Chemical degradation and chromophores of 18th century window glasses

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Three sets of glass samples from 18th century leaded windows from the Girona Cathedral, Reus Priory Church and the Vitoria Cathedral (Spain) have been studied. Chemical analyses and archaeometry of these glasses are of special interest due to both the scarcity of 18th century stained glass window production and to the particular orange colour of several glass pieces. Chemical degradation of glasses has been deduced from their composition and conservation state, directly observed using optical and electron microscopy. The chemical species responsible for colouring (chromophores) and other chromatic parameters have been investigated from optical spectroscopic data. The results indicated that glasses from Girona Cathedral are potassia lime silica glasses, whereas those of the Reus Priory Church and Vitoria Cathedral are soda lime silica glasses. The durability of the glasses studied is directly related to their respective chemical composition: potash glasses from Girona show advanced chemical degradation, compared with the other sets of glasses analysed. In addition to the assignment of chromophores for blue, violet, green and red ruby glasses, the chromophores responsible for the orange colour of glasses from stained windows have been characterised for the first time.

1. Introduction

Stained glass windows from the 18th century have been frequently denigrated in comparison with stained medieval glasses, due to the general decline in stained window standards during the 17th and 18th centuries. Several reasons can explain this situation: on the one hand, the new style of stained windows, as a consequence of changes in fashion, and on the other hand, the decline and even stopping of production in many glass workshops. A great number of glass windows were destroyed during various wars and coloured glass pieces were replaced with colourless ones. The aesthetic evolution of the Renaissance, Baroque and Rococo styles gave rise to the lack of division of the whole window into smaller panels. Certainly, this was the main technical difficulty with 18th century stained windows that affected the building security.

The general objective of the present study is the chemical and physical characterisation of the production technology used to produce coloured glasses in 18th century glass windows. Therefore, two aspects will be investigated: (i) the chemical composition and the degradation processes experienced by the glasses and (ii) the chromophores responsible for the colouring of these glasses, especially the orange colour that was used in glass windows for the first time in the 18th century. This is important since during former centuries orange coloured glasses were absent in glass windows, in which only yellow or red ruby colours have been characterised. These colours were obtained by applying an Ag(I) salt or a Cu(I) salt, respectively, mixed with a medium onto the glass surface and firing the panels at temperatures below the softening point of the glass. Moreover, the study of coloured glasses from glass windows of the 18th century is really interesting as such glasses are rare, as most of 18th century windows were produced using colourless glasses, while coloured glass pieces were reserved and used only for some central motifs or geometrical ornamentations in the borders. To the best of the authors’ knowledge, the chromophores giving the orange colour in 18th century glass windows have never been characterised from the chemical point of view.

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2. Experimental

2.1. Selection of set samples

The samples were selected as representative specimens of stained glasses from Girona Cathedral, Reus Priory Church and Vitoria Cathedral. The samples set from Girona Cathedral are from the stained glass rose window (Assumption of the Virgin Mary) located in the West façade of the cathedral. It was designed by Francesc Saladriga, a glass master of Barcelona, and produced by Aloi Xifreu ca. 1732. The glasses used in this stained glass window were imported from Venetia, according to some cathedral documents. This stained window was further restored in 2001 by the Glasmeri Peters Company (Paderborn, Germany). Macroscopic observation of coloured glass fragments revealed that most of them show a deterioration due to chemical attack of water known as crizzling. This kind of degradation, attributed to an excess of alkaline oxides and low percentages of calcium oxide, is common in glasses dated from the 17th and 18th centuries. The easy leaching of alkaline ions towards the glass surface causes the surface dealkalisation and a local pH increase. This basic pH enhances glass network decomposition by means of a chemical mechanism involving on alkaline attack that is able to break down the siloxane Si–O–Si bonds in the glass.

