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Prestige markers in art: subtle stratagems in material selection for fifteenth-century stained-glass windows

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Abstract

The understanding of the connection between the value of an image and the value of the materials that were used to make it is limited, especially for stained-glass windows. However, such information can bring-to-light how artistic and economic questions were intertwined and how the final artwork depended on the ranking of the materials.

With this paper, we aim to illustrate the benefit of combining art historical research with scientific analysis to retrieve the selection of the quality of the materials of stained-glass windows. Therefore, the main objective of this paper is to investigate the link between the materials and the iconography in order to recover artistic choices and highlight a possible hidden symbolism for a set of window panels, used as a first case-study. Glass quality is investigated according to the following parameters: (1) the glass composition, (2) the glass forming technique, (3) the transparency and hue of the colourless glass, and (4) the rarity and complexity of the colouring technology.

The results of our research indicate that the four-studied panels were originally assembled from two different glass compositional groups, K-rich glass and Ca-rich glass, and that specific attention was paid to select only high-quality materials and production techniques for the representation of the characters with higher positions in the religious hierarchy. A very interesting aspect concerns the way the bishop was rendered in one of the panels, because it seems that he actually upgraded his own prestige by requesting the use of specific materials and more attentiveness to his rendering in the panel.

By this research, we proposed a first case-study with a non-destructive tool to bring a discussion on the use of different glass qualities in stained glass window. We hope to further encourage such studies on window panels across Western Europe to verify if similar observations can be made.

Keywords: Stained glass, Quality, Prestige markers, UV–Vis-NIR absorption spectroscopy, p-XRF

Introduction

The period lasting from the mid-fifteenth until the end of the sixteenth century is considered the Golden Age of stained glass [1–3]. This phase coincides with notable changes in glass production, such as the transition from K-rich glass to Ca-rich glass. This composition change spread gradually all over Europe, except in Italy [4–9]. The new glass composition was probably first developed to improve glass properties and to save wood because Ca-rich glass requires less energy to be produced, and consequently less fuel. However, different historical sources give clues on the fact that the two productions were considered as having different qualities. In fact, K-rich glass, recalled as "French" or "Normandy glass" at that time, was preferred on Ca-rich glass or "Rhenish glass" by all nobles or royal families in Europe [10–13]. These mentions are

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only related to colourless glass [1] for plain glass windows, whereas coloured glass was also employed in stained-glass windows. Chromophores for colouring glass had a cost in themself and it is therefore commonly accepted that coloured glass was more expensive than colourless glass. This is also confirmed in archival documentation, such as from York, where coloured glass is mentioned as twice as expensive as colourless glass [14]. Different types of coloured glass also most probably had different prices. The most relevant example is blue glass, often recalled as precious material [15, 16], the price of which could reach up to six times the price of colourless glass [17, 18].

Behind the choice of colour, lies the selection of a colouring matter and technology linked to cost, which is connected to the importance of the image to be represented [19–21]. A perfect illustration of this concept in stained-glass windows is the Abbey Church of Saint Denis in Paris. The Twelfth-century windows are made with K-rich glass, with the exception of the blue parts. All of the blue glass pieces have a soda-rich composition [22]. At that period, soda-rich glass was very uncommon, and it is less sensitive to alteration; thus, soda-rich glass was certainly considered of a different quality than K-rich blue glass. The rationale for the selection of a specific blue glass for the windows of the Abbey Church of Saint Denis is in the theological and artistic reflexions of Abbot Suger, who designed the church. Indeed, blue was preferred for the stained-glass windows of Saint Denis because, for Abbot Suger, this colour recalled “the light where God lives” [16].

The connection between the value of an image and the value of the materials used to make it is much better understood in painting. For instance, we know of fifteenth-century contracts signed between painters and their clients, which often specified the nature and price of the pigments that needed to be used for a specific zone or element of the work [20]. Such documents highlight how artistic and economic questions were intertwined and how the final artwork depended on the ranking of the materials. As a result, a painting could become an instrument and sign of power because the used materials represented discrete layers of added value to the artwork. Analytical studies of mural, panel, and canvas paintings from the eleventh to the sixteenth centuries highlighted that expensive or rare pigments such as gold foil or lapis lazuli were used to render the most important characters in a picture [19, 23]. Such studies on stained-glass remain limited. We only noted a few recent studies focusing on the relation between glass composition and iconography. However, these papers mostly aim to retrieve the dating or region of production of the objects [24–27]. For stained-glass windows, we found a single and very recent reference suggesting the existence of a relation between the quality of the materials with the iconography. However, this indication exclusively relies on visual observations and on the conservation state of the glass pieces. Indeed, Gestels and colleagues [28] state that on a thirteenth-century panel representing a Visitation, a clear colourless glass without corrosion is used for the Virgin whereas the glass pieces used for angel show more defects and a slight pink colour. In the same panel a very high-quality glass without corrosion and an orange glass, a very rare colour at that time, are also used. Available agreements between promoters and glaziers mainly refer to the pricing and purchase of the raw materials and their quantities, to the duration of the work, to the names of the craftsmen, to the number of expected windows and their setting location inside the destination building, specifications about the transport, or to the iconographic program [14, 17, 29–31]. The link between the choices of the materials, their characteristics, and the iconography is missing. Hence, the need to follow an analytical approach.

The main objective of this paper is to investigate the link between the selected glass and the iconography to recover artistic choices and highlight a possible hidden symbolism for a set of window panels, used as a first case-study. Glass quality is investigated according to the following parameters: (1) the glass composition, (2) the glass forming technique, (3) the transparency and hue of the colourless glass, and (4) the rarity and complexity of the colouring technology.

Often, more than one stained-glass panel is used in the representation of a scene. Thus, studying a single panel could imply considering only a part of the picture. Therefore, we preferred to focus on roundels or central panels, as they consist of independent pictorial compositions that are smaller and easier to manipulate and examine. For the purpose of this research, it is crucial to investigate exclusively authentic parts of stained-glass windows. We selected a case study with panels that were produced and implemented in a region with a broad trade network of glass suppliers to ensure that the choices of the materials do not rely on availability. To be able to compare them, the windows are originating from the same initial setting, or at least from the same stained-glass workshop region (see Additional file 1: Sect. 1).

Consequently, we selected four Rhenish round panels with borders of approximately 30–31 cm diameter kept in the MAS | Collection Vleeshuis in Antwerp (Fig. 1). The four investigated panels are considered from the fifteenth century but were at least partly repainted and

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[1] By colourless glass, we comprise either naturally or voluntarily decoloured glass, as well as naturally coloured glass having a slight greenish, yellowish, blueish, or greyish hue.

Fig. 1 The four investigated panels AV.1163, AV.1164, AV.1665, and AV.1166 (MAS I Collection Vleeshuis, Antwerp)

refired. A few glass pieces are suspected to be restoration infills (for more details about the provenance of the four panels and the past conservation-restoration interventions, see the Additional file 1: Sect. 1.1).

Methodology

A multidisciplinary approach is of major importance to successfully investigate the specified research points. The data related to art historical research, as well as chemical and optical analyses, are holistically interpreted, allowing cross-discipline comparison in examining technological and stylistic properties of the four panels.

In this paper, we are investigating the hierarchy of glass materials in four aspects. First, we determine the glass composition by combining ultra-violet visible near infra-red (UV–Vis-NIR) absorption spectroscopy with portable X-ray fluorescence spectroscopy (p-XRF). Second, we unravel information regarding the glass-forming technique. Third, optical parameters such as the intrinsic (i.e., normalised to 1 mm) and perceived colour coordinates (i.e., for the real thickness of the original glass piece) and transparency are calculated from the optical spectra for colourless glass. Fourth, we focus attention on the chromophore types and techniques used in the colouring processes. The identification of the chromophores is mainly based on the study of fingerprinting absorption bands of the recorded UV–Vis-NIR absorption spectra. In the final research step, the emphasis is focused on studying the relation between the different facets of glass production and iconography.

UV–Vis-NIR absorption spectroscopy

The optical set-up consists of a spectral broadband light source (AvaLight-DH-S-BAL deuterium lamp combined with the Avalight-HAL halogen source, Avantes), a focusing lens, an integrating sphere that collects transmitted light, and a portable spectrometer [32]. The light is guided through optical fibres, and the diameter of the light beam on the sample is smaller than 4 mm. The integrating sphere allows collecting all the light transmitted, minimising the effects of the curvature of the glass fragments. A second optical fibre guides the light from the integrating sphere towards the entrance slit of the optical spectrum analyser as a detector (compact combination of AvaSpec-3648 and AvaSpect-256-NIR1.7, Avantes for the coloured glass and colourless glass and Spectro 320 Scanning Spectrometer, Instrument Systems measurements for the stained parts). The spectral resolution is 1.4 nm in the UV–visible and 4 nm in the infrared regions. For each defined location (see Additional file 2: Figure S1, Additional file 3: Figure S2, Additional file 4: Figure S3, Additional file 5: Figure S4), we record the transmittance spectrum T(λ) between 200–1750 nm, i.e., the spectral region where most glass chromophores' absorption bands are located. The transmitted intensity is measured as a function of the wavelength. Afterwards, we calculate the absorbance spectra using the Lambert–Beer law and the formula $A(\lambda) = -\log_{10}T(\lambda)$. To quantitatively interpret the optical spectra, they must be normalised (to 1 mm thickness), and losses due to Fresnel reflections at the surfaces must be subtracted. The removal of reflection losses is approximated using an average refractive index of 1.5; considering that the maximum incident angle is 20° , the average reflectance is $R = 0.04$ at each surface [33, 34].

