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Assessing the decorative techniques of two Art Nouveau glass windows by optical coherence tomography (OCT)

Teresa Palomar[1,2*], Magdalena Iwanicka[3], Isabel Pombo Cardoso[4,5], Marcia Vilarigues[1,4] and Piotr Targowski[6]

Abstract

This work presents an assessment of the different decoration techniques applied in the two glass windows from the Casa-Museu Dr. Anastácio Gonçalves (Lisbon, Portugal) by Optical coherence tomography (OCT). The Dining Room glass window was found to be decorated with grisailles and acid etching, and the *Atelier* window with grisaille, enamel, and cold painting. The alteration state of the surface decorations was also assessed. The thicker surface decorations (grisailles and enamels) presented cracks and detachments, in contrast to the thinner lines which are normally well preserved. OCT is a suitable technique for characterizing glass decoration in situ without dismounting the stained-glass window; and able to reveal the condition and methods of manufacture that cannot be detected simply by visual inspection.

Keywords Art Nouveau, Glass windows, Optical coherence tomography, Grisaille, Enamel

Introduction

The decorative techniques applied to stained-glass windows are very diverse. The most ancient windows were made with coloured glasses mounted with lead cames. By the twelfth century, the use of grisaille as a dark painting to trace contours with a thick line (grisaille *à contourner*) and shadows with a thin and watery layer (grisaille *à modeler*) was widespread in Europe. The paint was prepared by mixing dark metal oxides, normally of iron and/or copper, with powdered colourless glass, and this mixture fixed to the glass support by thermal treatment. [1, 2]. Another common decorative technique introduced during the fifteenth century is the use of enamels for colouring glass. Enamels are layers of glass that melt at lower temperatures than the glass onto which they are applied [3–5]. A different method to colour stained-glass windows is the application of yellow-silver staining composed of a mixture of silver salts and clays (ochres). After thermal treatment, silver nanoparticles are formed inside the glass matrix by a two-step process of exchange with alkaline ions and cementation [6–8]. Finally sanguine, a decorative technique applied to obtain yellowish-brownish-reddish colours, became popular at the end of the fifteenth or beginning of the sixteenth century for decorating skin colours, hair, and beards [9]. Sanguine is generally produced by grinding iron oxides with lead-silica glass. The tone and opacity of the paint are directly related to the thickness of the paint layer and the size of the Fe_2O_3

*Correspondence:
Teresa Palomar
t.palomar@fct.unl.pt
[1] Research Group VICARTE "Vidro e Cerâmica para as Artes", FCT-UNL, Campus de Caparica, Quinta da Torre, 2829-516 Caparica, Portugal
[2] Institute of Ceramic and Glass (ICV-CSIC), c/Kelsen 5, Campus de Cantoblanco, 28049 Madrid, Spain
[3] Faculty of Fine Arts, Nicolaus Copernicus University in Toruń, ul. Sienkiewicza 30/32, 87-100 Toruń, Poland
[4] Department of Conservation and Restoration, Universidade NOVA de Lisboa, FCT-UNL, Campus de Caparica, Quinta da Torre, 2829-516 Caparica, Portugal
[5] LAQV-REQUIMTE, Universidade NOVA de Lisboa, FCT-UNL, Campus de Caparica, Quinta da Torre, 2829-516 Caparica, Portugal
[6] Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, ul. Grudziądzka 5, 87-100 Toruń, Poland

particles [5, 9, 10]. All the above decorative techniques require high temperatures to fix the colouration.

By contrast, the 'cold' paints such as tempera or watercolour are directly applied onto the glass with an organic binder but not fused in a kiln [11]. Their most important characteristic is that they should be transparent enough to give colour to the glass without darkening it. These paints are normally used to retouch the decoration or to restore it [12].

In addition to painting techniques, it is common to use mechanical or chemical procedures, which induce modifications to the light that passes through the glass sheet, in order to obtain different decoration effects. For example, frosting, sandblasting, and etching produce frosted glass through controlled pitting while engraving and grooving techniques use diamond tools to make the decorations by cutting the glass [13]. Among these techniques, acid etching has been widely used in stained-glass windows to remove the thin coloured layer in glasses (flash glasses) or to induce different colourations in the same glass piece by controlled acid attack of the surface with hydrofluoric acid. The use of acid etching in stained-glass windows has been recorded from, at least as early as, the fourteenth century [14].

The decorative techniques used for stained-glass windows have been studied from a stylistic point of view [15]. In addition, the characterization of these decorative techniques provides information about their production practices in ancient workshops [16, 17]. For most of the characterization methods, stained-glass windows need to be dismounted and/or samples must be collected in order to study their surface and cross-section. However, in recent years the development of non-destructive techniques, such as visible hyperspectral imaging [18], laser-based techniques [19, 20] or multiphoton excitation fluorescence microscopy [21], have made it possible to perform such studies without sampling and even in situ [18, 20, 21].

Another promising non-invasive technique for the study of stained-glass windows is optical coherence tomography (OCT), which is an interferometric imaging technique that provides cross-sectional images of the internal microstructure of an object [22]. It was developed for biomedical optics and medicine because it allows the analysis of biological tissues in situ and in real-time at axial resolutions of 1–15 µm [23]. However, since the beginning of the twenty-first century, OCT has been applied to objects of cultural heritage as it is a non-destructive technique with fast data collection and easy object preparation with no need for the use of a sample/object chamber. It permits the examination of the structure of historic samples without sampling when the materials on the surface are transparent to infrared light [24–27].

OCT has been broadly applied to easel paintings since it gives insight into the varnish layers and semitransparent glazes underneath [28]. In the case of glass items, Egyptian faience objects have been characterized by OCT to determine their microstructure and production method [29]. In addition, the different IR absorption of the opacifiers has permitted observation of the different decorative layers of Egyptian glass objects [30] or stratified glass eye beads from the Warring States Period (China) [31]. OCT is also capable of detecting different layers of glazy enamels having an approximately 800 µm total optical thickness [30].

OCT has also been applied to characterize alterations of glass objects. The formation of silica gel layers on the glass surface as a result of their interaction with the environment commonly diminishes the surface refractive index [32–34]; the difference, though, used not to be significant enough to be resolvable in OCT. However, the formation of fissures in the interface of the alteration layers and the bulk glass makes it possible to estimate their depth. For example, in the study of post-medieval *façon de Venice* goblets, the thickness of their alteration layers was assessed, being found to be lower than 9 µm in stable glasses and between 50 and 70 µm in the altered one [35]. Similarly, the leaching layers in an Egyptian glass scarab were found to have a thickness of around 110 µm [30]. Another case study was provided by the crizzled glass flutes made by Claude Laurent in the nineteenth century. OCT detected cracks, delaminations, and different alteration layers, which could be correlated to the intensity of the hydration band detected by short-wave Infrared fiber optics reflectance spectroscopy (SWIR FORS) [36]. A similar relationship was observed in a piece made with Limoges enamels, where the most hydrated areas presented crizzling with broken gel layers and surface deposits [37]. OCT was also capable of detecting the droplets and dry particulates produced by weeping, the first stage of crizzling, in a 19th-century daguerreotype without opening the encasement [38]. Finally, a 17th-century Antwerp *Façon de Venice* glass showed multiple corrosion fronts, a typical deterioration pattern exhibited in buried glasses [39].

Alteration in stained-glass windows has also been characterized by OCT [26, 27, 35, 40]. The presence of silica gel layers on stained glass from the Basilica of St. Mary in Cracow (fourteenth century) resulted in a high level of scattering in the analysis, obscuring significantly the ability of OCT to detect the reach of alteration. However, examination through the glass allowed observation of the silica gel layers including the gel-glass boundary and pitting on the glass surface [27]. A 19th-century stained glass from a church window in Powidz (Poland), whose surface was severely crizzled, was also analysed. Here again, analysis by OCT showed the presence of a high level of scattering as well as small cracks parallel to the surface which indicated the gradual and localized delamination of the glass [35]. Targowski et al. also determined the morphology of grisaille layers by analysis of the OCT scans taken from both sides of the glass piece, since glasses are transparent enough to permit deep penetration of the examining IR light [26]. This procedure is not always possible, especially with the in situ analysis of stained-glass windows, but it is useful to characterize the painting used on Reverse glass paintings (*Hinterglasmalerei*) and their delamination without touching the fragile painted surface [25], and also to monitor the consolidation of detachments in this type of object [41].