The set of samples from Reus Priory Church belonged to the stained windows located in the dome of the Saint Sacrament Chapel (1700). After the Spanish Civil War (1936–1939) these stained windows were removed due to severe damage. Nowadays new stained glasses substitute the original ones. The original glass fragments selected have neither grisailles nor any kind of ornamental elements or painting. These stained glass windows have never been restored before and their state of conservation is extremely poor.

2.2. Characterisation of the glass samples

Table 1 summarises the most important selected samples and their macroscopic characteristics and deterioration pathologies. Chemical composition of glasses was semi quantitatively determined by X-ray fluorescence spectrometry (XRF) using either a Philips PW-1404 or a PANalytical Axios instrument. In both cases the glass samples were cleaned of deposits and decorations and ground to a fine powder. Such powders were pressed into boric acid pellets with n-buthyl-methacrylate and acetone (10:90 wt%) as binders. The semi quantitative results obtained correspond to the average chemical composition of the bulk glasses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Provenance</th>
<th>Colour</th>
<th>Dimensions (mm)</th>
<th>Thickness (mm)</th>
<th>Conservation state</th>
<th>Indoors surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>1G (2 fragments)</td>
<td>Girona Cathedral (1732) West Rose</td>
<td>Blue</td>
<td>3.0×2.0</td>
<td>1.9–2.2</td>
<td>Dirt and scratches</td>
<td>Deep grey grisaille and pits</td>
</tr>
<tr>
<td>2G (2 fragments)</td>
<td>Assumption of the Virgin Mary</td>
<td>Clear orange</td>
<td>3.0×2.0</td>
<td>1.8–2.3</td>
<td>Few pits</td>
<td>Dirt near the print of the lead came profile</td>
</tr>
<tr>
<td>3G (2 fragments)</td>
<td>Violet</td>
<td>2.0×2.0</td>
<td>1.6</td>
<td>Dirt and putty remains</td>
<td>Pits, scratches and dirt near the print of the lead came profile</td>
<td></td>
</tr>
<tr>
<td>4G (2 fragments)</td>
<td>Deep orange</td>
<td>3.0×2.0</td>
<td>1.8–2.0</td>
<td>Many pits</td>
<td>Dirt, few pits and putty remains</td>
<td></td>
</tr>
<tr>
<td>1R (2 fragments)</td>
<td>Priory Church Sant Pere, Reus (1700) Stained windows of the Saint Sacrament Chapel</td>
<td>Green</td>
<td>5.0×1.0</td>
<td>1.8</td>
<td>Good State</td>
<td>Idem outdoors surface</td>
</tr>
<tr>
<td>2R (3 fragments)</td>
<td>Orange</td>
<td>2.0×1.0</td>
<td>1.7–2.0</td>
<td>Good state</td>
<td>Idem outdoors surface</td>
<td></td>
</tr>
<tr>
<td>3R (3 fragments)</td>
<td>Blue</td>
<td>2.0×1.0</td>
<td>1.9–2.0</td>
<td>Dirt</td>
<td>Idem outdoors surface</td>
<td></td>
</tr>
<tr>
<td>4R (3 fragments)</td>
<td>Red plaqué</td>
<td>2.0×1.0</td>
<td>1.6–2.8</td>
<td>Good state</td>
<td>Idem outdoors surface</td>
<td></td>
</tr>
<tr>
<td>1V (1 fragment)</td>
<td>Vitoria Cathedral (1733?) Stained windows of Reconciliatorio and Sacristry</td>
<td>Orange</td>
<td>6.0×4.0</td>
<td>1.9–2.0</td>
<td>Good state, Dirt</td>
<td>Dirt and small pits</td>
</tr>
<tr>
<td>2V (1 fragment)</td>
<td>Red</td>
<td>6.0×5.0</td>
<td>1.7–1.8</td>
<td>Dirt and putty remains</td>
<td>Dirt and scratches</td>
<td></td>
</tr>
<tr>
<td>3V (1 fragment)</td>
<td>Red</td>
<td>6.0×3.0</td>
<td>1.6–1.7</td>
<td>Dirt</td>
<td>Good state, Scratches</td>
<td></td>
</tr>
</tbody>
</table>
The state of both surfaces of the glass samples was observed by optical microscopy (OM) with a Leica model DM-LM reflected light microscope, equipped with a Leica DFC 480 digital camera. Microscopic analyses of the surface texture of glass samples were carried out with a scanning electron microscope (SEM; Hitachi model S-3400-N at CCHS-CSIC), and with a field emission scanning electron microscope (FESEM; Jeol JMS 6500F). Local microanalyses, both on the glass surfaces and on cross-sections, were undertaken with an energy dispersive x-ray spectrometer (EDS) Pentafet Link attached to the FESEM equipment. The spectrometer was equipped with a windowless Si (Li) detector operating at 15 kV. Semi quantitative results were obtained by means of the ZAF correction method. For electron microscopy and EDS analyses the samples were coated with gold or carbon respectively to prevent charging.

