The classification and characterisation of archaeological glass using multi-elemental analysis

Volume 1 of 2

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Submitted for the Degree of Master of Science (Research)

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Submitted to Institute of Technology, Sligo, May 2015

Abstract

The main aim of this thesis was to use non-destructive multi-elemental analysis to determine the major and trace elements contained in archaeological glass. There has been very little work done on elemental analysis of glass in Ireland, not least because destructive techniques are usually necessary in order to obtain a quantitative result which is representative of the entire glass object. For the purpose of this study, X-ray fluorescence (XRF) was chosen as the analytical method as it is capable of carrying out completely non-destructive multi-elemental analysis, something which is highly desirable for archaeological material.

A total of 328 beads, artefacts and fragments were analysed by XRF. The objects came from a range of sites from various locations across Ireland and included glass from the Iron Age through to modern times. Using elemental analysis, it was possible to identify the raw materials, including the type of modifiers that were used as well as the colourants and opacifiers used. It was also possible to examine levels of corrosion that the surface layers had undergone, based on the amount of elements such as aluminium that they contained.

The results from the analysis highlighted some interesting trends such as increased levels of aluminium over time in glass due to corrosion. Further analysis of larger groups of samples would make it easier to identify trends and changes in glass objects and could potentially highlight further indicators of chronology or geographical origin based on elemental composition.

Acknowledgements

I would like to thank the following people for their contributions, support and assistance during the course of this study;

-My supervisors, Dr. Fiona Beglane and Dr. Carmel Moran, for their continuing support, advice and encouragement.

-Dr. Marion Dowd and Chris Read of Institute of Technology, Sligo, Dr Matthew Stout, Geraldine Stout, Bairbre Mullee and the staff at the Irish Archaeological Field School, Paul Duffy and the Grassroots Archaeology Committee and Cóilín O'Drisceoil for providing the glass assemblages as well as their time and their expertise.

-The staff at the National Museum of Ireland for providing the glass assemblages from Dún Ailinne and Lagore Crannog, as well as their assistance in obtaining licences for the washing technique used on the artefacts.

-Dr. Ted McGowan and Maria Keeney, for their advice on analytical methods.

-The research staff at Institute of Technology, Sligo, in particular Mary McLoughlin for her unending patience and encouragement.

-The laboratory technicians at Institute of Technology, Sligo for their assistance and advice.

-My fellow post-graduate students, in particular Rita, Lisa, Micheal and Thorston, for all their support as well as their fresh insights and advice.

-My family for their support and encouragement.

Declaration

I declare that I am the sole author of this thesis and all the research presented within is my own, unless otherwise referenced. This work has not been submitted, in whole or in part, to any other University or Institute for any degree or qualification

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1. Introduction

This thesis will discuss the elemental analysis that was carried out on a variety of archaeological glass artefacts and examine the merits of carrying out such analysis on different types of glass. Since ancient times, glass has been a highly valued material, owing to its many desirable properties and pleasing aesthetic qualities. These include the ability to affect the colour, translucency and brilliance of glass objects by adding different materials when producing them. The atomic arrangement of glass is identical to a liquid rather than a solid, which allows it to be cut and shaped in a way that other solids cannot (Freestone 2009, 38). The composition of glass has remained fairly consistent over a long period of time, comprising of a glass former, like sand or crushed quartz, a modifier such as soda or potash, and finally a stabiliser such as lime. A variety of other inclusions, added either intentionally or unintentionally, are usually found, some of which can act as colouring agents and opacifiers (Goffer 2007, 124). Glass has been produced by ancient civilisations since the third millennium BC. Ancient Egypt and Mesopotamia are responsible for some of the earliest examples that are known, areas where ample raw materials existed for the craft. Later on, the Romans too had extensive knowledge of how to create a wide range of glass and evidence of the objects they created can be found all over Europe. They also developed the means to produce glass a lot more quickly and cheaply than had been done before (Renfrew and Bahn 2004, 345). This kind of expertise would not be matched again until the beginning of the Post Medieval period when highly decorative and more chemically pure glassware such as Venetian glass was produced.

In Ireland, as everywhere else, it seems that glass was a prestige item and was often associated with high status. From early prehistoric faience and blue-glass beads uncovered in burial contexts such as at the Bronze Age burial in Kilcroagh (Williams *et al.* 1991, 48), to medieval stained-glass windows (Moran 2010, 15), to the production of glass in one of the many glassworks which developed in the Post-Medieval period such as the Cork glassworks (Rynne 2010, 135), Ireland has plenty of evidence for a long association with glass objects. While there is little evidence of

what, if any glass, was actually produced in Ireland before the 16th century, there is at the very least evidence for the working of glass at some sites and there is no denying that they were objects of high importance given that they are often found at high status sites. For example, a wide range of beads were found at Lagore Crannog, Co. Meath and the royal site of Dún Ailinne in Co. Kildare (Hencken *et al.* 1950, Johnston 2007). Unfortunately, little is known about the elemental composition of archaeological glass in many cases in Ireland. While there has been some work done on categorising and examining collections, such as those found at the royal site of Dún Ailinne (Johnston 2007, 115), very few analytical studies have been carried out on glass assemblages. An example of one such study was scientific XRF analysis which was carried out on a group of glass beads uncovered from different sites including Garranes, Lagore and Clogher. The results determined what type of colourants were used and also allowed the beads, which ranged widely in colour and shape, to be classified according to percentages of trace elements (Warner and Meighan 1994, 53).

1.1 Aim of the study

The main aim of this study was to determine the materials which were used to make archaeological glass as well as the trace elements that they contained. The study also examined how non-destructive elemental analysis can be used to further understand the function of glass objects as part of the economy and society of past communities. These aims were be achieved by carrying out the following objectives;

- Creating a database of excavated glass samples from Irish archaeological contexts with the aim of evaluating what kinds of glass are most prevalent on sites and where best to focus the elemental analysis.
- Determining the materials used to produce archaeological glass sourced from a range of different time periods and locations in Ireland.
- Classifying the glass into different categories based on their major and trace elements.

- Investigating the social and economic contexts in which these glass artefacts were created and utilised.
- Creating a database of analytical results from excavated archaeological samples which can be used to compare future samples to.

A multi-disciplinary approach was necessary to carry out this research; integrating scientific analytical techniques with what was known about the artefacts from the archaeological reports and their context within the sites they were found in. The first important aspect of the research involved compiling a database of excavated archaeological glass samples to analyse the potential for analysing glass artefacts in Ireland. This helped to evaluate what kinds of glass are most prevalent on Irish archaeological sites and how to best focus the scope of the scientific analysis. Glass artefacts from a range of different sites underwent elemental analysis in order to determine the materials which were used to make them as well as to determine the trace elements they contained. This involved identifying the major ingredients of the glass as well as elements and substances associated with the colour, opaqueness and translucency of the glass. By examining these, it was possible in some instances to classify the glass into categories. This data could then be further used to investigate the social and economic contexts in which the glass was created and used. The final objective of the thesis was to create a database of results which can be used to compare future samples to.

The analysis of the glass involved using XRF (X-ray fluorescence), a non-destructive method capable of multi-elemental analysis, making it ideal for fragile archaeological material. It has additional advantages in that it is relatively cheap to run, requires little or no pre-treatment of samples and produces results quickly compared to other techniques. XRF has been used to great success in the study of not only archaeological glass, but metals, ceramics, pigments, stone and textiles to name just a few. The technique works by exciting part of a sample using X-rays and then analysing the backscattered radiation which is characteristic of the type and quantity of elements in the sample (Healey and Mecholsky 1984, 142, Janssens 2004, 129). This provides both quantitative and qualitative results. The success in the use of this

technique on archaeological material to date was examined and different methodologies were investigated with regards choosing and treating glass prior to examination.

All of the glass that was analysed during this study was done so with no destructive preparation beforehand. The elemental composition of glass is highly susceptible to corrosion and leaching of elements from its surface layers. Ideally, samples should have their outermost layers removed as archaeological glass will have a leached layer on its surface where the proportions of elements are significantly altered from the bulk of the glass (Henderson 2013, 614). The extent of this leaching is variable and depends on a number of factors including the original composition of the glass, surface area and environmental factors. Removing these layers using destructive polishing techniques is the only way to get an accurate, quantitative result of the original composition of the glass. However, such destructive techniques are neither desirable nor oftentimes feasible when dealing with precious archaeological material. In particular, small glass objects such as Iron Age beads, may have suffered corrosion right through to the innermost layers. There is no way to know if a result representative of the original composition would be obtainable before polishing and analysing the sample. This study aimed to investigate whether or not non-destructive analysis would be useful for gaining information about ancient glass, while bearing in mind that the outer layers of the glass may not be representative of the entire glass if corrosion is prevalent.

As mentioned, glass was a highly-valued material and analysis of it when found in archaeological contexts can provide information of trading routes and economies in past societies. This can be best achieved by performing scientific analysis on as wide a range of samples as is possible. Such work has been used to great success elsewhere such as in Britain and in mainland Europe, on various different types of archaeological glass (Henderson 1991, 123, Hirst 2000, 121, Henderson 2005, 475, Foster and Jackson 2009, 189, Bertini *et al.* 2011, 2750) . Since work has already been carried out classifying glass based on physical appearance in Ireland, it would be a basis for performing scientific analysis to see if the elemental compositions vary

according to these groups. It is hoped that utilising scientific analysis with desk based research will provide an multi-disciplinary approach which can be used to put the results into a social context.

2. Background to the study

2.1 Science of glass

2.1.1 Manufacture of glass

Much of what is known about ancient production of glass, and in particular about medieval production of stained glass windows, comes from the twelfth century writings of a German Benedictine monk called Theophilus (Kemp 2000, 108). His work, entitled '*On the Diverse Arts*' detailed how glass was made using one part washed sand to two parts beechwood ash, which produced a soda-lime glass (Charleston 1991, 239). From ancient times, glass has been consistently made up of a glass former, such as sand or quartz pebbles (SiO_2), a modifier, such as soda (Na_2O) or potash (K_2O), and a stabilizer such as lime ($CaCO_3$). In addition, glass may contain a variety of colouring agents or opacifiers, either intentionally or unintentionally. Sometimes cullet (broken pieces of glass) would also have been added with the effect of lowering the overall melting point (Goffer 2007, 124). From a scientific point of view, the composition of ancient glass was typically a soda-lime glass with elemental composition of approximately 73% SiO_2, 23% Na_2O and 5% CaO (Gratuze and Janssens 2004, 665).

It is likely in ancient times that often only two materials were purposely added in glass production; the sand/crushed quartz for silica and the plant/mineral deposits for the soda, with the lime most likely introduced as impurities (Gratuze and Janssens 2004, 665). The unusual structure of glass allowed it to be worked in ways which were not possible with other materials available to ancient people. Most solids have crystalline structures, which causes them to break preferentially in certain ways, parallel to rows of atoms. In the case of glass, this arrangement of atoms is such that it is more like that of a liquid, a condition which can be described as being 'amorphous'. This allows glass to be cut or ground in any way or shape with the right skill, and it also means that components can be incorporated in the structure that affect the colour, brilliance, hardness and transparency of the finished product

(Goffer 2007, 114-115). A diagram illustrating the structure of glass compared to a crystalline structure can be seen in Figure 2.1.

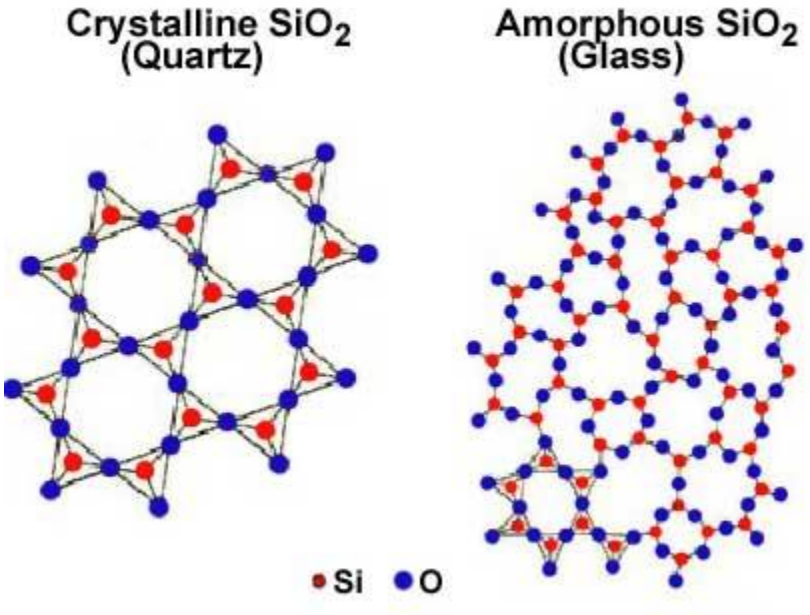

Figure 2.1: Structure of glass compared to crystalline solids (*Structure of glass*)

When heated until melted and then cooled rapidly, silica sand forms silica glass. The soda or potash is added to the silica sand in order to lower its melting point from 1700°C to 1000°C, a temperature which was attainable in ancient furnaces (Goffer 2007, 115). This makes the soda/potash a flux; a material which has the effect of lowering the melting temperature (Bray 2001, 42). Lime has the benefit of 'stabilizing' the glass, making it more resistant to dissolution or weathering as well as making the glass easier to shape before it cools down. Most ancient glasses that do not contain lime are generally in an advance stage of decay or do not survive at all, however a careful balance must be struck as too much lime in the glass structure will cause the object to quickly degrade (Goffer 2007, 117-8). The mixture is heated slowly to above 1000°C and held for several hours before being cooled back to about 1000°C. At this temperature, it is viscous and can be formed into various shapes by blowing and casting. The glass can also be subjected to thermal processes after cooling. This can be in the form of annealing to remove internal stresses and reduce hardness. Tempering, another type of thermal treatment, can also be carried out to

reduce brittleness and increase strength. Sintering is a process which causes the particles in the glass to conglomerate, which is desirable as it causes them to become a more coherent mass, making the glass more rigid and rugged. Both processes involve heating the glass to just below melting point, however tempering also involves rapid cooling to change the physical properties of the piece (Goffer 2007, 115, 125-126).

Glass is known to be a difficult material to provenance for several reasons. Firstly the main raw material it requires, sand, is highly likely to be composed of many different and varying amounts of minerals and rock particles depending on the topographical region of the source (Wilson and Pollard 2005, 513). There is always the possibility that glass from different sources will be added together and any colorant or broken glass, known as cullet, which is added to the mixture will further complicate the process (Pollard and Heron 2008, 183). All these potential variables in any given sample of glass indicate just why it is so difficult to provenance. Another reason is that molten glass will often partially flux any container it is in, introducing yet more impurities (Wilson and Pollard 2005, 513). The nature of glass which gives it the ability to take on so many different properties is the very reason that it can be so difficult to account for the vast variety of trace elements it may accumulate during its production.