As can be seen, OCT is a versatile non-destructive technique to characterize glass objects, mainly to quantify alteration of the glass. However, it is necessary to be cautious with possible multi-scattering events produced by silica gel layers that can render estimation of their thickness impossible [42].

The present study aims to explore the feasibility of non-destructive OCT analysis for the characterization of the different decorative techniques (grisaille, enamel, textured glass, and cold painting) by direct observation of two 20th-century vertical stained-glass windows. Additionally, the condition of some of the decorations was assessed aiming to relate their degree of alteration to their morphology and to the prior restoration interventions identified in some areas of the windows.

Fig. 1 Glass windows in the Dining Room of the Casa-Museu Dr. Anastácio Gonçalves with the areas analysed superimposed

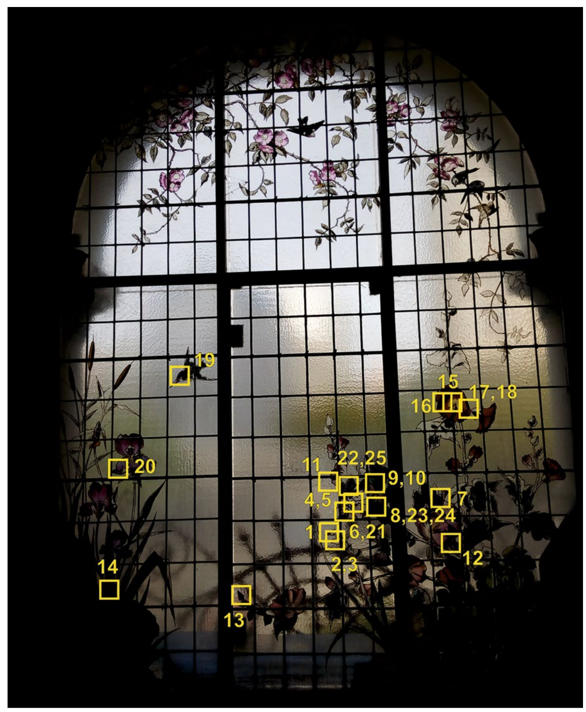

Fig. 2 Glass windows in the *Atelier* of the Casa-Museu Dr. Anastácio Gonçalves with the areas analysed superimposed

Materials and methods

Glass windows

The Casa-Museu Dr. Anastácio Gonçalves (CMAG) located in Lisbon (Portugal) has two glass windows in *Art Nouveau* style signed by the *Societé Artistique de Peinture sur Verre* in 1904. One is located on the first floor in the current Dining Room, and the other is in the *Atelier* on the second floor.

The stained-glass window in the Dining Room is a traditional window made with glasses coloured in bulk and mounted with lead cames, depicting a woman picking oranges from a tree (Fig. 1). The glasses were coloured with iron, manganese, cobalt, copper, and chromium to give greenish, bluish, and purplish hues. Silver staining, copper ruby and iron-amber glasses were also used to create warm colours [18]. The decorations were made with grisaille and textured glass and, in general, were in good condition, with the exception of some grisailles that showed fissures. The *Atelier* window exhibits a naturalistic painting with iris flowers, reeds, bellflowers, vines and birds. It was made with rectangular pieces of hammered glass decorated with grisailles, enamels and cold paintings coloured with iron, manganese, cobalt, copper and chromium [18]. This panel was in a very poor state of preservation in its lower part with loss of the bluish and purplish enamels. Some of these areas were probably retouched with dark paints (Fig. 2). Descriptions of the areas analysed in both windows are summarised in Table 1.

Table 1 Summary of OCT analyses of the Dining Room and *Atelier* windows

Window	Panel	Spot	Motif	Decoration
Dining room	Central	1	Pedestal	Cracked grisaille
		2	Grass	Grisaille *à modeler*
		3	Flower petal	Grisaille *à modeler*
		4	Flower petal	Grisaille *à modeler*
		5	Flower petal	Textured glass
		6	Flower petal	Textured glass
	Left	7	Flower	Cracked and repaired glass
		8	Flower	Cracked and repaired glass
		9	Flower petal	Textured glass
		10	Flower petal	Textured glass
	Right	11	Bird	Grisaille
		12	Water	Textured glass
		13	Decorative frame	Thick grisaille
		14	Decorative frame	Thick grisaille
		15	Decorative frame	Thick grisaille
		16	Decorative frame	Grisaille with degradation products
		17	Decorative frame	Thin altered grisaille
		18	Decorative frame	Thin and thick altered grisaille
Atelier	Central	1	Leaf	Enamel with grisaille contours
		2	Leaf	Enamel with grisaille contours
		3	Stem	Lost enamel with grisaille contours
		4	Leaf	2 colours in grisaille *à contourner*
		5	Leaf	2 colours in grisaille *à contourner*
		6	Leaf	Blue paint
		8	Flower	Pink paint
		9	Leaf	Green enamel
		10	Leaf	Green enamel
		11	Flower	Pink enamel
		13	Leaf	Blue enamel
	Right	7	Leaf	Blue enamel
		12	Brown leaf	Brown enamel
		15	Red flower	Yellow colour and grisaille
		16	Red flower	Red enamel and grisaille
		17	Red flower	Red enamel and grisaille
		18	Red flower	Red enamel and grisaille
	Left	14	Stems	Green enamel and grisaille
		19	Blue bird	Blue paint
		20	Purple flower	Purple enamel
	Central (from external side)	21	Blue flower	Blue painting
		22	Blue leaf	Blue painting
		23	Pink flower	Pink enamel
		24	Pink flower	Pink enamel
		25	Blue leaf	Blue painting

Optical coherence tomography

The OCT examination was made with a prototype high-resolution portable Spectral domain (SdOCT), an instrument built under the EU FP7 CHARISMA Programme to be used for the examination of cultural heritage objects. In brief, OCT is an interferometric technique capable of localising structures which scatter or reflect IR radiation within media of moderate light absorption. This is accomplished by registration of the time (or optical path) needed for propagation to the object, reflection from an element of its structure, and propagation back to the instrument. The spectral range of the probing light is 770–970 nm. The axial resolution is 3.3 µm in air and 2.1 µm in a material with a refraction index of 1.6, such as glass. In the case of using the OCT technique to assess the thickness of the glass layer, the location of the two interfaces should be determined and, consequently, the error in the determination of the glass layer thickness is ± 4 µm, which applies to all glass thicknesses given in this work. The lateral resolution is 15 µm. It is specific for the OCT technique that the axial resolution is decoupled from the lateral one. The former depends entirely on the spectral properties of the probing light: the broader the spectrum, the higher the axial resolution. Furthermore, this resolution deteriorates quickly on increasing the central wavelength, which very often leads to an enforced trade-off between the penetration range (usually better for long wavelengths) and the axial resolution. The lateral resolution depends on the focal length of the objective and thus it is usually kept reasonably low to ensure a large imaging area [23] (up to 17×17 mm^2 for this instrument). The axial imaging range is 1.4 mm and for spectral domain OCT it depends mostly on the spectral resolution of the detection channel. For the measurements described in this contribution, the power of the probing light at the object was lower than 1 mW and the distance to the object from the most protruding element of the instrument was 43 mm.

In every spot (numbered independently for both windows, as in Table 1) a narrow beam of the probing light was fast-scanned over a set of 100 parallel linear trajectories covering an area of 12×12 mm^2 (except for Spot 1 in the *Atelier* window which was collected over an area of 10×10 mm^2). Most of the scans were performed in the horizontal direction, except for that of Spot 18 in the Dining Room window, which was analysed twice in both directions (horizontal and vertical). The resultant 3D data cube could be exploited in two ways: by extracting a single 2D cross-section slice, hereinafter referred to as the OCT tomogram (Fig. 3) or by extracting the glass surface profile (Fig. 4).