The colours of the glasses and the chemical species responsible for such colours (chromophores) were determined by ultraviolet-visible-near infrared (UV-VIS-NIR) spectrophotometry using an Ocean Optics model HR400CG-UV-NIR spectrophotometer. Absorption and transmission spectra were recorded in the 230–1050 nm wavelength range. Chromatic coordinates and other colour parameters were determined by using the Ocean Optics Spectra-Suite software and the transmission spectroscopic data obtained with a D65 standard illuminant D65 and a 10° observation angle.

The bulk glass microstructure of the orange glasses was observed using a transmission electron microscope (TEM; Hitachi model H-7100) operating at 125 kV. Carbon direct replicas of fresh fracture of the glasses were prepared and then etched for 15 s using 5 vol% HF.

3. Results and discussion

3.1. Chemical composition of the bulk glasses

Table 2 shows the average chemical composition of the most representative glass samples studied. Semi quantitative data were obtained by XRF spectrometry. All the glass samples from Girona Cathedral contain on average 65 wt% SiO₂, 23 wt% K₂O and 5 wt% CaO. This proportion of major components corresponds to that of potash lime silicate glasses with very low Na₂O contents (2 wt% on average). With the aim of clarifying whether the glass fragments analysed came from earlier centuries and had been re-used during the 18th century, some comparison with medieval glass compositions was carried out. However, the chemical compositions determined (Table 2) cannot be assigned to any of the medieval glass types described by Müller et al. Among the five compositions given in Ref. 8, the most similar contains in wt% 45–55 SiO₂, 15–25 CaO, 15–25 K₂O, 0–2 Na₂O, 0–1PbO and 0–4 P₂O₅. The SiO₂ content in the glass samples from Girona Cathedral is higher, while the CaO content is much lower, and PbO and P₂O₅ were not detected. Therefore, the assignment of the Girona glass samples as re-used medieval pieces is not consistent. Although Girona samples are potash lime silicate glasses, they are not typical of medieval potash glasses. In the Girona glass samples the relatively high percentage of SiO₂ provided stable glasses with the use of high percentage of K₂O as a flux and the almost complete absence of Na₂O. Simultaneously, in these glasses it was possible to use lower percentages of CaO as a glass stabiliser, compared with the usual large amounts found in medieval glasses. Summarising, the glasses from Girona Cathedral can be considered to be potassia lime silica glasses with a more stable composition as compared to medieval potash glasses. The higher SiO₂ percentage in the Girona glasses means they have a higher chemical resistance. The production of such SiO₂-rich glasses was probably possible thanks to 18th century advances in the design and technology of melting furnaces, and also to new refractory materials. With respect to the minor components, the Girona glasses contain 0–15 wt% MgO and 1–6 wt% Al₂O₃ on average, which are normal percentages of these oxides in glasses used in stained glass windows. Other minor components are chromophore oxides that are discussed in Section 3.3, As₂O₃ (probably used as a refining substance), BaO and Bi₂O₃ (probably incorporated as impurities in the raw materials). The presence of small amounts of