The thickness is measured at the position of each measurement area. For that purpose, we use an Olympus 45MG ultrasonic thickness gauge equipped with a contact V260-SM Sonopen® transducer with 0.001 mm resolution. Acetone is used as a couplant and it helps to reduce weathering or dust traces potentially affecting the transmission signals [35]. Only few drops of acetone are necessary because the analysed area has a circular surface close to 5×5 mm^2. The peak positions are determined by identifying the local extrema of the obtained optical spectra. Glass transparency is calculated from the non-normalised transmission spectra. A fully transparent window is characterised by 100% transmission in the visible wavelength range (380–780 nm), consequently having a transparency value of 100%. The colour coordinates are also calculated from the optical spectra in both the CIE 1931 xyz and the CIE Lab colour spaces, and normalised to the standard illuminant D65 [36]. Objective hue descriptions are given in the text based on the approximate colour areas of the *Commission Internationale de l'Eclairage* (CIE). The colour difference between two samples (ΔE) is calculated in the CIE Lab colour system for the real thickness of the material following the CIE76 formula.[2] Additional optical parameters are calculated from the normalised spectra, i.e., the Ultra-violet Absorption Edge (UVAE), the [Fe^{2+}] from the absorbance at 1100 nm [34, 36].

Finally, for the silver-stained parts, we report the position and the full-width half-maximum (FWHM) of the peak and the calculated silver nanoparticle (np) size when available. The silver nanoparticle sizes are calculated from the spectra using the formula

$$R = \frac{V_f \lambda_p^2}{2\pi C \Delta\lambda}$$

where C is the speed of light in vacuum, V_f is the Fermi velocity of the electrons in bulk metal (i.e., 1.39×10^8 cm s^{-1} for silver), Δλ is the FWHM of the silver peak, and λ_p is the peak position [37].

The main optical parameters calculated and used in the following text are available in the Additional file 6: Tables S2, S4, S6, and S8).

p-XRF spectroscopy

The p-XRF data are recorded for all possible glass pieces, i.e., pieces without painting or corrosion with a surface of at least 22×22 mm^2 (see Additional file 2: Figure S1, Additional file 3: Figure S2, Additional file 4: Figure S3, Additional file 5: Figure S4). The p-XRF measurements are performed with a Bruker Tracer IV. Adding a 3D-printed attachment to the instrument head ensures the measurement distance between the device and the tested sample is kept constant to minimise signal fluctuations and maximise repeatability [38]. The time measurement is automatically set to 60 s. The analyses are performed in ambient air conditions with the Bruker factory "Soil" mode with an X-ray generator voltage of 45 kV and 30 μA current, an excitation energy of 40 keV, and a Ti/Al filter. Preliminary calibrations were applied to the quantified data obtained from the "Soil" mode for ten elements (K, Ca, Mn, Fe, Co, Cu, Rb, Sr, Zr, and Ag) based on the analysis of multiple glass standards (see Additional file 6: Table S1). All calibrated p-XRF values are available in the Additional file 6: Tables S3, S5, S7, and S9).

To highlight surface colouration as flashed glass, i.e., glass manufactured by layering, measurements are performed on both sides of the glass. The presence of a colouring agent (such as metallic copper or cobalt) on only one side implies the use of flashed glass (or *plaqué*), which refers to a homogeneous red glass layer that was either poured on a glass support or sandwiched between a thick support and a glass coating. On the other hand, we can identify streaky glass (or *feuilleté*), i.e., a striated red and colourless glass, if no or very low concentrations of chromophore(s) are present.

Combining two portable techniques

Up to this stage of the research it has not been possible to sample the panels. This is due to the lack of available fundings either for the dismantling—and restoration—of the window panels (which are currently sealed in a lead came), and for organising chemical analysis, including sample preparation, transport, and cost of the analysis itself. Moreover, we also do not have the permission for such a sampling action.

However, due to nowadays advancements in technology, we reckon that portable techniques—such as UV–Vis-NIR spectroscopy and p-XRF—offer the possibility to get sufficient information, to answer specific questions with far-reaching conclusions. Indeed, recent studies show that similar conclusions can be made from high-end lab device analysis and different portable methods, although the type of information obtained is different. In fact, we showed that UV–Vis-NIR absorption spectroscopy allows the distinction of optical groups that are consistent with glass compositional groups [39], but the exact glass composition group cannot be identified (yet). For that purpose, we combined the optical study with p-XRF measurements for which Adlington and Freestone [40] demonstrated the great potential in recognising different K-glass subgroups by considering rubidium, strontium, and zirconium (Rb, Sr, and Zr) as substitutes for glass major elements, i.e., K, Ca and Ti.

Unfortunately, not all of the glass pieces in the four panels could be measured by both analytic techniques because of the large spot size of the p-XRF instrument or because of the presence of painting layers on both sides of the glass. Therefore, UV–Vis-NIR was applied as the first-line technique. The evaluation of the optical results was performed in situ to distinguish major groupings. Then, p-XRF was applied on a limited number of glass pieces, to confirm the grouping and identify the glass composition. By undertaking both forms of analysis on the same samples, we were able to gather a fuller analytic profile spanning a broad range of information, including the calculation of the colour coordinates and material transparency, the chemical subgroup of the glass, and identification of the chromophores.

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[2] Although this formula does not correct the non-uniformity of the CIE Lab space, we decided to use it instead of the CIEDE2000 for which a coefficient specific to the material is needed.

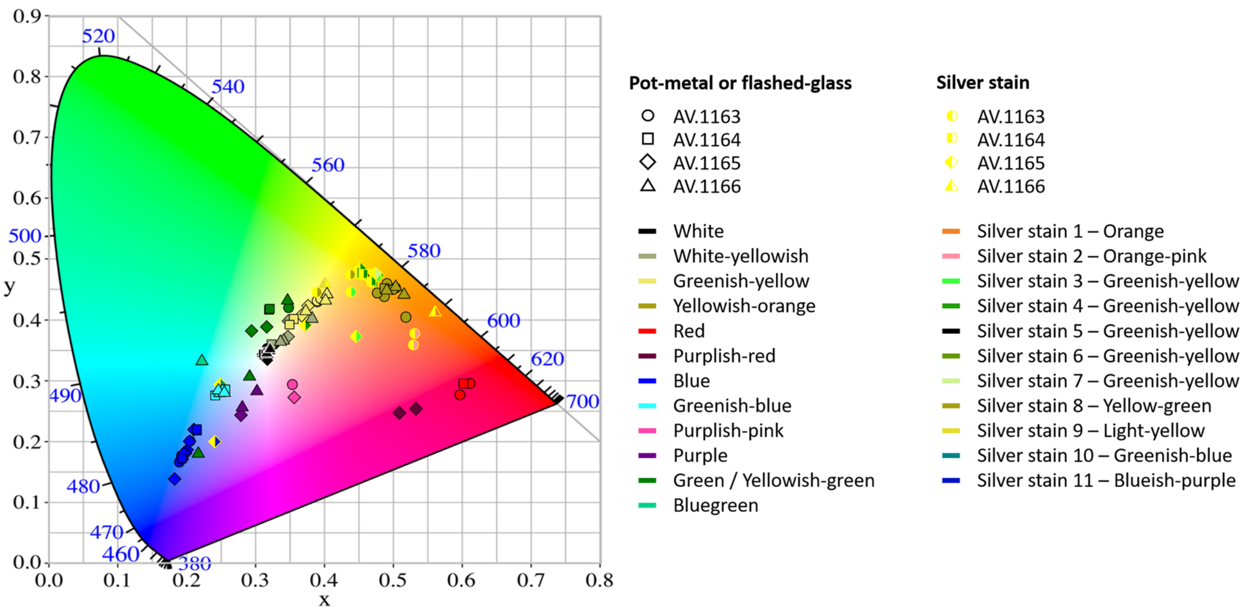

Fig. 2 Real-thickness colourimetric coordinates of the investigated glass pieces on the CIE 1931 xy colour diagram

Discerning the forming technique

The study of macroscopic production traces can help reveal the glass-forming technique [41–43]. The production of crown glass consists of forming a disc by blowing and spinning a bubble of glass. Though the technique produces a fine fire-finish glass, the obtained sheet thickens towards the central pontil mark, and the surface tends to be wavy with concentric curves of imperfections, including striations and circular air bubbles. Cylinder glass is made by blowing the glass as a cylinder. In the following stage, both extremities are clipped off, after which the cylinder is cut vertically, opened up, and poured on to a flat surface. One side of the cylinder surface is rougher and can present inclusions from the contact surface. The cylinder technique also leads to the formation of elongated air bubbles in the glass, which are often arranged in straight, parallel lines. In comparing the two techniques, cylinder glass is flatter than crown glass, and a cylinder glass plate is thinner (1.5 to 3 mm on average) and more uniform. In addition, the cylinder glass-forming technique allows the production of larger proportions of usable glass in each plate. By contrast, crown glass sheets usually appear to be cleaner due to the lower risk of contamination during the production.

To identify the forming technique, the panels were observed in reflective and transmitted light on both sides to identify the presence of bubbles, inclusions, or striations.