2.1.2 Colouring of glass

The production of glass would certainly have included the use of closely monitored and controlled quantities of colorants, opacifiers and more to produce the various tints and colours of glasses (Henderson 1991, 123). Colouring of a glass is usually achieved with either the presence of transition metal ions or metallic atoms which are added during its production. Opaqueness on the other hand occurs when a homogenous immiscible phase is distributed within the structure (Pollard and Heron 2008, 163). Sometimes colourants were added in the form of natural minerals such as malachite. In other cases the additive was produced synthetically, such as by

heating bronze to produce copper oxide (Shortland 2012, 105-106). Different colours could be achieved from the same element depending on its oxidation state and its position within the glass (Pollard and Heron 2008, 163).

The most common and generally unintentional colouring of glass was the distinctive 'bottle green' colour, which was caused by iron impurities, both ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions, in the sand (Goffer 2007, 120). A dark green tint would likely be caused be ferrous iron as ferric iron tends to give only a weak yellow colour. It is a mixture of these two which creates glass which has an olive green hue (Bhardwaj 1979, 42). The Romans discovered that they could neutralise this colour by adding small amounts of pyrolusite to the glass mixture, a mineral made up of mainly manganese oxide (MnO_2). Used on its own without the presence of iron, pyrolusite would give a violet tinge to the glass, but when added to a glass mixture with iron in it, it would mask the green colour caused by the iron, giving the glass a grey/clear colour.

Bright blues also appeared in ancient glasses, often caused by the addition of cobalt (Co) (Goffer 2007, 121-122). Blue tones ranging from bluish-green to a very pale blue could also be achieved by adding cupric oxide (CuO) to the glass while adding cuprous (Cu_2O) oxide resulted in a reddish brown colour. Nickel oxide (NiO) is another powerful colourant, usually producing a brownish green colour. However in cases where there are several colourants used in the glass, it can be difficult to determine how they interacted to produce the specific colour of the object (Bhardwaj 1979, 42-43). Other factors in the production of the glass will also affect its colour, such as the atmosphere in the furnace, the chemical environment and the variations in the heating cycle (Henderson 2000b, 29).

There is substantial evidence to show that ancient people were very much aware of how to control colour and other aesthetic properties of glass. The Egyptians are known to have utilised cobalt, manganese and copper to achieved different colours and they were also aware of the use of stibnite (antimony sulphide; Sb_2S_3) to give glass an opaque white colour. Antimony was also discovered to be a decolourant when used in the right amount (Lambert 1997, 111). The study of both colourless and

blue glass from Malkata in Egypt allowed the additives which gave the blue glass its distinctive hue to be distinguished. It was found that some of the blue glass was coloured by adding cobalt. This was produced from alum sourced in the Western Desert of Egypt (Henderson 2013, 56). The Romans also displayed great skill when it came to knowledge of colourants and other minerals. They were known to add small quantities of silver mineral when producing glass to give it a yellow colour. They even discovered that adding small amounts of gold could result in a variety of different shades of red or even a dichroic quality in the glass. Dichroism in glass means it appears two different colours; one when light is reflecting off it and another when light is transmitting through it This is caused by adding metallic elements such as gold and silver to the glass during production (Goffer 2007, 122). While the Romans were by no means the only ancient peoples capable of producing dichroic properties in glass, the vessels they created were particularly impressive. From analysis of the Lycurgus cup, a fourth century AD artefact, it was determined that the effect was achieved by adding small amounts of metallic silver and gold to cause selective absorption and scattering of light (Goffer 2007, 132).

Aside from the highly unique and decorative pieces that were produced during this time, there is considerable evidence that Roman glassmakers continued to innovate and experiment with ways to more easily achieve results that had already been obtained. Different substances from different sources were added to glass mixtures gain the same desired end results. One such example can be seen as in glass objects recovered at a high-status Roman burial in Bocholtz in the Netherlands. Analysis of a variety of colourless glass artefacts from this site showed that while the objects were most likely made using the same silica and lime sources, varying trace elements present were indicative of using different sources and types of antimony to decolour it (Huisman *et al.* 2009, 413). Examples of Roman coloured glass can be seen in Plates 2.1 and 2.2.

Plate 2.1: Bottle green Roman glass (http://ancientglass.wordpress.com/category/ancient-glass/roman-glass/)

Plate 2.2: Cobalt blue Roman glass vessel (http://pinterest.com/shouning/archeology/)

Glass, and in particular window glass, was sometimes painted to achieve a desired colour. The paint was initially made by mixing copper oxide (CuO or Cu_2O) or iron oxide (Fe_2O_3), ground cullet and gum arabic (a type of hardened tree sap) with a binder such as urine or wine, before applying the mixture with an animal hair brush (Wigelsworth 2006, 38). This produced a layer of reddish-brown colour which was then 'burnt' on to the glass to help preserve the colour (Tallis 2011, 96). This term is actually misleading as the paint fuses with the glass rather than burning to it (Caen 2005, 245). Other coloured paints came later, including a particularly common paint known as 'yellow stain' or 'silver stain', which was achieved using a solution of silver nitrate ($AgNO_3$) or silver oxide (Ag_2O) instead of iron oxide. This could be used on uncoloured glass to achieve a range of colours, from yellow to bright vivid orange, and was particularly well-used after its introduction in the fourteenth century (Kibler 1995, 889).

2.1.3 Glass corrosion

Corrosion develops on glass due to the selective leaching of elements from its surface (Plate 2.3). The corrosion layer is essentially a 'leached' layer where the ratios of the elements are significantly altered from the bulk glass (Henderson 2013, 614). Corrosion layers may develop on glass for a number of reasons many of which relate to the environment that the glass is in. However, the most important factor in most cases is the original elemental composition of the glass which determines the resistance of the glass to agents which can cause corrosion such as water, acidic and basic solutions and other atmospheric substances (Pollard and Heron 2008, 166). With regards to medieval window glass for example, potash-based examples were highly susceptible to weathering due to the high alkalinity of the glass (Moran 2010, 17). The extent of corrosion can also be dependent on the thermal processes to which

Plate 2.3: Glass objects with corrosion (http://www.cmog.org/blog/tag/iridescence/)

an object was subjected to. For example, glass which has been annealed corrodes more slowly than glass which has not been. Weathering occurs when glass is affected by water combined with atmospheric gases such as sulphur trioxide (SO_3) and carbon dioxide (CO_2) (Pollard and Heron 2008, 166-168). It can result in changes in the elemental concentration of the glass such as variation in the silica content (Bhardwaj 1979, 39). Soda lime glass is not as vulnerable to this kind of weathering as potash glass. Examples of window glass made of soda lime glass were recovered in England and Scotland on Early Medieval sites which were found to have been in almost perfect condition with regards to colour and translucency (Moran 2010, 17)

While weathering of medieval windows has received some attention, corrosion in buried glass has received very little. Ground water can interact with buried glass material affecting the stability of the object. This includes development of a flaky coating and iridescence on the surface of the object (Pollard and Heron 2008, 178). This is due to the sodium or potassium in the glass leaching out and leaving only porous, hydrated silica behind. The decay of glass is a complex matter, affected by many different factors and it is not perfectly understood. However most experts would agree that it occurs due to the preferential leaching of alkali ions to be replaced by hydrogen ions, as was already discussed above (Wayne Smith 2003, 94). The reaction begins at the surface of the object and spreads inwards (Varshneya 1994, 398). Studies of corrosion in ancient Roman glass fragments revealed a series of corrosion layers continuing steadily down to a depth of around 400μm, with spaces between each layer and a crust of precipitation on the surface. Micro XRF scans down through the corrosion layers showed that several cycles of leaching seemed to have caused the formation of the corrosion on the fragments (Zucchiatti 2004, 549).

Investigations into the reaction of soda lime glass showed that a double diffusion takes place in which sodium ions (Na^+) move from out of the glass to be replaced by hydrogen ions (H^+). This results in an increase in the amount of hydroxyl anions in the corrosion layer which in turn increases the pH. This increasingly basic solution causes the process to accelerate. In general, glasses are very resistant to damage in acid solutions, as the hydroxyl anions are usually neutralised quickly. Pure silica is highly resistant to aqueous solutions when at neutral pH but once the pH reaches above 9, it begins to dissolve and moves into the solution as $Si(OH)_4$. The depth to which the weathering occurs varies a great deal, depending on the elemental composition of the glass and the environment around it (Pollard and Heron 2008, 166). Potash glass is even more susceptible to corrosion than soda-based glass. It is thought that potash-based glass has a more open chemical structure owing to the larger size of the potassium ions compared to sodium ions. This allows the glass to be more easily affected by ground water (Pollard and Heron 2008, 173).

2.2 Principles of X-ray fluorescence (XRF)

X-ray fluorescence (XRF) analysis is a method of qualitative and quantitative elemental analysis which is based on the ionisation of the atoms of the material in question by a beam of primary X-rays. By analysing characteristic radiation emitted by the material, it is possible to determine the identity and abundance of the elements present (Janssens 2004, 129). It can be used to identify not only the major raw materials such as sand and fluxing agents, but also additives including colourants and opacifiers. This in turn can provide information about the technology used in the production of the glass. XRF can also be used to study glass corrosion, specifically by analysis of the elemental composition to better understand the mechanism of the corrosion. XRF has been successfully used on not only archaeological glass, but ceramics, paintings, stone, metals, pigments and paper to name just a few (Stuart 2007, 238).

Within atoms of any given element, the electrons circle the nucleus in fixed paths known as orbits or shells. Electrons in a shell have a fixed amount of energy. If an electron absorbs energy, it will move to a higher shell and is said to be 'excited'. Excited electrons are unstable and will quickly fall back to the fixed lower shell, releasing a definite amount of energy in doing so. The underlying principle of the XRF technique involves the release of a beam of energy in the form of an X-ray. This X-ray is referred to as the primary X-ray and is emitted from an X-ray tube (comprised of an anode such as tungsten) in the machine. The primary X-ray hits the sample and as a result, atoms have vacancies created in their inner shells due to electrons becoming excited and moving to a higher shell. As these electrons return to the ground state (or 'deexcite') they release the energy in the form of a secondary X-ray. This secondary X-ray is characteristic of the element in the sample. When some of these secondary X-rays escape from the sample, they are measured and compared to known values for each element, which can identify and quantify the sample in question (Pollard *et al.* 2007, 101, Pollard and Heron 2008, 38) (Figure 2.2).

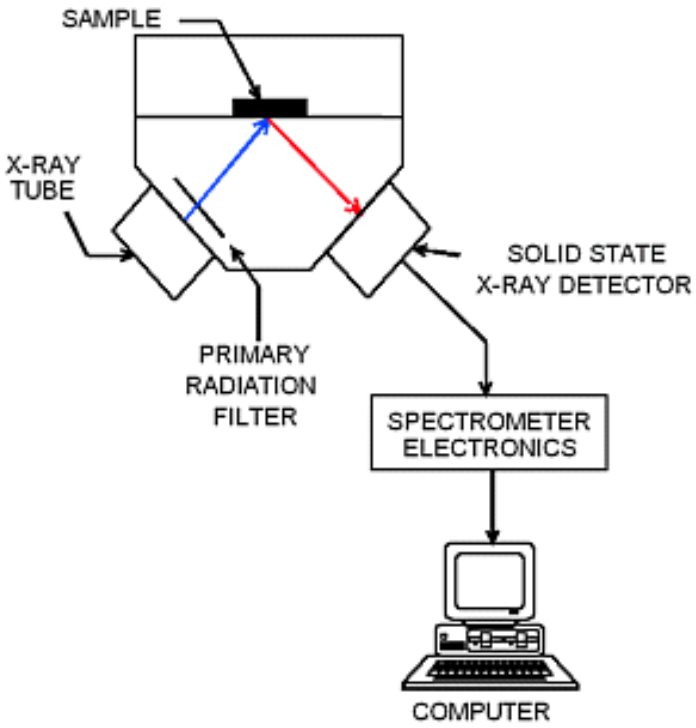

Figure 2.2: Diagram of how XRF works (http://www.swxrflab.net/xrfinstrument.htm)

The major advantage of this analytical technique is that it can allow an entirely non-destructive analysis (Polikreti *et al.* 2011, 2890). While X-rays deposit relatively large amounts of energy in a sample, observation over years of carrying out this kind of analysis has shown that the effects on the appearance and integrity of the objects are negligible (Zucchiatti 2004, 546). In addition to this, the technique also has the added advantages of its high sensitivity and the fact that the material under study requires little or no pre-treatment prior to being analysed (Carmona *et al.* 2010, 257). Many alternative analytical techniques require dissolution procedures which may include costly reagents or acids that are destructive to the samples. XRF testing also has an advantage in its speed; results obtained by the instrument are available almost immediately and the technique is cost effective when compared to other laboratory techniques (Jacobs 1996, 6-7). XRF does have its share of limitations however. It cannot, for example, carry out isotopic analysis. Another disadvantage of XRF comes from the fact that it is not very effective when attempting to test very small samples, for example layers of paint (Zieba-Palus 2006, 718). As well as this, elements lighter than sodium cannot be detected and any element lighter than

magnesium (atomic number = 24) require a vacuum to be detected (Lee and Quirke 2000, 106). Another limitation is that XRF is a surface technique, as it only measures the components of the glass to a depth of around 30μm and corrosion layers can extent well below that depth (Kaiser and Shugar 2012, 458).

According to Craig et al (2007, 2013) most elemental XRF studies carried out on archaeological material have been focused on obsidian and metals. He states that XRF is capable of measuring ten to thirty elements in obsidian with great precision. This sort of standard has been consistently achieved in studies of obsidian from Mesoamerica and New Mexico (Craig *et al.* 2007, 2013). The instrumental limit of detection (ILD), which refers to the lowest quantity of an element that can be detected but not necessarily accurately measured, is in the low parts per million (ppm) range for most elements. For example, Rosseau (2001, 42) notes ILDs of 3.9 ppm, 9.8 ppm and 1.3 ppm for silica, chromium and copper respectively. The limit of determination (LOD) which refers to the lowest amount that can be accurately measured, is several times higher than the ILD but still in the low ppm for most elements. Silica, chromium and copper have LODs of 267 ppm, 20 ppm and 24 ppm respectively (Rousseau 2001, 42). Silica which has an atomic number of 14, has a much higher ILD than either chromium or copper which have atomic numbers of 24 and 27 respectively.