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>SO₂</th>
<th>K₂O</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>MnO</th>
<th>Fe₂O₃</th>
<th>CoO</th>
<th>NiO</th>
<th>CuO</th>
<th>As₂O₃</th>
<th>BaO</th>
<th>PbO</th>
<th>Bi₂O₃</th>
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<td>1G</td>
<td>1·41</td>
<td>0·12</td>
<td>1·57</td>
<td>64·55</td>
<td>0·32</td>
<td>0·29</td>
<td>24·36</td>
<td>5·19</td>
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<td>0·65</td>
<td>0·47</td>
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<td>0·03</td>
<td>0·07</td>
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<tr>
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<td>2·16</td>
<td>0·24</td>
<td>1·98</td>
<td>67·51</td>
<td>0·08</td>
<td>0·19</td>
<td>21·68</td>
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<td>-</td>
<td>-</td>
<td>0·02</td>
<td>0·02</td>
<td>-</td>
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</tr>
<tr>
<td>3G</td>
<td>2·26</td>
<td>0·11</td>
<td>2·12</td>
<td>62·72</td>
<td>0·16</td>
<td>0·52</td>
<td>24·01</td>
<td>5·09</td>
<td>-</td>
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<td>0·16</td>
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<td>-</td>
<td>0·05</td>
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<td>2·20</td>
<td>0·15</td>
<td>1·57</td>
<td>66·68</td>
<td>0·83</td>
<td>0·51</td>
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<td></td>
</tr>
<tr>
<td>1R</td>
<td>17·41</td>
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<td>1·66</td>
<td>66·72</td>
<td>0·21</td>
<td>0·21</td>
<td>0·78</td>
<td>9·79</td>
<td>0·76</td>
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<td>1·40</td>
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<td>2·48</td>
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<td>0·11</td>
<td>0·37</td>
<td>1·39</td>
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<tr>
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<td>12·44</td>
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<td>0·23</td>
<td>-</td>
<td>0·05</td>
<td>0·06</td>
<td>0·13</td>
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<td>0·99</td>
<td>0·81</td>
<td>1·72</td>
<td>16·32</td>
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<td>-</td>
<td>0·03</td>
<td>0·13</td>
<td>-</td>
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</tr>
<tr>
<td>2V</td>
<td>11·77</td>
<td>0·10</td>
<td>0·93</td>
<td>68·15</td>
<td>0·40</td>
<td>0·09</td>
<td>0·44</td>
<td>13·86</td>
<td>-</td>
<td>1·31</td>
<td>0·34</td>
<td>0·20</td>
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<td>0·53</td>
<td></td>
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<tr>
<td>3V</td>
<td>12·51</td>
<td>0·14</td>
<td>0·53</td>
<td>69·53</td>
<td>0·96</td>
<td>0·14</td>
<td>0·14</td>
<td>15·46</td>
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<td>0·19</td>
<td>0·01</td>
<td>-</td>
<td>0·08</td>
<td>0·01</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
Cl\(^-\) and SO\(_2\) could be due to some minor raw materials such as NaCl and Na\(_2\)SO\(_4\).

