A transparent dialogue between iconography and chemical characterisation: a set of foreign stained glasses in Portugal

Alexandra Rodrigues, Mathilda Coutinho, Andreia Machado, Bruno A. Martinho, Luís Cerqueira, Maria Filomena Macedo and MÁrcia Vilarigues

Abstract
This work presents the first results of the iconographic study and analytical characterisation of a set of four stained-glass panels that are part of the collection of National Palace of Pena (Sintra, Portugal). These panels were collected by the King Ferdinand II in the mid-19th century, for his main residence the Palace of Necessidades (Lisbon, Portugal), and only first presented to the general public in 2011. This study contributes with the knowledge of Technical Art History and Heritage Science to a better and deeper understanding of their history, materials and techniques used in the production, where an art-historical and a scientific approach are applied to attribute their origins. Based on the analysis of the formal and stylistic characteristic of the panels, it is proposed that the drawings used for the production of three of these panels may be based on the design and painting being carried out in the same workshop, and that the four panels have the same provenance (Germany). The composition of the glass and grisaille was determined and colourising elements were identified. Through this approach, conclusive correlation among the analysed glasses was possible: all are calcium rich or calcium-potassium rich types, and the results also suggest that the same source of silica was used for their production. A typical mixture of glass and lead oxide was found on the grisaille applied on the painted panels. However, less usual was the use of a copper oxide pigment for the black grisaille. All these findings support the proposals made regarding provenance and production period (15th century).

Keywords: stained glass; iconography; chemical composition; µ-EDXRF; UV-Vis spectroscopy; PCA

Introduction
The art of stained glass has always sought to interact with the surrounding space by creating architectural planes that allowed illumination while transforming the experience of light into one specific and meaningful to the purpose of a building [1]. From the beginning, production of stained glass developed side by side with economic, social and cultural innovations. In the Middle Ages, stained glass gained an important role with the construction of cathedrals, reaching its peak in the 15th century with Gothic architecture. During the Renaissance period, single glass sheet panels and roundels showing themes of family and local interest brought stained glass into a more intimate and domestic setting with highly personalised imagery. From the 18th century onwards, medieval and later stained-glass panels were collected in order to decorate private houses and chapels [1–3], often bought in the art market and/or through an intricate network of dealers which grew throughout the 19th century [4]. This was the case of Ferdinand II’s stained-glass collection, housed today at the Pen National Palace (PNP) [5]. These stained-glass panels – produced in central Europe (namely, in the territories of modern Switzerland, Germany and the Netherlands) – had been originally installed in churches, monasteries, manor houses, and artisan’s workshops, prior to their disposal in the Portuguese Palaces, which is merely a short chapter in their long history [5].

The history of this unique stained-glass collection begins with King Ferdinand II (1816-1885) – born and raised in Vienna, married to Queen Maria II (1819-1843) since 1836, and King of Portugal since 1837 [6] –, who dedicated part of his life to collect and finance
works of art and his vast collection of glassware and stained glass occupied a place of pride [5].

Ferdinand II kept the greater part of the objects acquired in Portugal and overseas – collections of paintings, armour, sculptures, porcelain and others – in his royal residence, the Palace of Necessidades (located in Lisbon). These collecting activities included a group of stained-glass panels of different origins and sizes, with which he decorated the windows of the Palace’s dining room, very much in the style of the other Saxe-Coburgs’ castles [5, 6]. Later in his life, he lived in the old cloister of Pena (restored and turned into a Palace), where he also ordered to be mounted another group of stained-glass panels in the windows of the Great Hall [6]. The choice for the use of stained-glass windows in the openings of the main rooms of residences reflected a central and northern European tradition [6].

Unlike the windows installed in the main hall of Pena Palace’s, the stained-glass windows first located in Palace of Necessidades remained unknown to the general public until very recently. As such, the transfer of the panels to PNP is a story in and of itself [6]. The stained-glass windows were transferred by 1949, since during the Republic (after 1910), the Palace of Necessidades was handed over to the Ministry of Foreign Affairs and its contents were stored and gradually dispersed. It was in 1949 that, after being requested by the conservator of PNP, the ‘eight wooden frames with stained-glass windows’ arrived at this Palace. Unfortunately, their poor state of preservation required an intervention before they could be installed, and so they were to lie forgotten in the store-room for the next sixty years [6]. It was only in 2010-2011 that this important and unique group of stained glass panels was restored and displayed [6]. The collection’s main group currently consists of thirty-seven glass panels was restored and displayed [6]. The coloration’s main group currently consists of thirty-seven glass panels was restored and displayed [6].

This study aims to contribute to the knowledge of the history, materials, and techniques used in the production of a group of four panels within this collection. In the present work, a relation between the stylistic, formal and iconographic studies, and the chemical characterisation of some of the glass fragments allowed to attribute the set to the same origins, highlighting the widely recognised and used potential of heritage scientific studies for solving historical complex questions (e.g. [8, 9]).