OCT tomograms illustrate reflective and scattering properties of the material examined. Here, these are presented in a scale of false colours, where warm colours indicate strong reflection or scattering areas, and cold colours mark weaker reflecting or scattering areas. Regions that do not scatter light, such as air, glass, and areas inaccessible to radiation, are imaged in black. In the figures, light is incident from the top, and the first visible structure is the surface of the glass. Due to the big difference in the refractive index of air and glass, the reflection signal from the surface is usually the strongest. For the same reason, cracks in glass structure are highly visible. Another feature specific to OCT tomograms are structures visible directly under the surface as vertical, gradually fading lines Figs. 5, 6c. They are caused by multiple scattering of the probing light in the structure directly above. The boundary of two media (*e.g.*, air–glass) is represented in the OCT tomogram as a thin, strong line in two cases: either the probing light propagates further in non-absorbing media—like a transparent glass—or the glass at the surface absorbs so strongly that only light scattered by or reflected from the surface can be registered. In the case of multiple scattering, the light propagates for longer in the medium, which results in the visualization of seeming structures deeper in the glass layer. It must be also admitted that OCT does not visualize the refractive index of medium directly, but only by back reflection if there is a boundary for which the change in refractive index is rapid. Thus, in the case of small changes in glass composition (e.g., leaded *versus* alkali glasses), this boundary is not detectable.

For the convenience of the reader and due to the axial resolution being higher than the lateral, the tomograms are nine-fold vertically stretched. In principle, OCT as an optical detection method, retrieves optical distances as opposed to geometrical ones. The tomograms presented here are corrected for this effect with a common refractive index $n_R = 1.6$ [43]. Since the vertical distances imagined are small, the possible error caused by the approximation of n_R is below the axial resolution and thus not significant.

A detailed description of the instrument and data processing procedures can be found in Targowski et al. [44]. A graphical description of how to interpret the tomograms can be found in Fig. 7.

OCT data collections were performed in the absence of direct solar light. In the Dining Room window, wood panels were placed in the windows to block the sun, since that façade receives sunlight over several hours during the afternoon [45]. The *Atelier* window, oriented to the northwest, received sunlight in the evening, so those data collections were made during the morning and afternoon (Fig. 8) because, due to the architectural distribution of the façade, it was not possible to protect the window.

Other techniques

The condition of the decorative elements was assessed using the naked eye. Photographic records were made using Canon EOS 1200D camera, with Canon EFS 18–55 mm objectives, and with the 8MPx camera of a BQ Aquaris A4.5 phone, without the use of special lighting. Pictures were usually taken with natural illumination; however, the figures referred to in the text as by

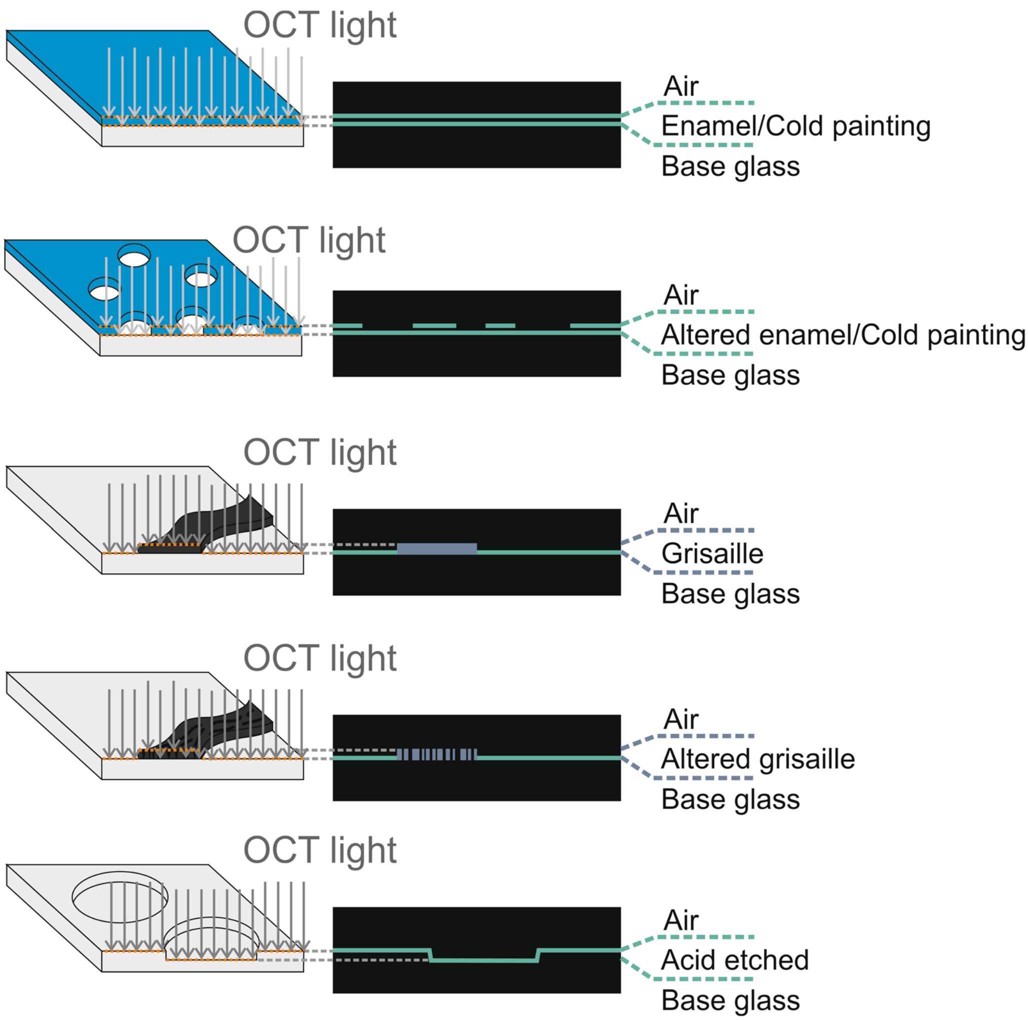

Fig. 3 Visual interpretation of the tomograms as a function of the decoration on the glass surface

reflected light were taken with artificial lamp illumination with wood panels blocking the sun.

Results

Dining Room window

Grisaille

Grisaille is a dark paint, usually black or brown, formed by small grains of iron and copper oxides fixed to the glass surface with lead glass [2]. It is used in the form of thick lines to define the contours of the figures, and in the form of thinner layers to produce shades and volumes.

The presence of crystals of metal oxides distributed heterogeneously inside the grisaille produces dispersion of incident light, creating the aspect of a dark, rough, and dull painting. It results in some propagation of OCT light inside the layer where it is partially absorbed. Therefore, the OCT response is less intense, resulting in a bluish hue in the tomogram. For the surface of the glass, light is reflected/scattered directly, without absorption, the back signal is stronger and is visible in the tomogram by a yellowish-greenish hue (Fig. 5b–d). Light scattering produced by grisaille has previously been observed by Targowski et al. who analysed the glass from both sides of a glass window piece to characterize its morphology [26].

