Stained glasses from Monastery of Batalha: Non-destructive characterisation of glasses and glass paintings

Paula Fernandes a, Mária Vilarigues a,*, Luís C. Alves b, Rui C. da Silva b

a Depto de Conservação e Restauro and Centro do Vidro e da Cerâmica para as Artes, FCT-UNL, Quinta da Torre, 2829-516 Caparica, Portugal
b Dep. Física, LFI, ITN, E.N.10, 2686-953 Sacavém, Portugal

Received 30 March 2008; accepted 24 July 2008

Abstract

The characterisation of stained glass fragments belonging to the lateral north wing, to the Capela-Mor and to the Capela do Fundador of the Monastery of Santa Maria da Vitória, Batalha, Portugal, was performed by non-destructive analyses. The work aimed at finding the composition of the glasses and decorations, and relating these with the corresponding production periods.

The chemical compositions of the glass fragments were obtained by micro X-Ray Fluorescence Analysis (µ-XRF), completed with the distribution maps obtained from selected cross-sections by means of micro-beam Particle Induced X-ray Emission Analysis (µ-PIXE). Colour characterisation was performed by optical absorption spectroscopy in the UV–vis range, while corrosion products were characterised with optical microscopy and µ-Raman.

The combination of the different analyses on the different glass samples allowed knowing the composition of the glasses and glass paintings. Using UV–vis spectroscopy, both the oxidation state of an element and its coordination, which are responsible for the colours displayed, could be determined. The presence and distribution of silver and copper in glass surfaces painted with yellow silver stain were also studied.

Keywords: Stained glass; Grisailles; Yellow silver stain; XRF; Ion beam microprobe analysis

1. Introduction

This study intends to contribute to a better and deeper knowledge of the materials and techniques used for the stained glass production in Portugal. For such purpose, several samples of stained glasses from the Monastery of Santa Maria da Vitória were analysed. The Monastery of Santa Maria da Vitória, best known as Monastery of Batalha, is one of the symbols of the Dynasty of Avis. It was raised by the initiative of King D. João I, under the direction of the Portuguese architect Afonso Domingues, following a promise made to the Holy Virgin, for the victory in the Battle of Aljubarrota (1385). The Monastery holds the most important and old nucleus of Portuguese stained glass, being the earliest example of this art in Portugal. It is considered a treasure, for the rarity of this art form in Portugal and for its artistic importance and value [1–3]. The history of these windows has been studied by Carlos Barros [1] and, more recently by Pedro Redol [2]. At the material level, Robert Brill investigated the composition of some glasses from the 16th century [4], while the most recent characterisation studies have been performed by M. Vilarigues et al. [5]. The possibility of analysing samples from original glasses, as well as samples from glasses inserted during conservation—restoration works performed in the beginning of the 20th century, allowed performing a complete material and technical study. This in turn allowed the comparison of the new results with data presented in published works, in particular with the dating presented by Carlos Barros [1].

The study started with the characterisation of small fragments of stained glasses from the first half of the 15th century, belonging to the lateral north wing of the Monastery, and continued with the characterisation of samples of stained glasses from the Capela-Mor and the Capela do Fundador.

* Corresponding author.
E-mail address: mgv@fct.unl.pt (M. Vilarigues).

© 2008 Elsevier Masson SAS. All rights reserved.

Available online at www.sciencedirect.com

Journal of Cultural Heritage 9 (2008) e5–e9
glasses from Capela-Mor and Capela do Fundador, dated from the 16th and 20th centuries. The stained glasses from the 15th and 16th centuries are original, while the remaining were incorporated in the 20th century by the workshop of Ricardo Leone. The fragments analysed were not re-incorporated, having been substituted for new glasses during the conservation—restoration campaigns carried through 1998 and 2007.

2. Experimental

The samples were analysed by X-ray fluorescence spectrometry using one ArTAX, 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 μm by means of polycapillary X-ray mini lens. In all cases the spectrometer was operated at 40 kV, 0.6 mA and 300 s acquisition time, in a He atmosphere. Quantitative analysis was carried out with the WinAXIL program, making use of spectra obtained from CMOG C and D glass standards. The analytical capability of the equipment is limited to elements with atomic number \( Z > 13 \), thus being unable to detect sodium. Quantification of this element was calculated by the method of differences. This is a less rigorous method as other light elements may also exist in the glass composition.

Proton Induced X-ray Emission (PIXE) was used to determine elemental compositions of the painted layers. The elemental maps of the glass surfaces and grisailles were obtained from PIXE spectra excited by 2 MeV H\(^+\) micro-beams with intensities \( \sim 100 \) pA, delivered by a 2.5 MV Van de Graaff accelerator, and focused to \( \sim 3 \) μm cross-section at the target position. The X-rays were collected with a Si(Li) detector of 145 eV energy resolution, protected from scattered protons by a 50 μm thick Mylar® stopping foil. Accurate charge integration required for quantitative analysis was provided by Rutherford Backscattering Spectrometry (RBS) spectra collected simultaneously, with a surface barrier detector of 13 keV energy resolution.