There are two different types of XRF based on the way the secondary X-ray is analysed. Wavelength dispersive X-ray fluorescence (WDXRF) measures the wavelength of the secondary X-ray and energy dispersive X-ray fluorescence (EDXRF) measures its energy (Pollard *et al.* 2007, 102). Generally speaking, WDXRF has better limits of detection and is more precise than EDXRF. However, the difference is small enough to often be considered an acceptable compromise, since EDXRF is usually quicker to generate results and is cheaper to purchase. An XRF instrument is generally intended for the analysis of solid samples, most commonly in the shape of a disk but the instrument can be modified to accommodate larger or irregular shaped samples (Pollard and Heron 2008, 44-45, 107).

2.3 Preparation of glass samples

Despite the fact that XRF is a non-destructive technique, preparation of glass samples is often carried out to varying extents, usually involving polishing or drilling of the surface layers. This may be done in order to provide a more homogenous sample, to examine under a layer of corrosion or thick dirt or simply to provide a sample suited to fitting in the machine. Corroded layers on the glass must also be removed if a result representative of the entire glass is to be obtained, as they may have had alkali elements leached out into the environment. One example was the XRF analysis of two glass artefacts from the Hessisches Landesmuseum Kassel, known as the Reichsadlerhumpen and the Flacon. Tiny grains of around 100µg were removed from the base of each with a diamond drill which provide a quantitative result for the glass (Wegstein *et al.* 1997, 1057-58).

Sample preparation of glass which is much more destructive is sometimes used. Such was the case in the analysis of a range of window glass fragments recovered from the excavations from Basing Grange in Hampshire, England (Dungworth 2009). Here, the forty-seven fragments under analysis were mounted in resin and then ground and polished to expose a cross-section. While there is no specific reason given for this particular treatment, the fragments are described as having been 'highly weathered with flaky iridescent surfaces' so it is likely the treatment was carried out for the purpose of removing the corrosion layer. Pollard *et al* (2007, 111) note that most analysis using electron beam is carried out on prepared samples of thin polished sections which have been cut and mounted to fit standard sample holders. They also note that some instruments have larger sample chambers to allow analysis of large unprepared samples, suggesting that the process may sometimes be due to a requirement to fit the sample into the instrument rather than a necessity needed to gain accurate results (Pollard *et al.* 2007, 111).

Analysis of glass which is not pre-treated by polishing or grinding is possible but it may depend on the state of the sample. For example, in the analysis of the glass beads from Pylos, as was discussed in Section 2.2.2, seven of the eighteen beads

analysed were not considered to have given accurate results, due to the heavy corrosion they contained (Polikreti *et al.* 2011, 2891).

Some experimental work has highlighted that care must be taken in interpreting results obtained from XRF analysis, even if the surface appears non-weathered or has been subjected to light polishing. Even if there is no visible indication of corrosion, depletion or enrichment of certain elements may have occurred in the surface layers of the object, either through age, environmental factors or even in the method of production. Cox and Pollard (1977, 45) examined six samples of flat glass, of varying colours and dates, which were subjected to XRF analysis. Prior to the initial analysis, the samples were washed in acetone. A second analysis was carried out after polishing the same surface to a depth of 6μm and a third analysis on the same surface polished to a depth of 500μm (Cox and Pollard 1977, 45). The results of the experiment showed that in some samples, the surface layers, even those exposed with light polishing had been depleted of some lighter elements such as sodium. However they did not have particularly high levels of heavier elements in their composition.

Scientific analysis can be used in conjunction with typological studies which have been carried out in order to better understand assemblages of glass beads. Work into classifying beads by type has been published by many different authors including Kohl in 1977 and Guido in 1999 (Hirst 2000, 121). Guido's 1999 account of Anglo-Saxon glass beads and parallels which occur on the continent provides a comprehensive and chronological study of beads. Typological and statistical analysis of glass beads on sites is the simplest type of analysis of finds, and publication of such findings can help in analysis of distribution within regions. It also provides a basis for choosing samples on which to perform elemental analysis. Different criteria for classifying beads include colour, translucency/opaqueness, shape, perforation or lack thereof, size, decoration and more.

2.4 History of glass

The ability to make small glass objects such as beads and bracelets is known to have existed in certain parts of the world since the third millennium BC but it was only in the 2nd millennium BC that glass started to be produced in any quantity (Henderson 2000b, 52). Obsidian, a natural glass formed under intense geological pressure, was the only such material used by prehistoric people prior to this (Gratuze and Janssens 2004, 670). This black volcanic substance was often used to manufacture weapons and tools such as those found on Milos Island, Greece (Plate 2.4). Faience, a sort of '*pre-glass*', was first produced before 3000BC in Egypt and was created by coating a powdered quartz core with a vitreous alkaline glaze (Renfrew and Bahn 2004, 344). An example can be seen in Plate 2.5 which depicts two different Egyptian faience ushabtis. It was populations in the Near East which most likely produced the first artificial glasses, comprised of glazed quartz, steatite and faience (Gratuze and Janssens 2004, 670).

It cannot be said with absolute certainty how glass making was first discovered although there are several suggestions as to how it may have come about. Some suggest it was during the melting of metal ores containing silica, while others propose that it was a continuation of the glazed pottery craft. Early glazes, such as those found on ceramic tiles from Egypt and Mesopotamia, have a very similar composition to glasses, which would support the latter idea (Luckner 1994, 79). Glass was often used for decorative rather than functional reasons and was often seen as a substitute for precious stones. There are records of ancient Mesopotamian cuneiform glassmaking recipes which refer to glass as 'artificial lapis lazuli' (Henderson 2013, 9). Henderson (2013, 10) suggests that other colours of glass were also produced by ancient people in an attempt to emulate semi-precious stones. He likens pale blue glass to turquoise, cobalt-blue glass to lapis lazuli and possibly opaque yellow glass to gold.

Plate 2.4: Obsidian tools from Milos Island, Greece. (Zekkos and Athansopoulos 2004)

Plate 2.5: Egyptian blue faience ushabtis (*Egyptian blue faience ushabtis*)

A common theory regarding glass making is that the raw material was produced in primary workshops or centres throughout the Middle East and then traded to other areas of the Mediterranean and elsewhere in Europe. This glass could then be used in 'secondary' workshops to create various glass objects (Huisman *et al.* 2009, 414). This theory is supported by the remains of a number of ovens found in Palestine which may have been used for large-scale primary glass production. There are also documented sources from ancient writers including Strabo, the Greek geographer (born c. 64BC) and Pliny the Elder, the Roman philosopher (born c. 23AD), which mention the Levant as being a major source of glass (Freestone 2009, 77, Huisman *et al.* 2009, 414). It is through analysis of the raw materials and in particular trace elements within glass samples that greater knowledge can be gained as to where glass may have been sourced, as this factor varies based on geography and geology.

Some of the most intricate and skilfully crafted examples of ancient glass were created by the Egyptians. The technology was likely introduced to Egypt from Syria and was particularly well known after *c.* 1450BC (Tait 1991, 26). It was around this time and place that the first real glass vessels started to appear. The oldest known glass furnace, located at Tell el-Amarna and dating to 1350BC, shows that these vessels were made by shaping the molten glass around a core made of clay which was later scraped away (Renfrew and Bahn 2004, 345). The raw materials were melted in furnaces built of sand and clay, such as the reconstruction shown in Plate 2.6. The vessels could be reheated at a later time and decoration applied to the

Plate 2.6: Reconstruction of an Egyptian glass furnace (http://www.interestingthings.org/page/2/)

exterior (Lambert 1997, 109). True casting, achieved by pouring molten glass into a clay mould, developed soon after this. The sand used by Egyptians in their glass production is known to have had a high iron content, and the alkali source most likely came mainly from natron or sodium bicarbonate ($NaHCO_3$), both of which the country had access to in abundance (Lambert 1997, 110). Natron is a mineral which occurs in locations such as the Wadi el-Natrun Desert and in areas in the Besheira province of Lower Egypt which is a source known to have been worked in antiquity. It has a composition of mainly sodium carbonate, sodium bicarbonate and impurities of sodium chloride and sodium sulphate (Henderson 2000b, 26).

Another prehistoric civilisation which produced high quality glass and contributed greatly to glassmaking was the Roman Empire. Large and varied collections of Roman glass have been found throughout the Roman world (Plate 2.7). The Roman World was likely introduced to glass following conquests of Syria and Egypt beginning in 63BC (Lambert 1997, 110). It was the Romans who developed the quick and cheap method of glass-blowing, sometime around 50BC (Renfrew and Bahn 2004, 345) (Plate 2.8). Their expertise with the production of glass was unrivalled in the ancient world. Despite this however, finds of Roman glass vessels are relatively rare compared to other types of glass (Renfrew and Bahn 2004, 345). The Romans also developed a tool known as a 'cutting wheel' which far surpassed the decorating techniques which had been utilised previously and was used to carve designs into the glass by holding the object to the wheel as it was turned (Chown 1988, 51). A

Plate 2.7: Collection of Roman glass vessels (*Collection of Roman glass vessels*, 2009)

good example of the skill of Roman glassmarkers is the Lycurgus cup, a vessel with a delicate glass frieze which depicts a scene from the myth of King Lycurgus (Quinten 2010, 404). It also has a striking and impressive dichroic property. The Lycurgus cup appears green under normal conditions, but red when held to the light as can be seen in Plate 2.9.

Plate 2.8: Glassblowing technique (*Glassblowing technique*)

Enamelling, the process of fusing glass to an object of copper alloy, silver or gold to decorate it, was another use of glass. It first occurred in Mycenaean goldwork from the mid-second millennium BC and there are some particular fine examples dating from medieval times. It was achieved by either applying a fine wire outline to the substrate or else by carving out a hollow in the metal. This was then filled with powdered glass, heated in a furnace to melt the glass and then polished (Ogden 1992, 39). One of the most striking examples is the Battersea shield, a decorative Iron Age bronze shield with inlays of red enamel (Plate 2.10).

Plate 2.9: The Lycurgus cup, showing its dichroic properties (*The Lycurgus Cup*)

Plate 2.10: The Battersea shield with red enamelling, an Iron Age shield found in the River Thames (*The Battersea shield*)

Glass-making industries in the medieval period were often in isolated locations, situated near woodlands within reach of a local sand source. One of the most important factors when it came to the quality of the sand was how much iron oxide it contained as even trace amounts would impart a green hue to the finished product. As such, most medieval glass has a distinctive green hue unless other colourants or decolourants were added. While the average medieval glass-maker most like did not need to be too discerning with their raw materials, there is evidence of some sand sources in particular being utilised due to their purity. In England, it was found that white sand from Lodsworth Common and Hambledon Common were used which were able to produce glasses with very pale green colours (Charleston 1991, 238)

Advances in glass-making techniques during the medieval period in Europe was closely associated with the expansion of Christianity, as coloured glass started to be used in stained-glass windows in churches (Plates 2.11 and 2.12). This could include coloured glass which was cut and arranged into a pattern as well as that which had paint fired on to it (Kemp 2000, 108). Most commonly, windows were found in churches, depicting biblical scenes and early Christian saints (Bunson 2004, 847). Stained glass has the ability to create a unique lighting, one which was believed to have a special significance in a religious context, as well as having mystical and mysterious qualities (Rebold-Benton 2009, 174). These windows were also able to impart religious knowledge and stories to those in attendance at the church, many of whom could not read or write. There are records of stained glass being described in Europe as the 'Bible of the Unlearned' (Bunson 2004, 847). In many parts of Europe there are numerous fabulous stained-glass windows and fragments preserved *in situ* such as in Sante Creus in Spain, Obazine and Bonlieu in France and Altenberg and Doberan in Germany. In Britain there have also been many impressive stained glass windows and fragments found at monasteries such as those at Fountains and Winchcombe (Wouters *et al.* 2008, 101-103). In fact, glass production as a whole seems to have been strongly linked to Christianity, with the only evidence for glass furnaces of this period coming from monastic sites. One of the most important was

Plate 2.11: Stained glass window depicting Daniel from Altenberg, 12th century AD (*Altenberg stained glass window*)

Plate 2.12: 13th century window from Chartres Cathedral (*13th century window from Chartres Cathedral*)

at Glastonbury Abbey where four furnaces were found with fragments of crucible and molten glass (Willmott and Welham 2011).

The next main advancement in glass production technology came in the mid-seventeenth century, which saw the production of so called 'lead crystal' in England, a glass with a high proportion of lead oxide (Wouters *et al.* 2008, 127). The lead content allows the glass to be worked over a wider range of temperatures as well as giving the finished product a higher density (Campbell 2006, 23). The raised density also raises the refractive index of the glass which causes the glass to appear more '*brilliant*' than other glass. Full lead-crystal is traditionally defined as containing at a minimum 30% lead oxide although any glass containing at least 24% can be described as lead crystal. Glasses containing less than 24% lead oxide are simply called crystal glass (Lefteri 2002, 147).

2.5 Analysis of glass found outside Ireland

XRF has been used extensively to analyse archaeological material. Examples of the use of XRF in determining production methods and sources of materials for glass production includes work carried out on Mycenaean sites such as Pylos in Greece (Polikreti *et al.* 2011). Pylos was a significant part of the trade network of Mycenean and Minoan centres during the Bronze Age and large amounts of glass beads had been recovered at this site. What was unusual about this was that no moulds were ever found, leading to the belief that the glass had been imported. The aim of the scientific analysis was to determine the composition of a number of glass beads and compare this data to that of other glasses from Egypt, Mesopotamia and mainland Greece. A number of uncorroded beads which had survived at the site were analysed using XRF analysis. From this analysis, the raw materials of the glass could be determined; a silica source, a soda flux and a colorant. Eleven of the beads were of a composition similar to late Bronze Age glasses which were commonly found in the Eastern Mediterranean. Some of the glasses were found to be most likely of Mesopotamian origin due to a characteristic low level of zirconium (Zr) and titanium (Ti). From these objects, a number of blue examples were found to be coloured using copper additives. In contrast, four dark blue beads showed titanium and zirconium levels similar to those found in Egyptian glasses of the same period. In addition, the dark blue colour was found to have been due to cobalt additives. The lack of arsenic in the cobalt-coloured beads excluded many potential sources of cobalt including the Erzgebirge ores from eastern Germany. The ratios of cobalt, manganese, nickel and zinc were in fact consistant with coralliferous alums found in parts of Egypt. These results show that these particular blue glass beads were imported from Egypt (Polikreti *et al.* 2011, 2890-2894). This is a good example of how XRF can be used to provenance glass, and in this particular case highlighted how the populations at Pylos traded in both Egyptian and Mesopotamian glass.

