Accepted Manuscript

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PII: S0168-583X(09)00387-5
DOI: 10.1016/j.nimb.2009.03.049
Reference: NIMB 56519


Please cite this article as: M. Vilarigues, P. Fernandes, L.C. Alves, R.C.d. Silva, Stained glasses under the nuclear microprobe: a window into history, Nucl. Instr. and Meth. in Phys. Res. B (2009), doi: 10.1016/j.nimb.2009.03.049

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Stained glasses under the nuclear microprobe: a window into history

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Abstract

Stained glass fragments from the 15th, 16th and 20th centuries, belonging to Mosteiro de Santa Maria da Vitória, Batalha (Portugal), were characterised non-destructively in a nuclear microprobe. The work aimed at finding the composition of the glasses and glass paintings and relating these with the corresponding production periods.

The elemental compositions of the glass fragments were obtained by means of scanning micro-beam Particle Induced X-ray Emission (μ-PIXE) spectrometry in selected cross sections. These were complemented by micro X-Ray Fluorescence spectrometry. Characterisation of colour was performed by optical absorption spectroscopy in the UV-Vis range, while the corrosion products were identified by optical microscopy and μ-FTIR (Fourier Transform Infra Red) spectroscopy in combination with the data generated by μ-PIXE.

Nuclear microprobe analysis allowed unveiling the compositions and structures, in particular of glass paintings and corrosion products. While it is not surprising that Fe, Cu and Pb were the main elements identified in the grisaille paintings of all studied periods, as well as Ag and Cu found in the glasses decorated with yellow silver painting, their distribution gave important clues on the materials and techniques used to manufacture these stained glasses. Furthermore, it allowed establishing a definite relation between the compositions found and the periods of production, with the added bonus of correctly reassigning the manufacturing period of some samples.

Keywords: Stained glass; grisaille; yellow silver stain; glass corrosion.

PACS: 81.05.Kf; 82.80
1. Introduction

The introduction of the art of the stained glass in Portugal was due to a major architectural project from the Royal House: building the Monastery of Santa Maria da Vitória, best known as Monastery of Batalha. 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, thanksgiving for the victory in the Battle of Aljubarrota (1385). The history of these windows was first studied by Carlos Barros [1], more recently by Pedro Redol [2] and through our own work [3,4].

The program for the stained glass windows was probably launched at the end of the 1430s when a german “master of glass windows” (Luís Alemão) started working at the workshops in Batalha. Some panels from that period are still in existence, namely fragments from the windows on the lateral wings with figurative creations, representing biblical scenes. A large number of heraldic panels were also discovered. From the 16th century on the monastery gained a group of panels of the highest artistic value, in particular the panels of the main altar of the church and the stained glasses that fill the main window in the Chapter room. Due to the growing indifference of the royal house for the religious institutions, the earthquake of 1755 and the devastation left by the invading French troops in 1810, along with the extinction of religious orders in 1834, the Monastery was in a general state of decay all through the 18th century until 1840. During his first visit to the north of Portugal, in 1836, D. Fernando II visited the Monastery of Batalha. After returning to Lisbon he made every effort to save the monument and in the following Luís da Silva Mouzinho de Albuquerque was appointed in 1840 to oversee all restoration works. Later, already in the 20th century, Ricardo Leone became responsible for the restoration from 1931 and 1939. Eight panels were produced for the main chapel during this
period, using original glasses from the 16th century and new ones, put together in the spirit of the original stained glass windows. Finally, new restoration works were performed between 1996 and 1998, and more recently in 2001 and 2007.

At the material level, these glasses have been studied by Robert Brill who determined the composition of some glasses from the 16th century [5]. More recent studies of characterisation have been performed by M. Vilarigues et al. [3,4].

Ion Beam Analysis, both in broad beam and focused beam, is a remarkable tool for the investigation of objects of cultural heritage [6,7]. In particular, the nuclear microprobe combines the analytical capabilities of essentially non-destructive PIXE and RBS spectroscopies with mapping capabilities with micrometer lateral resolution. This combined information may contribute to a deeper understanding of ancient glass technology and its corrosion behaviour. In this work we present and discuss the results obtained from the characterisation of small original fragments of stained glasses from the first half of the 15th century and of the 16th century, belonging respectively to the lateral north wing of the Monastery of Batalha, and to two chapels, Capela-Mor and Capela do Fundador. The study continued with the characterisation of stained glass fragments from the latter locations that have been incorporated in the 20th century by the workshop of Ricardo Leone. The analysed fragments had been substituted for new glasses in the conservation-restoration campaigns carried through 1998 and 2007.