Micro Energy Dispersive X-Ray Fluorescence (μ-EDXRF) was used in order to obtain a non-destructive characterisation of the composition of the glass and grisaille used in the production of three of the panels (Virgin of the Apocalypse, Saint Ambrose, Saint Gregory). This information was, in turn, used to help establish the origins, art schools and artistic trends involved in the manufacture of the panels, as well as its recently established relation with the fourth element (Sigmund von Schönfels’ coat of arms).

Materials and Methods
Visual observation and art-historical approach
The four panels under study are nowadays held by PNP (acc. nrs. PNP2809, PNP2810, PNP2821 and PNP2822) (figs. 1 to 2). These stained glasses were observed with the aim of understanding their production technology and evaluating their state of conservation. An iconographic analysis (an art historical analysis) also made use of observation, and of what could be seen in the objects being considered. On the basis of these observations, the objects were related to other primary sources (images and texts), and since this work is published elsewhere [10], it will herein be used as single reference, providing it is an authoritative secondary source.

Chemical analyses and statistical methods
Energy Dispersive X-ray Fluorescence
Concerning the chemical characterisation, several fragments of the panels of Virgin of the Apocalypse, Saint Ambrose, Saint Gregory (fig. 1) were accessible to be analysed by μ-EDXRF. The analyses were carried out using an ArtTAX, Intax® spectrometer, equipped with an air-cooled low-power X-ray tube with a Mo target and Xflash® Peltier cooled silicon drift detector. The primary X-ray beam is focused to a diameter of 70 micrometers by means of a polycapillary X-ray mini lens. The spectrometer was operated at 40 kV, 0.6 mA and 360 s acquisition time, in a He atmosphere. At least three different measurements were made in each glass fragment selected, based on their visual aspect (colour, etc.).

Quantitative analyses were carried out with the WinAXIL program, making use of spectra obtained from CMOG A, B, C and D glass standards. The analytical capability of the equipment is limited to elements with atomic number Z ≥ 13, thus making detection of sodium and magnesium impossible. The concentration of these elements was calculated by the method of ‘matrix by difference’ [11]. This is a less rigorous method, because it is not possible to separate both elements from other light elements that may also exist in the glass composition. The error associated with the analysis was calculated for SiO₂, K₂O, BaO.
and CoO, and is below 5%. Calculated error for CaO, Fe$_2$O$_3$, MnO and SrO is below 10%. For the remaining elements or oxides, Al$_2$O$_3$, CuO, PbO, Sb$_2$O$_5$, SnO$_2$, TiO$_2$ the error is below 25%, which was verified by analysing standard glasses (Corning A, B, C and D) under the same experimental conditions as the samples, and calculating experimentally the concentration values of the certified samples. P$_2$O$_5$ and other light elements standard deviations calculated by the same method were much higher, and therefore this is considered to be a semi-quantitative method.

In this paper, only the results obtained for the glass thought to be from the original production of the panels are presented. Nevertheless, in all four panels several modern glass insets (probably introduced during the 19th century in the assemblage of the windows) were found.

**Principal Component Analysis**

The chemometric study was performed through the statistical treatment of the data collected on the $\mu$-EDXRF spectra, using Principal Component Analysis (PCA). This technique was applied to the peaks of the identified elements obtained through the $\mu$-EDXRF analysis. PCA is known to be useful in reducing the dimensionality of the datasets, increasing interpretability and at the same time minimizing information loss [12]. As elemental peak intensity variations from sample to sample result from the variation of their chemical composition, these were used in PCA in order to identify groups based on the glass chemical composition. The freeware R-statistica under the terms of Free Software Foundation’s GNU General Public License and Statistica from StatSoft (Dell software) were used to accomplish the statistical analyses.

**Figure 1** Photographs of the panels under study: (left) Saint Ambrose (PNP2821), (middle) Virgin of the Apocalypse (PNP2822), and (right) Saint Gregory (PNP2809). Below, details of the faces of the depicted figures. Photograph credits © PSML – Luís Pavão.
UV-Visible Spectroscopy
UV-Visible absorption spectroscopy (UV-Vis) was used to confirm the presence of the transition metal ions responsible for the colours on the glass fragments. An Avantes AvaSpec-2048 fibre optic spectrometer with a 300 lines/mm grating was used. The operational range used was between 200-800 nm and the instrument has a FWHM resolution of 2.4 nm. The light transmitted was measured using a 200 µm transmission probe (Avantes FC-UV600-2).