Results

The four panels are made from colourless and pot-metal yellow, green, blue, and purple glass, as well as a few flashed red pieces. Additionally, the details are depicted in black with grisaille and in yellow, orange, or red by silver staining. The real-thickness colourimetric coordinates of the investigated glass pieces are shown in Fig. 2 on the CIE 1931 xy colour diagram. The objective description of the colours proposed in the subsequent text is based on the approximate colour areas of the CIE.

The analytical results are presented in four sections, following the four quality parameters: (1) the glass composition, (2) the glass forming technique, (3) the transparency and hue of the colourless glass, and (4) the characteristics of the colouring technology.

Compositional characteristics

The analytical study of the four panels by combining UV–Vis-NIR absorption spectroscopy with p-XRF reveals that glass of different compositional groups was employed to build each panel. In the first step, we distinguished seven optical groups for colourless glass, four for blue glass, three for purple glass, two for red glass, three for green glass, and six for yellow glass (see Additional file 7: Figure S5). These groupings were made based on optical parameters, namely the [Fe^{2+}] calculated from the Fe^{2+} absorption at 1100 nm [34], the UVAE, the colour coordinates, the Co^{2+} absorption bands in the visible region [39, 44], and the presence of any other chromophore absorption band (see Additional file 6: Tables S2, S4, S6, and S8 and Additional file 7: Figure S5) [33, 45]. This approach showed its potential to distinguish optical groups that are consistent with the different glass compositional groups [39, 46]. Therefore, we consider that glass pieces with the same optical characteristics (i.e., belonging to the same optical group) have the same composition.

In the second step, we attempt to link the optical groups with the glass composition. For that purpose, at least one piece of glass from each optical group was measured via p-XRF. The results were first interpreted following the approach of Dungworth [47] and then confirmed with the method of Adlington and Freestone [40]. The former is based on the measured K_2O:CaO ratio, whereas the latter consists of considering Rb, Sr, and Zr as substitutes for K_2O, CaO and Ti respectively, to overcome the p-XRF unreliability of the lighter elements because of the effect of the glass corrosion. The glass composition groups were identified based on the flowcharts proposed by Dungworth [47] and Schalm and colleagues [48]. The results indicate that the four panels were assembled from two different glass compositional groups, K-rich glass and Ca-rich glass. K-rich glass shows three compositionally distinct groups, whereas Ca-rich glass shows two groups that are consistent between the four panels and coherent with the dating (see Additional file 6: Tables S3, S5, S7, and S9 and Additional file 8: Figure S7). The two infills in the border of panel AV.1165 (glass pieces 21 and 22) show a nineteenth- or twentieth-century composition, probably industrial soda, because their K_2O and Rb contents measured by p-XRF are close or equal to 0.

The repartition of the glass composition groups in the four panels is reported in Fig. 3. An interesting aspect highlighted by the study of the glass composition groups is the fact that for panels AV.1164, AV.1165, and AV.1166 the backgrounds (landscape and borders) are almost exclusively rendered with Ca-rich glass. In addition, Ca-rich glass is the only glass composition group used for the depiction of the two nuns, i.e., the characters with the lower position in the religious hierarchy (in panels AV.1164 and AV.1166). Most of panel AV.1163 is made from K-rich glass, including the background. Only the green pieces of panel AV.1163 have a Ca-rich glass composition.

Figure 4 shows the repartition of the subgroups for the K-rich and Ca-rich glass groups, emphasising the use of a specific K-rich glass subgroup (K2) for the

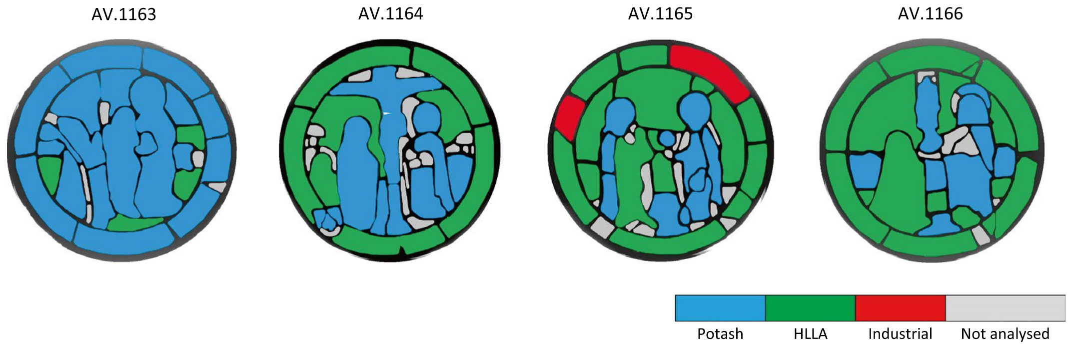

Fig. 3 Outline of the four panels showing the distribution of the compositional glass groups, K-rich glass, Ca-rich glass and Industrial glass in the four panels: **a** AV.1163, **b** AV.1164, **c** AV.1165, and **d** AV.1166

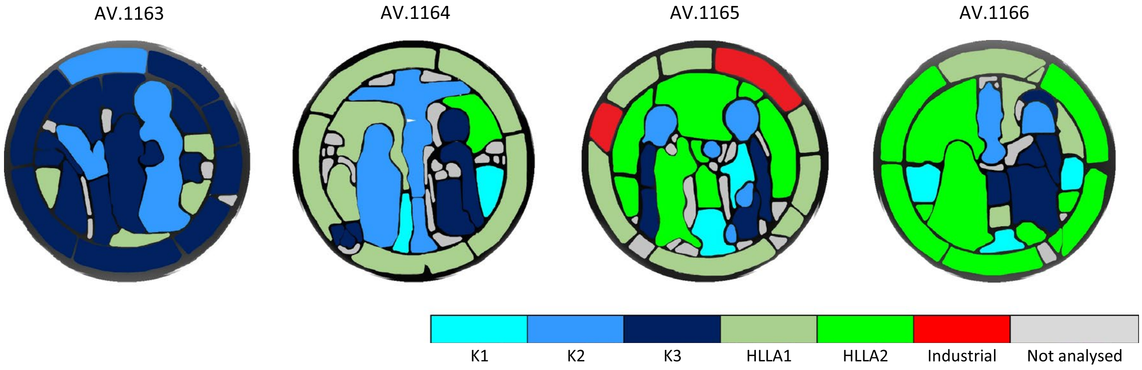

Fig. 4 Outline of the four panels showing the distribution of the compositional glass subgroups for K-rich glass (K1, K2, and K3), Ca-rich glass (Ca1 and Ca2) and industrial glass compositions in the four panels: **a** AV.1163, **b** AV.1164, **c** AV.1165, and **d** AV.1166

Fig. 5 Elongated bubbles arranged in straight and parallel lines suggesting the Ca-rich yellow glass pieces were produced with the cylinder forming technique. As an example, we picture the exterior side of the piece 25 from panel AV.1165, in reflective light

most important characters (Virgin and bishop in panel AV.1163, Virgin and Christ in panel AV.1164) or for parts of the images highlighted by the artistic composition (heads and attributes in AV.1165 and AV.1166). The K-rich glass subgroup K3 is used for two other characters of high status: the Christ (AV.1163) and Saint John (AV.1164). The same glass chemical subgroup is used for the bodies of Saint Dorothy (AV.1165) and Saint Clare (AV.1166). This raises the question of whether the stained-glass makers were able to recognise, to some extent, differences in the glass sheets prior to composing the window, giving them the possibility of a material selection. Can we link the glass composition to the glass-forming technique? Particularly concerning the colourless glass parts, which are mostly used for the characters, were the stained-glass makers able to distinguish K-rich glass from Ca-rich glass based on their colour and/or transparency, as reported in historical sources? These two aspects, the glass-forming technique, and the transparency and hue are investigated in the next two sections.

Forming technique and visual characteristics

Concerning the glass-forming technique, two main types of production traces could be observed on the glass pieces from the four panels. First, we observed numerous elongated bubbles arranged in straight and parallel lines, suggesting the glass was produced with the cylinder forming technique (Fig. 5). These bubbles are visible on the exterior side of most of the yellow glass pieces used for the borders (panels AV.1164, AV.1165, and AV.1166) and for the landscape of panel AV.1163. All these glass pieces have a Ca-rich glass composition.

Second, blue glass pieces used for the sky in panels AV.1164 and AV.1165 show many inclusions on the interior side of the glass surface (Fig. 6). A high number of inclusions is a typical accidental feature of the cylinder glass-forming technique that happens when pouring the glass on an uncleaned stretching table. These glass pieces also have a Ca-rich glass composition and belong to different optical groups (B2, B3, and B4).

Two pieces show a single isolated inclusion on their surface (Fig. 7). The presence of a single inclusion is not sufficient to identify the glass forming method, as it could come either from the crucible, glass-making tools, or stretching table in the cylinder technique.

None of the other glass pieces show bubbles, inclusions, or production traces. This is especially true for the K-rich glass pieces. Visually, the K-rich glass pieces are also very clear, smooth, and even. In addition, K-rich glass is, on average, slightly thicker and discrepant in thickness than Ca-rich glass (2.37 ± 0.51 vs 2.20 ± 0.34). These observations lead us to think that the K-rich glass was probably produced with the crown glass-forming technique.

Most of the glass pieces are very well conserved and show no corrosion. This is rather surprising because K-rich glass is more sensitive to alteration than Ca-rich glass. Only glass pieces with a K-rich glass K1 composition show substantial pitting.