Obsidian, as mentioned already, is a kind of naturally occurring glass and XRF has been successfully used to analysis the elemental composition of artefacts made from this material also. WDXRF was used to determine the provenance of obsidian

artefacts from the Lake Urmia region in Iran, which led to the identification of three different source locations for the large quantities of these objects recovered there. This in turn led to the conclusion that the people of the area were reliant on local resources as well as engaging in short distance trading alliances (Niknami *et al.* 2010, 28). XRF was also used in the analysis of sixty eight obsidian artefacts from Jiskairumoko in southern Peru. Two techniques were used; laboratory based XRF and portable XRF, both of which identified sixty-six of the artefacts as coming from a nearby obsidian source at Chivay and two artefacts as being unassignable to source (Craig *et al.* 2007, 2012-2013). XRF analysis of obsidian has some advantages over that of glass. Since obsidian is naturally formed, its chemical signature tends to be homogeneous unlike glass which can have many variables added during its production. Obsidian sources also are limited to areas where there was volcanic activity, making them easier to identify. In addition, obsidian artefacts tend to survive very well in most archaeological contexts (Craig *et al.* 2007, 2012-2013).

XRF analysis was also carried out on a collection of very well preserved Roman glass finds recovered in the Canton Ticino area in Switzerland (Arletti *et al.* 2010, 606-612, 624-628)). The main objective of this analysis was to determine the elemental composition of these pieces and whether there were significant differences from the compositions of other glass of the same period in other regions. The methodology involved WDXRF analysis of 300mg of powdered samples of glass. The results that were obtained seemed to suggest continuity of use of raw resources over time. This conflicts with written accounts in other parts of Europe and with samples from Aquileia which show a change in the composition of glass of the first to second centuries and the fourth century AD. The elemental analysis also highlighted the use of impure sands during the glass production, due to the presence of potash (K_2O) and magnesium (MgO).

An XRF study of Roman glass samples uncovered in Israel was used to categorise the artefacts using their trace and major elements (Stuart 2007, 238). The major elemental composition was found to be typical of Roman glass (66-72% silicon dioxide, 16-18% sodium oxide and 7-8% calcium oxide). More specific knowledge

about the glass was provided by the trace elemental analysis. Cluster analysis was performed on the data and two distinct groups were found, each with significant differences in the amounts of copper, tin, lead and antimony. These elements are associated with the different colours and levels of translucency in the glass and the differences in the trace element components would suggest that the glass was sourced from two different origins. The analysis was also able to determine that the green colour of the glass was likely caused by adding bronze chips and antimony to the mixture during production.

XRF is not the only instrumental technique used in the elemental analysis of archaeological glass. Schalm *et al. (2007, 663)* used electron probe microanalysis for the analysis of archaeological glass from Belgium. Around 500 window glass fragments from different sites were included. This study found that the fragments did not contain lead or soda glass, which are what stained windows were commonly made of, but instead found them to be of calco-potassic type (Schalm *et al.* 2007, 663-666). This type of glass occurs when potash (K_2O) has been used as the alkali flux to completely or partially replace soda.

A benefit of using potash was that it raised the refractive index of the glass, making it aesthetically pleasing, however it was more prone to corrosion than soda-lime glass (Bray 2001, 133). It was also possible to identify three distinct periods from the fragments (pre-fifteenth century, fifteenth-seventeenth century and eighteenth century onwards) due to changes in the composition in the glass at these times. These could be noted by examining the concentrations of soda, silica, magnesium oxide, potash and calcium in the samples (Schalm *et al.* 2007, 663-666).

Work done on analysing glass colourants in different parts of the world has shown promise in categorising the origins of the raw material. Cobalt for example is commonly found with other minerals, most likely impurities obtained along with it at its geological source (Henderson 2005, 475). For example, in Ancient Egypt blue cobalt objects were found to be associated with manganese, zinc, nickel and aluminium in the New Kingdom period, which suggested a source of alum with a large cobalt impurity for the use of glass colouration at this time (Henderson 2005,

475). In contrast, later glasses from the same area are noted to have used a natron-based blue glass. In Iron Age Europe, studies on blue glass have highlighted how there was a change around the second century BC, in which it appears that ancient people began exploiting new areas of cobalt mineral sources (Henderson 1991, 131). The chemical analysis suggested that there was a change from an antimony-rich source of cobalt to a manganese-rich one (Henderson 2005, 475).

Evidence from places such as Britain suggests that different workshops may have specialised in specific types or colours of beads (Henderson 1991, 123). For example, an Iron Age workshop at Meare Lake Village in Somerset was found to have a range of glass bead types, the majority of which were either colourless or opaque yellow glass. Chemical analysis determined that antimony trioxide was responsible for the colourless glass, while lead pyroantimonate was used as both a colorant and an opacifier in the yellow opaque beads. Furthermore, by examining trace chemical impurities in the beads, it was possible to classify the beads found elsewhere as belonging to the Meare workshop. This made it possible to track the distribution

Plate 2.13: Selection of Meare beads (http://www.academia.edu/1488066/Celtic_Beads_from_the_British_Isles)

Plate 2.14: Northern Scottish annular beads (http://www.academia.edu/1488066/Celtic_Beads_from_the_British_Isles)

patterns of these specific beads and also to determine how long they may have been in use for, even after production at the site itself was believed to have been stopped. The elemental classification of these beads is important in identifying them on sites. Yellow opaque beads were also produced at a site called Culbin Sands in Scotland which, although looking nearly identical to the Meare beads, have a much different elemental composition, particularly with the yellow colourants. The distribution patterns for the two types overlap and it would almost certainly be impossible to distinguish the two were it not for chemical analysis (Henderson 1991, 124-125). The similarities between the two types of beads can be seen in Plates 2.13 and 2.14.

Elemental analysis was also used to investigate whether characteristic Iron Age Scottish glass beads were produced locally or imported (Bertini *et al.* 2011, 2750). The beads, which were taken from areas in Aberdeenshire and Moray, were visually distinct from other glass found in Britain, making them ideal for elemental analysis. Elemental analysis showed that all the samples were consistent with each other and typical of Roman glass, with sand which may have originated in the Levant. The consistency of the amount of colourant used in beads of the same colour would suggest that the producers of the glass were following a recipe of sorts, in that they knew how much colourant to add each time as opposed to experimenting to achieve different colours. The style of the beads was much more characteristic of the local production rather than elsewhere however, which suggests that slabs of Roman glass may have been imported in, or Roman vessels reused, in order to produce these beads locally (Bertini *et al.* 2011, 2765). It has been found that there are many similarities between glass vessels which were produced throughout the north-west provinces of the Roman Empire, but some features of glass artefacts or indeed entire types of artefacts are unique to Britain, such as a small globular jug with one handle (Price 2000, 21). This makes it almost definite that vessel production was taking place in Roman Britain and in all likelihood much of the ordinary vessel glass discovered in Britain was probably made locally.

As the above examples show, elemental analysis can be highly useful in determining the raw materials in glass, distinguishing between similar looking glass based on

elemental composition, identifying changes in glass composition over time and can even provide knowledge of where certain raw materials can be sourced from. However, it is also important to keep in mind that as a surface technique, XRF results will always be indicative of the very surface layers of the glass only and this may be problematic if corrosion has taken place.

2.6 History of glass in Ireland

Ireland has produced many beautiful examples of archaeological glass; some which were made here and some which were likely imported from elsewhere. The earliest examples of glass artefacts in Ireland were simple glass beads which appear in the archaeological record as early as the Late Bronze Age, but more commonly date to the Iron Age (Raftery 1994, 22). Examples of such finds include eighty blue and also a few yellow glass examples which were found along with a token deposit of cremated bone at a ring barrow in Oran Beg, Co. Galway (Rynne 1970). Small blue translucent glass beads are the most common type found, and are often associated with Iron Age burials, such as those at Knowth, Co. Meath (Bray 2001, 65). The problem with such small, plain objects is that it can be hard to date them to a particular period, unless they are provenanced or are found in very clear context, since blue examples are common in the Early Medieval period also. White or colourless beads are another common example which appear both in Iron Age and later contexts (O'Kelly 1989, 280).

Many collections of beads dating to the Early Medieval period in Ireland have been found, most notably perhaps the large collection found at Lagore, Co Meath, of which there were blue, white, yellow and green in many different shapes including tubular and dumbbell shaped. Some of the larger ones, for example the blue melon-shaped ones, might be continuations of earlier Iron Age glass-making. However some of the others such as the tubular ones are common in Anglo-Saxon contexts, which may suggests that they are in fact imports (Hencken *et al.* 1950, 139). There was also a sizable quantity of beads found at Ballinderry crannog, Co. Offaly. This

assemblage included many different types such as melon, zigzag and dumb-bell examples, in a range of colours (O'Neill *et al.* 1942, 51) The occurrence of glass in high-status burials both in Ireland and throughout Europe, and its use as inlays on extremely decorative and prestigious metal artefacts would suggest that glass was regarded as both exotic and high-status material (Henderson 1991, 107). Examples of some Irish beads recovered from excavations can be seen in Plate 2.15. It is likely that these may represent high status material as they were uncovered in excavations of a multi-phased, high status enclosure complex at Roestown, Co. Meath (O'Hara 2005, 74).

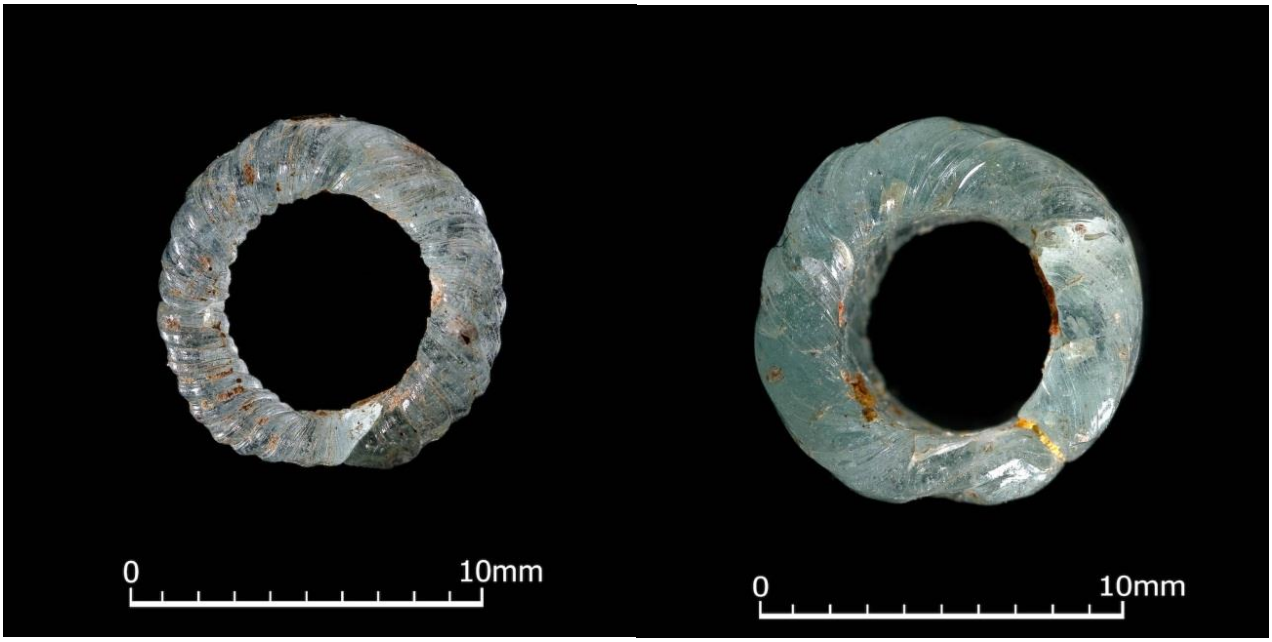

Plate 2.15: Coloured glass beads, recovered from Roestown, Co. Meath (*Roestown, Co. Meath*, Photographer John Sunderland, courtesy NRA)

One type of artefact worth particular mention is the so-called 'dumbbell bead' which is most likely unique to Ireland. Elsewhere they occur only very rarely, and may have been imported to these places from Ireland. Examples include one recovered from a dun at Kildalloig, in Western Scotland (Ritchie 1991, 153) and several which were found at an Iron Age roundhouse on the Isle of Man. These kind of beads are sometimes referred to as toggles and are often technically not beads at all, as many examples are not perforated (Gelling 1958, 95-96). These artefacts are particularly problematic as it is unknown what their function was, such as whether they were used for personal adornment. There is also a problem in that they have no set name

and are quite often grouped in with beads. One suggestion has been that they are in fact manufacturing debris; the ends of glass rods which had been used for producing beads, which were clipped off while the glass was still soft. The narrowest centre, which prompted the name dumbbell, is suggested to have been caused by whatever held the rod, such as forceps, while the glass was soft (Johnston 2007, 121). An example found at Scrabo Hill, Co. Down can be seen in Plate 2.16.

Plate 2.16: Dumbbell bead from Scrabo Hill, Co. Down (*Dumbbell bead. Scrabo Hill, Co. Down*)

An issue that arises from trying to determine if glass production took place in an area, is trying to differentiate between primary and secondary production of glass. Primary production would involve fusing raw materials into blocks of glass, while secondary production would involve re-melting and working these blocks into finished products (Willmott 2010, 2). For a material like glass, which was most likely highly prestigious, it is possible that power was gained by restricting access to and controlling the acquisition of its raw materials. It is also likely to have required

skilled producers (Henderson 1991, 107). It is difficult to say what glass, if any, was made in Ireland in prehistoric and early historical times and there was certainly glass being imported from abroad. This includes the small numbers of Roman glass finds in Ireland, which are a reflection of the great glass-making abilities that existed elsewhere. These objects include a glass urn containing a cremation and accompanied by a small glass phial which were uncovered in a Roman burial at Stonyford, Co. Kilkenny (Waddell 2005, 276). Bourke (1994, 163) has argued that glass vessels are among the most common glass artefacts from Medieval Ireland although there is no evidence to suggest that they were manufactured in Ireland at the time. Initially, the majority of glass produced was of a soda-lime-silica type until it began to be replaced by potash glass. This would follow a similar trend in Britain, where analysis shows that potash was being produced in quantity from the thirteenth or fourteenth century, although there was likely an overlap in the two different techniques (Moran 2010, 17).

The first possible evidence for simple glass working from the Early Medieval in Ireland comes from Dunmisk fort, where a collection of glass including failed glass beads, glass rods, a failed glass stud and scrap glass, as well as the remains of glass making crucibles was uncovered (Henderson 1988, 115). Primary glass production involved producing glass from its raw materials as opposed to re-working blocks or rods of glass. It is unlikely that there was much primary production being carried out in Ireland at this time and the majority of glass that is found from these periods most likely was imported from elsewhere. The only evidence for primary glass production in Ireland is found at Dunmisk fort, in the form of crucibles containing partially melted primary raw materials along with fully formed yellow glass (Henderson 2000a, 144). The finds were found concentrated in the North-East section of the site along with evidence of hearths. One of the hearths produced a radiocarbon date of 570-890 AD. Elemental analysis carried out on the material revealed three main types of glass: soda-lime silica glass, high lead-high tin oxide glass and high tin oxide glass. Several colorants were also determined including cobalt oxide and copper and lead-tin crystals. The trace levels of lead, tin and antimony found in the glass is significant as these sorts of impurities are found in

many examples of Early Medieval glass. This means that the pattern could be used to compare these glass artefacts with other contemporary material both from Ireland and abroad (Henderson 2000a, 115-119). Dunmisk appears to have had a small monastic community and this would correlate with glass production in Britain, where production and working of glass was carried out almost solely at monastic sites and centres. There is more evidence of secondary processing, or reworking, of glass in Ireland. This includes the Early Medieval ringfort site at Garranes, Co. Cork (Ó'Ríordáin and Ryan 1942, 121) and as well as the Late Medieval remains at Scotch Street, Co. Antrim (Lynn 1979, 81) where polychrome rods which would have been used to create beads or create decoration on glass vessels were found.