Results and Discussion
The Iconographic Analysis: from questions to answers
Of the four panels under study – Virgin of the Apocalypse, Saint Ambrose, Saint Gregory and Sigmund von Schönfels’ coat of arms – the former three are proposed to have the same manufacture, due their formal and stylistic characteristics (fig. 1). The three panes Virgin of the Apocalypse, Saint Ambrose, Saint Gregory share common elements in the architectural design illustrated within each panel. The framing seen in the lateral and upper level uses Gothic arches of stone and wood and respective uprights. Several details also suggest that perhaps the same artist could have painted the entire series; for instance the hair and eyebrows and the vestments. It is well known that stained-glass workers could design panels by copying a cartoon made by an artist or by inspiring themselves in famous engravings within the iconographic program ordered by the commissioner [1]. In the present case, it is proposed that the design of these three panels may be based and strongly influenced by the works of German engravers active in the Upper Rhine – namely Master E.S., known to be active between 1450-1467 based on the monogram on eighteen of his surviving prints. Master E.S. was a very well known engraver and influenced many others, and some similarities between these panels and several of his prints may be found [13], as further presented. Simultaneously, an influence from Nuremberg artists seems also to be present, such as the works from the Era of Dürer [14]. The forth panel, Sigmund von Schönfels’ coat of arms (fig. 2), was recently directly related with the glazing of the windows of the Marienkirche at Zwickau [10], presenting himself as the link between the acquisition of Ferdinand II in the 19th century and the Medieval origins of these four panels. The study and interpretation of the iconographic program, the stylistic features and the design of the panels were the first clues to unravel the historical mystery.

Panel of the Virgin of the Apocalypse
This panel, recovered after a complex restoration, shows a way of representing the Virgin that was highly popular in the late 15th century. The iconography is taken from a passage in the Book of Revelation that describes ‘a woman clothed with the sun, and the moon under her feet, and upon her head a crown of twelve stars’ [Revelation 12:1] – the signs of the Apocalyptic woman were later transferred to the Virgin Mary [10, 15]. In this panel the Virgin holding the Child is represented inside an altarpiece with a late-Gothic architectural design, dressed in a red tunic symbolising her great love, a white robe that symbolises Purity, and a blue background of truth [16]. We might easily recognise the depiction of sunlight as a surrounding brilliance (to compensate for the inability to portray a garment of sun), as well as the moon under her feet and the crown over her head. On the contrary, the twelve stars that usually ornament the crown and ‘the wings of a great eagle’ offered to ‘the woman clothed with the sun’ [Revelation 12:14] are absent in this representation [15, 17]. The non-existence of some of the attributes or the simplicity of the depictions is one of the main peculiarities of the three stained glass panels here correlated.

Panel of Saint Gregory
This panel depicts Saint Gregory, a Father of the Latin Church. The depiction of the four Fathers in the same series is usual [14]. Saint Gregory is sitting on a bench at a desk, writing in a book in a very similar architectural space to that of Saint Ambrose and with the same iconographic characteristics. The papal red tunic together with a blue...
robe, a bordeaux lining, and the papal tiara are his most recognisable attributes, together with a crosier with the double cross. At his feet lies what appears to be an eagle. His special attribute is the dove; in ancient pictures this symbol is never far from his ear, sometimes apparently whispering to him, or hovering about his head and shoulders [16].

The eagle is thought to be the representation of Saint John the Evangelist by this symbol. The depiction of this Doctor of the Church associated with Saint John, or his symbol, is uncommon to find but it may be seen for example in the frescoes paintings of the ceiling of Basilica San Giulio in Piedmont, Italy, dating from 1500. In 16th century German stained-glass representations, Saint Gregory is usually depicted associated with St. Matthew the Evangelist (or his symbol, the angel) [14].

**Panel of Saint Ambrose** In this panel, Saint Ambrose is thought to be represented. Like the previously described panels, this one is also illustrated in an architectural space: under the roof of a small late-Gothic chapel, the Saint is sitting at a desk, on a bench which is decorated with quatrefoil, similar to the one that he wears his collar. The environment of the scene recalls a *scriptorium*, girded with a bay window and an ambience that is created by the three small windows arranged in a diamond shape shown in background. The saint wears white tunic, a red robe with a blue lining, and an Episcopal white mitre. He writes with the right hand on one folio of an open book and leans his left hand in the previous folio. By his feet lies what seems to be an ox. Although it is depicted without wings, it is thought to be the symbol representing Saint Luke the Evangelist, since this type of representation of the symbol becomes usual during Romanesque and Gothic eras [18]. Ahead, we may see a small depiction of the Virgin holding the Child on a damask background. She wears a white robe, which also covers the Child, and the small proportion of the figures suggests perhaps a Marian apparition.

Saint Ambrose’s representation in this panel is a direct reference to his comments drawn from the Gospel of Saint Luke: he is surrounded by attributes related to Saint Luke the Evangelist including the image of the Virgin and Child, books and the ox [18]. The depiction of Saint Ambrose associated with Saint Luke the Evangelist, more precisely his symbol the ox, may be seen in several 16th century German stained glasses [14].