In synthesis, we see coherence between the glass-forming technique and its composition. The tendency observed is that Ca-rich glass was produced via the cylinder forming technique as it shows more accidents (bubbles or inclusions). On the opposite, the K-rich glass pieces—except of the presence of a single isolated inclusion at the surface of a purple piece of panel AV.1166—visually appear flawless, and thicker, and were most probably produced with the crown glass-forming technique. This means that the glaziers could visually distinguish different glass qualities based on the glass surface characteristics.

Transparency and hue

In addition to the better visual properties of K-rich glass, literature [13] indicates that K-rich glass is also clearer (i.e., better decoloured) and more transparent. Therefore, in this paragraph we aim to verify if this statement is correct, specifically for colourless glass, based on optical parameters.

First, the calculation of the optical transparency reveals that K-rich glass (mostly related to crown glass production) is not always the most transparent glass; on average,

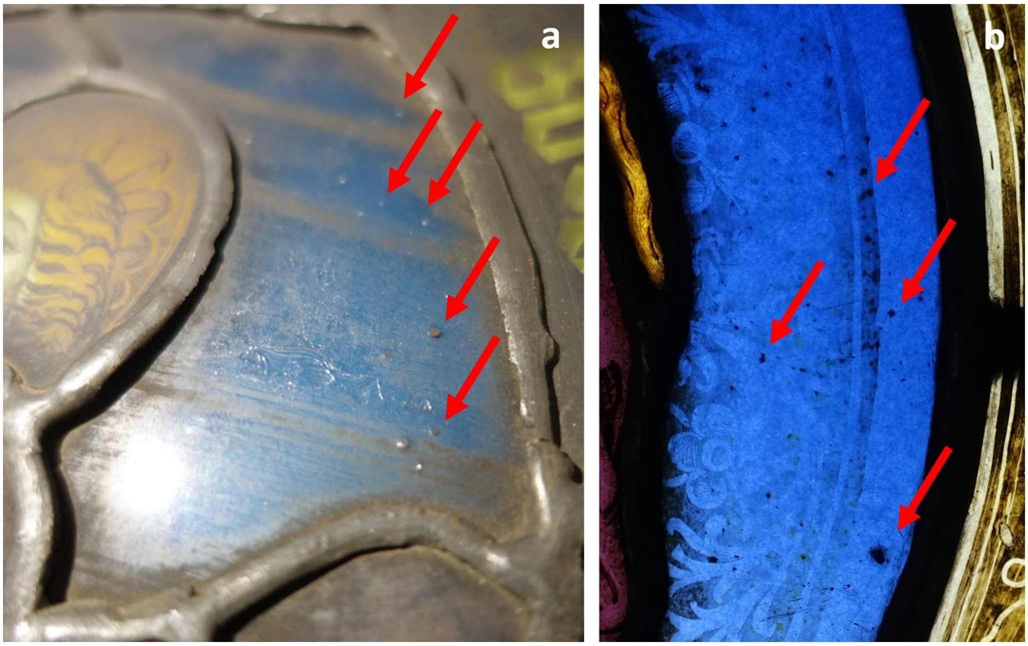

Fig. 6 Inclusions on interior side of the glass surface suggesting the Ca-rich blue glass pieces were produced with the cylinder forming technique. As examples, we picture the interior side of **a** piece 7 from panel AV.1164 in reflective light and **b** piece 10 from panel AV.1165 in transmitted light

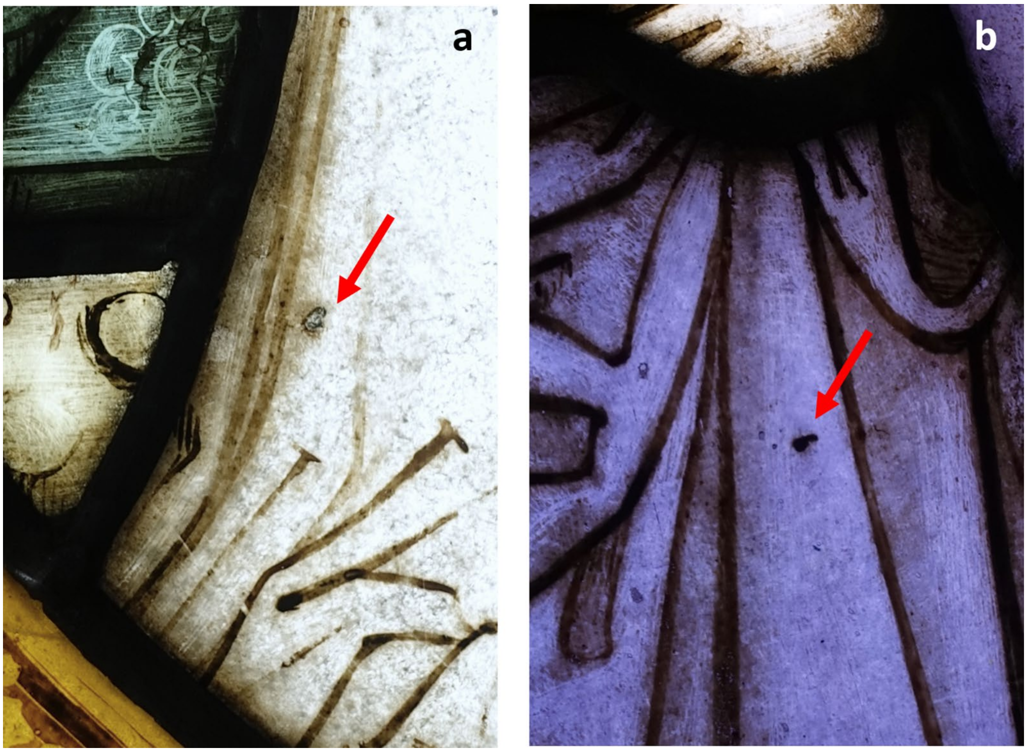

Fig. 7 Single isolated inclusion on the surface of pieces 1 and 8 from panel AV.1166 in transmitted light

Ca-rich glass has a transparency value of 51.9 ± 2.6% (44.3 ± 8.8% for K-rich glass).[3]

Second, we investigate hue. Although all of the colourless glass pieces have a "white" colour (see Fig. 2), we can observe differences in hue. In colourless glass, the hue is given by iron and manganese. Iron is the main impurity of glass; it enters the glass through the sand and imparts a yellowish, greenish, or blue hue to the glass, depending on the redox conditions of the batch and furnace [33]. Manganese was added to the glass batch either to oxidise iron, leading to a more yellowish colour, or to compensate for the effect of iron colouring, resulting in a more greyish hue [49, 50].

For all the investigated colourless glass pieces, the decolouration with manganese is confirmed by the normalised a colour coordinate ranging between -1 and -5 and the presence of the quite well-defined Mn^{2+} absorption band at 430 nm (see Additional file 6: Tables S2, S4, S6, and S8 and Additional file 7: Figure S5a) [51]. Besides, although the glass pieces from both compositional groups contain similar iron contents (0.42 ± 0.08 wt% for K-rich glass and 0.48 ± 0.09 wt% for Ca-rich glass), Ca-rich glass appears slightly yellow or green (see Fig. 2). This last observation is in accordance with what historical sources report, i.e., that Ca-rich or Rhenish glass was greener [13].

The calculations of the colour differences (ΔE) in the CIE Lab colour system for the real thickness of the material highlights that Ca-rich glass could easily be distinguished from K-rich glass with the naked eye ($\Delta E = 5.8$[4]). Thus, stained-glass makers were able to recognise, to a certain extent, colour differences in the colourless glass sheets prior to composing the window, giving them the possibility of material selection for the colourless glass.

The four studied panels were assembled from glass pieces having different compositions. Not only there seems to be a link between the glass compositions and the parts of the image represented, but also between the glass composition, the forming technique, and the transparency and hue of colourless glass. We highlighted that the stained-glass makers were able to recognise differences in the glass sheets based on their surface appearance, and the transparency and hue of colourless glass. In the next section we investigate the characteristics of the coloured glass pieces.

Glass colouring

In ancient glassmaking, the chromophore palette available to pot-metal glass was limited. Nevertheless, a wide range of colours could be produced by combining chromophores in different concentrations and by applying different production processes [52]. With this in mind, one might expect that the colouring process selection was related to the targeted colour. We aim to verify if the glaziers indeed selected a colour, or a glass coloured in a specific way.

Yellow

Two distinct colouring methods were applied to obtain the yellow colour in the four panels: pot-metal glass and silver staining.

All of the yellow glass pieces of the four panels show a broad absorption tail before 600 nm, which originates from the strong absorption in the UV region and at 380, 420, and 440 nm due to Fe^{3+} [33]. However, six separate spectral groups (i.e., Y1, Y2, Y3, Y4, Y5, and Y6) can be recognised (see Additional file 7: Figure S5b), highlighting distinct production conditions but leading to only two colour groups. The first group of glass, which has a white, greenish-yellow hue, concerns the optical groups Y1 and Y2, which both belong to the Ca-rich glass family. Glass pieces from these optical groups present a strong Fe^{2+} absorption peak around 1100 nm. These glass optical groups were probably produced in oxidising conditions. Glass pieces from the optical group Y3 are also characterised by a Ca-rich composition and by a strong Fe^{2+} absorption peak around 1100 nm. However, the spectra show a stronger ferri-sulphide complex absorption band, typical for reduced samples [35], leading to a darker, yellowish-orange hue. Three other optical groups (i.e., Y4, Y5, and Y6) also show a strong ferri-sulphide complex absorption band and a yellowish-orange hue. Glass pieces from these groups all have a K-rich composition. The spectra are characterised by the presence of weak Co^{2+} absorption bands and lower Fe^{2+} absorption in respect to the white, greenish-yellow glass pieces. Groups Y4, Y5, and Y6 are differentiated by their ferri-sulphide and Fe^{2+} absorption strengths.

