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# Analytical Report
## Red Stained Glass

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# Content

## Introduction

Stained glasses are commonly used for churches and cathedrals window panels. Stained glasses are coloured glasses that are cut and pieces together to create a design for decorative windows or doors. Glasses are made of a mixture of mainly silica mixing with other minerals depending on the type of glass. The mixture is then melted in a very high temperature, 1700 degree Celsius (British Glass, n.d). Stained glass is made by cutting sheets of coloured glass tracing the wanted designs. After that, it is painted over to create detail designs. The painted pieces are then fired in a kiln to fuse the painting on to the surface of the glass (Khan Academy, n.d.). The glass pieces are joined together with lead strips, forming a single panel. Cement glaze is applied to the panel to secure the glass with the lead and making it waterproof (Khan Academy, n.d.).

The investigate question focus in this report was to find out what are the elemental compositions of the glass sample. The technique used to answer the question was by using X-ray fluorescence spectroscopy (XRF). The finding of the glass sample composition could help to identify the raw materials that make up the glass. The purpose is to identify how the elemental compositions in the glass effect its characteristic. This could be acquired by comparing the result to a known information.

## Materials and Method

### Sample

The stained glass sample that was used for testing is a small broken piece of a red stained glass. It is 2.8cm wide at the widest part of the sample and 1.8cm long at the longest part (see figure 1 and 2). This stained glass sample was one of many pieces that came from St. Michaels on the Mount, which located in Lincoln, Lincolnshire. St. Michaels on the Mount was a church that was built in 1855-56 by Samuel Sanders Teulon (Historic England, n.d.). Now the place was renovated to be a hotel called 'The Old Palace' (Franklin Ellis Architects, 2012). According to the information from Historic England, all the stained glass window panels in the church were made and installed in the early $19^{th}$ century.


*Figure 1: Front side of the stained glass sample*


*Figure 2: Back side of the stained glass sample*

The red stained glass sample was painted over, which could be identified from the brush stroke left on the glass. This shows that this piece of glass was a part of a stained glass with painting design on it. In term of the glass sample condition, there are some white corrosions on the edge of the glass, which probably occur from the lead used for the stained glass framing. On the back side of the glass, there are also some white corrosions. The area contained dirt and dust which is probably was attracted by moisture.

**X-ray fluorescence spectroscopy (XRF)**

A XRF machine was used to analyse the stained glass sample. It is a non-destructive technique used to analyse materials surface for their elemental composition. The XRF machine work by projecting a primary x-rays energy on to the sample. The atoms in the sample react and are excited when it is hit by the beam, which generates secondary x-rays that are collected and analysed by the machine detector (Petiot, 2017).

XRF was chosen over other techniques because of many of its advantages. As mentioned it is a non-destructive technique. This means that the object being tested could be safe for future analysis. It also helps safe object with historic value or significant from being damaged. Furthermore, XRF is a very simple and quick method, while also producing accurate results. However, there are some limitations to this technique. XRF could only analyse the surface of the materials, it is not capable of adjusting the level of penetration. Another limitation is that it could not detect light element. The lightest elements that the XRF could detect is sodium (Na) with atomic number 11 (Roberts & Thornton, 2014). However, sodium may not be detected depending on XRF machine and also the material being tested and its element concentration.

XRF is a suitable analytical technique for the stained glass sample as it could identify the glass elemental composition. In addition, the technique is easy and quick to use without damaging the object in any way. The test was done using portable XRF Bruker S1 Titan. This portable XRF could be used in two ways. The first is handheld and pointing it to the material wanted to analyse. The second way is to stand the XRF with benchtop stand kit that comes with the product. Since the glass sample is small, the option of standing the XRF could be used. This option is more accurate than handheld method. This is because by holding the XRF window could move around, which may result in a less accurate data. Nothing was done to prepare the glass sample, the corrosions were not cleaned. The testing duration was set for 60 seconds. The elemental composition of the material tested is shown in a form of weight percent. The XRF analysis was carried out two times. Only the result from the second analysis is being focused in this report (see table 1). The reason why only the second result of XRF is used was because the data from each analysis were completely different. The elements detected were different and for the element that were detected in both analysis have different percentages. This shows that the data received from XRF may depend on the location where the XRF window is pointing at. It also the result of not cleaning the sample corrosion, which the XRF could pick up instead.