**Panel with Sigmund von Schönfels’ coat of arms** This panel does not belong to the iconographic group as the other three, but it is the only one that has survived and can directly be related with the glazing of the windows of the Marienkirche at Zwickau. The rectangular field shows the coat of arms of the Saxon family of Schönfels, a silver oblique bar in black, within a frame of columns and above them – later added – an arch. When the pane came to Portugal, the panels were restored and the black background was incorrectly replaced by blue glass [10]. The panel is dated from 1517, and in the inscription can be read ‘Sigmund von Schönfels 151?’. Not much is known about Sigmund, the founder of the coat of arms – a noble from the family inhabiting the Schönfels Castle, located southwest of Zwickau, which owned several properties near the town since the 14th century. Why Sigmund, who died in 1519, started a window foundation in the Marienkirche remains a mystery. However, the donated panel and its inscription is nowadays the connection with the church documents and the testimony of Lorenz Wilhelm (Zwickau cantor), that in 1633 refers to this stained-glass window – and from the documents, the inscribed year is ‘1517’ [10].

The other three panes – the Madonna and the two Church fathers – were created in a joint program, something that seems clearly evidenced by technology, composition and style. According to written sources, a total of six other stained-glass windows were sold to Silesia in 1819/20, including the coat of arms of Sigmund von Schönfels. There are short descriptions of the panels sold, but unfortunately when Crown Prince Friedrich August became chairman of the Royal Saxon Antiquities Association by 1825, and realised the mistake made by selling these medieval windows, it was already too late and the reacquisition negotiations happening between 1839-40 failed. Thus, for the next 170 years, nothing was known about the whereabouts of the sold panels [10], and the attribution was lacking one final link.

**Chemical characterisation and chemometrics approach**

The three panels – *Virgin of the Apocalypse, Saint Ambrose, Saint Gregory* – were able to be chemically analysed by µ-EDXRF (table 1). The identified medieval colours of the coloured glass fragments were two red hues, light purple, blue, two brown hues, yellow and colourless glass. All the other coloured fragments are thought having been added later, probably when the whole collection was gathered in the window sashes of Palace of Necessidades. The ancient fragments were easily recognisable, by their very even thickness and by the presence of fine design work in the grisaille painting. Almost all of them were found in a good state of preservation in terms of the corrosion process, showing no significant signs of iridescence, and few signs of corrosion products despite the poor storage conditions in which these panels remained for six decades.
By observation of the production defects (e.g. bubbles), we can deduce that these stained-glass panels were produced with coloured blown flat glass, obtained with cylinder glassmaking, since the bubbles in the glass tend to be elongated due to the extension of the original sphere into a cylinder. This widely used middle ages technique consisted of a sphere being extended into a cylinder, with the glass blower carefully swinging a blowing iron and stretching the still soft glass with centrifugal force. Although the bubbles can return to the original spherical shape by further reheating treatment, it is known that the long axes of the bubbles indicate the direction of the original cylindrical axis [19].

Glass Composition: unveiling similarities
As can be seen in fig. 1, the majority of the analysed glasses are coloured. As aforementioned, in the present case, six different colours can be distinguished: a bright red, two types of brown (hereafter Types 1 and 2), a dark hue of yellow, light purple and a dark red or bordeaux, and blue glass. It is well known that glass was produced by melting together a silica rich material as a network former (e.g. quartz sand), a fluxing agent (e.g. coastal plants or wood ashes), and a stabiliser (usually deriving from either a calcareous sand or from plant ash), and that coloured glass was obtained by adding one or more colourant substances (metal oxides) [1].

Glass compositional data (table 1) suggest that flux used was probably wood ash (e.g. bracken, oak and
The glass of the analysed samples can be classified in two compositional groups: (i) high-lime low-alkali (HLLA) or (ii) K-Ca-rich silica type (with mixture of alkali: K and Na). For the classification of these glasses, the authors considered that Na$_2$O content is lower than 6 wt%, since an amount of MgO between 3 wt% and 4 wt% (associated with the chlorophyll) is expected in wood ash glass [20]. Thus, the colourless, red and blue glasses are HLLA glasses, following Schalm et al. [21] classification (the ratio between K$_2$O and Na$_2$O is, in that case, under 0.5). The purple/bordeaux, yellow and brown glasses are then considered Ca-K-rich glasses, since they have high contents of K$_2$O and the ratio between this and CaO is higher than 0.5 [21]. The concentration of P$_2$O$_5$ of about 2 wt% and above points to the use of unpurified wood ash [21].

Despite using $\mu$-EDXRF analysis, a technique which only allows surface analysis, data points were acquired on both sides of the glass fragments (and cross-section whenever possible) and no significant differences were found, allowing one to assume that alkali leaching (associated to corrosion processes) had few consequences on the currently performed comparison [22]. Overall (cf. table 1), glasses revealed contents of SiO$_2$ from ca. 52-60 wt%, K$_2$O from ca. 4.5-6 wt% in a first group (HLLA), and ca. 10-13 wt% in a second group (K-Ca-rich), (Na$_2$O + MgO) from ca. 2.5-8.6 wt% in the HLLA type, and ca. 7-10 wt% in the K-Ca-rich type, and CaO from ca. 19-25 wt% in the HLLA type and ca. 13-19 wt% in the K-Ca-rich type.