Pot-metal yellow glass was only used for the landscape and all the borders. Two exceptions concern the halo of Saint Clare in panel AV.1166 (glass piece 18, belonging to the optical group Y5) and the golden pastoral staff of the bishop in panel AV.1163 (glass piece 12 measured, belonging to the optical group Y5). In all the other cases, the halos and golden objects were rendered by silver

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[3] Transparency can also be affected by the presence of a very thin layer of grisaille, which covers most of the glass pieces. We tried to avoid this effect by not considering the glass measurements taken from the glass piece 19 of panel AV.1165 (largely covered by grisaille and silver stain) and glass pieces 20 and 21 of panel AV.1166 (covered by a thin layer of grisaille on both sides of the glass).

[4] When the ΔE is comprised between 0 and 0.5, it means that there is no colour difference. Between 0.5 and 1, the difference is only perceivable by experienced observers; between 1 and 2, there is minimal colour difference, between 2 and 4, there is a perceivable colour difference, and between 4 and 5, the colours are significantly different. Finally, a ΔE superior to 4 characterises different colours.

stain. Silver stain was also applied to represent the hairs of the characters, the cross of the crucifixion, and only in AV.1165, for clothes, basket, and flowers related to Saint Dorothy. Silver staining is a complex colouring technology that involves metallic silver and empirical knowledge to produce the exact desired shade. Indeed, the final silver stain colour depends on numerous parameters, including the silver compound type, the base glass composition, the firing temperature, and the baking process's duration. A variation of one parameter is considered a change of recipe. The study reveals that the silver stain was mainly applied on K-rich glass. On Ca-rich glass, the stain was applied in two specific occurrences on panel AV.1165: for the clothes of St John and on the blue glass to represent the leaves and the stem of the flower held by St Dorothy. The silver staining has a typical optical signature linked to the silver absorption band at around 470 nm, but previous analytical researches have also stressed that the silver stain technology is responsible for variations in the distribution and size of silver nanoparticles inside the glass matrix, resulting in different optical spectra and, consequently, different glass colours [37, 53]. The optical analysis of the investigated stained parts reveals three groups of colours, two darker yellow hues (orange and orange-pink), two lighter ones (greenish-yellow and yellow-green), and two blue-green hues (greenish-blue and blueish-purple) because the stain was applied on blue glass (see Fig. 2). The stains applied on blue glass will be discussed in the section on green glass.

Based on the silver absorption peak characteristics (i.e., peak position and shape) combined with the Ag:Cu ratio, we further subdivided each colour group into recipes (see Additional file 6: Tables S2, S4, S6, and S8 and Additional file 9: Figure S6). It clearly appears that the painters selected the stain recipes based on the targeted colour and on the specific iconographic part they wanted to depict. The first recipe (silver stain 1) stands for gold because it was used to render the monstrance in AV.1166. It has a pure orange hue. This stain recipe has the highest Ag:Cu ratio (7.11), indicating that the content of silver is much more important than the content of copper (with concentrations of 1372 ppm and 193 ppm, respectively). Darker, and especially orange or red, staining layers are attributed to the presence of copper [45, 54] but can be obtained from silver depending on the rate of dilution in ochre, the temperature, and number of firings [12, 54, 55]. The second recipe (silver stain 2) produces an orange-pink hue. It was applied to parts that could be red in reality, i.e., the bishop's mitre and his cope's embroideries (AV.1163). The optical spectra from stains 2 and 3 look alike, but silver stain recipe 3 leads to a greenish-yellow hue. This stain was also applied for the bishop's clothing in panel AV.1163. However, the glass is slightly different because the silver stain 2 was applied on a K-rich glass K3, whereas silver stain 3 was applied on K-rich K2. The Ag:Cu ratio calculated for both stains is also different (2.62 for silver stain 2 and 0.01 for silver stain 3). However, we have to remark that the area of this stain was very small, and despite our effort to align the p-XRF spot on the stain layer, it is possible, but not certain, that the measurement area was shifted. Six other recipes lead to a greenish-yellow colour. First, the silver stain 4 was applied to render the saints' halos and hair in both panels AV.1164 and AV.1165, and for the bottom part of the cross in panel AV.1164. This stain is characterised by an Ag:Cu ratio of 4.38 ± 0.8 and a silver peak position at 414.1 ± 0.2 nm. Second, silver stain 5 shows a close silver peak position (at 416 nm) but shows a secondary silver peak [53]. The Lorentzian-shaped silver peak is complete, allowing us to estimate the very small silver nanoparticle size to around 0.81 nm [37]. This stain was identified for the rendering of the flowers in the basket of the child accompanying St Dorothy (panel AV.1165). Another, and peculiar, greenish-yellow stain was used for the Christ and the Virgin in panel AV.1164. It is a copper-rich stain. Indeed, the Ag:Cu ratio of the third recipe for greenish-yellow stain (silver stain 6) is very low (0.20 ± 0.2), indicating that the stain contains more copper than silver in proportions, which is unexpected for a light-yellow stain. In this case, there is less probability that the p-XRF spot dimensions caused an error because the measured stained area was relatively large. Silver stain 6 has a Lorentzian-line shape peak located at 418 nm. The silver nanoparticle size of 1.9 nm was calculated from the FWHM of the peak (66 nm). The fourth and fifth greenish-yellow stains (silver stains 7 and 8) have silver peaks with a silver shape. However, the Ag:Cu ratio calculated from the p-XRF measurements are completely different. Silver stain 7 shows a ratio of 4.3, whereas silver stain 8's Ag:Cu ratio is 0.4. In addition, the silver stain 8 also leads to a slightly different hue (yellow-green). Although silver stain 7 was used for the Virgin in panel AV.1163 and the child's head in AV.1165, stain 3b was applied for the Christ in panel AV.1163. A last light-yellow recipe (silver stain 9) corresponds to the clothes of Saint John in panel AV.1165. This stain shows a silver peak position at 424 nm, i.e., shifted 10 nm in respect to the other stains that leads to a lighter colour. The switch in peak position could be due to the different glass matrix (here, Ca-rich) or to a different production parameter. Moreover, this stain tends more towards the yellow-green hue than the greenish-yellow hue.

Red

The red glass's colouration is a direct result of copper. Indeed, the strong absorbance before 600 nm in the optical spectra of the four analysed red glass pieces (see Additional file 7: Figure S5c) indicates that the glass colouration is due to Cu^0 [33]. In addition, all of the red glass pieces of the four panels are likely to be flashed glass. This type of red glass is more often reported as being used in stained-glass windows.[5] In addition, we observed the colourless layer on the edges of a glass piece from panel AV.1165.

The p-XRF measurements performed on the red glass pieces indicate that both sides of the flashed glass pieces were made from the same subgroup of K-rich glass (K3). However, the red glass pieces could be separated into two optical groups. Optical group R2 has a purplish-red hue (see Fig. 2), and optical group R1 has a purer red colour. The difference in colour may be linked to different iron concentrations, which is indicated by the differences in absorbance strength for Fe^{2+} (see Additional file 7: Figure S5c).

Blue

We observe two shades of blue. Light blue glass was used for the sky in panels AV.1164 (nine pieces) and AV.1166 (four pieces). Dark blue pieces were used for the sky (five pieces in panel AV.1163 and eight pieces in panel AV.1165) and for the clothes and the coat of arms in panel AV.1164 (6 pieces in total).

Cobalt is the blue chromophore used in the four panels (see Additional file 7: Figure S5d). When linking the blue hue with the glass composition, it appears that light blue glass always has a Ca-rich signature (optical groups B3 and B4), whereas Ca-rich (optical group B1) and K-rich (optical group B2) glass groups were used for dark coloured blue pieces. The cobalt contents measured by p-XRF highlight that to produce a deep blue colour, more cobalt is needed in Ca-rich glass than in K-rich glass. Indeed, to obtain the same dark blue colour, 1700 ppm of cobalt is needed in Ca-rich glass, versus 800 ppm in K-rich glass. In Ca-rich, 800 ppm of cobalt leads to a light blue colour. This phenomenon, as mentioned in the literature, is due to, according to their sizes, different alkali ions exerting different influences on oxygen, which reflect the Co–O bond strength [45]. Because Ca-rich glass typically contains less potassium than K-rich glass, it is de facto less efficient than other glass-compositional groups in producing a blue colour.

Purple

Visually, it was possible to distinguish two shades of purple, substantiated by the colour coordinate calculations (see Fig. 2). Four glass pieces were cut in a lighter reddish-purple or purplish-pink glass and used to represent the Virgin's clothes (AV.1163) and those of Saint Dorothy (AV.1165). Conversely, the clothing of the child accompanying Saint Dorothy in panel AV.1165 was made from a dark blueish-purple piece, the colour of which can be described as a true purple. The same purple colour was used to render Saint Clare's habit (AV.1166).