| **Oxides** | **Weight percent (wt %)** | **Oxides** | **Weight percent (wt %)** |
|---|---|---|---|
| $SiO_2$ | 45.231 | $As_2O_5$ | 0.7721 |
| MnO | 0.0264 | $ZrO_2$ | 0.045 |
| $Fe_2O_3$ | 0.706 | $SnO_2$ | 2.004 |
| CuO | 1.3524 | PbO | 44.331 |

*Table 1: Result of XRF analysis on stained glass sample*

**Result and Discussion**

The result from the XRF analysis shows the elemental composition of the glass sample. The glass sample contains a high level of Silicon (Si), 45.231%, and lead (Pb), 44.331%. The minor elements present in the glass are copper (Cu), 1.3524%, tin (Sn), 2.004%, Iron (Fe), 0.706%, and Arsenic (As), 0.7721%. The other elements detected are of very low percentages. These include manganese (Mn), 0.0264%, and zirconium (Zr), 0.045%. To explain the why these elements were detected in the glass sample, some information obtained from researching could be compared and applied.

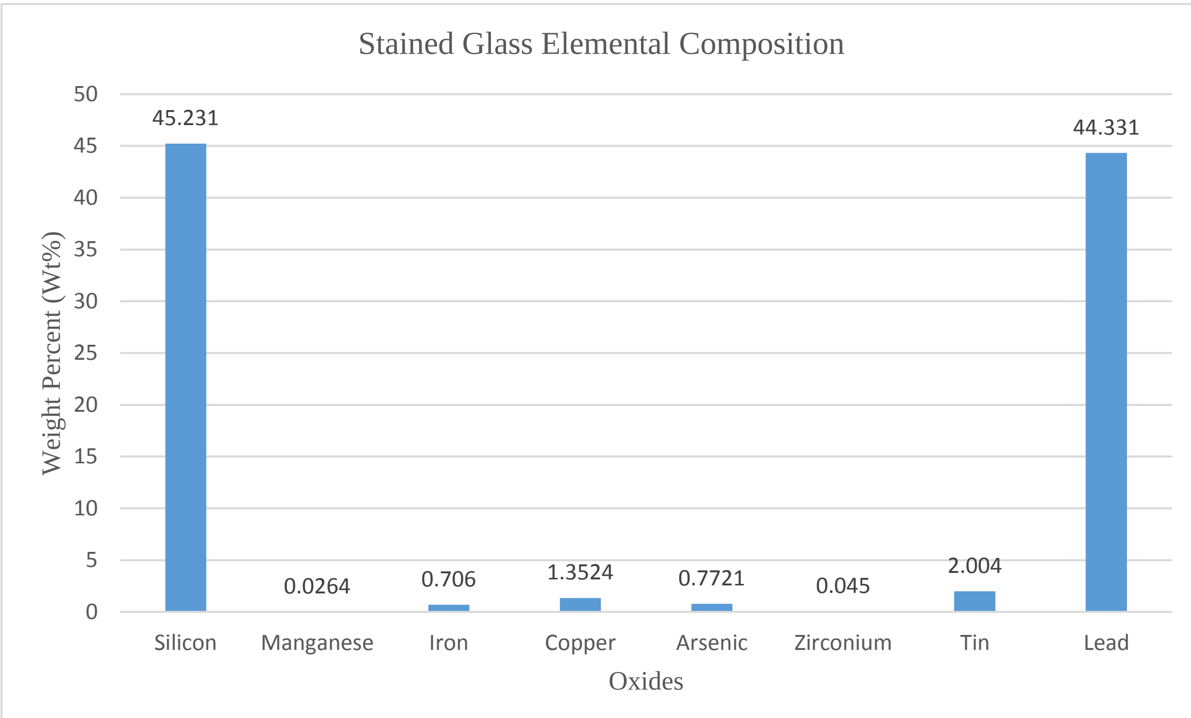


*Figure 3: Stained glass sample elemental composition*

Chapter 16 in a book called 'Through a Glass Brightly: Studies in Byzantine and Medieval Art and Archaeology Presented to David Buckton' gather some tests data and information that helped to explain the stained glass sample composition. The tests data were acquired by using Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDXA). Although the tests shown was done on an opaque red glass, the information could still be applied to explain the composition of the glass. This is because the elemental composition of opaque glass and the stained glass sample have a similar composition with a relatable pattern, but they are not exactly the same. For example, the opaque glass data shows a higher percentage of copper than the stained glass sample. This explains why the opaque glasses are opaque as copper does not only colour the glass, but also render it opaque. Also, more elemental compositions were detected in opaque glasses. The information acquired helped to reveal that the composition of copper in the glass is the source of the red colour. It also helped explain reasons of why each element was added to the glass composition. The advantage of adding lead oxide to the glass is it could help reduce the probability of the glass being devitrified (Freestone, et al., 2003). Tins are added to the mixture to prevent the glass from turning blue or yellow when melted (Bring, 2006). Adding too much tin could also make glass turn opaque (Bring, 2006). Tins act as a reducing agent. Some of tin detected may be a deposit element from bronze (copper-tin alloys). Iron is also used as a reducing agent for copper glass (Freestone, et al., 2003). Another book called 'Modern Methods for Analysing Archaeological and Historical Glass' also support that copper oxide was used for glass colouring. The copper oxide could be used to produce red glass for both transparent (rosechiero) and opaque (haematinone) glass (Moretti & Hreglich, 2013). It also supports that the iron oxide is used as a reducing agent.