The evaluation of the major set of results considering all compound oxides obtained from the panels in situ or to ascertained glass fragments by $\mu$-EDXRF was performed by PCA. In fig. 3, the resulting plot of the two first components allow the interpretation of the variance among data points, explaining approximately 92% of the results. Analysing the relation between pan-
els, it is clear that clusters are being formed based on compositional groups (i) and (ii), which in turn seem to group by sets of fragments’ colours. On PC1 axis, the variance is mainly explained by Ca and Fe contents opposed to K (or the corresponding oxides in the glass matrix). This axis clearly distinguishes the two compositional groups. HLLA and Ca-K-rich glasses – the two different glass compositions used – have respectively lower and higher contents of potash (K$_2$O) in relation to a less variable amount of lime (CaO). The two different compositions seem to be related in all cases with the different fragments’ colours. PC2 axis presents the inverse correlation between K (with greater influence), Rb and Sr oxides, and Mn and Fe oxides, which mainly seems to represent the spread among colours used (or the element oxides associated with the production of colour).

The variance of the associated elements pointed by the arrows in fig. 3 is in accordance with what would be expected for different glass types, where two different flux or recipes were applied. The influence of the silica (SiO$_2$) and alumina (Al$_2$O$_3$) seems to be rather small, which suggests the use of the same silica source. Ca and K represent both the most variable elements (corresponding to their respective oxides in glass composition) and the most common leachates (even low degree corrosion can produce small variations on light elements). Given the spreading of the data points associated with the same fragment of each panel through a diagonal line (scores plot, fig. 3), the relation among the similarly-coloured fragments seems clear.

**Raw materials and the origins of production**

The semi-quantitative chemical composition of the studied glasses obtained by μ-EDXRF analysis, illustrated in table 1, are helpful in the interpretation of the raw material sources used. The plot K$_2$O vs. CaO (fig. 4a) shows a general disposition of compositional groups similar to that of PCA in fig. 3. As will be presented, there is a good correspondence between the multivariate statistical and geochemically based analyses. It is possible to assume that two different glass compositions were used – one with a higher content of potash (K-Ca-rich) and another with a lower content of potash (HLLA) – from these two consistent results, providing strong evidence that the PCA groups are robust. The two different batches may be associated with two different recipes, or different raw materials used for the same recipe.

The high-lime levels in the HLLA samples compared to a lower level in proportion to the increase in K$_2$O could result from: (i) the use of a mixture of high-lime ash with a high-potash ash (either by using different parts of the same wood, where differences in the ratio K$_2$O/CaO are expected to occur [20], or by mixing different species), (ii) the use of a lime-containing silica source or (iii) a separate addition of lime, such as by adding limestone. It is difficult to determine from compositional data whether the groups here formed are due primarily to the variability of the raw materials, the choice of specific raw materials by the glassmaker or the use these sources in different recipes, or a combination of these factors.

The binary plot in fig. 4b using the relations between Sr, Ba and Ca was used to clarify the differences observed, and it becomes clear that two different lime sources were applied. The elements Ba, Cu, Rb are known to accompany K in beech-tree trunks, whilst P, Mn, Ba and Sr are related to Ca in the bark. Ba is accumulated in both trunks and bark in almost equal proportions [20]. A high CaO/Sr is observed for HLLA glasses (low in Sr), whilst Ca-K glass has higher Sr and Ba contents (according to the lower Ca/Sr or Ba ratios, fig. 4b). This trend seems contradictory with the use of different parts of the same tree, since Sr contents are higher in the K-rich glasses. It is also known that ashes were mixed for glassmaking, still for unclear purposes, being assumed that perhaps they were in short supply or that different combinations produced a desired colour or working property [23], and being the most typical wood beech, oak, birch and bracken [20, 23, 24]. The use of fern as a source of K$_2$O is also mentioned, but it is still unclear if or why glassmakers actually made use of this source [25, 26]. Higher Ca:K proportions follow the trend oak > birch > beech > bracken > fern, whilst the Si and Sr contributions follow the opposite trend; and Ba content is usually higher in birch > beech > oak > bracken [24, 27, 28]. Figure 4d and fig. 4e present higher values of iron oxide and alumina in HLLA glass. Whilst in the first case (Fe$_2$O$_3$) it seems to be related with the higher content in CaO, the increase in alumina seems independent of this factor, being similar to the Ca-K-rich glass. This could suggest a contribution of the K-rich ashes in Ca-K glass to the SiO$_2$ content, but not for alumina. In the current scenario, the expected proportions upon mixture of two wood ashes [24] only do not correspond to the observed trends in fig. 4b. Since interpretation should be made with caution and taking into account the great number of variables involved and the analytical technique applied, a mixture of wood-ashes may still be a plausible hypothesis.