The microprobe analyses were performed without the need of coating, thus allowing identifying the composition of the paintings with grisailles and yellow silver stain, without altering important historical material.

2. Experimental

Proton Induced X-ray Emission (PIXE) and Rutherford Backscattering Spectrometry (RBS) were simultaneously used to determine elemental compositions of the painted layers, corrosion products and some glasses. The elemental maps of the glass surfaces and painted layers were obtained from PIXE and RBS spectra excited by 2 MeV H+ microbeams with intensities ~ 100 pA, delivered by a 2.5 MV Van de Graaff accelerator, and focused to ~3 μm cross-section at the
target position. The X-rays were collected with a Si(Li) detector of 145 eV energy resolution, positioned 45º from the beam direction. Accurate charge integration required for quantitative PIXE analysis was ascertained using the RBS spectra collected simultaneously with a Si surface barrier detector of 25 keV energy resolution, positioned at 40º to the incoming beam direction. Further details of the microprobe set-up can be found elsewhere [8]. Spectra analysis and elemental quantification was performed with DAN32 computer code through the analysis of K and L X-rays [9]. The composition of the glasses was determined by X-ray fluorescence spectrometry using an ArtTAX, Intax® spectrometer, equipped with a Mo target and XFlash® Peltier cooled silicon drifted detector of 170 eV energy resolution. The primary X-ray beam is focused to a diameter of 70 μm by means of a polycapillary X-ray mini lens. Quantitative analysis was carried out with the WinAXIL program, making use of spectra obtained from glass standards from The Corning Museum of Glass (CMOG C and D). The analytical capacity 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. No aluminium was detected in these glasses. Composition cross-checking by PIXE always proved fully consistent with XRF analysis.

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

The corrosion products were identified by μ-FTIR (Fourier Transform Infra Red) spectra obtained with a Nicolet Nexus spectrometer equipped with a Continuum microscope, in reflectance mode using an Attenuated Total Reflectance (ATR) slide-on accessory with Si crystal.

3. Results and Discussion

Table 1 summarises the compositions of glasses found from μ-PIXE and μ-XRF analyses for glasses produced in the 15th, 16th and 20th centuries. Clearly, the chemical compositions of the samples present great differences in accordance with the fact that they originate from different historical periods. Although the process of making stained glass has changed very little over the
centuries the glass recipes (in particular raw materials used) have constantly changed and evolved through time. In fact, it is still possible to read “De Diversis Artibus”, written by the monk Theophilus in the 12th century, for a basic understanding of the steps required both to make sheets of transparent coloured glass and to fabricate a window. It was possible to establish groups of similarity, which can be associated with the different historical periods. The glasses analysed during this study may be divided in two major groups: Potash or mixed alkali glasses, produced during the 15th and 16th centuries (groups I, II and III in Table 1, respectively) and soda-lime glasses, introduced during conservation-restoration works performed by the workshop of Ricardo Leone (group IV in Table 1). More detailed results can be found in M. Vilarigues et al. [4,5].

The study of the decoration elements present in these samples was also performed, in particular of the grisailles and yellow silver staining.

Figure 1 shows an example of the X-ray maps obtained from a cross-section of a 20th century glass fragment painted with grisaille. The region of the grisaille is easily identifiable in these maps by the presence of the elements Pb, Fe, Cu and also Co. The structure of the grisaille can be perceived as an homogeneous mixture of Cu, Co and Pb, with Fe in the form of grains. This can be understood taking into account that the grisailles, consist of a mixture of melting agent (glass powder and lead oxide) and one or more pigments (in general metallic oxides of iron or copper), allowing the artist to mix it with water, vinegar, wine or arabic gum as binders. It was applied on the glass surface and fired at temperatures between 600 ºC and 750 ºC [10]. These temperatures are enough to make the mixture of fondant combine with the glass but not enough to melt the Fe.