Even if there is little physical evidence for glass production or working on sites in Ireland, there is some indirect evidence in the form of the glass objects themselves. Toggles or dumbbell beads, which have been discussed already, are unique to Ireland and may suggest that there was glass working being carried out here. As well as this, a bead type which was found at the Iron Age burial site at Loughey, which consisted of yellow spiral decoration on a colourless background, was found to be unique to Ireland. This would suggest that the beads may have been produced in Ireland using imported glass blocks or reused imported vessels (Henderson 1991, 132).

In Later Medieval Ireland, there is still little archaeological evidence for primary glass production, however documentary evidence suggests a concentration of glass workers around Dublin. The earliest reference being to a 'William the Glassmaker', who received a grant of land for making glass in 1258 (Thorpe 1969, 268).

Some of the most impressive coloured archaeological glass found in the Irish archaeological record comes from stained glass windows or fragments which remain of them. Often these windows were sponsored by wealthy patrons as high-status gifts to the church, which in return afforded them prestige (O'Clabaigh 2008, 78). While soda window glass has been noted elsewhere, including England and Scotland, early Irish church or monastery coloured window fragments uncovered so far have been manufactured using potash. This results in any surviving fragments

often being badly weathered, caused by the high alkalinity of the potash glass (Moran 2010, 17). While medieval stained glass windows occasionally survive in their original position they usually fell into disrepair or were even intentionally destroyed (Crabtree 2008, 83). In 1846, a quantity of decorative glass was found at the Cathedral of St. Canice, Co. Kilkenny. In 1850, the window was described in a paper by Rev. James Graves (1850, 210) as being 'a gift…. [of which] in no other part of Ireland does there exist an example…so ancient and so unquestionably genuine'. The fragments were believed to have been from famous painted windows, which apparently displayed the history of Jesus and were created in the fourteenth century before being demolished later by Cromwell's soldiers. Fragments were discovered at the site during excavations to examine some ancient foundations. It seemed that even during the wanton destruction, those who tore down the windows took the time to attempt to melt down the lead in the windows, with evidence of a fire and melted glass also found at the site (Graves 1850, 210). Indeed, many magnificent examples of Irish Medieval stained glass are recorded to have met a similar destruction, including at Clonmacnoise, which the Annals of the Four Masters described as 'not left… even glass in a window' (*Annals of the Four Masters*, 2002). Sometimes, windows are discovered walled up during later alterations, or panels are found intentionally buried where they have fallen, but it is usually only fragmentary evidence which remains (Crabtree 2008, 83). One example from excavations near Adare friary uncovered fifteenth century pieces including some coloured with a yellow stain wash and a fragment of red flashed glass (Dunne and Kiely 2009, 177). At the Dominican friary in Limerick, glass finds from the fifteenth century were uncovered including large diamonds of white glass painted with a yellow stain. This glass seems to date to a time when patronage was received from the Fitzgeralds of Desmond (O'Clabaigh 2008, 80).

Roche (2007, 184) argues that the majority of glass found in archaeological contexts in Ireland is post-seventeenth century in date. In terms of quality and quantity, Ireland had a relatively good post-medieval glass industry for such a small country and several glass-houses were founded during this time which produced four main types; bottle glass, flint glass, crown glass and plate glass. Bottle glass was cheaply

manufactured and widely used (Rynne 2006, 184). Glass used for making bottles was almost always of a lower quality than that of other vessels and usually had a very dark green colour, caused by varying iron impurities (Roche 2007, 411). Although there is not much documentary evidence for the production of bottles in Ireland compared to elsewhere by the end of the seventeenth century, there are records of it being carried out by the eighteenth century in Dublin and in Waterford City (Thorpe 1969, 272). Flint glass was made with silica that contained a low iron content and was well suited to being worked for decorative purposes by engravers and glass cutters (Rynne 2006, 184). The first record of flint glass being produced in Ireland was in Dublin around 1690, although it is likely to have been produced at an earlier date, as supported by glassmaking debris excavated from Smithfield, Co. Dublin (Myles 2003). Crown glass was formed by blowing, heating and rolling the molten glass on a metal surface and was carefully formed into a flat disc. It was often used for making windows and was sometimes referred to simply as window glass. Plate glass was made of finer materials than the others and was used for manufacturing mirrors and coach windows (Rynne 2006, 185). It was first by casting and rolling the glass and then grinding and polishing both surfaces of the glass to remove any flaws and create a flat surface (Roche 2010, 59).

One of the earliest post-medieval glass furnaces is an upstanding late-sixteenth/early-seventeenth century glass furnace, which was found near Shinrone in Co. Offaly (Rynne 2006, 181) (Plate 2.17). Archaeological evidence for when the earliest glass furnaces were constructed is very limited but documentary evidence would suggest that glass production of this nature began at the end of the sixteenth century (Farrelly *et al.* 2014, 47). By the end of the eighteenth century, glassworks had been founded in Dublin, Cork, Waterford, Belfast, Newry, Drumrea and Ballycastle, however there are many gaps in the knowledge of these structures due to their poor survival rate. Glass furnaces have a notoriously low rate of survival with most known examples having only a few courses of brickwork remaining at best. This may be due to their simple nature, generally consisting of basic rubble-stone structures (O'Brien and Farrelly 1997, 21). Excavations were carried out at the Shinrone furnace in 1999. The finds from this excavation included light green

window glass, as well as waste glass within the stroking trench of the furnace. Other finds included crucibles, pottery sherds, slates, bricks and other waste material (Farrelly 1999). Rynne (2010, 138) describes the establishment of glassworks in Cork, as well as many of the other glassworking centres, as a direct transfer of English glassworking knowledge to Ireland, with much of the knowledge of how to produce their products coming from skilled glassworkers recruited from England. In addition, many of the raw materials used to produce the glass was sourced and imported from England (Rynne 2010, 138). One of the most internationally famous glassworks ever in existence was the Waterford glassworks which was in operation between 1743 and 1851. This would later be revived as Waterford Crystal in the twentieth century. Other famous glassworks include Cork Glass Company which was established in 1783 as well as Benjamin Edward's works in Belfast which he started in 1776 (Elville 1953, 60-61). The late eighteenth and early nineteenth centuries saw the pinnacle of Irish glass making due to the introduction of excise duties on glass produced in England, while glass exported from Ireland faced no such restriction. The industry went into steep decline due to the introduction of taxes on manufactured glass in 1825 (Roche 2007, 405).

Plate 2.17: Glass furnace at Shinrone, Co. Offaly from the late sixteenth century. (O'Brien and Farrelly 1997, 21)

2.7 Analysis of glass found in Ireland

There has not been as much scientific work done on glass found in Irish archaeological contexts compared to elsewhere in Europe. One example of the use of XRF was on a group of forty-eight Early and Late Medieval glass beads and bracelets from various sites including Garranes, Lagore, Garryduff and Clogher (Warner and Meighan 1994). These beads ranged greatly in colour and in shape which included dumb-bell, tripartite and mottled. From the analysis, the beads could be divided into different groups; based on their percentages of antimony and manganese. Other colourants were also determined, such as a yellow bead which was coloured by lead antimonate and a red bead which been coloured by the addition of cuprous oxide. The work also highlighted the increased use of antimony as a decolourant in beads found in Ireland from after the seventh or eight century AD (Warner and Meighan 1994. 53-54, 60-65). This is similar to trends elsewhere in North and Western Europe (Henderson 2000b, 70)

A range of glass samples from Early Medieval Ireland, including translucent blue, green, and turquoise, and opaque yellow, white and red examples from monasteries, raths, crannogs and royal status hillforts were scientifically examined using SEM and electron probe microanalysis (EPMA) (Henderson 2000a, 147). The relatively small variations in the chemical compositions of the 160 samples showed that a small range of primary raw materials must have been used to produce them. The chemical compositions of the translucent glasses were found to be typical of Roman silica-soda-lime glass and indeed were similar in composition to samples found in a late fourth century Roman glass-working site at Jalame, Palestine. It was found that colourants used in the glass included cobalt for blue, copper for turquoise and manganese for a purple hew, and it appears the quantities of colourants were added deliberately. The opaque glass was similarly found to have been of a typical Roman type. Both yellow and white opaque glass were found to be similar to samples which were first introduced for glass bead production and enamelling purposes in the late Iron Age in Europe which points to the movement of both the objects themselves and the knowledge of how to manufacture them (Henderson 2000a, 147-150).

Different work has been done on categorising and examining archaeological glass or glass collections in Ireland. At NUI Galway, post-graduate researcher Margaret Mannion has carried out work towards a database which would help facilitate a system for national classification of glass beads. The study involved the first dedicated database of chronology, typology, dating and social context of these artefacts(Mannion 2013). This ambitious project looked at the visual appearance of medieval beads in great detail. Another project which was carried out was Johanna O'Sullivan's examination of Viking glass beads at UCC as evidence for interaction between existing Irish communities and Vikings (O'Sullivan 2015). Some of the Viking glass that was looked at from a trade perspective, the Viking beads from Glencurran cave, was analysed as part of this study.

An analysis of opaque red glass was carried out on a number of Early Medieval samples from Britain and Ireland (Stapleton *et al.* 1999, 913). Among the artefacts analysed with XRF and SEM was a red enamel ingot supposedly recovered from the Hill of Tara, although it was unprovenanced (Johnston 2007, 115). While opaque red beads are common Germanic types and are found in Anglo-Saxon graves, red glass is very rare in Ireland particularly for this period (Laing 1975, 337). There are two types of red enamel found in use in Ireland from this time; liverish-red glass and sealing-wax red glass, of which the Tara ingot is the latter (Henderson 2000a, 150). Sealing-wax red enamel was used mainly to decorate Iron Age metalwork such as shields on the continent, and continued in use in Early Medieval Ireland. It was not used for bead decoration or millefiori, although the liverish-red colour type was. The Tara ingot, an undated and unprovenanced find, was found to be comprised of a typical soda-lime-silica glass with 27% lead oxide and 9% copper oxide added to it (Stapleton *et al.* 1999, 915). Analysis of the lead was also carried out on the ingot as well as on two Irish brooches with red enamel. The results from this showed that the brooches were closely similar to each other but both were distinctly different from the Hill of Tara ingot making it highly unlikely to have been from the same source. The results of the ingot had no comparable match from Ireland and indeed it is possible it was sourced outside of the British Isles entirely.

2.8 Conclusions

Since it was first produced in antiquity, glass has been prized for both decorative and functional purposes because of its translucent and durable properties. It is also capable of taking on many different colours and can be formed into many different shapes and sizes. There is substantial evidence that people were very much aware of how to influence these factors. This chapter has demonstrated that Ireland has a rich quantity of archaeological glass, from Bronze Age beads right up to finds from the Post-Medieval period.

Analytical scientific techniques can help in a much wider sense in that the results that are obtained from individual assemblages can provide information on economies and trading routes in the past. Work done in Britain and elsewhere has highlighted how successful this kind of analysis can be. Glass objects were a highly valued and prestigious commodity for a long time in prehistory and early history, and their presence on archaeological sites is worth closer examination. While very little analytical work has been carried out on Irish glass artefacts, the examples which have been mentioned, both in Ireland and abroad, highlight the great potential there is in examining chemical compositions of glass. It can be seen that glass can be a difficult material to provenance but that does not mean that nothing can be gained from elemental analysis. On the contrary, it can provide a lot of valuable information on the production methods and origins of a piece.

The principles behind XRF have been discussed to show its usefulness and advantages compared to other techniques when it comes to analysing glass and samples in general. It is their ease of use, relative speed, highly sensitive detection and, in particular, their non-destructive nature which make them suitable for the work which was intended within this project. While these instruments also have their limitations, such as not being able to detect some of the lightest elements, they are still considered the best methods for multi-elemental analysis in this circumstance.

Other limitations too, such as the possibility that the sample area analysed may not be representative of the entire object, also have to be taken into account. Ancient glassmakers undoubtedly had a vast knowledge of their craft to produce some of the remarkable specimens which remain today and chemical analysis can help to determine more about what processes caused these objects to exist where and how they did.

3. Methodology

3.1 Database of archaeological glass finds

A database of glass finds recovered on archaeological sites in the past number of years was compiled, both by looking through reports on www.excavations.ie as well as the *Excavation Bulletins*. The years covered were 1997 to 2008 inclusive which included a total of 17807 sites. For the purpose of putting together this database, glass finds which were listed as 'modern' or late-twentieth/twenty-first century were excluded from the results, so as to better focus on artefacts which are more likely of archaeological importance. The results were compiled in an Excel document and arranged alphabetically, first by county and then by townland. Some basic statistical analysis including barplots and pie charts were also applied to the results with the aim of identifying trends in the data as well as gaps in what is known about the objects. The information is outlined in detail in Appendix A.

3.2 Development of preparation techniques using analysis of modern glass

Despite the fact that XRF is a non-destructive technique; removal of corroded layers of glass or dirt on the surface of the glass is often desirable in order to provide a more homogenous sample. Analysis of glass which has not been subjected to pre-treatment is certainly possible but it depends on the state of the sample as to whether the results are representative or not. As part of the research carried out, different types of preparation techniques were utilised on modern glass was to determine which, if any, preparation methods should be used on archaeological glass objects when undertaking XRF analysis. A number of modern glass samples of various colours were collected for this study. Some were taken from newly bought glass bottles while others were left exposed in an outdoor environment for a number of weeks. This was so as to introduce the samples to impurities from the soil, rain water, pollution and other such contaminants. Each sample was analysed using the XRF and all analysis was carried out in triplicate. First, the samples were rinsed in deionised water and analysed. They were then rinsed in ethanol and analysed again.

