0.4**	**1.3**	**0.3**	**1.1**
Coimbra	[2-3[	17th	6	52.4	6.9	2.5	12.6	2.6	2.7	0.7	2.1	0.3	0.2	0.1	0.8
Beja	[2-3[	14-15th	2	66.8	4.4	2.9	16.2	2.4	3.3	0.5	1.5	0.6	0.0	0.1	0.9
Beja	[2-3[	16-17th	3	63.2	8.3	2.3	16.0	5.1	2.9	0.4	0.4	0.2	0.1	0.1	0.9
Lamego	[2-3[	17th	7	62.8	7.0	2.5	16.7	5.6	3.0	0.4	0.6	0.2	0.1	0.1	0.8
São Francisco	**≥ 6**	**16th**	**6**	**60.8**	**7.9**	**6.6**	**13.0**	**4.0**	**3.7**	**0.6**	**0.9**	**0.6**	**0.5**	**0.5**	**0.9**
Coimbra	[3-6[	17th	14	55.4	7.0	4.3	14.2	4.0	2.9	0.5	2.6	0.4	0.1	0.2	0.8
Coimbra	≥ 6	17th	3	57.6	6.5	7.2	16.5	3.1	4.4	1.0	1.7	0.5	0.1	0.4	0.8
Beja	[3-6[	14-15th	2	64.5	4.2	3.4	18.3	3.3	2.2	0.2	0.9	0.6	0.0	0.5	1.2
Beja	[3-6[	16-17th	9	65.6	6.2	3.7	16.2	3.1	2.6	0.5	0.6	0.3	0.1	0.1	1.0
Beja	≥ 6	16-17th	1	62.9	3.22	6.0	18.6	3.76	1.9	0.92	0.82	0.42	0.02	0.16	1.3

Sources: Coimbra glass [42]; Beja and Lamego glass [41].

4.3. The glass and the painting practice

The soda-ash glass used in the panel paintings studied, is of a type extensively used by Italian painters [6,12,14] and it has also been found in a painting by the Spaniard Luis de Morales [9,16]. It shows no correspondence with northern schools, which, although also resorting to this type of glass (probably imported), mainly used potash or mixed-alkali glass [12–14]. Regarding the particle size, the glass is similar to that found in some Italian works, while in Netherlandish and German paintings the particles are finer, of around 2–5 μm [12,14].

Although falling in the same soda-ash category, the glass from these Portuguese paintings shows compositional differences relative to the soda-ash glass so far analysed in European painting. Considering glass particles with no significant leaching, an alumina concentration of 2.7 wt % as the one in the Machede glass has only been found in three German works produced between c.1485–1510; in a painting by Morales dating from 1560–70 and in a single painting by Tintoretto (1518–1594) [12,14]. However, if we consider the CaO content of these paintings, only the glass used in the painting by Morales has similarities with the Machede glass (5.8 and 6.8 wt % CaO, respectively), as the German and Italian works have a higher lime concentration (9–10 wt %) [12,14].

The very high alumina level of the S. Francisco glass (above 6 wt %) has so far not been found in European paintings [12,14]. An Al_2O_3 concentration between 3.6 and 5.5 wt % has nevertheless been reported in soda-ash glass used by a few Italian painters – especially Raphael (1483–1520) and Perugino (1446–1523), but also the Master of the Story of Griselda (c. 1493–1500), Pontormo (1494–1557) and Beccafumi (1486–1551) – in works produced between the end of the 15th century and the mid-1520s [14]. However, this high alumina Italian glass possesses a much higher manganese content (1.1–2.4 wt %) than the Portuguese glass (0.6 wt %) [14].

Even if the provenance of the glass used in these Portuguese paintings could not be determined, its chemical composition shows differences with the soda-ash glass of Italian, German and Netherlandish paintings. Marika Spring has noted a geographical correspondence between the glass used in paintings and glass manufacturing and trading in Europe, suggesting that painters used locally available material [6,10,14]. As a result, the possibility that the painter intentionally added a local glass to his red lakes, as advised in the two Portuguese painting treatises of this period, remains open to further research, especially when considering the chemical similarity between the glass used in the Machede paintings and in the work by Luis de Morales, a painter who worked in Évora and strongly influenced Francisco João, whom he possibly met [2,14].