In the thinner layers of grisaille, the material is transparent to the OCT illumination, and therefore the thickness of these layers can be measured: it can be estimated to be about 7 µm in Spots 2, 3 and 4 and around 11 µm in Spot 14 (Table 2). The thickness of thicker grisailles, used to define contours, was difficult to determine due to the opacity of this material to OCT light. As these thick grisailles usually exhibited fissures and cracks, we determined the thickness of cracked grisailles using the detached areas for the glass surface. Previous analyses of historical grisailles showed that the altered cracks are commonly formed along the glass/grisaille interface [46],

Fig. 4 Setups of the OCT technique in the **a** Dining Room window, and **b** *Atelier* window

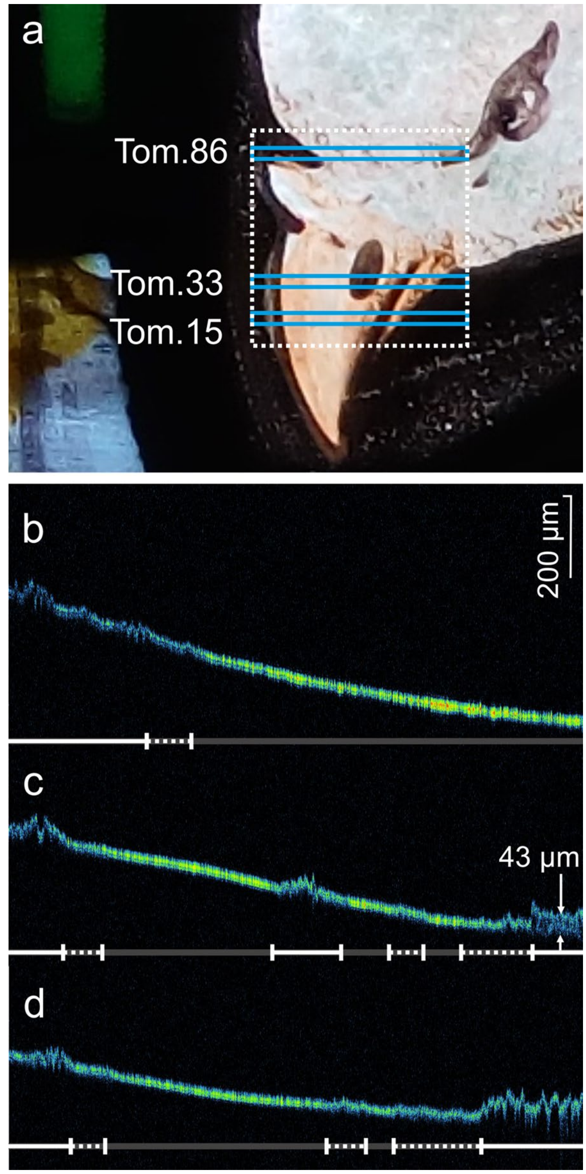

Fig. 5 **a** Detail of the pigeon head in the right panel in the Dining Room window (Spot 11). OCT tomograms: **b** Tomogram 86, showing the thick grisaille in the pigeon head. **c** Tomogram 33, showing the thick grisaille contouring the beak of the pigeon, defining its nares and its mouth; some areas also have thin grisaille which yield volume to the beak. **d** Tomogram 15, showing the presence of thick grisaille contouring the beak and defining the mouth, and thin grisaille yielding its volume. Solid line: thick grisaille; dotted line: thin grisaille. The tomograms are presented on the same scale

this being a good baseline for the measurement of thickness. The measurements varied between 50 and 70 µm (Spots 13, 14, 15) (Table 2), but it was detected as up to 200 µm in a thick line in the decorative frame. Here, though, the material was substantially altered by several grisaille detachments (Fig. 6).

Finally, some of the grisailles (Spots 1, 16 and 17) had a whitish hue, probably due to their degradation with formation of whitish alteration products. The different observed absorption of IR OCT light by the whitish alteration products of the grisaille arises due to increased scattering, which creates multi-scattering artefacts in comparison to areas of better-preserved grisaille (Fig. 7) (Spots 16 and 17). However, some areas have higher transparency to IR (*e.g.*, Spots 1, 11). According to the literature, the alteration products could be carbonates and sulphates [2, 47].

Textured glass

The flowers and the lake represented in the stained-glass window have textured decoration (Figs. 1 and 8a). This type of decoration could have been made by either decreasing the thickness of the glass with treatment by hydrofluoric acid called acid etching, or by increasing it by fusing, i.e., adding small glass pieces at high temperatures.

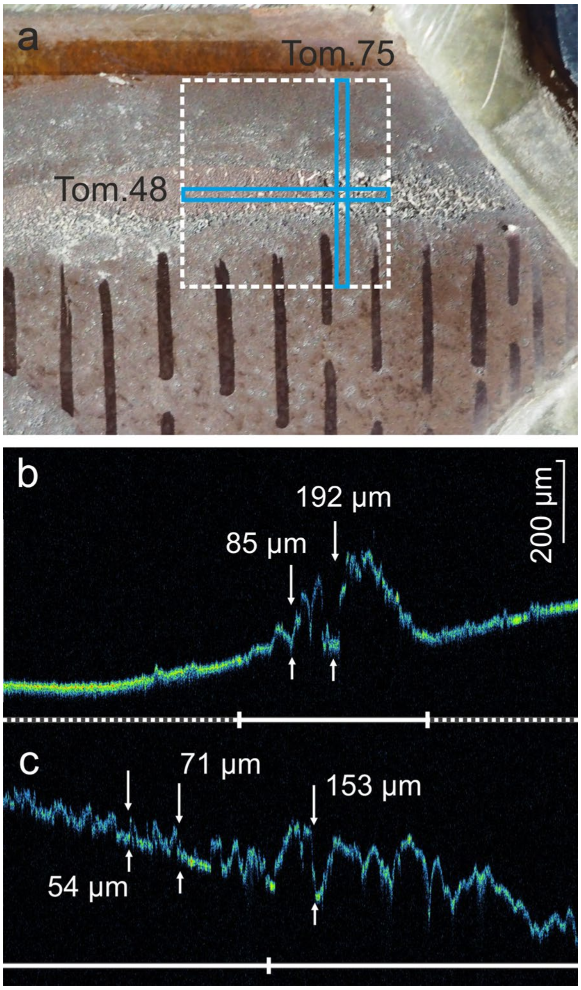

Fig. 6 **a** Detail of the decorative frame in the right panel in the Dining Room window (Spot 18). OCT tomograms: **b** Tomogram 48, in horizontal analysis, showing the morphology of the altered thick grisaille; **c** Tomogram 75, in vertical analysis, showing the difference between the area in which the grisaille has been detached and the thick cracked grisaille. Solid line: thick altered grisaille; Dotted line: thin grisaille. The tomograms have the same scale

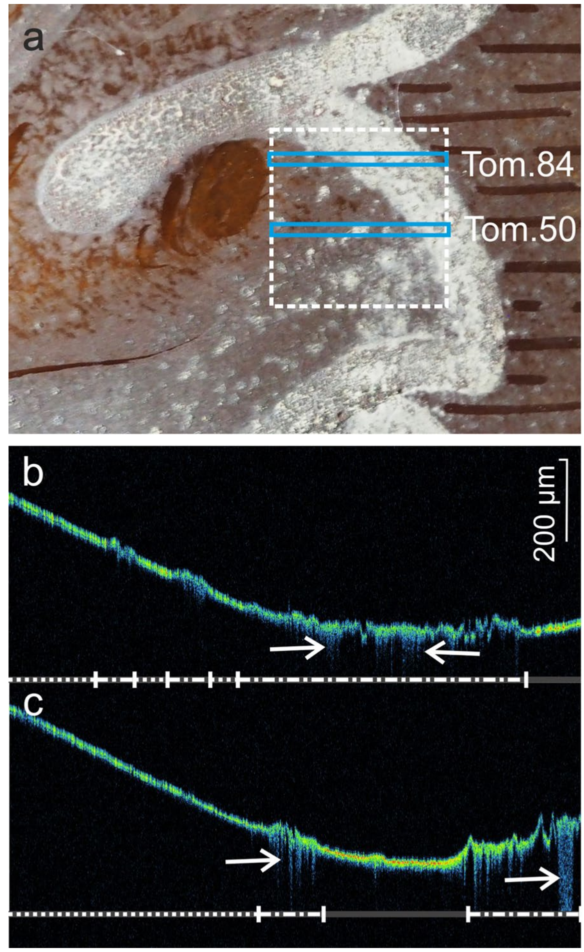

Fig. 7 **a** Detail of the grisaille decoration in the central panel in the Dining Room window in reflected light (Spot 16). OCT tomograms: **b** Tomogram 84, showing the presence of alteration products that cause the multi-scattering artefacts (arrows). **c** Tomogram 50, showing the same alteration products also formed in the thin layer of grisaille. Solid line: thick grisaille; Dotted line: thin grisaille; Dash-dot line: alteration products. The tomograms have the same scale

The OCT analyses showed that the glass surface was flat in thicker and darker areas as well as in thinner and clearer ones. In the joint of the two areas, rounded edges were observed as if material had been removed (Fig. 8). The colour of these pieces depended on the thickness of the glass in each area. The difference in thickness between the thinner and thicker glasses varied between 29 and 95 µm (Spots 5, 6, 9, 10, and 12) (Table 2). According to the Lambert–Beer law, the absorbance of a material is directly proportional to its thickness, for this reason, the areas with greater thickness (depicting stamens) have a more intense hue than those of petals with lesser thickness [48]. In some motifs, the grisaille layer is apparently lying on top of the textured glass decoration, as indicated by the difference in scattering properties visible at the surface of the stained glass (e.g., Spots 9, 10). This behaviour also pointed to the fact that no interface inside the glass could be related to the presence of adhered glass. These observations provide evidence pointing to the use of acid etching rather than fusing to give additional texture to the flowers and lake.