The glass samples from the Priory Church of Sant Pere of Reus can be considered to be soda lime silica glasses (Table 2). These glasses are much more stable than potassia lime silica glasses, which accounts for their better conservation state compared with glasses from Girona Cathedral. The glass sample 2R contains a lower SiO\(_2\) percentage (63.08 wt\%) and a higher Al\(_2\)O\(_3\) percentage (2.48 wt\%) than the other samples. Other glasses from Reus have average SiO\(_2\) and Al\(_2\)O\(_3\) contents of 67.98 and 1.08 wt\%, respectively. Since both SiO\(_2\) and Al\(_2\)O\(_3\) are glass forming network oxides, the sum of their percentages is the total content of oxides that give the glass chemical stability. Following this criterion, such a sum of percentages varies between 65.56 and 69.75 wt\% and, hence, all the glasses from Reus have a similar chemical stability and can be classified into the same group of soda lime silite glasses. Other major components in the Reus glasses are the following (average %) 15.86 Na\(_2\)O and 12.25 CaO, which fit with the composition of common soda–lime–silica glasses. The main minor components are MgO (0.15 wt\%), Cl\(^-\) (0.19 wt\%) and K\(_2\)O (0.88 wt\%). Oxides incorporating potential chromophore agents are discussed in Section 3.3. Finally, other minor oxides introduced as impurities in the raw materials are As\(_2\)O\(_3\) (0.09 wt\%), BaO (0.18 wt\%) and Bi\(_2\)O\(_3\) (0.04 wt\%). In three Reus glass samples PbO has been detected up to a maximum of 1.46 wt\% (e.g. in sample 4R).

Analytical results for the glasses from Vitoria Cathedrals (Table 2) indicated a soda–lime–silica composition that accounts for their relatively good state of conservativite. The average sum of SiO\(_2\) and Al\(_2\)O\(_3\) (the main glass forming oxides) is 69.37 wt\%, the average CaO content is 15.21 wt\% and the average Na\(_2\)O content is 12.90 wt\%. With regards to minor components, the average weight percentages were: 0.13 MgO, 0.37 SO\(_2\), 0.36 Cl\(^-\), 0.06 BaO and 1.72–0.14 K\(_2\)O. Lead oxide was detected in two samples (0.13 and 0.01 wt\%, respectively). Chromophore oxides are discussed in Section 3.3.

### 3.2. Chemical degradation of the surface of glasses

#### 3.2.1. Optical microscopy observations

Glasses from Girona Cathedral exhibited alterations on their outdoor surfaces with many scratches, dark deposits (dirt), interconnected cracks, etc. (Figure 1). Some fragments from cracked areas were detached leaving concave prints or giving rise to interference colours. They are due to the light diffraction in superimposed silica gel layers formed as a consequence of hydrolytic attack on the glass surface and further dealkalinisation. Indoor surfaces also showed cracks and deposits in which the presence of grisailles and remains of other decorations can not be neglected.

Glasses from Reus showed deposits on their outdoor side, shallow to deep scratches and small pits, while on the indoor surfaces dark deposits and light scratches were observed (Figure 1). The outdoor surface of glasses from Vitoria Cathedral exhibited different pathologies as compared with glasses from Girona and from Reus. Apart from dirt, dendritic interconnected forms appear and alternate with dispersed pits. On indoor surfaces of glasses from Vitoria the same pathologies as on the outdoor surfaces can be observed and cracks, detachments and interference colours also appear (Figure 1). Red ruby glasses (plaqué glasses were in a better state of conservation than the orange ones (e.g. 1V), whose surface is the most deteriorated.

In general, all the pathologies detected confirm the crizzling phenomenon observed visually (section 2.1).

#### 3.2.2. Scanning electron microscopy observations and energy dispersive x-ray spectrometry

The microstructure of glasses from Girona Cathedral consists of an interconnected network of cracks with some detached areas (crizzling) where dirt particles are deposited (Figures 2(a) and (b)). EDS microanalyses confirmed that in plate-like areas (zone 2 in Figure 2(b)) high SiO\(_2\) and Al\(_2\)O\(_3\) contents and low K\(_2\)O percentages are detected. This indicates that a surface dealkalisation process has taken place as a consequence of hydrolytic attack enhanced by...
environmental moisture. This situation generated a surface layer of silica gel. In areas with detachments (bottom area in Figure 2(a) and zone 1 in Figure 2(b)), the chemical composition is similar to that of zone 2, and other deposits of dirt or products from the hydrolytic attack (mainly sulphates) are detected.