Another selection of samples had a thin layer removed from them using the Dremel polishing tool and the samples analysed in triplicate. The results of the analysis show that rinsing the samples in deionised water can affect the results that are obtained when the samples are analysed. The trace elements are the most affected by this washing. This is unsurprising due to the small amounts which the sample contains, which leaves a greater scope for percentage error. As well as this, it can be expected that deionised water may aid washing away trace contaminants on the surface of the sample and it certainly seems to be doing so in this case. Ethanol seems to have a similar effect as the deionised water as it has comparable results (Tables 3.1 and 3.2). In fact the results from both deionised water washing and ethanol washing were broadly interchangeable. The polishing technique, was deemed too destructive for the delicate glass that was sourced as part of this thesis, however results obtained from this method are detailed in Table 3.3. A negative %change indicates a lower concentration obtained after washing. This is particularly significant for trace elements.

	Exposed Green glass %Change	**Exposed Brown Glass %Change**	**Exposed Clear glass %Change**	**Unexposed green glass %Change**	**Unexposed clear glass %Change**	**Unexposed brown glass %Change**
SiO_2	-0.71	0.87	0.81	-0.39	1.06	0.17
Na_2O	12.22	-3.58	-5.03	1.63	-4.42	-1.94
CaO	-9.43	-0.11	0.45	0.41	0.74	1.58
Al_2O_3	10.90	-2.41	-0.18	1.73	-7.71	0.69
K_2O	19.862	-1.475	nd	-0.065	nd	0.644
MgO	nd	nd	-87.34	nd	-1.84	-3.48
Fe_2O_3	3.321	2.013	-13.1054	-1.873	-11.7048	1.373
Cr_2O_3	4.545	-15.6863	nd	-2.581	nd	10.8808
TiO_2	5.3140	-2.6090	-22.109	8.6475	-3.0093	7.8140
MnO	22.0884	.8636	nd	-5.6314	nd	4.3393
BaO	25.0883	-4.6229	nd	-3.3520	nd	5.6434
ZrO_2	23.9506	-1.6181	-2.6820	-2.2500	-7.7922	1.7766
PbO	50.4762	-14.3552	nd	nd	nd	nd
SrO	23.6271	-1.3793	nd	-1.7621	nd	0.6309
ZnO	nd	-34.6154	nd	nd	nd	nd

Table 3.1. Modern glass %change with water washing

	Unexposed Green glass %Change	Unexposed Brown glass %Change	Unexposed Clear glass %Change	Exposed Green glass %Change	Exposed Clear glass %Change	Exposed Brown glass %Change
SiO_2	-1.12	0.92	0.87	1.18	0.86	-1.41
Na_2O	-6.96	-7.23	-5.52	18.00	2.48	7.83
CaO	13.01	1.82	0.73	-31.15	-10.47	-5.19
Al_2O_3	11.69	3.83	-0.92	13.99	-11.21	2.71
K_2O	21.382	-1.475	nd	-29.406	nd	25.919
MgO	nd	nd	-83.12	-44.90	1.91	4.42
Fe_2O_3	3.084	-0.906	-11.9658	-54.743	2.5806	25.077
Cr_2O_3	4.377	7.3529	nd	-53.9171	nd	nd
TiO_2	-4.0843	-0.8496	-22.449	-48.7273	0.3817	4.294
MnO	37.3494	4.1969	nd	-57.8822	nd	-1.292
BaO	24.8528	7.2993	nd	-64.596	nd	-19.446
ZrO_2	18.1893	-2.5485	-4.4700	-58.8342	-12.8514	-5.0193
PbO	52.9252	-10.2190	nd	-55.9585	nd	-8.1340
SrO	24.1379	-1.2069	nd	1.18	0.86	-1.41
ZnO	nd	-118.2692	nd	18.00	2.48	7.83

Table 3.2: Modern glass %change with ethanol washing

	Unexposed green glass %Change	Unexposed clear glass %Change	Unexposed brown glass %Change	Exposed brown glass %Change	Exposed clear glass %Change	Exposed green glass %Change
SiO_2	0.85	0.91	1.02	0.11	0.25	1.39
Na_2O	-10.84	-2.93	-5.11	1.73	-3.52	11.33
CaO	4.29	-0.85	0.07	-4.32	0.32	-29.83
Al_2O_3	19.05	-11.71	-3.47	0.70	6.91	11.78
K_2O	10.039	nd	8.615	2.294	-40.820	-18.728
MgO	nd	-1.84	2.32	nd	nd	nd
Fe_2O_3	10.086	2.7990	0.125	-8.853	1.7684	-52.324
Cr_2O_3	-2.581	nd	-11.9171	-5.5300	nd	-50.2488
TiO_2	9.6452	-1.6204	-1.2093	-2.9818	7.9318	-42.1801
MnO	10.7509	nd	-1.2821	-10.4299	-2.8345	-61.0568
BaO	-2.2346	nd	0.5130	-12.422	-10.5000	-85.0000
ZrO_2	9.5000	31.8182	-0.7614	-9.8361	-4.6036	-65.7471
SrO	7.0485	nd	0.0000	-7.7720	-5.7011	-59.6774

Table 3.3: Modern glass %change with polishing

3.3 Sample washing and preparation

As a result of extensive experimentation with washing trials on modern material, and in consultation with the National Museum of Ireland, it was decided that a basic washing technique using an ethanol-deionised water solution would be used to remove dirt from the surface of the glass objects. Prior to cleaning any of the objects, licenses to alter the material were obtained from the National Museum.

A solution consisting of a 1:1 ratio of deionised water and 99% ethanol solution was prepared. The surface of each sample was gently cleaned using a clean cotton swab dipped in the deionised water/ethanol solution prior to being analysed in the XRF. The samples were left to dry completely before undergoing analysis. All samples were handled using gloves to avoid adding any further surface contamination. The purpose of this technique was to remove surface contamination on the surface of the glass. Different trace elements can be left on the glass from many processes such as salts left behind from washing with ordinary water or chlorine transferred from handling the samples with bare hands. By removing such elements, a clearer result of the elemental composition of the surface layers of the glass can be obtained.

3.4 Calibration and Quality Control

The instrument used was an ARL Quant'X EDXRF Spectrometer. The XRF was calibrated monthly using the standard procedure for this instrument. This involves analysing ten standard metal discs which are copper, aluminium, titanium, chromium, iron, nickel, mobylium, tin, tungsten and lead. The accuracy of the instrument was also tested regularly using glass reference material. These consisted of two pieces of clear soda-lime-silica class which contained trace amounts of various oxides including iron, aluminium, titanium, magnesium, sulphur and potassium. The concentrations for these two reference samples; Standard glass 1 and Standard glass 2, are listed in Appendix B. The accuracy and precision of the instrument were monitored by comparing the results obtained from analysing the reference material to its given composition. The reference material was run five

times and an average taken of the results. The percentage difference and relative standard deviation was then calculated from the results. This was done regularly to ensure that the instrument was accurately detecting elements. Standard 2 was used most frequently for this purpose as it has a lower soda concentration than Standard 1, which was more consistent with what would be expected from ancient glass. An example of these calculations can be seen in Table 3.4.

	Stated concentration (%w/w)	**Average obtained (%w/w)**	**Relative Standard Deviation%**	**%Error**
SiO_2	72.26	72.62	0.360	0.503
Na_2O	13.78	12.88	1.399	-6.516
CaO	10.05	10.71	0.598	7.000
MgO	3.40	3.64	2.423	-0.0549
SO_3	0.270	0.027	9.658	-90.074
TiO_2	0.033	0.0237	7.413	-28.121
Fe_2O_3	0.021	0.0177	4.058	-15.619

Table 3.4 Reference material results

$\%\ \text{error} = ((T - E) \div (T)) \times 100$

where T is the known true composition of the glass and E is the experimental quantity

3.5 Analysis of archaeological glass samples using XRF

A total of 328 glass samples from nine archaeological excavations were obtained from a number of sources including excavation companies, the National Museum of Ireland research institutions and archaeologists. These ranged widely in their age, from potentially Iron Age beads to Post-Medieval samples, however the majority of the glass tested was Post-Medieval. Each sample was analysed by XRF in triplicate and the results averaged. The standard error for elements calculated in this manner was calculated and deemed to be within an acceptable range. The % standard error for most elements with concentrations over 1% w/w was found to be less than 2%. The exception to this was soda (Na_2O) which could be anything from <1% to 15%. Sodium is the lightest element detectable by the instrument which could explain the lower reliability of the results obtained for it. Trace elements generally had relatively

good standard errors with the exception of those with only very small traces. Elements with concentrations of <100ppm tended to have much higher standard errors, however such elements were not used in the interpretation of the results.

The results were reported as elements in a %w/w format with a standard error calculated for each individual element. As the instrument cannot detect oxygen or any other element lighter than sodium, it was necessary to input parameters so that the results were displayed as oxides. A set of parameters optimised for the ancient glass in this study was created by compiling empirical data obtained by analysing reference material.

3.6 Statistical analysis of the results

Correlation statistics were carried out to determine if there was association between certain elements contained in specific groups of glass (Townsend 2013, 140-143). For this purpose, SPSS software was used. For each instance, the results for the two elements in question were used to produce a scatter diagram. The correlation coefficient, which is a numerical measure of the degree of association, was then calculated. Spearman's coefficient was used as it was the most appropriate for the results in this study which were not normally distributed (Rees 2001, 211 - 215). The following values were assigned to the r value.

r = 0.7 to 1.0	Strong correlation
r = 0.3 to 0.7	Weak to moderate correlation
r = 0.0 to 0.3	No correlation

4. Case Studies

4.1 Database of archaeological glass finds

Appendix A contains a list of sites compiled from excavations.ie and the *Excavation Bulletins* where archaeological glass was found between the years 1997-2008 inclusive. The total number of sites which contained glass was found to be 487, out of a total of 17807 excavations which were carried out in the course of these twelve years. This accounts for just 2.73% of the sites listed. This total does not include sites where only modern glass finds were listed however and not all glass found would have been recorded in these brief summaries of the excavations. While different types of glass on a single excavation were taken into account, on excavations where more than one sherd of a type of glass was found, or where several beads were uncovered, the groups were counted as a single occurrence and not individually. The number of sites and the types of glass that were found during the excavations are summarised in Table 4.1. Unsurprisingly, the majority of the glass was Post-Medieval in date, most of which came from low-quality glass bottles which were cheaply manufactured and widely distributed. Many of the finds from earlier periods were isolated ones, consisting of just fragments or single beads. There were some exceptions to this, such as a case where over fifty glass beads were uncovered in Ferns Lower, Ferns, Co. Wexford and the find of over fifty glass beads in Glencurran Cave, Tullycommon (No. 478 and No. 36 respectively in Appendix A).

	Bottle	**Bead**	**Window**	**Vessel**	**Unspecified fragments**	**Other**
Iron Age	0	3	0	0	0	0
Early Medieval	0	6	0	0	1	1
Late Medieval	0	1	1	0	2	0
Post Medieval	39	1	8	6	159	0
Unknown date	18	116	15	4	99	12
Total	**57**	**127**	**24**	**10**	**261**	**13**

Table 4.1 Number of sites where archaeological glass has been identified

Figure 4.1 illustrates the time periods the glass finds came from and Figure 4.2 shows the type of objects the glass came from. As mentioned already, the majority of the glass was Post-Medieval in date; however a sizable proportion of the glass was from an unknown date. These objects consisted mainly of isolated sherds of glass and blue glass beads for which there were no discernable diagnostic features or definite context.

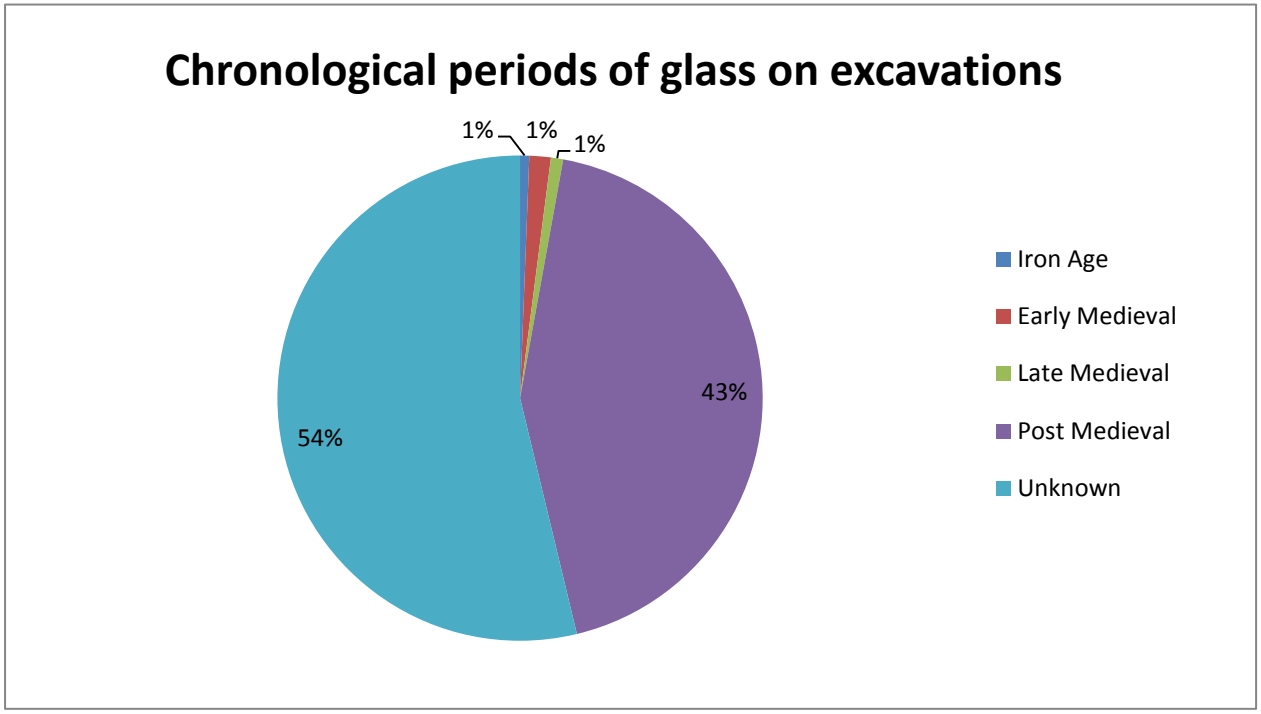

Figure 4.1: Chronological periods of glass on excavations

Figure 4.2 illustrates how the majority of the archaeological glass found on sites was fragmentary, with no obvious function listed in the excavation reports. Of those for which a type of glass was determined, the largest group was glass beads, making up 26%. Beads are notoriously difficult to accurately date without a very clear context, particularly plain blue examples which are among the most common. Bottle glass also made up a sizable percentage with 11% of the glass in the database. Window and vessel glass from objects other than bottles were not very common but they generally do not survive intact in the archaeological record and it is possible that they are simply not recognised and remain unspecified. Other types of glass, including bracelet fragments and a glass inkpot, made up 3% of the finds.