The precise quantification of the grisailles compositions was obtained by µ-PIXE point analyses and allowed concluding that the lead oxide content has increased from 5 mol% in the 15th century to contents higher than 10 mol% in the 20th century grisailles. In addition, zinc was found in the composition of the grisaille produced in the 15th century, whilst in the 20th century grisailles chromium and cobalt were detected instead.
Figure 2 presents typical depth profiles of Ag, Cu and Si, derived from the elemental distributions obtained from cross sections of glass samples painted with yellow silver stain. It is possible to identify the simultaneous presence of Cu and Ag in a near surface region. The presence of Cu may be attributed to the use of an Ag-Cu mixture (probably as an alloy as used in coinage). In these profiles it is possible to see that Cu is confined to the superficial region, while Ag distributes also in the glass bulk, indicating diffusion of Ag into the glass matrix (the presence of Ag in the bulk glass is confirmed by point spectra analyses). In this diffusion region, the areal density of Ag X-rays intensity appears constant, indicating that the distribution of Ag is approximately uniform. The annealing process allowed Ag to penetrate into the glass – precipitating as a relatively homogeneous colloidal dispersion of Ag particles – and conferring the characteristic yellow colour to the glass [11,12].

Silver staining developed around the beginning of the 14th century. A diluted silver compound was applied in the glass surface and fired at temperatures between 500 ºC and 600 ºC. During the firing silver ions penetrate through the glass surface by ion exchange with K or Na, then reduced to their metallic form. Finally, neutral silver aggregates and form clusters with a diameter between 2 nm and 100 nm. The silver nanoparticles in the glass matrix are responsible for a bright colour that can be varied from yellow to red [11,12].

The colours of these glass fragments were studied by UV-Vis spectroscopy. One UV-Vis spectrum obtained from a glass sample painted with yellow silver stain is shown in Figure 3. The absorption band located around 420 nm is due to a well known surface plasmon resonance of colloidal silver particles [11, 13].

Usually, grisailles and yellow silver stains were applied in opposite sides of glass panels, and annealed in two steps, first the grisaille and then the yellow silver stain. Sometimes however it is also possible to find glasses where this procedure was not followed and silver stain and grisailles may be found in only one side of the painted glass panels. Figure 4 illustrates this displaying the depth profiles of Si, Ag, Cu and Fe, obtained from a cross-section of a 20th century glass sample painted with grisaille and yellow silver stain. The Cu profile is the result of
two distinct contributions: Cu present in the Ag-Cu mixture, confined to the superficial region of the glass, and also Cu from the grisaille, mixed with Fe (and also with Pb).

This work also included the identification of the main corrosion morphologies and products present in the surface of the glasses, since its identification is crucial to an adequate conservation-restoration action. 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. The X-ray maps of Si, K and Ca shown in Figure 5 reveal the existence of areas with a reduced concentration of Si and K and a corresponding enhancement in the Ca content, corresponding to the corrosion processes described. Analysis of these structures by μ-FTIR allowed concluding that these are CaCO$_3$ crystallites [4,5]. Corrosion starts when the surface of glass is put in contact with water. Alkali and alkaline earth ions are leached out of the glass, with hydronium ions replacing them in the glass structure, leading to the formation of a hydrated layer at the surface. This layer can retract and yield, creating fissures through which the solution can reach the inner glass, allowing the alteration to propagate further. In addition, leached cations can combine with SO$_2$ or CO$_2$ gases present in the atmosphere to crystallize at the surface forming gypsum or syngenite.

4. Conclusions
The glasses analysed during this study may be divided into two major groups: potash glasses (produced during the 15$^{th}$ and 16$^{th}$ centuries) and soda-lime glasses, introduced during conservation-restoration works performed by the workshop of Ricardo Leone in the beginning of the 20$^{th}$ century.

The use of a nuclear microprobe and the associated μ-PIXE technique allowed unveiling also the composition and structure of the glass painting: grisailles and yellow silver stains.

It was established that the grisailles were produced with a mixture of Fe, Cu and Pb. The main difference determined in the chemical composition of the grisailles through the ages, lays in the content of Pb, about 5 mol% in the original grisailles and more than 10 mol% for the grisailles produced in the 20$^{th}$ century. The structure of the grisailles does not vary with the production
period: a ~30 μm thick lead silicate fondant layer, with Fe and Cu pigments concentrated in the
centre most region. The temperatures used were sufficient to bind the fondant mixture to the
glass substrate, with the Fe and Cu colorants being part of a ~15 μm thick dispersion of solid
grains that remained solid in the melt.