All purple glass pieces have a K-rich composition (K3). The difference in the observed colours is linked to the addition of a second colouring agent for the blueish-purple parts (optical group P3). Indeed, optical spectroscopy highlights the presence of Mn^{3+} absorption bands close to 490 nm [51] in all of the purple glass pieces; instead, the Co^{2+} bands around 525, 595, and 645 nm [33] are present for the blueish-coloured pieces. The Co^{2+} absorption bands are also present, but almost imperceptible, in reddish purple glass pieces belonging to optical group P2 (see Additional file 7: Fig. S5e). Due to its low absorption, the effect of Co^{2+} on the glass colour is mostly negligible. Therefore, we can conclude that the lighter reddish was obtained by colouring with manganese, whereas the darker purple glass appears more blueish because it was coloured with manganese and cobalt. The lighter and the darker blueish-purple pieces have a similar thickness, with an average thickness of 1.95 ± 0.3 mm. This means that adjusting the thickness of the material was not enough to create a variation in the observed colours. Moreover, the hues are different: the darker shade is more blueish, as indicated by its lower normalised b colour coordinate (-11.16 ± 3.1 versus -4.06 ± 1.8), whereas the normalised a colour coordinate, corresponding to the red component, is much higher in lighter purple glass (18.15 ± 1.4 versus 8.28 ± 1.2). Deep purple glass obtained from cobalt has only been found once, namely in a stained glass rose window from the Siena Cathedral in Italy, dating from the end of the thirteenth century [56]. No other existence of pot-metal cobalt-manganese glass from the fifteenth century was found in the literature. Technologically, the addition of cobalt to a purple glass batch typically relates to enamel productions, which only occurred from the end of the sixteenth century onwards [57].

Green

Except for one piece, i.e., the habit of Saint Dorothy in panel AV.1165, all of the 16 green glass pieces are connected to the rendering of the landscape.

One single piece (glass piece number 10 of AV.1166) was coloured with Cu^{2+} (see Additional file 7: Figure S5f,

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[5] Ruby glass is considered not transparent enough to be used in stained-glass windows. Actually, ruby glass for windows is only mentioned for York in approximately 1470 by Knowles, without any reference to a specific building or panel, leading other authors to question the use of other types of red glass than flashed red glass in windows before the nineteenth century [10, 14].

optical group G3). This colouring agent shows a large absorption band at 780–800 nm [33, 58, 59], giving the glass a blue-green hue (see Fig. 2). For all the other green pieces, the recorded optical spectra show high absorption values, especially around the iron and cobalt bands, indicating that the green glass pieces were coloured by iron and cobalt (see Additional file 7: Figure S5f). They all belong to the K-rich composition group (optical group G1), except one piece that has a Ca-rich composition (optical group G2).

Finally, two blue pieces were stained in panel AV.1165 with the objective of producing a green colour [55] to represent the leaves and the stem held by St Dorothy. We recognise two recipes because the shape of the silver peak appears to be different. Silver stain 10 shows only one silver peak, whereas silver stain 11 also presents a secondary silver peak. No additional information could be retrieved about these recipes because the stained layers could not be measured by p-XRF.

Discussion

In the results section, we investigated the glass composition, the forming technique, the transparency and hue of the colourless glass, and the colouring technology. In this section, we aim to link these parameters with the use of the glass in the four panels to assess if the researched glass quality aspects relate to the iconography. We also aim to bring clues on the use of lower quality glass and propose some reasons to explain why people would still want and use lower quality material if higher quality material was available on the market.

K-rich glass: a higher quality glass?

The two involved glass compositional groups (i.e., K-rich and Ca-rich) are obtained using different raw materials and, in particular, different fluxing agents, i.e., plant ashes. The various types of used ashes are documented in several medieval manuscripts on glass production. Oak and beech are the two most frequently mentioned trees in historical sources [60]. Thereupon, Theophilus Presbyter [61 Book 2, Chapters III–V] specifically recommends using beech trunk to obtain ashes. Beech trunk ashes, as well as bracken (member of the fern family), have the highest potassium content, which is the best alkaline to lower the melting temperature. This means that when these ashes were used, it was easier to melt the glass, requesting less time and technical progress. Thus, the glass produced chemically corresponds to K-rich glass [60]. As reported by various authors [60, 62], glassmakers were skilled and competent artisans who understood their materials; they probably considered beech trunk and bracken ashes as better raw materials, in the sense of workability, not of purity. The addition of lime (leading to a Ca-rich glass composition) increases the glass durability but makes the glass harder to manufacture [11].

We already mentioned that colourless Ca-rich glass is reported to be greener than K-rich glass in historical sources and that this colour difference expresses a difference in quality for stained-glass window production [13]. In the Escorial palace archives in Spain, Normandy glass (i.e., K-rich glass) was selected and declared to be the purest in respect to other glass production from Spain, Burgundy and Lorraine. The 'purity' of this glass was probably determined by colour rather than chemistry [10, 11]. This difference in hue between K-rich glass and Ca-rich glass is observed in the here-studied material. The greenish hue of decoloured glass is related to the iron which is naturally present in the glass batch as sand impurities. Iron can also enter the glass via the plant ashes. However, the content of this element, among others, can be lowered during ash purification [63], hence the fact that a glass that did not include a purifying a step (whole-ash glass) shows a greenish or yellowish hue. Here, both K-rich and Ca-rich glass pieces show similar iron contents, excluding that ash treatment was responsible for the difference in colours. Caen and colleagues [13] suggested that the reported difference in quality between K-rich glass and Ca-rich glass could indeed be due to the 'whiter' colour of K-rich glass, but also its regularity. The glass surface appearance (presence or absence of defects such as inclusions and bubbles, the dimensions and flatness of the sheets, etc.) is a direct consequence of the forming technique [10, 41–43] and Caen [10] advocates that for the fifteenth–sixteenth centuries, K-rich glass was produced with the crown method. Actually, the production traces on the studied glass pieces hint that K-rich glass was indeed produced with the crown glass technique, whereas the cylinder forming technique was most probably used for Ca-rich glass.

Another reason to explain why K-rich glass was preferred on Ca-rich glass could be that, empirically, stained-glass makers knew that K-rich glass took stain better than Ca-rich glass; therefore, it was easier to achieve a colour on K-rich glass with the same amount of silver. Indeed, with K-rich glass composition groups, it is technologically easier to achieve a colour, either in pale or dark shades, independently from the applied silver compound. On the one hand, the staining process takes place at a temperature close to the glass transition temperature. For K-rich glass, this transition temperature is approximately 600 °C. Thus, the stain can be fired at a rather low temperature, and that by using this glass, no matter the silver compounds, it is possible to get a darker colour by firing at a higher temperature just above 600 °C [64, 65]. On the other hand, silver penetration in glass is favoured in presence of interstitial ions, i.e., alkali in the glass [45, 66]. Because K-rich glass contains more potassium ions than Ca-rich glass, the silver diffusion in the glass is more intense, meaning it is easier to achieve a colour with silver stain on K-rich than it is on Ca-rich glass. On the four panels, the silver stain was exclusively applied on K-rich glass except for two minor exceptions. Similarly, as shown in the result section, K-rich glass is more efficient than other glass-composition groups, including Ca-rich, in producing a blue colour.

The repartition of the K-rich and Ca-rich glass groups in the four panels highlight that Ca-rich glass was almost exclusively used for the panel backgrounds (e.g., landscape and borders) and was the only glass composition group used for the depiction of the two nuns, i.e., the characters with the lower position in the religious hierarchy (in panels AV.1164 and AV.1166). However, K-rich glass, even a specific K-rich glass subgroup (K2), was used for the most important characters (i.e., Virgin and bishop in panel AV.1163, and Virgin and Christ in panel AV.1164), and for parts of the images highlighted by the artistic composition (i.e., heads and attributes in AV.1165 and AV.1166).

Although the historical documents from the period of production of the panels give clues on the fact that Ca-rich glass might have been considered of lower quality at that time in Europe, the lower compositional, visual, optical, and technological quality of Ca-rich glass was verified only for the case-study panels. Other examples are reported in the literature. Indeed, there are mentions that coloured glass must be imported to England, and Normandy pot-metal glass (i.e., K-rich coloured glass) was considered as the best [12].

Discerning the hidden symbolic meaning behind glass colouring

The price of coloured glass

Documentation has shown that colourless glass was cheaper than coloured glass. For example, we found mentions that, at York (1338), the price for coloured glass was twice the price for "glazing white glass", i.e., colourless glass [14]; at Westminster (approximately 1351–2), blue glass was six times the price of colourless glass [17, 18]. However, this evidence questions the reason for such a price difference. Was the difference related to the price of chromophores or to the complexity of the technology? Do we observe a relation between the documented price of coloured glass and its use in the four panels? Can we point out specific colours or types of coloured glass with a higher status?

There is little documentation concerning the costs of different colours of glass. An interesting work was conducted by Brain and Brain [67] on the costs of glass-making materials in mid-seventeenth century England. Their interpretation of the costs shows that manganese dioxide, used to decolour glass, was more than twice as expensive as saffre ($CoO + impurities$),[6] a source of cobaltous oxide to produce the blue colour [67]. Cobalt is commonly considered an expensive pigment [16], but the low concentration necessary to lead to a blue colour [15, 58] means that it might not have added much to the cost of a glass sheet. Therefore, the price of the raw materials cannot be directly related to the final price of the glass.