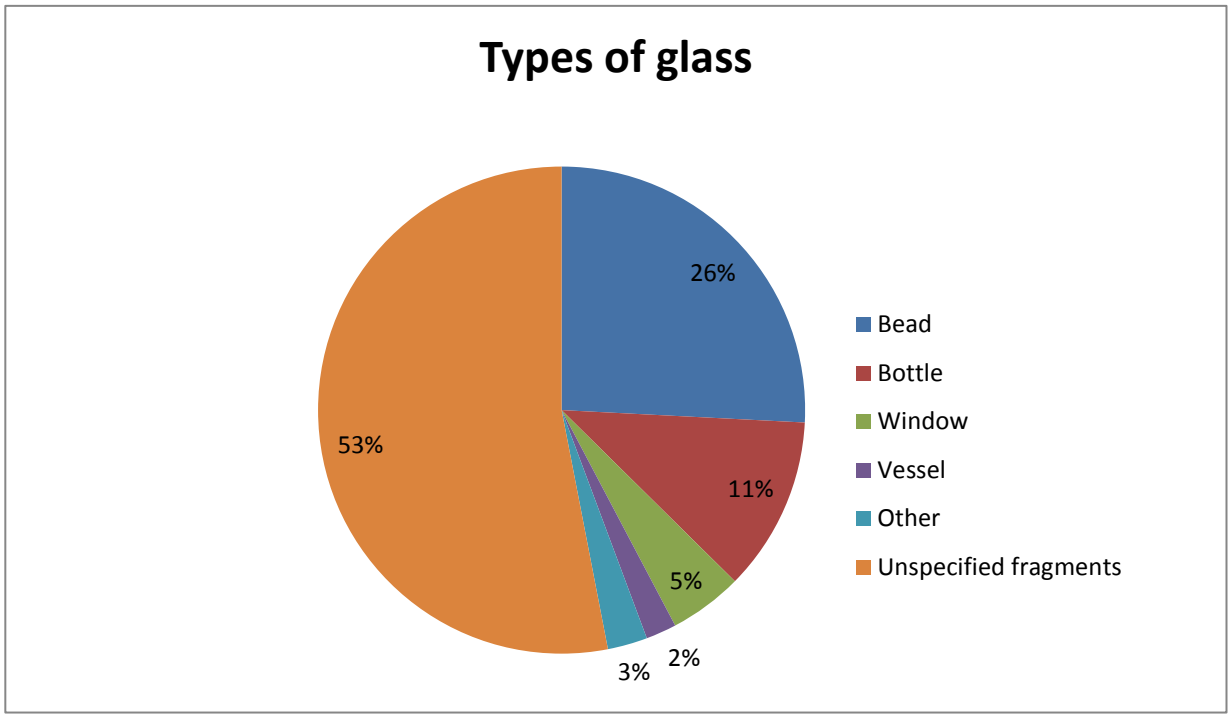

Figure 4.2: Types of glass on excavations

4.2 Case Studies

Glass assemblages from nine different sites were analysed as part of this research. This section will briefly discuss the backgrounds of these sites and the contexts in which the glass artefacts were found. Detailed technical reports were prepared and supplied to the archaeological companies and individual archaeologists who supplied the glass assemblages for the purpose of this study. The full reports which have all the analytical results and details are contained in Appendices C to K. The major points and findings of the study will be outlined here. A summary of the sites including their excavation numbers and chronological periods can be seen in Table 4.2.

Name	Date of contexts that glass was recovered from:	Excavation no.
Dún Ailinne	Late Iron Age/Early Medieval	n/a
Glencurran	Viking bead assemblage	04E0432
Lagore	Early Medieval	E14
Kilteasheen	Early Medieval to Modern	05E0531
Blackfriary	Late Medieval to Post-Medieval	E4127
Bective Abbey	Late Medieval to Modern	E4028
Moygara Castle	Post-Medieval to Modern	13E161
Seagrange	Post- Medieval to Modern	13E238
Rothe House	Post-Medieval	05E598

Table 4.2 Archaeological sites with chronologies and excavation numbers

4.2.1 Dún Ailinne, Co. Kildare. Late Iron Age/Early Medieval (Full Report, Appendix C)

Dún Ailinne is a site of around thirty-four acres on a hilltop, which is enclosed by a ditch and bank. The site is often referred to as a hill-fort however the position of the bank downhill and outside of the ditch would indicate that its primary purpose was not defensive. Four major stages of construction on the summit were discovered upon excavation; a Neolithic structure and three subsequent Iron Age timber structures. Throughout the excavations, artefacts were discovered which indicated heavy use of the site during the Iron Age and Early Medieval (Wailes 2007b, xxv-xxix). The most prominent features dating to the Iron Age were the three successive construction phases which were, dating from early to late, the White, Rose and Mauve phases. Each of these was shown to contain circular palisade trenches which would have held upright timbers. A low mound, roughly 20m diameter and barely 1m above ground level, was completely excavated and was found to contain a series of complex layers which were likely accumulated while the timber structure of the Mauve phase was still standing. However its uppermost level, which shows extensive evidence of feasting, post-dates the deconstruction of all of the structures

associated with the Mauve phase and is classified as the Flame phase (Wailes 2007a, 22).

In total, forty-three artefacts from a total of fifty in the assemblage were analysed. This included twenty beads, eleven bracelet fragments, eight toggles and four unidentified fragments. The remaining seven artefacts were either too small or too fragmented for analysis. Of the fifty glass artefacts which were discovered during the Dún Ailinne excavations, eighteen came from unknown phases. Of the remaining thirty-two, seventeen came from the Flame phase contexts, which represent the latest Iron Age deposits on the site that were associated with feasting, and it has been suggested that they represent items of personal adornment that were lost. Other finds that were deposited during feasting activities were well represented in this phase. The Mauve and Rose phases, which also dated to the Iron Age although earlier than the Flame phase, contained three and four glass artefacts respectively. The remaining eight glass artefacts were uncovered from complex levels in the low mound which occured under the Flame phase deposits (Johnston 2007, 115).

A total of twenty beads were analysed with a range of colours and sizes represented. Most of these, fourteen of the twenty, were blue in colour, but there was also one green, two orange/amber, one blue-green, one colourless and one purple. Seven beads were potash-based and the remaining thirteen were most mixed-alkali. Of the fourteen blue examples, thirteen were found to have been coloured using cobalt oxide, with only one most likely having gotten its hue from copper oxide (Bhardwaj 1979, 42-43) (Plate 4.1). This particular bead also has a much higher level of aluminium oxide than the other blue examples, indicating it had undergone more corrosion of its surface layers than the others. This would suggest that it had a different original elemental composition, as the susceptibility of glass to corrosion is influenced most by its original elemental composition. Johnston notes that this bead is of unknown date. She states that it may be modern but that its condition, with surface etching, may suggest an ancient origin (Johnston 2007, 119). Given the

elemental corrosion it has suffered, it is highly unlikely to be modern and indeed may be one of the oldest blue beads from the assemblage.

A single blue-green example, with an appearance typical of that found in Bronze Age glass, was analysed (Barber 1991, 235, Bellintani 2013, 283, Henderson 2013, 75)(Plate 4.1). Magnesium oxide, a characteristic component of Bronze Age blue-green glass was not detected in this bead however. This makes it difficult to ascertain whether this bead was truly a Bronze Age example. There was also no cobalt oxide found in its structure and like the earlier single blue example, it most likely got its hue from the copper oxides in its structure.

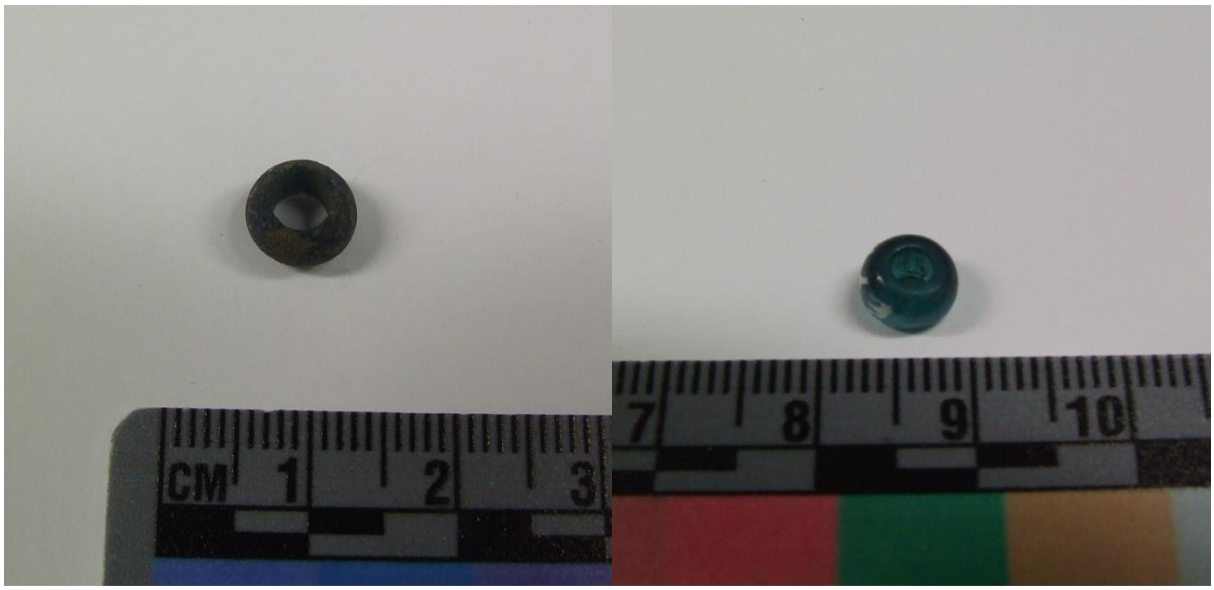

Plate 4.1: Blue bead coloured with copper (left) and bluish-green bead (right)

There was no definite colourant determined for the two amber-coloured beads. Both contained manganese oxide which, when added to other elements such as carbon and sulphur, is known to impart an amber hue. However the concentration of manganese was comparable or even lower than many of the other bead samples. It is possible that the amber colour was caused by the addition of a reducing agent, such as carbon, to the glass furnace. When carbon is added to a glass mix containing iron and sulphur for example, it can result in varying shades of amber (Bray 2001, 65).

Unfortunately, carbon is too light an element to be detected by the XRF, so further investigation would be required in order to determine the level of carbon present.

The single purple bead was most likely coloured by the relatively high level of manganese oxide it contained. Manganese oxide was found in trace quantities in all of the beads, however the purple bead had the highest concentration with more than double what was found in any of the others. While manganese is sometimes added intentionally as a decolourant in glass production as it masks the green colour caused by iron, it can be used on its own without significant levels of iron to give a purple colour (Goffer 2007, 121).

The most elaborately decorated Dún Ailinne bead was a light green example with yellow-white decoration. The green colour was most likely due to substantial iron oxide contaminants in the glass melt, as other substances known to act as green colourants, such as oxides of copper, chromium and nickel, were absent. The yellowish-white decoration was most likely caused by tin oxide and lead oxide.

There were eleven glass bracelet fragments analysed and these were found to have less evidence of corrosion than any of the beads that were analysed. Like the Lagore glass bracelets, this may be due to the original composition of the glass being different to the beads or to the different relative surface area (Plate 4.2). Three of the fragments had particularly high levels of soda compared to the rest of the glass and were likely soda-based glass. The majority of the bracelet fragments were produced using a mixed-alkali glass.

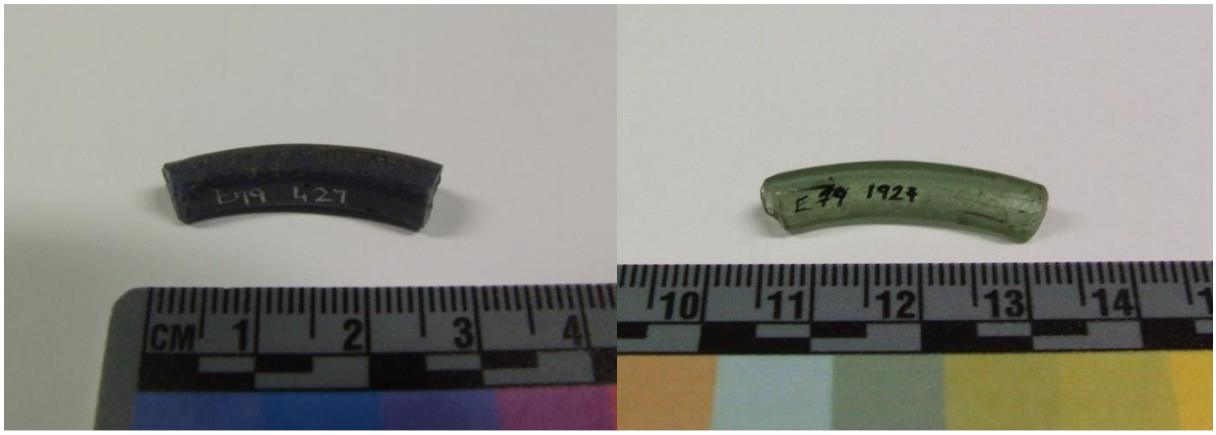

Plate 4.2: Examples of bracelet fragments; blue (left) and clear with green tinge (right)

Six of the bracelet fragments were blue in colour and contained significant traces of cobalt oxide. They also contained varying amounts of copper oxide which may have further enhanced their blue hue. Overall, their concentrations of major and trace elements were very similar to each other which would suggest they had a similar production method.

There was only example of a colourless glass bracelet fragment. Another bracelet fragment, which was green in colour, was found to have a similar elemental composition to it, however it had almost double the amount of iron oxide. This manifested visually in the glass as a light green tinge. Both samples were made of soda-based glass and lacked many of the trace elements found in the other glass bracelet fragments, such as sulphur, cobalt oxide, tin oxide, lead oxide and copper oxide. Manganese oxide was found in both but the concentration was particularly high in the light green example. As mentioned already, manganese was sometimes used as a decolourant and this was likely an attempt to counteract the green colour caused by the iron oxide, an attempt that was not entirely successful.

A purple bracelet fragment, similar to the purple bead was also found to contain significant quantities of manganese oxide. It was one of the best preserved artefacts within this assemblage from an elemental point of view, containing a relatively high level of soda and a low concentration of aluminium oxide showing that the surface layers had not been corroded to as great an extent as some of the other glass in the assemblage. Visually, it did not appear better preserved than any of the other bracelet fragments, none of which showed any signs of corrosion.