Restoration areas

Damage on one of the flowers in the left panel had been restored (Fig. 9a) (Spots 7 and 8). The restoration was visible to the naked eye, and the OCT analyses showed

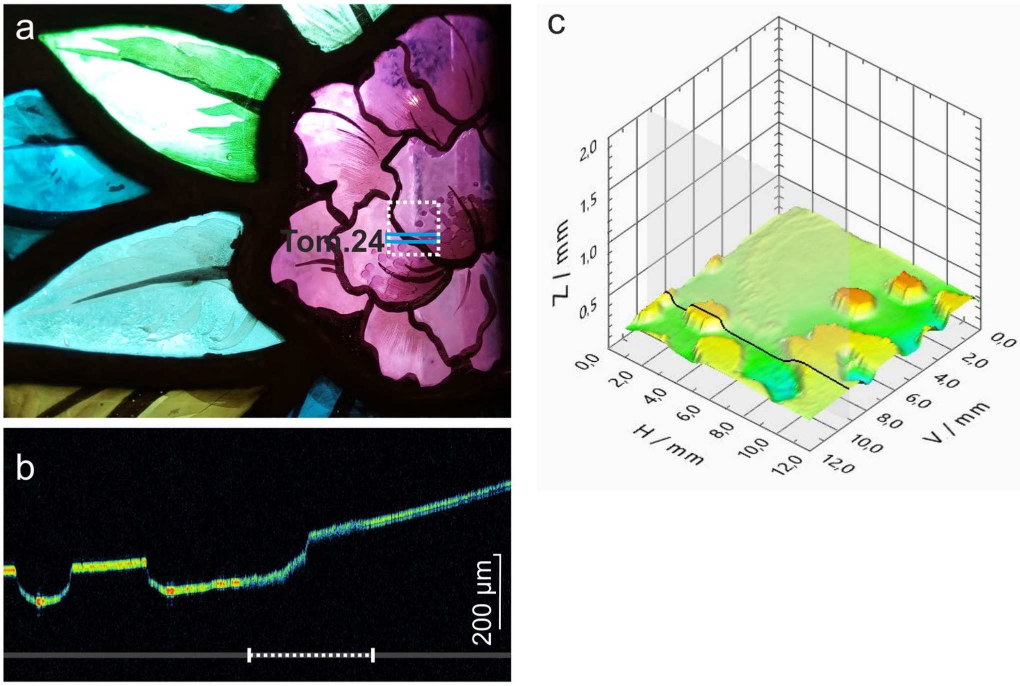

Fig. 8 **a** Detail of a flower in the left panel in the Dining Room window (Spot 10). **b** OCT tomogram 24, showing the two-level decoration and the presence of a thick grisaille on it; dotted line: thin grisaille. **c** 3D representation of the glass surface showing the circular decoration on the upper level. The colours code the elevation of the surface. The position at which tomogram 24 was taken is shown as a black line

Table 2 Analyses performed on the Dining Room window

Grisaille	Spot	Thickness ±4 (µm)	Acid attack	Spot	Thickness ±4 (µm)
Light	2	7	Purple	5	54
Light	3	7	Purple	5	56
Light	4	7	Purple	5	66
Light	14	11	Purple	6	27
Black thick	11	43	Purple	6	30
Black thick	1	43	Purple	6	33
Black thick cracked	13	50	Purple	9	89
Black thick cracked	13	70	Blue	12	60
Black thick cracked	14	52			
Black thick cracked	15	51			
Black thick cracked	15	83			
Black thick cracked	15	62			
Black thick cracked	18	54			
Black thick cracked	18	71			
Black thick cracked	18	153			
Black thick cracked	18	85			
Black thick cracked	18	192			
Average		61			52
Standard deviation		50			21
Minimum		7			27
Maximum		192			89

that the repair was not properly levelled with the rest of the panel (Fig. 9b and c) and that it presented some voids which could have affected the physical stability of the glass (Fig. 9b). The remains of lumps along with transparent layers, probably of glue, were also observed in this area. It is possible that this restoration was performed in situ, without removing the panel, despite all the difficulty of working in a vertical position.

Atelier window

Grisaille

The grisaille was applied to the window in the form of thick lines to define the contours of the figures, and their volume was brought out by the use of enamels of different colours (Fig. 2). In a similar way to the other stained-glass window (Sect. "Grisaille"), the grisaille produced light dispersion and, therefore, it was perceived in the tomogram as a bluish colouration (Fig. 10b). In the thicker grisaille lines, the detachments exposed the subjacent glass (Fig. 10b).

The well-preserved grisailles had a thickness of around 20 µm, and the detachments were observed in lines with thicknesses larger than 30 µm (Table 3). Grisailles with thicknesses larger than 60 µm were also identified (e.g. Spot 5) (Table 3).

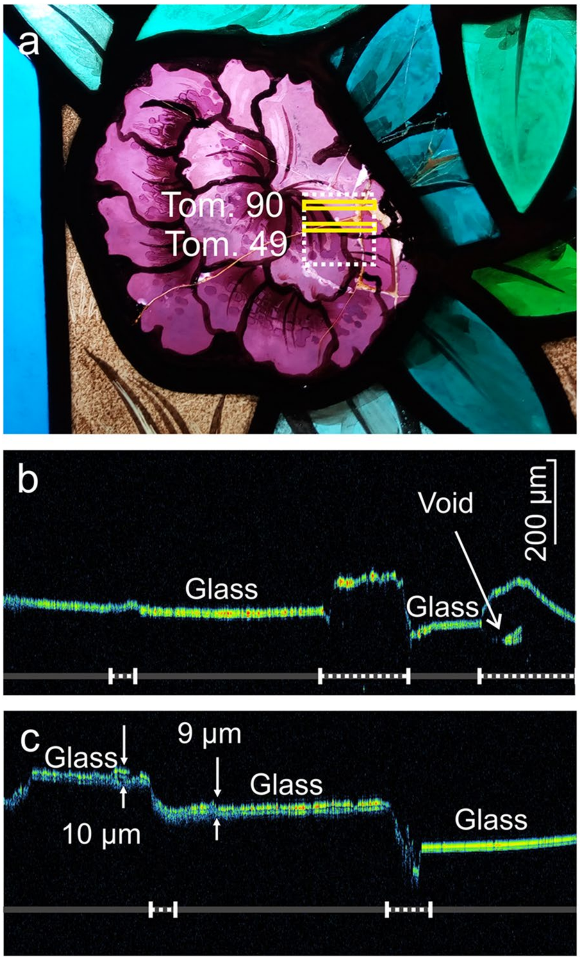

Fig. 9 **a** Detail of a restored flower on the left panel in the Dining Room window (Spot 8). OCT tomograms: **b** Tomogram 90, showing the incorrect alignment of glass pieces and the presence of a void on the glue-glass boundary (however, the presence of a bubble inside the adhesive cannot be excluded); **c** Tomogram 49, showing the glass pieces at different levels due to a careless restoration. Dotted line: cracks fixed with glue. The tomograms are shown on the same scale