The use of calcareous sand or the separate addition of lime is here also considered. In fig. 4e, the ratios of TiO$_2$/Al$_2$O$_3$ vs. Al$_2$O$_3$/SiO$_2$ are plotted against the SiO$_2$/CaO ratio. The former ratios are extremely powerful in identifying production groups, since they relate the chemical composition to the glassmaking
sands mineralogy (silica from quartz, alumina from the feldspars and titania from heavy minerals in the silica source) [29]. It is possible to observe in fig. 4e that the silica-lime and titania/alumina ratios are similar in the two glass types, despite the division of the two groups by the higher alumina/silica ratio in HLLA glass, as in fig. 4d. Hence, this suggests that only one source of silica was used in the manufacture of the analysed glasses. Additionally, there is no clear relation between the contents of CaO and Al₂O₃, which may indicate the use of non-calcareous sand in both glass types. Instead, it appears more plausible to consider the separate addition of lime. External sources of lime included travertine (high in Sr and low in Ba, P, Cu, and Rb) [20], limestone (low in Sr and Ba) [30, 31], and even dolomitic limestones are mentioned to have been used in the medieval period [32]. In the current case, limestone would probably increase the Ca/Ba and Ca/Sr ratios if mixed with sand and ash. According to Wedepohl (1997) [33] a transition from wood-ash to wood-ash-lime glass occurred in Germany after about 1400, which reflected the shortage of wood-ash due to its increasing demand. Wood-ash-lime glass seem to have been produced by addition of quartz, lime and soda-ash (or Na-glass cullet), and probably to the simultaneous replacement of beech by spruce due to its higher productivity [33]. Proportions of 1:1 or 1:2 (sand:ash) [24, 33] in wood-ash-glass and 1:1:3 (ash:limestone:sand) in the transitional wood-ash-lime (Hartmann 1994 apud [34, 35]) – later HLLA – have been suggested. Both the latter or the mixture of different wood-ashes seem reasonable possible reasons for the variations in oxides content observed between the two glass types.

Finally, the relatively high Cl concentration, predominantly in HLLA glass (see fig. 4f), suggests that the low K₂O as alkali flux in this case was supplemented by NaCl, the same way as in cases reported elsewhere [21].

**Colours and painting techniques: helpful tools on provenance and dating**

According to the resulting compositions, manganese oxide (MnO) is present in all analysed glasses in concentrations from ca. 0.4-1.8 wt%. This oxide could be
added either as a decolourising agent, to neutralise the colour given by iron contaminations (e.g. sand, crucible), or with the purpose of altering the hue of a colour. Batch composition and melting conditions are the key parameters controlling the oxidation state. In the case of light purple and bordeaux glass, this oxide seems to have been added as a colourant to a K-Ca-rich glass, and the glass was produced in a kiln with an oxidant environment, since Mn$^{3+}$ is usually the ion responsible for purple colour in glass [36, 37] – fig. 5a. The case of the bordeaux colour of the robes in the panels of Saint Gregory and Virgin of the Apocalypse and the light purple of the ox in the panel of Saint Ambrose are different colour hues obtained by addition of MnO in oxidising environments.

The brown colours in glass could be obtained by changing the proportions of MnO and iron oxide. A yellowish hue is present in Brown T1, (the lighter brown used in the bench and desk of the Church Fathers) and a deeper brown hue can also be observed (Brown T, as in the architectural elements), all sharing a similar composition (see table 1). It is likely that the same colouring strategy was used for these colours by the glassmaker, and that different equilibria of the oxidising states are found in the two hues produced, as is suggested by the different intensities of the Fe$^{2+}$ bands the UV-Vis spectra in fig. 5b. High alkaline glasses favour a closer bound of the Fe$_2$O$_3$ with the alkali, which means the formation of ferrites. Ferrite corresponds to the presence of iron with coordination number 4 (Fe$^{3+}$O$_4$), with a strong absorption in the ultraviolet region, which extends into the blue, so that brown colour results. At the same time, MnO in a glass batch acts an oxidising agent changing FeO to Fe$_2$O$_3$. An increase in MnO content decreases the infrared absorption and increases the absorption in the violet and blue, corresponding to an increase in Fe$^{3+}$ ions also resulting in a brown colour [36, 37].

The blue colour is given by cobalt Co$^{2+}$ in a tetrahedral environment [37] (fig. 5c), since cobalt oxide is present only in the composition of the blue glass analysed (table 1). In the glasses where cobalt is present,
Ni and Fe were also detected (in higher amounts than other cases where Fe is also present), most probably because they coexist in the mineral from which cobalt is extracted. According to comparative studies, performed by Gratuze [38], the association of Co and Ni indicates the use of cobalt extracted from the mines of Erzgebirge, Germany.