Glasses from Reus showed few microstructural features. This is explained by the stable chemical composition of these soda–lime–silica glasses. However small holes are observed which are attributed to mechanical impacts from the external environment, since they show some geometrical morphologies and concave fracture lines (Figure 2(c)). EDS analyses revealed evidence of the same dealkalinisation phenomena and formation of a silica gel layer as already described for the Girona glasses (e.g. zone 1 in Figure 2(c)), which combine dealkalinisation products and other oxides from corrosion of the lead came profiles, putties and supporting bars.

Apart from dirt and common deposits (Figure 2(d)), glasses from Vitoria Cathedral Vitoria do not exhibit microstructures attributable to chemical degradation mechanisms or to other kinds of degradation. This is in agreement with chemical stability of soda lime silica glasses.

SEM observation of a cross-section of the grisaille of the Girona glasses indicated that it is formed by an agglomerated mixture of relatively big grains and small grains (Figure 2(e)). EDS analyses of the larger grains (zone 1 in Figure 2(f)) detected very high proportions of antimony and sulphur (40–50 wt%), and a low percentage of SiO₂ (<1 wt%). Moreover, EDS analyses of the small grains also indicated antimony and sulphur as major components, while SiO₂ and CaO contents were as low as <1.5 wt%.

The whole analysis of the grisaille (zone 2 in Figure 2(f)) revealed high antimony and sulphur contents (37–49 wt%), a low SiO₂ content (~1.7 wt%) and a relatively high content of mercury (~8 wt%). In some areas iron, cobalt and arsenic oxides were detected at low percentages. These results indicate that both the large grains and the small grains could have the same or similar compositions, and that some mercury mineral or raw material (possibly cinnabar, HgS) was used to intensify the red and brown colours of the grisaille. The amounts of antimony, sulphur and oxygen detected in the grisaille maintain proportions very close to the stoichiometry of antimony (III) sulphate [Sb₂(SO₄)₃]. Thus, this salt could have been used for preparation of the grisaille. In Figure 2(e) a clean interface between the glass and the grisaille can be observed (line above the upper part of the grisaille), as well as angular forms in the grain boundaries. These facts demonstrate that the grisaille was not densified to an adequately high temperature, or even that it was a grisaille applied at room temperature and never fired (cold paints). This is one of the characteristics of 18th century stained glasses: the absence of authentic grisailles fired at high temperatures and the use of cold paints.

3.3. Characterisation of the chromophores

The chromophores in the glasses studied were determined by VIS spectrophotometry and assigned according to Weyl and Fernandez-Navarro. In the case of orange glasses they were confirmed by TEM.

The blue glasses (e.g. 1G and 3R) have visible spectra dominated by a triplet at 540, 590 and 640 nm (Figure 3) attributed to Co²⁺ ions in [CoO₄]⁶⁻ coordinated, responsible for the well known cobalt blue colour. This assignment is confirmed by the analytical results shown in Table 2 (CoO contents at about 0.2 wt%). Other possible contributions to colour from other oxides such as MnO, Fe₂O₃, NiO and CuO were masked by the higher extinction coefficient of Co²⁺ ions (intense blue glasses can be obtained with CoO contents as low as 0.005 wt%).

The violet glasses (e.g. 3G) exhibit a unique absorption band at 499 nm (Figure 4), which is assigned to Mn³⁺ ions. The chemical analyses of that glass (table II) confirm the content of manganese oxide (~3 wt%) and a small percentage of Fe₂O₃, which can contribute to the total colour, but is masked by the intense violet colour of Mn³⁺ ions.