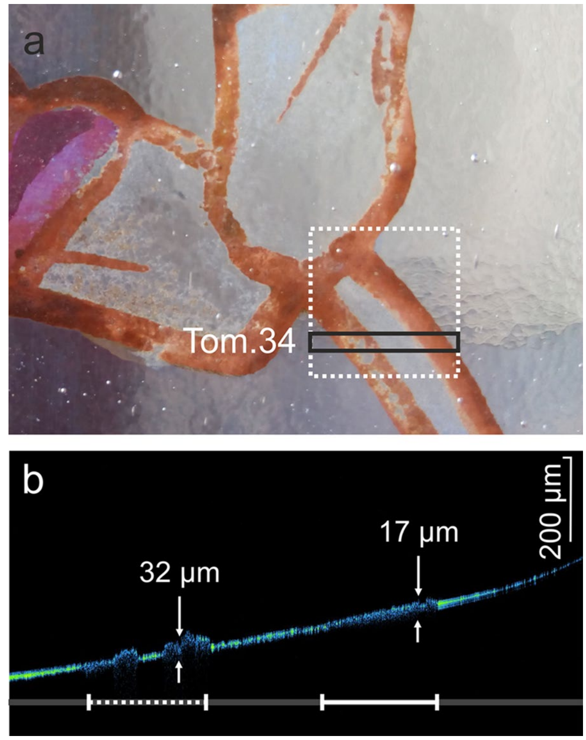

Fig. 10 **a** Detail of the grisaille decoration in the *Atelier* window (Spot 3). **b** OCT tomogram 34, showing the thick grisaille that creates the contour of the flower, in the left line the grisaille has been partially lost. Solid line: well-preserved grisaille; Dotted line: altered grisaille

Enamels

In contrast with grisailles, the enamels analysed showed a better translucency to the OCT light, showing a similar thickness in the different areas analysed. Layers as assigned to original enamels had thicknesses around 7–15 µm (Spots 1, 2, 4, 7–14, 16–18, 20, 21, 23, 24) (Table 3). No correlation was found between the degree of alteration and the thickness of the enamel layers, but it was observed that their state of preservation is related to their colour. Reddish, pinkish and pale enamels look stable (Spots 1, 2, 4, 11, 16, 17) (Fig. 11a–c); however, some of the brownish and bluish ones are damaged (Spots 7, 12, 13, 14, 18) or have been lost (Fig. 12a). In most of the altered areas, the enamel exhibited paint losses with circular shapes, creating a speckled appearance on the surface of the glass. These spots tended to merge in groups, creating larger sections of loss (Fig. 12a). These detachments can easily be observed by OCT (Fig. 12b). Similar alterations were observed in Spots 7, 12, and 18. In some areas of the bottom part of the window, well-preserved enamels near significantly altered ones were observed. The analysis of these areas, such as Spot 13, showed the presence of two transparent layers (Fig. 13a and b). This result can be related to the application of two different enamels, or a retouching by cold painting of the altered enamel. Individual enamel layers had an approximately 12 µm thickness, similar to the original layers.

In another area, some enamels seemed to be very heterogeneous, and their colours were brighter in comparison with other colours found in the window (Fig. 14a). The OCT analyses in these areas revealed a very irregular surface (thickness 7–17 µm) with the presence of large drops of enamel on the surface and two layers in some areas that might correspond to the grisaille and the enamel (Fig. 14b). Some of these pieces were analysed from

Table 3 Analyses made on the *Atelier* window

Grisaille	Spot	Thickness ±4 (μm)	Enamel	Spot	Thickness (μm)	Painting	Spot	Thickness ± 4 (μm)
Brown (well)	3	17	Red	1	8	Blue	6	23
Brown (well)	5	23	Red	2	10	Blue	6	34
Dark Rose	11	15	Dark	4	7	Blue	6	52
Dark Rose lump	11	17	Blue	7	14	Blue	19	47
Black	15	19	Blue	7	15	Dark purple	20	30
Brown (cracked)	3	32	Rose	11	9	Dark purple	20	36
Brown-Dark (double layer)	4	44	Brown	12	14	Blue	21	56
Brown-Dark (double layer)	5	57	Brown	12	14			
Black (double layer)	14	28	Greenish	13	11			
Black (upper layer)	14	18	Double layer	13	31			
			Blue	14	9			
			Red	16	11			
			Red	16	13			
			Pale red	17	10			
			Pale red	18	10			
			Pale red	18	10			
			Blue	21	9			
			Rose (restoration)	8	7			
			Rose (restoration)	8	51			
			Green (restoration)	9	14			
			Blue (restoration)	10	14			
			Green (restoration)	10	16			
			Pink (restoration)	23	38			
			Pink (restoration)	24	30			
Average		27.0			15.7			39.6
Standard deviation		13.9			10.7			12.1
Minimum		15			7			23
Maximum		57			51			56

outside (Spots 23 and 24) and a layer of approximately 30 μm thickness was detected (Fig. 14c and d). This coating is thicker than the layer identified as the original enamel (10–15 μm) and it was applied irregularly, resulting in the unusual appearance of their colour. Similar results were also observed in Spots 9 and 10. These areas might correspond to past restoration attempts.

Restoration areas

In the lower part of the glass panel, some opaque areas were detected (Fig. 15a). The analyses of these areas (Spots 6, 8, 19 and 21) identified the presence of thick, 25–60 μm, layers (Fig. 15b). Additionally, these layers are not completely fixed to the glass substrate, being locally detached from the surface (Fig. 16a and b). The analyses from the external side showed a change in refractive index in the whitish areas, indicating the presence of delamination, that is, a separation of the paint layer from the glass substrate, but without detachment due to the plastic behaviour of the layer (Fig. 16). The opaque appearance, the greater thickness and different detachment behaviour of these layers with respect to enamels allowed us to identify them as cold paintings, which could have been applied during a restoration [11, 49].

Discussion

The two windows have completely different decorative techniques. The Dining Room window (Sect. "Dining Room window") is made with coloured glasses decorated with grisailles and acid etching; the *Atelier* window (Sect. "Atelier window"), on the other hand, is decorated with grisailles, enamels, and cold paintings. The characteristics of the materials used and their state of preservation are summarized in Table 4.

According to OCT characterization, the thickness of the grisaille *à modeler* is around 10 μm, and that of the grisaille *à contourner* is 30–100 μm. From the literature, analyses made to cross-section and analyses by laser

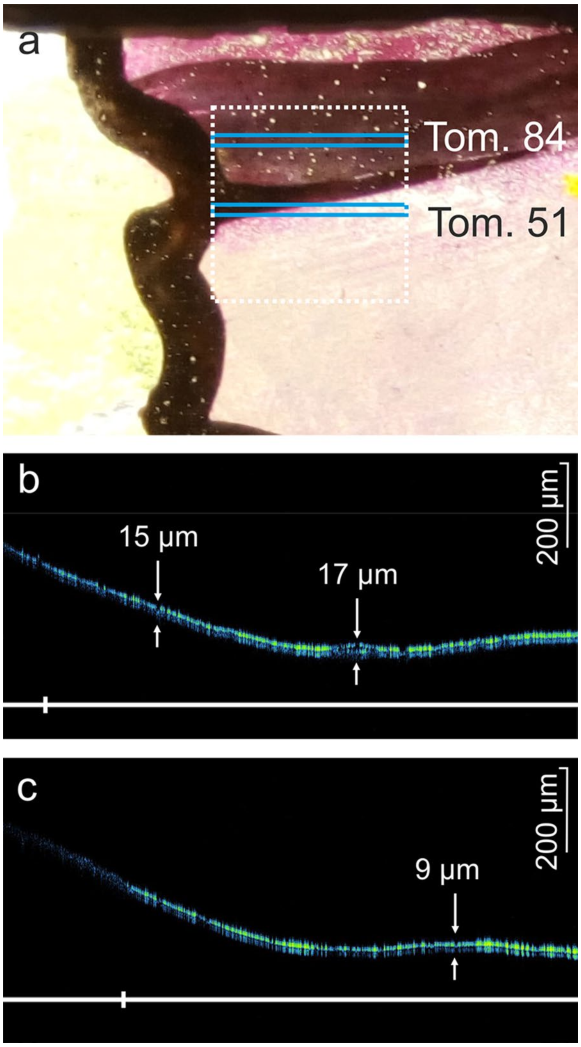

Fig. 11 **a** Detail of the enamel decoration in the *Atelier* window (Spot 11). OCT tomograms: **b** Tomogram 84, showing a continuous layer of well-preserved purple enamel; **c** Tomogram 51, showing a continuous layer of well-preserved pink enamel. Solid line: well-preserved grisaille/enamel. The tomograms are shown on the same scale