Consistent with analytical studies on historical red glass in the panel of Saint Ambrose, this colouration was probably produced by nanoparticles of metallic copper dispersed in the glass matrix [37]. The red glass composition has a CuO content varying from ca. 0.2 to ca. 0.50 wt%, which is much higher than in any other analysed glass. This is an indication that copper is the element responsible for red colour in the glasses, together with the correlated UV-Vis absorption bands presented in fig. 5d.

The absence of silver staining for yellow and brown hues, with the use of iron coloured glass fragments instead (fig. 5b), points to dating these panels to the period before the dissemination of the use of silver staining [1, 39]. A time gap between the beginning and third quarter of the 15th century is consistent with the iconographic program and the typical glass composition being produced in the Germanic region [33, 40].

**Grisaille.** For the three panels here compared, the same painting technique was applied; the lines and shades being obtained through the use of grisaille upon the glass surface to elaborate designs, lines and shadows of the iconographic representation, and two types are applied: black and white hues (fig. 6). In the particular case of the analysed panels, the black grisaille was very heterogeneous, having SiO$_2$ content varying from 12 wt% to 30 wt%, PbO between 23 wt% and 30 wt%, CaO from 8 wt% to 12 wt% and K$_2$O content of about 1 wt%. The most significant characteristic of this grisaille is the fact that no relevant amount of iron oxide was detected. This oxide is normally responsible for the colour of black grisaille [1, 41]. However, in this case the iron oxide it was substituted by copper oxide (see fig. 6), present in a concentration from varying from 10 wt% to 18 wt%. To the best of our knowledge, this composition of grisaille was only reported fashionable in the stained-glass panels of Central Europe during the 15th century [42], such as the church of Salvatorkirche in Munich [43], in St. James’ Church, Prague [44], as well as in Batalha Monastery in Portugal [45], where a German glass-manufacturer probably originating from Nuremberg have settled and worked in the production of the latter stained-glass windows in this period [46].

It is worth mentioning that the two grisailles in fig. 6 were compared with a Nuremberg Schwarzlot painting on hollow glass signed with the monogram of Johann Schapper, also in Ferdinand II’s collection. Values normalised between white and black grisaille by the Ca peak, whilst the whole spectra is normalised to the maximum peak, in the present case being the Cu peak.

![Figure 6 EDXRF spectra of the two types of grisailles (representative spectra were chosen from Saint Gregory – SG – panel)](image)

**On solving an historical mystery**

These four late-medieval windows are now being attributed to the Marienkirche (Saint Mary’s Church) in Zwickau, in the German state of Saxony. On the one hand, Sigmund von Schönfels’ coat of arms is undoubtedly correlated, and on the other hand the three other panels integration seems very likely.

Documents attest the Zwickau panels were sold about 200 years ago, and a relation with the acquisitions of Ferdinand II in the 19th century may be drawn [10]. Despite some authors, as Michael Kühn (apud. [10]), suspect that Albrecht Dürer has designed at least one of the glass paintings of the cathedral, it seems now confirmed that windows were placed in Zwickau a few years after the altar, which the Nuremberg-based Michael Wolgemut created around 1479, and where, interestingly, the young Dürer had worked. However, dismissing the so-desired possibility, the church documents attest for the commission for the ‘window fillings’ of the ‘liberey’ and ‘new chapel’ to a ‘glazier’ named ‘Jacoff’ (Jakob) on October 21, 1481, who received a remarkable amount of 75 guilders for the job. Jakob was probably settled on site with
his workshop, perhaps covering the entire area around Zwickau, due to the close-by flourishing silver mining, which created large demand of stained-glass manufacturers and painters, providing numerous new churches arising in the second half of the 15th century [10]. The influence of the already mentioned Masters and glass-artists in the three stained-glass panels here considered seems clear, and the integration on Zwickau’s cathedral iconographic program is presumed: the Virgin Mary as an apocalyptic woman, relating more with the Ecclesia, whilst the Church Fathers stand for the teaching authority of this very Church, being represented on their scriptoria attuned with their placement in the library [10].

Together with the art-historical interpretation, the almost certain relation of the four panels and a Zwickauer production can now also be extended from the chemical analysis’s results. The fact that both Ca-K-rich and HLLA (or wood-ash and wood-ash-lime classification by [33]) were being used in the three panels analysed supports the correlation with the dating of the windows of Zwickau of 1481 [10], since the period of interest (the course of the 15th century) represents the transition towards the widely recognised HLLA glass, a technological development that became increasingly established in the regions of Germany and Bohemia/Czechia. [20, 21, 40, 47]. Both types are known to have been used simultaneously during the transitional period [33].