One type of the red coloured glass that contains copper is known as copper ruby glass. Copper ruby glasses were manufactured from 1500 BC in Egypt (Bring, 2006). The recipe was lost when gold ruby glass was introduced and was revived again at a later time (Bring, 2006). Research done in the 18th century finds that lead and tin were an important component of making the colour (Bring, 2006). In the 1840s, a glass decorator Friedrich Egermann from Bohemian invented a ruby red colour that was made of copper instead of gold and used it to stain glass surface (Kerssenbrock-Krosigk, 2013). By using copper instead of gold help cut down the price of production making it easy to be mass produced. According to The Conservation and Art Materials Encyclopedia Online (CAMEO) copper ruby glass could contain arsenic, which could help explain why arsenic was detected. Arsenic could also be a deposit element from lead alloys.

Silicon detected is the main raw material composition that makes up the glass. The high level of lead in the glass sample suggest that it may be a lead base glass. However, the reason why sodium was not detected may be because the XRF have difficulty to detect element with a low atomic number. Another reason why the lead may be high is because of the white corrosion on the glass that is likely to come from lead corrosion. Some of the element could also be picked up from the paint on the glass, but it is not likely as the paint layer is very thin and the XRF easily penetrate through it.

## Conclusion

The XRF was an effective way of identifying the stained glass elemental composition. Though, the result may not be as accurate as it could be considering that the corrosions on the glass were not removed. In addition, the XRF limitation of not detecting light elements may cause the XRF to miss out some of the composition element contained in the object, such as sodium. The result data of elemental composition of the glass does correspond to the glass characteristic. There are data and information that supported that coppers were used as colouring source of red in glasses. One of the reason copper was used may be because of that coppers could be used instead of gold allowing it to be mass produced as it is a cheaper alternative. The other elements detected in low percentages are mainly added to add strength to the glass or act as a reducing agent for copper. The high percentage of silicon was expected as silica is the main component that makes up a glass. The high percentage of lead suggest that it a lead based glass or it could be the result of an inaccurate analysis.

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