UV—vis spectra from the samples were obtained with a Perkin Elmer® Lambda 35 spectrometer.

The morphology of the corroded surfaces was characterised by optical microscopy using a Zeiss®, Axioplan 2 microscope with a Nikon DMX photographic digital camera attached. Raman spectra of the corrosion products were obtained with a micro-Raman, LabRam 300, Horiba Jobin Yvon spectrometer, with a He—Ne laser (632.8 nm), and a Peltier cooled 1024 × 256 pixel CCD array.

3. Results and discussion

The analysed glass samples originate from different historical periods, in which the techniques of glass production changed and evolved. Thus the chemical compositions of the different samples present great variations. However, as Fig. 1 shows it is possible to establish groups of similarity, i.e. associations of similar glass compositions, which are clearly distinct and disjointive among each other, and can be associated to individualised historical periods. As seen in Fig. 1 these samples can be grouped in four sets in a \( \text{K}_2\text{O} \) vs. \( \text{CaO} \) composition diagram. Two of these group samples with higher contents of \( \text{K}_2\text{O} \) have been recognised as originating from the 15th and 16th centuries (groups I and II in the plot of Fig. 1, respectively). In the 15th century group, all the samples belonged to the lateral north wing of the Monastery, while those of the 16th century group belonged to the panel *Fuga para o Egipto* from Capela-Mor. There are also fragments of the same panel that certainly have been introduced during the conservation—restoration works of the 20th century, as they group together (group III in the plot of Fig. 1) and are characterised by a lower content of \( \text{K}_2\text{O} \) (by substitution for \( \text{Na}_2\text{O} \)). Some samples of the same panel — belonging to the face of St. Joseph — sit in group IV and may be dated as post
16th century, implying they were probably introduced in some unregistered conservation–restoration work [1,2].

Considering that the glasses of the 15th and 16th centuries may be characterised as potash-lime glasses and the remaining as soda-lime or mixed alkali glasses [6], the obtained results were compared with the dating of the same panels by Carlos Barros [1]. The comparison has revealed that some fragments originally dated as being from the 16th century were most probably produced by the workshop of Ricardo Leone in the 20th century. To confirm these results a study of glasses from this workshop will be carried out in a near future.

The colours of these glasses were studied by UV–vis spectroscopy making possible associating them with the different transition metal ions present in the glass matrix: cobalt, copper, and a mixture of cobalt and manganese in the blue, green and purple glasses, respectively. The UV–vis spectra are presented in Fig. 2 and show the characteristic absorption bands of (a) Co²⁺ ions in the tetrahedral configuration [CoIIΟ₄], displaying a triple band with maxima located at 540 nm, 590 nm and 640 nm, (b) Cu²⁺ in the octahedral configuration [CuIIΟ₆] with maximum absorption around 800 nm. Spectrum (c) in the same figure presents the optical absorption of the purple glasses, produced with a mixture of cobalt and manganese. Cobalt exhibits the same triple band as in spectrum (a) due to the [CoIIΟ₄] configuration, while the Mn³⁺ ions in octahedral configuration, [MnIIΟ₆], contribute with the band peaking at 500 nm [7].

Study of the decoration elements present in these samples was also performed, in particular of the grisailles and yellow staining. Analyses of cross-sections of the samples by means of nuclear microprobe allowed identifying the composition of the grisailles and the paintings with yellow silver stain, as well as understanding its production techniques. A typical example of the X-ray maps obtained from a cross-section of a sample painted with grisaille is presented in Fig. 3. The region of the grisaille is easily identified by the abundance of the elements detected, Fe, Cu and Pb. The grisaille structure shows a homogeneous mixture of Cu and Pb, with Fe incorporated in the form of grains. This structure is consistent with the temperatures used to produce the grisailles (between 600 and 750 °C) [8] which, although allowing the mixture of fondant to combine with the glass, are not enough to melt the Fe. Additionally, the μ-PIXE maps for Fe, Cu, Zn and Pb show 20–30 μm thicknesses for grisailles of all periods, both medieval and from the 20th century.

Table 1 summarises representative examples of the compositions of grisailles produced in the 15th, 16th and 20th centuries, obtained from μ-PIXE analyses. Clearly the lead oxide content has increased from 5 mol% in the 15th century grisailles to contents higher than 10 mol% in the 20th century grisailles. In addition, Zn was found in the composition of the grisaille produced in the 15th century, while in the 20th century grisaille, chromium and cobalt oxides were detected instead.