The two hypothesis related with flux raw materials also provide interesting connections with the Zwickau site – either by the use of mixed wood ashes (beech, oak, spruce were certainly abundant in the region and being explored in the glasshouses settled there during the 15th century [48]), or the addition of lime through an external source to produce HLLA glass (limestone was explored in the nearby areas of the Ore Mountains [49, 50], and curiously dolomitic limestone was even applied in the mortars of the Marienkirche itself [51]).

Finally, the colouring agents in glass and painting techniques also allow to support the established relation. The chemical results point to the use of a cobalt-mineral extracted from the mines of Erzgebirge, and to establish a link through the proximity to the production site (either nearby Zwickau or Nuremberg) would be very tempting. Nonetheless, it is well known that the mineral was exported to other sites in Europe and at use around 1500 [38]. Perhaps on the contrary, the use of copper in the black grisaille may be a regional trend – an hypothesis inferred from the previously presented examples of Batalha’s grisailles, where possibly a Nuremberg artist worked [45], or the later application of Schwarzlot on tridimensional glass, a technique that became notorious in the 17th century at Nuremberg. It is possible to correlate this information with the ‘southern German, Franconian influences’ on the handwriting of the glassmaker Jakob, and to the close relationship between Zwickau and Nuremberg in the end-15th and early-16th centuries [10]. The use of copper in colouration of the black grisaille may be a strong indication of the production of these panels in that same region for the proposed Marienkirche.

Deeper research would be necessary to undoubtedly attribute the production to a Zwickau-based workshop solely from a chemical point of view – perhaps with the use of more invasive chemical analyses that would provide information on trace and rare-earth elements (e.g. Laser Ablation Inductively Coupled Plasma Mass Spectrometry, La-ICP-MS). However, to the authors present knowledge, the composition of local raw-materials used for glassmaking is not yet studied to allow the establishment of direct relations.

Conclusion

The study of the four medieval panels in the collection of Ferdinand II of Portugal with a multidisciplinary approach (art historical and chemical characterisation) strongly points to a common provenance – now attributed to Zwickau’s cathedral in Germany. The current results suggest all panels belong to the same group, three of them sharing common elements in design. The latter points to the work of the same artist, probably influence by coeval artists such as Master E.S., or the contemporary young Albrecht Dürer, working on the workshop of the Nuremberg-based Michael Wolgemut, who provided the great altarpiece of Zwickau’s Marienkirche. The iconographic program also points to a production of the panels during the late 15th century, early 16th century.

Results from the glass composition analysis are in accordance with the proposed date and, most likely, provenance. The glass of the analysed samples has a HLLA or Ca-K-rich silica type, coloured with manganese, iron, cobalt and copper. The panels are all painted with a black grisaille that presents a peculiar composition, since copper oxide was used as the pigment instead of iron oxide, and this is common in all three analysed panels. The possible regional use of copper-based black paints, might strengthen the relations established with a possibly Nuremberg-master or a closely workshop, such as in the Zwickau area.

It thus becomes evident that the origins of these stained glasses most likely corresponds to the one proposed, being attributed to the same manufacture and region of production, as well as to the Marienkirche.
site, through the combination of art-historical research, stylistical features and chemical analysis results.

Abbreviations

- µ-EDXRF: Micro Energy Dispersive X-Ray Fluorescence
- HLLA: high-line low-alkali
- PCA: Principal Component Analysis
- PNP: Pena National Palace
- UV-Vis: UV-Visible absorption spectroscopy

Competing interests

The authors declare that they have no competing interests.

Data Availability

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Authors’ Contributions

First and corresponding author (AR) has worked on the conception, design, acquisition, analysis and interpretation of data and main contributor in writing the manuscript. Second (MC) and third (AM) authors have made substantial contributions to the acquisition, analysis, and interpretation of data. Fourth author (BM) substantially contributed to the art-historical interpretation. Fifth (LC) and sixth (FM) authors contributed the acquisition and analysis, and FM has substantially revised this work. Sixth and last author (MV), as scientific responsible for the funded project and this work, has made substantial contributions to the work design, data acquisition, interpretation and manuscript revision. All authors read and approved the final manuscript.

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Author details

1. VICARTE, Research Unit Vidro e Cerâmica para as Artes, Hangar III, FCT-NOVA, campus da Caparica, 2829-516 Caparica, Portugal.
2. Laboratório HERCULES, Universidade de Évora, Palácio do Vimioso, Largo Marquês de Marialva, 8, 7000-809 Évora, Portugal.
3. Parques de Sintra – Monte da Lua SA, Parque de Monserrate, 2710-405 Sintra, Largo Marquês de Marialva, 8, 7000-809 Évora, Portugal.
4. C2TN – Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10 (km 139.7), LRS, 2695-066 Bobadela, Portugal.
5. Department of Conservation and Restoration, Faculdade de Ciências e Tecnologia, NOVA University of Lisbon, Campus de Caparica, 2829-516 Caparica, Lisbon.

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