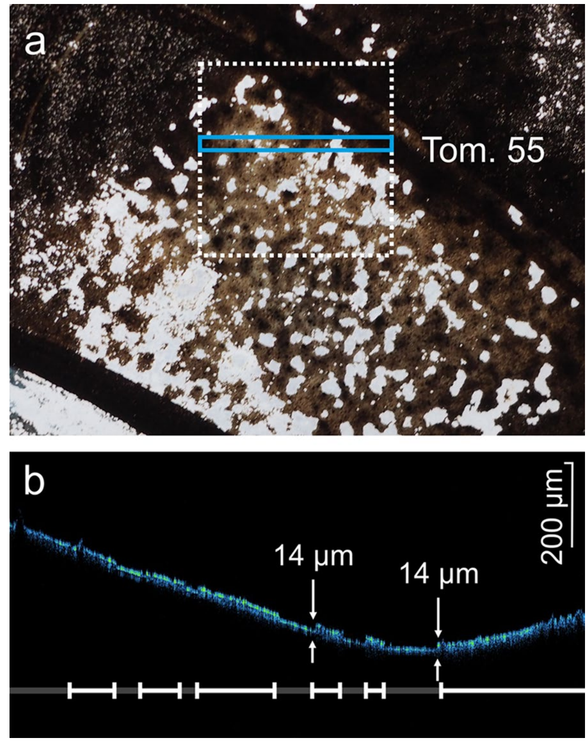

Fig. 12 **a** Detail of altered enamel decoration in the *Atelier* window (Spot 12). **b** OCT Tomogram 55, showing the homogeneous alteration to the brownish enamel. Solid line: preserved enamel

techniques of historical grisailles are consistent with the values measured by OCT [21, 50–52]. Regarding the enamels, the well-preserved ones have a thickness of 7–16 µm, similar to those of modern enamels, as measured in cross-section by Schalm et al. and Beltran et al. [53, 54]. One glass tile from the *Atelier* window showed enamels with a completely different appearance: they are thicker and rougher, and the colours do not match with those observed on the rest of the panel. Additionally, this specific tile was mounted wrongly upside down. For these reasons, it would appear that it is the result of a restoration made with non-original enamels. Finally, some of the enamels from the bottom part of the *Atelier* window have suffered excessive alteration over time, and in these areas a thick layer, that might reflect cold painting, was observed over the thin layer of original enamel.

Concerning the state of alteration, in general, the Dining Room window seems to be better preserved than the *Atelier* one. In the Dining Room window, the acid-etched glass is well preserved, as well as are the thinner grisailles; only the thicker grisaille lines showed cracks and detachments. This variable alteration of grisailles as a function of thickness has previously been reported in the literature and it is normally due to thermal stress [55–57]. Thermal evaluation of this window in the summer detected variations up to 10 °C due entirely to solar impact, with variations of approximately 2 °C every 20 min during the first hour of direct solar radiation, and a maximum decrease of 3.6 °C in 20 min with the arrival of sunset. Additionally, changes of > 15 °C from day to night were reported [45]. These recurrent variations can induce stresses in materials, especially in those with different thermal expansion coefficients [55, 56]. The presence of whitish alteration products on the thickest altered grisailles was also observed. These products may be carbonates or sulphates, which are the most common degradation products formed on high-lead glasses [2, 47]. Since these thick

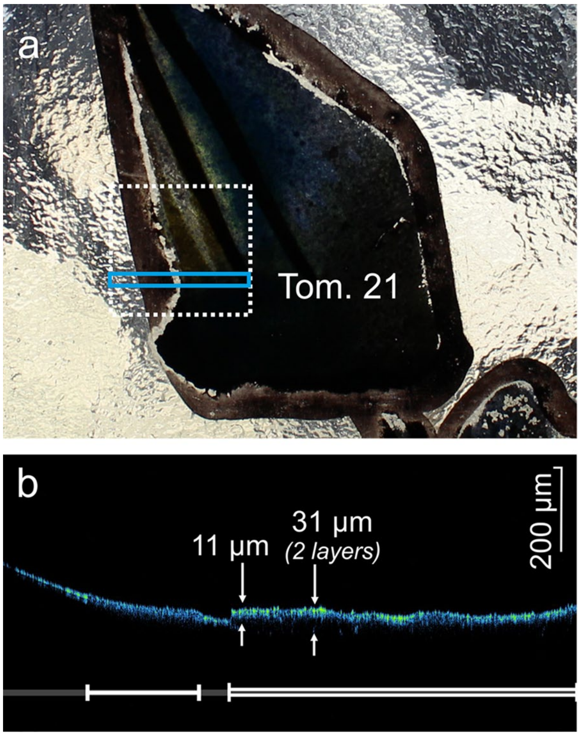

Fig. 13 **a** Detail of enamel decoration in the *Atelier* window (Spot 13). **b** OCT tomogram 21, showing the presence of two layers of enamel that could be related to a past restoration. Solid line: well-preserved enamel. Double line: two layers

grisailles were regularly subjected to high thermal stress, several fissures and cracks were created (Fig. 6).

In the *Atelier* window, on the other hand, only thin grisailles and the enamels with pinkish, reddish and pale hues are well preserved (Table 4). Interestingly, the enamels with bluish, greenish and brownish colour exhibited fissures and paint losses, which might result from thermal stress, because these colourations are the most sensitive ones to solar radiation [55, 56]. Previous studies with coloured glasses [56] proved that, under the same solar radiation, blue, green and turquoise glasses became the warmest ones because their chromophores induced the highest NIR absorption, and this would make them more thermally incompatible with the colourless glass support. Beltran et al. [53] also observed that the presence of cobalt and copper chromophores and spinel particles may be responsible for the large cracks filled with corrosion precipitates found in the Modernist green and blue enamels, and this could accelerate detachment of the enamel.

Due to the reduced solar impact, this window experienced a lesser increase in apparent surface temperature than the other window. Variations of up to 5 °C due to the solar impact, with variations of around 1.3 °C during each 20 min of the first 40 min of direct solar radiation, approximately 2 °C each 20 min during the hour following sunset, and changes of > 7 °C from day to night, were reported [45]. This difference in behaviour is due to the different orientation of the panel, the

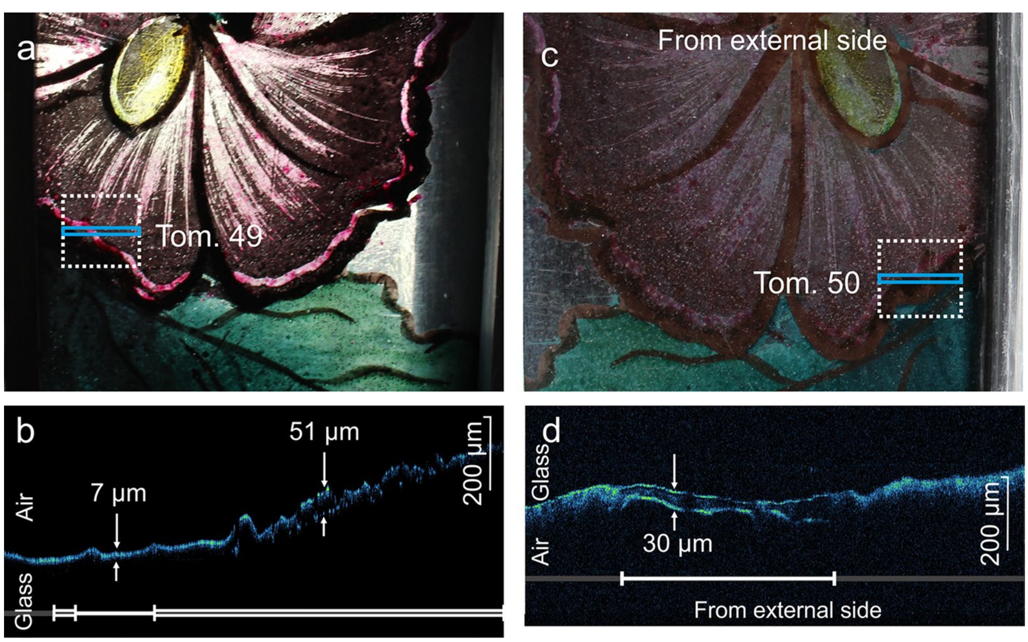

Fig. 14 **a** Detail of enamel decoration in the *Atelier* window (Spot 8). **b** OCT tomogram 49, showing the rough and thick pink enamel in the glass pieces that have been restored. **c** Detail of enamel decoration in the *Atelier* window from outside (Spot 24). **d** OCT tomogram 50, showing the same area but analysed from the external side of the window. Solid line: well-preserved enamel. Double line: two layers