The difference in price may have related to the thickness of the glass. Indeed, the price for glass was defined either by size or by weight. For example, the price for York window glass was given in feet [14] but in 'wey' (i.e., weight) for Winchester [17]. In the literature, dimension and thickness of the glass sheets are linked to the glass-forming technique. Indeed, it is reported that the thickness of a cylinder glass plate is thinner (1.5 to 3 mm on average) and that this forming technique produces larger glass sheets, consequently leading to a lower glass price. Visual observations of the four panels, combined with the study of the glass thickness, showed that K-rich glass was probably produced with the crown glass forming technique, leading to slightly thicker pieces, but Ca-rich glass was obtained with the cylinder technique, leading to less thickness variation. In the studied panels, primarily yellow glass was produced with the cylinder technique. In addition, yellow glass was only used for the images' minor parts, such as the panel borders and the landscapes. It was probably the cheaper of the coloured glass used in the panels. Interestingly, panel AV.1163 is the only one for which most of the glass pieces have a K-rich composition (even yellow pieces from the borders) and, therefore, made from crown glass (see Fig. 3). By contrast, in the other panels, a larger proportion of Ca-rich and cylinder glass was used, suggesting that panels AV.1164, AV.1165, and AV.1166 were made from less expensive glass.

Rarity and complexity of the colouring technology

Other aspects to evaluate the quality of coloured glass are the rarity and complexity of the colouring technology. As previously stated, blue glass is often mentioned as one of the most expensive glasses, but the price did not seem to limit its use. Indeed, it is largely used in stained-glass windows, including for the less important parts of the images such as the sky. In addition, blue glass colouring is not as complex as, for example, red glass obtained via the method of flashed glass. In the four studied panels, the green colouring using iron and cobalt can be considered relatively rare because, typically during the Middle Ages and the early modern period, green glass was obtained by using copper as a colouring agent. Furthermore, only

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[6] Or zaphir, recalled as 'saphirum vitreum' by Theophilus [56 Book II, Chapters XII-XIII].

one other occurrence was found in the literature, namely different glass pieces rendered the claws of the monster defeated by Saint Michael in a late 15th-century window. This panel was produced for the chapel of the Bruges guild of Saint Luke, patron of the painters and window makers, and historian researchers consider it a technical showcase for the guild of Bruges [10, 68]. Rather than thinking that this glass was selected for its peculiarity, we suspect that the selection of this glass composition group is the result of a mere colour selection or a material's availability in the workshop. This idea is supported by the fact that, in most cases, only low-quality material, here mostly Ca-rich glass, was used for the backgrounds. The single exception was the use of the unusual green glass used for the grass in the landscape. In addition, a specific subgroup of K-rich glass (K1) characterises the green parts. In respect to the other K-rich glass, the chemical subgroup K1 shows lower Zr content, highlighting a different sand source. Finally, a last clue is that AV.1166 was filled with a single green piece coloured with copper, with a K-rich K3 composition. This K-rich subgroup was also used in the four panels for other colours (see Fig. 4).

In medieval glass windows, the rarer colours are purple-pink, orange, and yellow, whereas blue, red, and green are well represented in most windows. The reason might be that the most frequently used colours are also the ones more diffused in nature. In the studied panels, yellow is also largely used in the landscapes and backgrounds parts. Although there are no direct clues on the price of this glass, from a raw material and technological point of view, pot-metal yellow glass might not have been an expensive coloured glass. Indeed, the yellow colour is due to the ferri-sulphide complex, which forms during firing (in reducing atmosphere) because of the presence of iron and sulphur naturally present in the batch as sand impurities. In the previous section, we also highlighted that the yellow glass from the four panels was made from Ca-rich/cylinder glass, corresponding in the case-study panels to low quality material. However, for the yellow colour, we observe that the production technology has a hidden meaning. This colour is extensively applied in the four panels and produced with not only the pot-metal method but also the silver-staining technique—both characterised by specific production processes and recipes. These differences in technology were, in most cases, not observable with the naked eye but were discovered after applying spectroscopy. Pot-metal glass was only used for the background and border parts, whereas silver staining was applied onto the figures and important objects, such as the saints' attributes. Silver stain was an expensive product because of its cost in time as much as in materials [12]. Moreover, it clearly appears that, in a few cases, the painters selected the stain recipes based on the targeted colour and on the specific iconographic part they wanted to depict. Indeed, the nine different silver-staining recipes applied on colourless glass can be classified in four groups based on their colour and use. First, the darker silver stain either represents gold (silver stain 1) or red (silver stain 2) and has very low copper content. Then, pale yellow stains (having either a greenish-yellow or a yellowish-green hue) were applied to render all the saint characters, including their halos, body parts (clothes), and hair. Noted differences in Ag:Cu and optical characteristics might be linked to the glass composition. Another explanation could be the influence of refiring during a conservation treatment. Refiring the panels is stated by Caen and Berserik [69]. Finally, we pointed out the application of a peculiar staining process (silver stain 8) for the depiction of the Christ and the Virgin in panel AV.1163. This stain shows the lowest Ag:Cu ratio (0.20 ± 0.2), indicating that it contains more copper than silver in proportion, in respect to the other stains. The success of producing a colour—the specific desired colour—from the stain depended on the glazier's knowledge and experience because each silver compound reacts differently to the constituents of each sheet of glass [12]. Thus, the application of different staining recipes with specific rational and colour goal in the four panels denotes production by highly skilled craftsmen.

The symbolic meaning of colours

The example of silver stain highlights the specific use of colour and colouring technology in relation to the iconography, although it is not possible to link the addition of copper in the silver stain used for the rendering of the Christ with a symbolic meaning. On that aspect, it is important to recall the specific name and use of coloured glass in stained-glass windows. Indeed, coloured glasses were named after precious stones, i.e., ruby, sapphire, emerald, and amethyst. The use of coloured glass in stained-glass windows is often seen as a symbolic of the Holy City of Jerusalem [12]. However, this is a general view, and the window commissioner may have had his own requests, as we described in the introduction with the Abbot Suger's specific theological and artistic reflexions about blue leading to the choices of special blue glass for the Abbey Church of Saint Denis. In the studied panels, the purple colour was distinctly meaningful. We saw that a lighter reddish-purple was coloured with manganese, whereas a dark blueish-purple was linked to the addition of a second colouring agent, cobalt. The purplish-pink glass, acknowledged as a more reddish hue, can be appreciated as the colour of the "Royal purple", a high-valued dye obtained from the murex, a sea snail from the Syro-Levantine coast. The dye was applied to elite clothing from Antiquity [70] and is represented in visual art by a red or a reddish-purple hue. In the fifteenth century, however, purple could also be seen as a "sub-black", especially in a liturgical context, and was thus considered a less prestigious colour [71]. Therefore, the study of purple glass led us to identify two different levels of symbolism, which recalls what Michel Pastoureau called the "chromatic status", referring to the colour's position in the socio-economic and cultural contexts [20]. In the first place, the reddish-purple glass pieces recall the murex dye and a noble reddish textile. Second, the blueish purple was utilised for the black clothes of Saint Clare, a character with a secondary position in the religious hierarchy, and typically, the Poor Clare's dress is black.

Relation between the iconography and the glass characteristics

Because the glaziers bought ready-made sheets to create stained-glass windows and were dependent on others for the supply of their raw materials, how can we confirm that the selective use of material does not simply reflect its availability? Good regional study on Ca-rich glass production in Southern Germany and Switzerland, as the ones available for K-rich glass [5, 27, 62] would be necessary to confirm that the here-noted lower quality of the Ca-rich glass could be a matter of supplier or local production. Still, we have clues that let us think that glass painters could have made material choices when building the four panels. First, there is already documentary evidence for the use of different qualities of glass in the fifteenth century because the price for making windows depended on whether it was a simple quarry work, a figure, a subject-window, or a small work with many details [14]. Second, the use of different glass qualities aimed to save production cost for luxury items, such as stained-glass windows. Knowles [14] suggested that perhaps low-quality glass was considered as good enough, for example, for parts hardly seen due to their positions in the window. Third, surviving contracts from the Southern Low Countries expressed specific requests about the materials used for windows and the impact of material selection on the panel's final price [10]. Michael Baxandall stated about 15th-century Italian painting that "money is very important in the History of Art"; also in stained-glass window production, the donor's choices and the way they chose to spend their money (e.g., material cost and technical and artistic skills of the painter) had a profound effect on the appearance of the window [18]. Fourth, we have proof that the glaziers used glass with special effects in relation to the iconography. A good example is the use of Venetian streaky, exclusively reported in stained-glass windows for the rendering of clothing (see for example, [72]).

In our research, we also showed that stained-glass makers were able to sort the colourless glass qualities based on visual observations to some degree, and, consequently, select a specific material for a character or part of the scene. Moreover, although window makers had no analytical techniques to find back the glass composition, we know from historical documentation of this period that Ca-rich glass was cheaper than K-rich glass [13] and, as with all craftsmen, glass painters knew the glass they had bought, at what price they had bought it, and the availability of glass in their workshops. Unfortunately, for the studied pieces we do not have information neither on the specific production workshop nor on the purchase of the glass sheets. In the specific context of fifteenth-century Constance area, a highly sophisticated organisation and material selection was possible because a broad range of glass composition subgroups and glass qualities were available on the market [see for example, 4, 62]. This let us think that it is not casual if the four investigated panels were built with different types and qualities of glass, but because glass painters had the possibility to choose, either based on their own observations and empirical knowledge, or relying on the producer/seller to distinguish more suitable glass sheets for colouring or painting.