Although in other paintings glass particles were also detected in opaque paint layers, primings and mordants, they have been mostly found in red glazes and appear to be related to oil painting [6,7]. The specific reason for their use is under debate since the 19th century [12,14,46]. The main purpose of glass addition could be related to the drying properties of the glass, as advertised in many Italian, Spanish, French, English and Netherlandish treatises from the late 16th and 17th centuries. Among other possibilities, the siccative effect of glass would depend on the role and contribution of metal ions present in the glass composition, a subject that needs research [12,46]. Other hypotheses are the glass' effect on the optical characteristics and working properties of the paint, especially in translucent glazes, and economic reasons, as the glass could be used as an extender in the case of expensive pigments such as red lakes [6–8,10–14].

In these Portuguese paintings, the exclusive addition of glass to translucent glazes containing a red lake as the only colouring material suggests, first of all, an optical intention of increasing transparency. However, considering that this type of glaze dries slowly, a translucent filler would have an indirect drying effect on the glaze layer due to the decrease in binder concentration. Glass appears to be the ideal material for that purpose, because it would maintain the glaze transparency without a perceivable change in hue, value or saturation of the paint. However, this plausible explanation, as far as we know, proposed here for the first time, still requires further investigation.

4.4. Deterioration of the glass particles

The glass particles of the paintings studied show a severe leaching of the alkali, especially in the case of Machede, where small particles (< 15 μm) are almost depleted of Na_2O. Alkali leaching, commonly recorded in the less durable potash glass smalt pigment [24,47], has only been reported in a few soda-ash glass particles, incorporated in glazes and paints containing lead-based pigments [12,14]. Unlike in these Portuguese paintings, the disruption of the layers containing leached soda-ash glass has not been observed [12,14].

Moisture is a primary factor involved in the beginning and sustaining of several forms of glass deterioration [47], mainly because it promotes alkali leaching. Damp environments also favour the development of microorganisms that can be responsible for oxalate formation, as detected in the μ-FTIR spectra of these glazes [26]. The oil-based medium that, in theory, could protect the glass particles, usually undergoes a complex ageing process that leads to an increase in the acidity and polarity of the binder and thus contributes to the ion exchange and makes the glaze more water sensitive [48–50]. In view of this mechanism, it is interesting to note that the paintings studied have been kept in churches with an uncontrolled atmosphere for more than four centuries. Moisture levels are higher in Machede, where the altarpiece hangs directly against a North facing outside wall. Furthermore, the possible direct contact with water from protein-bearing solutions or coatings used in conservation treatments (as stated above, proteins were detected in the μ-FTIR spectra of the Machede glazes) could have further accelerated the above-mentioned degradation processes in the more severely damaged Machede glazes.

Regarding the glass composition, a major factor affecting its durability [47], the Machede glass has a medium to low CaO and Al_2O_3 contents that would make it more susceptible to deterioration. In fact, leached particles with lower Al_2O_3 and, sometimes, similar CaO contents as those of the Machede glass have been reported in Italian paintings and in the Morales painting [14]. On the contrary, the very high amount of alumina in the S. Francisco glass might have contributed to its lesser degree of deterioration.

5. Conclusion

Glass particles were detected by OM and SEM-EDX in the red glazes of four paintings belonging to two altarpieces dated around 1570-80 and attributed to the Portuguese painter Francisco João. By SEM-EDX, the glass was characterised as being a soda-ash-based silica-soda-lime glass, different in the two altarpieces, and showed a medium to very high alumina content. Although the provenance of the glass could not be determined, the use of a local glass is suggested, as archaeological glass of the same period and similar composition has been found in southern Europe, notably Portugal. Furthermore, the glass from the Machede altarpiece closely matches the composition of glass found in a painting by Luis de Morales. The exclusive presence of glass in surface translucent glazes suggests that it was mainly used for its transparency and assumed siccative properties. Although the siccative properties of glass have not been proven, by lowering the oil concentration in the paint, the addition of glass may have indirectly assisted the drying of the glazes. The high moisture levels and uncontrolled environmental conditions of the churches where the works are preserved, combined with the glass composition and the paint formulation appear to have contributed to the degradation of the glazes and their glass particles, but further research is needed on this subject to fully understand the complex processes involved.

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