The green glasses (e.g. 1R) have visible spectra with a band centred at 435 nm and a triplet at 630, 650 and 675 nm (Figure 5). Such absorptions are attributed to Cr³⁺ ions, which produce the emerald green colour. The chemical analyses of Table 2 con-
firm that, for instance, the glass sample 1R contains about 0.7 wt% of Cr₂O₃. In the same way as in former cases, other possible chromophores from manganese, iron, nickel and copper oxides are masked by the intense green colour provided by Cr³⁺ ions. Since the first chromium minerals were discovered in around 1760–1770 and metallic chromium was isolated in 1798 by Louis Nicolas Vauquelin, the chromium-coloured glass fragments studied could be due to a modern restoration.

All the red plaqué glasses studied (e.g. 4R, 2V and 3V) show the typical colour of copper ruby glasses. This colouring is due to very small colloids or nanoparticles of Cu⁰ mixed with Cu⁺ ions that give rise to an absorption band due to the surface plasmon resonance of colloids. Such an absorption band appears at around 565 nm in Figure 6. The corresponding chemical analyses (Table 2) indicate the existence of small contents of copper oxide. However, the red colour cannot be attributed to such copper oxide detected in the bulk glasses because the XRF analyses were made of the colourless base glasses of the corresponding plaqué glasses (the copper percentages were determined in the colourless base glasses once the red layers were removed). Therefore, the copper detected in the light bluish base glasses can only be due to Cu²⁺ ions that would give rise to a pale turquoise blue colour, obviously masked by the intense red ruby colour of the plaqué layer. The contribution of other chromophores detected (manganese and iron oxides) to the total glass colour is also masked by the red ruby layer.

As is shown in Table 2, all the glasses contain iron oxide (0.12–1.40 wt%) probably incorporated as an impurity of the raw materials, e.g. the silica sand without a special purification. Iron oxide in glasses is always in the redox equilibrium Fe³+/Fe²⁺. Both ions can be responsible for the final glass colour: Fe³⁺ ions give rise to a pale yellow colour, while Fe²⁺ ions give a clear blue colour. The simultaneous presence of Fe²⁺ and Fe³⁺ ions results in chromatic addition, which yields different green hues depending on the relative proportions of both ions. In glasses with intense colours (blue, red, green) the contribution of iron ions is generally masked by other chromophores with higher molar absorptivities.

Characterisation of the orange glasses (e.g. 2G, 4G, 2R and 1V) using visible spectrophotometry
was first carried out. As shown in Figure 7, the VIS spectra were dominated by a wide band centred in the 400–450 nm range. The band of the glass samples 2G and 4G is shifted to higher wavelengths, while the corresponding bands of the glass samples 2R and 1V are very similar and centred at about 400 nm. The common absorption due to the surface plasmon resonance of silver colloids in glasses appears in the 400–430 nm range, which produces a yellow colour. Nevertheless, silver can provide other colours to glass. For instance, a well known case is the Lycurgus cup (dichroic glass) whose red/greenish colour has been demonstrated to be due to very small amounts of silver and gold. It is also known that the ‘gold lustre’ and ‘red ruby lustre’ of majolicas made during the Renaissance period do contain silver and/or copper nanocolloids in the 5–100 nm range, the copper particles having smaller dimensions than the silver ones. This indicates the ability and versatility of silver to produce different colours and even iridescent effects in glassy matrices and on ceramic materials.

To clarify the nature of the orange chromophores in the glasses studied, TEM observations were carried out. Figure 8 shows the micrographs of some orange samples in which dark rounded forms, more or less aggregated, attributed to silver colloids (after qualitative analysis provided by the x-ray energy dispersive microprobe of the TEM equipment) were confirmed. The larger the size of the colloids or the more aggregated, the longer the wavelength at which they absorb and the more intense the colour they produce. Taking this into account it is possible to explain that the glass in which the absorption band appears at the highest wavelength (glass sample 4G) is the one showing the deepest orange colour, due to larger and more aggregated colloids (~0.7–2.0 µm).