From the association of Cu with Ag displayed in the microprobe elemental maps, it was also
possible to conclude that an Ag-Cu mixture (probably an alloy as used in coinage) must have
been used for the production of yellow silver stain. Silver penetrated into the glass during the
annealing, and precipitated, leaving Cu behind, at the surface.

Use of the nuclear microprobe made also possible to obtain information about the structural
changes in the glasses surfaces due to corrosion processes. In particular evidence was found for
the formation of Ca rich structures associated with the formation of CaCO₃, confirmed with μ-
FTIR analysis.

Acknowledgment

This Project is supported by Fundação para a Ciência e Tecnologia (FCT) and POCI 2010 (co-

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

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Figure 1 – Elemental X-ray maps of the cross-section of a 20th century sample painted with grisaille (106×106 µm²).
Figure 2 – Si, Ag and Cu depth profiles obtained from the cross section of a 20\textsuperscript{th} century glass sample painted with yellow silver stain.

Figure 3 – UV-Vis spectrum obtained from a glass sample painted with yellow silver stain. The absorption band is attributed to the presence of silver nanoparticles.
Figure 4 – Si, Ag, Cu and Fe depth profiles obtained from the cross section of a 20th century glass sample painted with grisaille and yellow silver stain. The dashed line indicates the glass surface. Notice that it lays beneath the grisaille layer.

Figure 5 – 106 × 106 µm² µ-PIXE maps obtained from a corroded surface.
Table 1 – Representative examples of glass compositions (in wt%) produced in the 15th, 16th and 20th centuries obtained by µ-XRF and cross checked by µ-PIXE. Sodium content was calculated with WinAXIL by the method of differences. Groups I, II and III are potash or mixed alkali glasses, produced during the 15th and 16th centuries and Group IV corresponds to soda-lime glasses, introduced during conservation-restoration works performed by the workshop of Ricardo Leone.

<table>
<thead>
<tr>
<th></th>
<th>Group I</th>
<th>Group II</th>
<th>Group III</th>
<th>Group IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>60.22 ± 0.57</td>
<td>54.47 ± 0.45</td>
<td>56.47 ± 2.65</td>
<td>61.60 ± 0.54</td>
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<tr>
<td>CaO</td>
<td>12.23 ± 0.25</td>
<td>15.32 ± 1.02</td>
<td>18.54 ± 1.58</td>
<td>7.25 ± 0.67</td>
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<tr>
<td>K$_2$O</td>
<td>17.76 ± 0.19</td>
<td>12.68 ± 0.28</td>
<td>4.47 ± 0.19</td>
<td>3.12 ± 0.07</td>
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<tr>
<td>MnO</td>
<td>1.63 ± 0.05</td>
<td>1.59 ± 0.20</td>
<td>0.68 ± 0.05</td>
<td>0.60 ± 0.02</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.76 ± 0.03</td>
<td>0.46 ± 0.07</td>
<td>0.49 ± 0.04</td>
<td>0.55 ± 0.07</td>
</tr>
<tr>
<td>CuO</td>
<td>6.09 ± 0.22</td>
<td>1.7 × 10$^{-4}$</td>
<td>1.3 × 10$^{-4}$</td>
<td>3.82 ± 0.13</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.50 ± 0.02</td>
<td>2.2 × 10$^{-4}$</td>
<td>2.5 × 10$^{-4}$</td>
<td>4.0 × 10$^{-4}$</td>
</tr>
<tr>
<td>PbO</td>
<td>0.14 ± 0.04</td>
<td>4.6 × 10$^{-4}$</td>
<td>3.2 × 10$^{-4}$</td>
<td>5.9 × 10$^{-4}$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.16 ± 0.01</td>
<td>0.22 ± 0.01</td>
<td>0.18 ± 0.02</td>
<td>8.0 × 10$^{-4}$</td>
</tr>
<tr>
<td>Σ</td>
<td>100</td>
<td>84.74</td>
<td>81.13</td>
<td>77.59</td>
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<td>Na$_2$O</td>
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<td>15</td>
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<td>21</td>
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