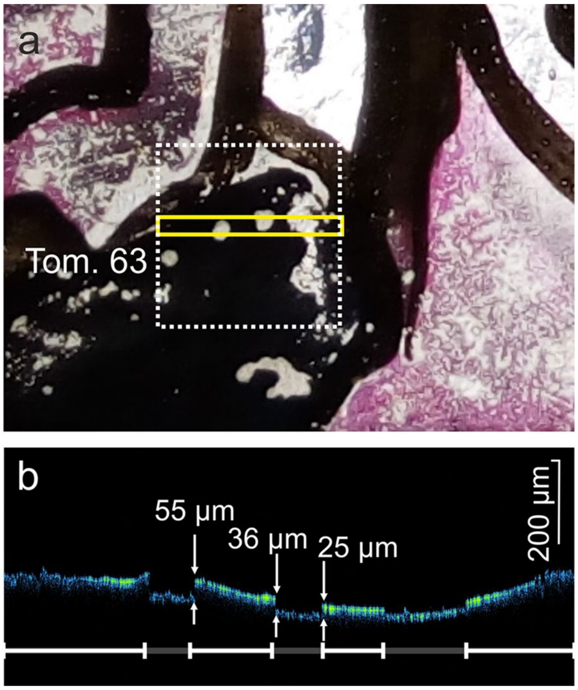

Fig. 15 **a** Detail of cold painting in the *Atelier* window (Spot 6). **b** OCT tomogram 63, showing a thick layer of cold painting and the areas where it was detached. Solid line: preserved cold painting

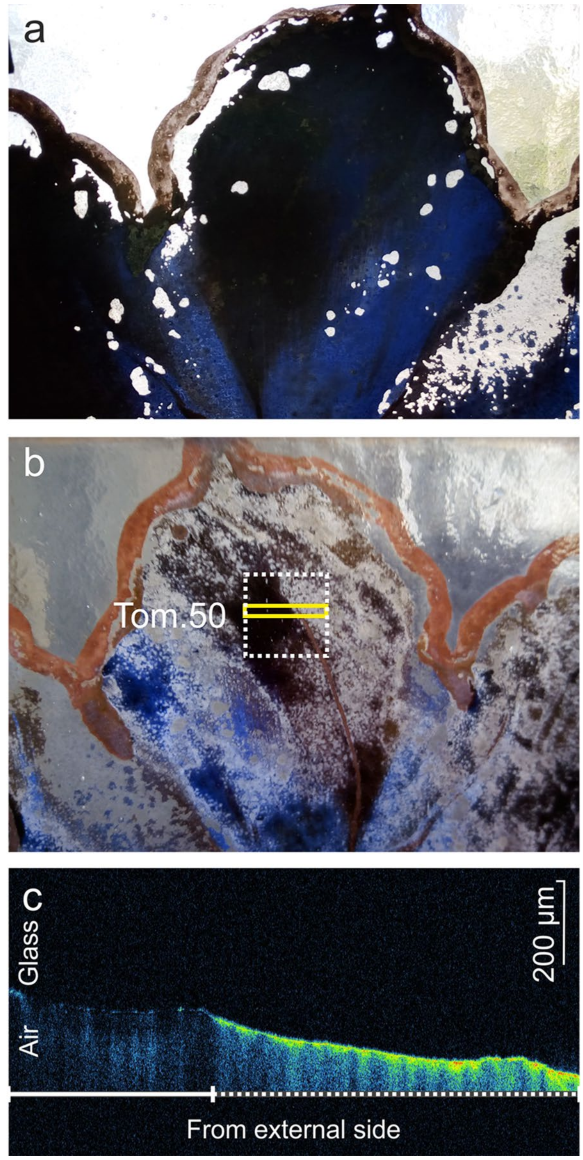

Fig. 16 Detail of the cold painting in the *Atelier* window from the **a** internal surface, **b** internal surface seen from the outside (Spot 25). **c** OCT tomogram 50, registered from the external side, therefore through glass, showing the internal surface of the glass with a thick layer of cold painting (absorbing strongly) and an area of very strong surface scattering. Structures below the surface, thus visible in the area where air is expected, are multi-scattered artefacts indicating strong surface scattering, possibly related to detachments. Solid line: well-preserved cold painting. Dotted line: possible detachments

shorter period of solar exposure, the lower greenhouse effect in the room due to its dimensions and, possibly, the lower outdoor temperature [45]. Enamels and cold paintings used for repairs were also identified as a function of their thickness, colour, and morphology (Table 4). Cold painting was observed predominantly in the lower part of the panel. For several years, this window was mounted inside out, with the painted surface facing outdoors, which could also have caused a faster deterioration of the enamels and grisailles in the bottom part of the panel, less protected from rain, wind and other external agents [58]. Recently, the development of fissures, cracks and delamination in dark cold paintings (Figs. 15 and 16), probably produced by thermal stress on the surface, has been observed [56].

An overall evaluation of the results reported here indicates that OCT may provide valuable information on the production methodologies of historical glasses and their degradation pathologies that cannot be revealed by other techniques.

Finally, the particularly novel result obtained by OCT and reported here, detailing the extent of alteration of grisailles and enamels in situ as a function of their thickness, without dismounting the window, is highlighted.

Conclusions

This study has established the feasibility of using the OCT technique to characterize different decorations directly on the glass windows in situ in a non-destructive way, while avoiding having to dismount them. The OCT analyses reported characterized grisailles, enamels, cold

Table 4 Summary of the characteristics of the materials and their state of alteration

Window	Material	Thickness	Condition
Dining room	Grisaille	< 15 µm (Thin lines)	Well preserved
		> 50 µm (Thick lines)	Cracked
	Acid etched glass	30–100 µm	Well preserved
Atelier	Grisaille	15–25 µm	Well preserved
		> 30 µm	Cracked or repainted
	Enamel	< 15 µm	Well preserved, original
		10–20 µm	Damaged
		15–40 µm (irregular)	Non original
	Cold painting	15–60 µm	Non original, delamination

paintings, textured glass, and a restored area. Original grisailles and enamels were in relatively good condition in both windows when they were applied in thin layers. However, thick grisailles and enamels presented fissures and detachments, probably as a consequence of thermal stress. In the *Atelier* window, different alterations depending on the colour of the enamel was observed, with darker colours altered more than reddish and purplish ones. Moreover, a thick dark layer on the bottom part of the *Atelier* window was identified as a cold painting, probably applied during a past restoration. In the Dining Room window, the textured glass of the flowers and the lake was identified as an acid-etched decoration since the holes appeared rounded and there was no interface between the thicker layers.

Abbreviations
CMAG Casa-Museu Dr. Anastácio Gonçalves
OCT Optical coherence tomography
SWIR FORS Short-wave infrared fiber optics reflectance spectroscopy

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Author contributions
TP, IPC, and MV designed the study; TP, MI and PT designed the methodology; MI and PT carried out the tests and analyses; TP and PT prepared the original draft. All authors read, reviewed and approved the final version of the manuscript.

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Availability of data and materials
The datasets used and/or analysed during the current study are available from the corresponding author and through Zenodo.

Declarations

Competing interests
The authors have declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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