The use of silver salts was well known by glass-makers of the Middle Ages and it probably continued during subsequent centuries. Following this medieval tradition, maybe in the 18th century the craftsmen producing stained glass windows added silver salts to the melt glass to obtain a bulk yellow glass, instead of producing a yellow coloured glass by means of a layer applied onto a colourless glass, which was the common medieval procedure (silver yellow glasses prepared by cementation, i.e. ion exchange of Ag⁺ ions from a silver salt by alkali ions from the glass surface). The appearance of an orange colour instead of yellow would be due to the simultaneous presence of silver ions and iron impurities in the glass melt. Such iron impurities probably came from the silica sand. Indeed, the chromatic result is due to two processes: (i) the iron ions can react with silver favouring the reduction of Ag⁺ ions (in silver salts) to Ag⁰ (in the glass melt), and (ii) the melt conditions at high temperature favour the further thermal aggregation of Ag⁰ to form larger colloids, i.e.

\[
\begin{align*}
(i) & \quad \text{Ag}^+ + \text{Fe}^{2+} \rightarrow \text{Ag}^0 + \text{Fe}^{3+} \\
(ii) & \quad \text{Ag}^0 \rightarrow (\text{Ag}^0)_n
\end{align*}
\]

Such larger colloids give rise to an orange hue rather than a yellow colour.

The use of silver as a chromophore agent for glasses, enamels and stains was stated by William Peckett of York (1731–1795) in his treatise, which contains many recipes. Newton & Taylor have pointed out the role of Fe²⁺ ions in providing adequate reducing conditions to produce silver based colours other than yellow (e.g. red).

In Table 3 the chromatic coordinates of the orange glasses are shown, as well as other parameters that define their colouring. These parameters allow the quantitative comparison of colour characteristics of each particular hue. In respect to chromatic coordinates x, y and z, the glass samples 2R and 1V are very similar, as is expected bearing in mind their corresponding visible spectra (Figure 7). However, the orange glass samples from Girona Cathedral have x and y coordinates that are relatively different from the former glass. This tendency is also confirmed by the dominant wavelength: glass samples 2R and 1V have a similar reddish orange hue compared to the Girona glasses, which have a yellowerish component (Figure 9). In regarding the colour purity percentage, the glass samples 2R and 1V have a purity intermediate to that of samples 2G and 4G. The latter is the glass
with the highest colour purity. The colour saturation of glass sample 4G is also the highest, followed by glass samples 2R and 1V with similar values, while glass sample 2G shows the clearest orange hue.

4. Conclusions

The application of characterisation techniques to historical stained glass windows from an archaeometric perspective demonstrated that glasses of the 18th century from Girona Cathedral fit well with a chemical composition of potassia lime silica glass with low CaO content. Therefore, they cannot be considered as medieval potash glasses, but as potassia lime silica glasses with higher chemical stabilities as compared with the medieval ones. However, their conservation state is very poor and show pathologies connected with chemical mechanisms such as hydrolytic attack and dealkalinisation, which cause many interconnected cracks and deposits in deteriorated areas formed as a consequence of detachments.

Glasses from Reus Priory Church and from Vitoria Cathedral have a soda–lime–silica glass chemical composition and their conservation state is acceptable. On the surface of the Reus glasses mechanical damage was observed, probably due to mechanical impacts on the outdoors side of the stained glass windows. As far as the grisailles are concerned, their chemical composition, morphology and poor thermal densification on the base glasses indicate that they were produced with cold paints.

Determination of the chromophores has indicated that blue colours are due to Co$^{2+}$ ions, violet to Mn$^{3+}$ ions, green to Cr$^{3+}$ ions, the plaqué red ruby contain Cu$^{+}$ ions and Cu$^{0}$ colloids and, finally, for the first time the orange colour of stained glass windows has been assigned to Ag$^{0}$ colloids of relatively large size and/or degree of aggregation. The formation of such Ag$^{0}$ colloids is attributed to the simultaneous action of reducing species in the glass melt (e.g. Fe$^{2+}$ ions from the silica sand impurities) and to the thermal aggregation of silver atoms during the melting process.

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