The X-ray maps of a cross-section with a yellow silver stain layer are depicted in Fig. 4. It is possible to identify the simultaneous presence of Cu and Ag in the near surface region. However, while the former is clearly confined to this region, the latter distributes also in the glass bulk, indicating that diffusion of Ag into the glass matrix has occurred. In this diffusion region, the areal density of Ag X-rays intensity looks constant (the presence of Ag in the bulk glass was confirmed by point spectra analyses), indicating that the distribution of Ag is approximately uniform. As in these glass substrates no Cu was found in the bulk glass composition and there is no grisaille in these surfaces, the conclusion is drawn that Cu was used in association with Ag in the production of the yellow silver stain. The annealing process allowed Ag to penetrate into the glass, precipitating as a relatively homogeneous colloidal dispersion of Ag particles, and conferring the glass its characteristic yellow colour [9]. Preliminary quantification of the yellow silver stain produced by the workshop of Ricardo Leone further indicates that an extra amount of Cu was intentionally added to its mixtures.

Table 1

<table>
<thead>
<tr>
<th>Compositions</th>
<th>15th Century</th>
<th>16th Century</th>
<th>20th Century</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brown</td>
<td>Black</td>
<td>Black</td>
</tr>
<tr>
<td>SiO₂</td>
<td>49.8 ± 1.6</td>
<td>47.4 ± 1.1</td>
<td>50.7 ± 0.9</td>
</tr>
<tr>
<td>CaO</td>
<td>21.5 ± 0.8</td>
<td>28.9 ± 0.9</td>
<td>21.9 ± 0.5</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.2 ± 0.9</td>
<td>11.9 ± 0.7</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td>MnO</td>
<td>1.6 ± 1.8</td>
<td>1.9 ± 0.3</td>
<td>6.2 ± 0.3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>10.3 ± 0.7</td>
<td>6.8 ± 0.8</td>
<td>7.6 ± 0.5</td>
</tr>
<tr>
<td>CuO</td>
<td>1.9 ± 2.0</td>
<td>1.2 ± 0.1</td>
<td>1.3 ± 0.3</td>
</tr>
<tr>
<td>ZnO</td>
<td>2.5 ± 2.2</td>
<td>0.3 ± 0.2</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>PbO</td>
<td>4.4 ± 1.9</td>
<td>1.7 ± 1.1</td>
<td>11.2 ± 1.2</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>nd</td>
<td>nd</td>
<td>2.3 ± 0.1</td>
</tr>
<tr>
<td>CoO</td>
<td>nd</td>
<td>0.15 ± 0.1</td>
<td>2.4 ± 0.7</td>
</tr>
</tbody>
</table>
Located in a place where the humidity levels are very high, the Monastery and its stained glasses are severely damaged by the subsequent corrosion processes. This work also focused on the identification of the main corrosion morphologies and products present in the surface of the glasses, since that is crucial to an adequate conservation restoration work. From the microscope images presented in Fig. 5 it was possible to identify fractured surfaces showing detachment, iridescent layers, and the formation and accumulation of crystalline looking elements. These were characterised by Raman spectroscopy as consisting of calcium carbonate formations [10] as can be seen from the spectra presented in Fig. 6.

4. Conclusions

The glasses analysed during this study may be divided into two major groups: potash glasses (produced during the 15th and 16th centuries) and soda-lime glasses, introduced during conservation—restoration works performed by the workshop of Ricardo Leone in the beginning of the 20th century. The comparison of the results obtained for the glass compositions of the different fragments with the dating of the same panels presented by Carlos Barros [1] revealed that some fragments originally dated as being from the 16th century were most probably produced by the workshop of Ricardo Leone in the 20th century. To confirm these results a systematic study of glasses from this workshop will be carried out.

It was established that the grisailles were produced with a mixture of Fe, Cu and Pb oxides. The main difference found in the chemical composition of the grisailles is the content of PbO, which changes from about 5 mol% in the original grisailles to more than 10 mol% for the grisailles produced in the 20th century.

From the association of Cu with Ag displayed in the microprobe elemental maps, it was also possible to conclude that a mix of Ag and Cu (probably as an alloy) must have been
used for the production of the yellow silver stain. Silver penetrated into the glass during the annealing and precipitated, leaving Cu behind, at the surface. Precipitated Ag formed a colloidal dispersion in the glass bulk giving it its characteristic yellow colouring. The obtained results also indicate that the yellow silver stain produced by the workshop of Ricardo Leone is richer in Cu, with the excess Cu intentionally added to the mixture.

Acknowledgement

This Project is supported by Fundação para a Ciência e Tecnologia (FCT) and POCI 2010 (co-financed by FEDER) under contract POCI/HAR/55882/2004.

We thank to IGESPAR for allowing us to analyse the samples from Monastery of Batalha.

References