Within the four studied panels, the represented characters can be hierarchised as follows: (1) the Christ and the Virgin, (2) the saints, (3) the Bishop Thomas Weldner, (4) the Abbess Anne Frigin, and (5) the religious sisters. This hierarchisation corresponds to the medieval cultural and religious hierarchy and is highlighted by the artistic composition of each individual panel. Actually, the research findings described in the previous paragraph made us conclude that specific attention was paid to select only high-quality materials and production techniques for the representation of the characters with higher positions in the religious hierarchy. This observation seems to be especially true for the panels representing either the Christ or the Virgin. Yet, in panel AV.1165, the use of colourless glass follows the iconographic hierarchy with another logic. A high-quality K-rich glass was exclusively employed for the heads of the two saints and the attributes of Saint Dorothy, i.e., the flower and the child accompanying the saint.

A very interesting aspect, however, is how the bishop was rendered in panel AV.1163 compared to the Virgin and Child in the same panel, and how the bishop related to the other characters in all the four panels. Indeed, much attention was paid to the bishop's rendering. First, his overall representation was made from six different pieces, including red flashed glass, whereas the Virgin and Child were made from two and one piece(s), respectively. Second, the colourless glass used for the Virgin and the bishop were both of the same composition; therefore, both were of the same quality. Although the artistic composition confirms the bishop's lower religious hierarchical level, it seems that he actually upgraded his own prestige by requesting the use of specific materials and more attentiveness to his rendering in the panel. In contrast, in panel AV.1164 the religious sister Elisabeth was represented as a so-called donor *in abisso*, which usually stands for false display of humility [73]. The choice of a simple production technology and materials of somewhat lower quality reflected this humility.

Conclusion

In this paper, we have shown that deliberate choices were made when selecting the materials for stained-glass window panels. The choices relied not only on the desired colours but also on the glass quality, in relation to the characters' hierarchy and the donor's requests. Obviously, the technical knowledge, the stained-glass protocols potentially linked to a specific workshop, and the availability of the materials on the market at a specific moment, all played their roles in the material selection. However, this paper demonstrates that two factors could have an additional impact. The first factor concerns the hierarchic position of the displayed characters or attributes in the image's artistic composition. In the case of the four window panels that formed the subject of our research, we have proven that the high-quality material (here, K-rich glass and even a specific K-rich glass subgroup) and silver-stain technologies were reserved for the characters positioned at the highest level in the religious hierarchy, i.e., the Christ and the Virgin.

The second factor that our research identified relates to the donor. Our findings suggest a potential deliberate request of the commissioner to the craftsmen to use a higher quality of materials and technology than his religious hierarchy would subscribe. A possible rationale is the highlighting of the donor's prestige. We already knew from the remaining contracts between panel, canvas, or mural painters and their clients that pigments were specified for a specific zone or element of the work based on their nature and price. For stained-glass windows, the link between the choices of the materials, their characteristics, and the iconography is missing in the available agreements between promoters and glaziers. For the first time in stained-glass window research, we showed that a client could have influenced, at least partly, the material selection, and it was possible to retrieve certain choices made in the glazing workshops. By this research, we proposed a first case-study with non-destructive tools to bring a discussion on stained-glass quality and the use of different glass qualities in stained-glass window. But the observations we made cannot be generalised for all stained-glass windows across Europe, but we expect similar outputs. Therefore, it would be interesting to study additional window panels from Western Europe to validate further if the use of different material qualities in relation to the character's religious hierarchy represented was exceptional or common practice in stained-glass window making.

The differences in qualities of the materials used, and especially the noted higher quality of K-rich glass over Ca-rich glass cannot be generalised to all the Ca-rich glass produced in Europe and in different timeframes. With time, and probably thanks to the glassmakers' empirical mastering of the Ca-rich production process, the differences in quality between Ca-rich and K-rich glass seems to be overcome. An explanation could be that the Ca-rich "defaults" became not so much problematic if the glass is painted because the glass was anyway obscured by the painting. Good regional study on Ca-rich glass production in Southern Germany and Switzerland could give a better view on the K- to Ca-rich glass transition, in relation with glass quality studies. While a study would require trace elements and chemical analysis, it appears that the data obtained using accessible and portable methods are sufficient to address wide issues on the quality and the use of glass in stained-glass window. Indeed, most of the observations and the main conclusions drawn in this paper were possible, because of the application of p-XRF and UV–Vis-NIR absorption spectroscopy. We selected these techniques because of their abilities to perform in situ and non-destructive signal recordings. We hope that, with this publication, we have illustrated the added benefit of combining art historical research with scientific analysis. In the particular case of these stained-glass window panels, we retrieved the glass quality by identifying the raw materials and the technological complexity, whereas it would have been impossible to draw the same conclusions from only visual observations.

Abbreviations

MAS: Museum Aan de Stroom; UV-Vis-NIR: Ultra-violet visible near infra-red; p-XRF: Portable X-ray fluorescence spectroscopy; CIE: Commission Internationale de l'Eclairage; FWHM: Full-width half-maximum; UVAE: Ultra-violet absorption edge; np: Nanoparticle; UV region: Ultra-violet region (100–400 nm).

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-022-00698-2.

Additional file 1: Additional historical information on the investigated panels.

Additional file 2: Figure S1. Numbering of the analysed glass pieces for panel AV.1163.

Additional file 3: Figure S2. Numbering of the analysed glass pieces for panel AV.1164.

Additional file 4: Figure S3. Numbering of the analysed glass pieces for panel AV.1165.

Additional file 5: Figure S4. Numbering of the analysed glass pieces for panel AV.1166.

Additional file 6: Table S1. Average values (μ) and standard deviations (σ) of seven glass standards analysed via p-XRF ($n \geq 5$) as calculated with the Bruker factory "Soil" mode with a a 3D-printed attachment added to the instrument head. The results are expressed in wt% for the major and minor elements (K_2O, CaO, MnO, and Fe_2O_3) and in ppm for the trace elements (Co, Cu, Rb, Sr, Zr, and Ag). Corning standards correspond to given data from [25] and NIST standards to given data from [26]. **Table S2.** Main optical values calculated from the recorded spectra of each analysed glass piece of AV.1163 grouped by colour. **Table S3.** Concentrations of selected elements measured by p-XRF of AV.1163 glass pieces grouped by colour. The results are expressed in wt% for the major and minor elements (K_2O, CaO, MnO, and Fe_2O_3) and in ppm for the trace elements (Co, Cu, Rb, Sr, Zr, and Ag). **Table S4.** Main optical values calculated from the recorded spectra of each analysed glass piece of AV.1164 grouped by colour. **Table S5.** Concentration of selected elements measured by p-XRF of AV.1164 glass pieces grouped by colour The results are expressed in wt% for the major and minor (K_2O, CaO, MnO, and Fe_2O_3) and in ppm for the trace elements (Co, Cu, Rb, Sr, Zr, and Ag). **Table S6.** Main optical values calculated from the recorded spectra of each analysed glass piece of AV.1165 grouped by colour. **Table S7.** Concentration of selected elements measured by p-XRF of AV.1165 glass pieces grouped by colour. The results are expressed in wt% for the major and minor elements (K_2O, CaO, MnO, and Fe_2O_3) and in ppm for the trace elements (Co, Cu, Rb, Sr, Zr, and Ag). **Table S8.** Main optical values calculated from the recorded spectra of each analysed glass piece of AV.1166 grouped by colour. **Table S9.** Concentration of selected elements measured by p-XRF of AV.1166 glass pieces grouped by colour. The results are expressed in wt% for the major and minor elements (K_2O, CaO, MnO, and Fe_2O_3) and in ppm for the trace elements (Co, Cu, Rb, Sr, Zr, and Ag).

Additional file 7: Figure S5. Optical groups for each colour a. Typical spectra of the seven colourless glass groups with indications of the Co^{2+} and Fe^{2+} absorption bands; b. Typical spectra of the six yellow glass groups with indications of the UVAE, the ferri-sulphide complex absorption band, the Co^{2+} and Fe^{2+} absorption bands; c. Typical spectra of the two red glass groups with indications of the Cu^0 and Fe^{2+} absorption bands; d. Typical spectra of the three purple glass groups with indications of the Mn^{3+}, Co^{2+} and Fe^{2+} absorptions bands; e. Typical spectra of the four blue glass groups with indications of the Co^{2+} and Fe^{2+} absorption bands; f. Typical spectra of the three green glass groups with indications of the UVAE, the Co^{2+}, Fe^{2+} and Cu^{2+} absorption bands.

Additional file 8: Figure S7. Identification of the glass composition and subgroups based on the biplot of a. K_2O and CaO contents, b. Rb and Sr contents, and c. Rb and Zr contents.

Additional file 9: Figure S6. Absorption spectra of the different silver stain recipes.

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Author contributions

MP: p-XRF measurements, data processing and result interpretation. Absorption measurements, data processing and result interpretation. Historical and art historical research. Was a major contributor in writing the manuscript. KN: facilitated the purchase of the instrumentation that was used for the p-XRF measurements. Supervisor of the historical and art-historical research part. German translation historical research. Contributed to the interpretation of the results and the writing of the manuscript. HT: director of the Brussels photonics research team B-PHOT. Facilitated the purchase of the instrumentation that was used for the absorption measurements. WM: facilitated the purchase of the instrumentation that was used for the absorption measurements. Supervisor of the spectroscopic research part. Contributed to the interpretation of the results and the writing of the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

Additional file 1. Additional file for Prestige markers in art: subtle stratagems in material selection for fifteenth-century stained-glass windows.

Declarations

Competing interests

The authors declare that they have no competing interests.

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