The final two bracelet fragments were described as amber-coloured on excavation (Johnston 2007, 120), although they appeared a very dark colour with almost a greenish tinge prior to analysis. Despite looking similar, there were clear differences in their elemental composition. One was potash-based while the other was mixed-alkali based. Both contained low levels of iron oxide and manganese oxide compared to the other bracelet fragments. They also lacked any obvious colouring agent, suggesting the elements they do contain may have reacted with elements such as

carbon in the furnace environment to produce their dark colour. As XRF cannot detect elements lighter than sodium, carbon would not be detected.

Eight toggles in total were analysed. Four of the eight were potash-based, three appeared to be mixed-alkali and a single example was a soda-based glass. With the exception of one red example (Plate 4.3), all the glass toggles had colours typical of Iron Age glass: blue, amber and green. Red glass is very rare in Ireland particularly for this period (Laing 1975, 337) and an example of a red toggle made it more unusual. An undated and unprovenanced red ingot reputedly from the Hill of Tara was found to be comprised of a typical soda-lime-silica glass with high levels of lead oxide and copper oxide added to it (Stapleton *et al.* 1999, 913-915). By comparison, the red toggle from Dún Ailinne had much lower concentrations of lead oxide and copper oxide, however it must be considered that the surface of the red toggle from Dún Ailinne has most definitely undergone corrosion and as such the results were not entirely representative of its original composition. This could be seen in the elevated level of aluminium oxide and low levels of modifier detected. The red toggle was also the only toggle to contain tin oxide, which may have caused its opaqueness. With regards the other toggles, the blue were coloured with cobalt oxide, much like most of the other blue glass samples. The green example was coloured with high concentrations of iron oxide. A light-greenish toggle was also coloured with iron oxides, albeit in much lower amounts.

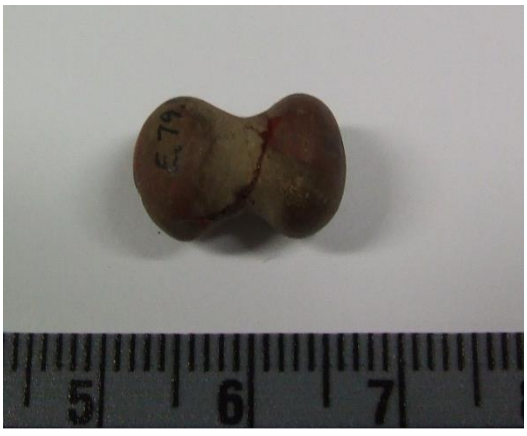

Plate 4.3: Red Toggle

The final group of finds consisted of four unidentified glass fragments of varying shades of blue. Three were small sherds and the fourth was a thin rod fragment.. Apart from the thin glass rod which was potash-based, the remaining three were mixed-alkali based. All four were found to contain both cobalt oxide and copper oxide, both of which could be responsible for the blue hues they exhibit. Two of the finds had slightly lighter shades of blue than the others and this corresponded with lower levels of cobalt oxide detected during analysis.

Overall, the XRF analysis revealed a varied glass assemblage containing potash-based, mixed alkali-based and soda-lime-based glasses which had undergone corrosion to varying degrees. Many of the objects were found to be in good condition, retaining much of their original composition. Many of the beads were found to show uniformity in the types of trace elements and raw materials that were used to produce them. This suggests similar production methods for many of them and furthermore similar origins. In addition, the elemental analysis also revealed some anomalies amongst the assemblage, such as the single blue bead which contained no cobalt and instead was coloured using copper oxide.

4.2.2 Glencurran Cave, Co. Clare. Viking bead assemblage. (Full Report, Appendix E)

Glencurran Cave is located within the Burren in Co. Clare. Rescue excavations were carried out in 2004 and 2005 by Dr. Marion Dowd of Institute of Technology, Sligo in response to human, animal and flood activity damaging the archaeological contexts of the cave. Most of the glass represented a Viking glass necklace (Dowd 2009, 90). A total of thirty-eight glass beads were analysed from this site. The majority of these were in a corroded state and exhibited an iridescent sheen to varying extents.

All of the beads, with the exception of two, were potash-based. The other two were most likely produced using mixed-alkali glass. The levels of soda and potash in all of the beads were found to be heavily depleted indicating a great deal of corrosion in their surface layers. In addition, high levels of aluminium oxide in all the beads

would suggest that certain elements had been preferentially leached from the surface layers, leaving mostly silica and aluminium behind. Manganese was also present in many of the glass fragments which in this case was most likely added in as part of the potash source.

The largest group of beads was a segmented type, with fifteen examples (Plate 4.4). Of these, twelve contained traces of silver, the only examples from the assemblage to contain this substance. This is known to cause a yellow colour when used in glass production (Goffer 2007, 122), however none of these beads exhibited this colour, instead having a variety of hues from brown to blue. It is possible that corrosion may have affected the original colour of these beads as examples of opaque-yellow segmented beads coloured using silver additives are known from elsewhere, such from a Viking burial on the Isle of Lewis in Scotland. The segmented beads are also unique in that none of them contain osmium oxide which was found in trace quantities in many of the non-segmented examples. This would have been added unintentionally as part of certain natural alloys or in igneous rock or soils. The segmented beads appeared to have corroded differently based on the amount of segments they contained; two, three or four. Those with two segments appeared to have corroded to a greater extent than those with three or four, possibly due to different surface-area-to-volume ratio or to their differing elemental compositions.

Plate 4.4: Segmented bead

The second largest group was comprised of oval and globular beads which varied widely in their elemental composition and had a range of colours from whitish, to bluish to brown. The iron concentration of these beads varied greatly and other trace elements such as cobalt, copper, sulphur and chromium were present in certain beads while not others.

The third group, which consisted of flat annular beads, were much more consistent in their elemental composition. While opaque cream in colour, it was thought that these beads may have undergone calcification which would have added calcium to the surface of the glass and altered their appearance. Due to their similarity in appearance to finds from other Viking sites such as Knowe of Moan, Scotland and the Isle of Man, O'Sullivan reasoned that originally they may have been blue (O'Sullivan (forthcoming)). The elemental analysis supported this as most of the beads contained blue colourants such as copper and cobalt, indicated they were probably blue in colour when they were first produced.

The final group consisted of three translucent blue beads. All were a rounded shape although not the same size and their blue colour varied considerably. The elemental analysis confirmed different raw materials and colourants used to produce them. Only the darkest one was coloured with cobalt while the other two were coloured with copper oxides. One of those containing copper also had a significant level of iron present which added a greenish tinge to its blue hue.

Overall all the XRF analysis shows a predominantly potash-based glass assemblage which had been heavily corroded. The Viking beads from Glencurran exhibited a wide variety in their elemental composition. Even finds which could be grouped together based on their appearance were not consistent, such as the segmented examples. The heavily corroded state of the surface layers of these beads may have compounded this, although given that they were found in close proximity to each other, they would most likely have been exposed to the same weathering conditions. Another thing of note was the surprisingly low levels of calcium detected, given the calcium-rich environment that they were found in. It is difficult to determine if the beads made up a single necklace or several, based on the wide variety of elements

detected in their structure upon analysis. It is possible that certain groups which were identified, such as the beads containing silver, may represent individual pieces of jewellery.

4.2.3 Lagore Crannog, Co. Meath. Early Medieval. (Full Report, Appendix E)

The site of Lagore consisted of a crannog which was located near Dunshauglin in Co. Meath. It was excavated by the Harvard Archaeological Expedition between 1934 and 1936 (Hencken *et al.* 1950, 3, 7). Both Hencken (1950, 6) and later Warner (1985/1986, 75) agreed on a date of no earlier than the seventh century and possibly as late as the eighth century for the earliest occupation of the site. In total, three periods of occupation were determined and designated as Period I, Period II and Period III. Period I includes the earliest occupation phase, which as mentioned would have been the seventh or eighth century. Only a few of the glass objects were found in Period I contexts and it was suggested by Hencken (1950, 9) that they were most likely imported as broken pieces for the production of studs for bronze ornaments. Moulds which would have been used for producing such studs were also found. Periods II and III did not give any evidence of date but instead coincide with reconstruction of the site on two different occasions after its initial construction. There are references in annal records of the structure having been destroyed twice; firstly in 850AD and then again in 934AD. This may mark the beginning of Periods II and III respectively (Hencken *et al.* 1950, 9). The majority of the glass that was analysed, forty-six out of the sixty-eight pieces, came from unstratified contexts, twelve pieces came from Period I contexts ten pieces came from Period II contexts. These included a range of glass beads, bracelet fragments and a few miscellaneous pieces.

The largest group of beads were undecorated blue examples, making up seventeen of the fifty-one beads (Plate 4.5). Eleven of these were potash-based examples, while the remaining six appeared to be mixed-alkali glass. The blue colour in all but one of these was caused by the presence of trace amounts of cobalt oxides in their structure.

The single example which was not coloured by cobalt oxide had a much lighter blue colour with a greyish tinge which was most likely achieved by using copper oxides in the glass mixture during its production. By examining other trace elements in the sixteen cobalt blue beads, it was possible to suggest what type of material was used as the cobalt sources in some cases. The presence of arsenic oxide in eight beads, seven of which also contained nickel oxide, would suggest that these beads were produced using a single type of cobalt ore, skutterdite. There was also evidence that tin oxide was used to produce blue beads which had a more opaque appearance. The two blue beads with the highest concentrations of tin oxide were noticeably lighter blue and more opaque than examples with much lower concentrations of tin oxide. Tin oxide was also utilised in producing white decoration for other beads on the site as will be discussed shortly. Three examples of segmented undecorated blue beads were also analysed. Like the other blue glass beads, there was a mixture of potash-based and mixed-alkali glass. The three were coloured with a mixture of cobalt oxide and copper oxide. They also contained significant traces of tin oxide which would account for their slightly opaque appearance. The did not contain any traces of arsenic which would suggest that they had not been produced using skutterdite as a cobalt ore and overall appeared different from the unsegmented blue beads. The difference in elemental composition would suggest that the two types of beads were essentially quite different from each other (Plate 4.5).

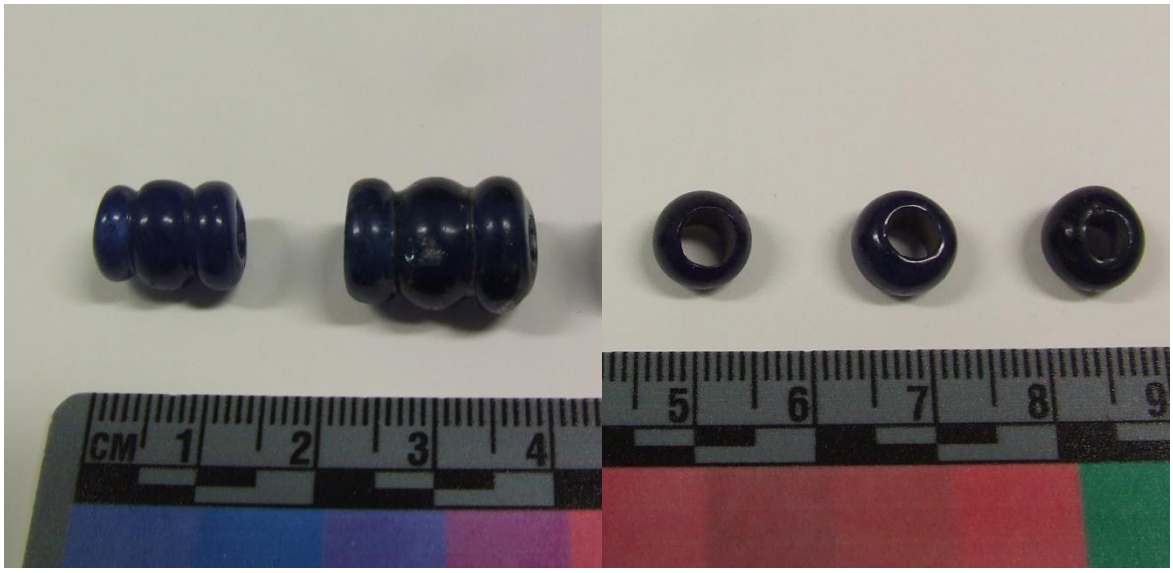

Plate 4.5: Segmented (left) and unsegmented (right) blue beads

The second largest group of beads consisted of decorated blue beads with a total of ten analysed. There was a greater variety in the shape and size of these and they had intricate red, white and yellow coloured glass within their structure. Like the undecorated blue beads, there was a mixture of potash-based and mixed-alkali glass with six potash-based and four mixed-alkali finds. The blue colour in all of these was also caused by trace amounts of cobalt oxide. Significant trace concentrations of tin oxide were also found in seven of the ten examples, which was unsurprising given that the beads had opaque white decoration and tin oxide was widely used to impart an opaque white colour to glass in antiquity. The yellow decoration was most likely caused by concentrations of lead oxide and tin oxide, which together are known to produce opaque yellows in glass. A single find had small amounts of red decoration on its surface but unfortunately it was not possible to detect the elements which would have caused this. Previous analysis of red glass from Early Medieval Ireland and Britain would suggest it was most likely produced using a mixture of lead and copper oxides in the glass structure (Stapleton *et al.* 1999, 913-915, Bertini *et al.* 2011, 2765).

The next two groups of beads were opaque yellow and opaque white with seven examples of each. These two groups had the most corrosion of any of the finds from this site. This was evident in the elevated levels of aluminium oxide and depleted levels of modifier substances, potash and soda, which they contained. The yellow hue of these beads was achieved with a mixture of tin oxide and lead oxide as these elements together are known to produce opaque whites and yellows (Henderson 2000b, 74). Four of the seven yellow beads contained small trace amounts of gallium. The four pieces of glass which contain it also had high levels of sulphur oxides. Given that these high levels of sulphur oxides distinguish them from the other finds, it is likely that they were both added to the substance as gallite ($CuGaS_2$). The white beads were produced using tin oxides in their structure with the exception of a single find. It is difficult to say what could have coloured this bead based on the results obtained. Perhaps it did contain tin oxide, just not in high enough concentrations to be detected by the XRF or leached away as the surface layers underwent corrosion. It is noteworthy that this bead was the only example to

contain traces of cadmium oxide , however this substance would usually impart a yellow tinge to the glass, not white (Henderson 2013, 113).

Two green-coloured beads were analysed, one having a light-green tinge and the other having a 'khaki' colour with more of a yellow tinge. Both had modifier concentrations consistent with mixed-alkali glass. The greenish colours in both were likely caused by iron oxides. The variation in the shade of green between the two was most likely caused by differing oxidation conditions in the furnace environment. It is also possible that the copper oxide, which was only present in one of the two beads, played a role. Copper has been found to impart a wide range of colours in glass (Bhardwaj 1979, 42-43). This includes blue tones ranging from bluish green to a very pale blue that could also be achieved by adding cupric oxide to the glass. Adding cuprous oxide, meanwhile, results in a reddish-brown colour (Bhardwaj 1979, 42-43). Finally, the yellowish-green colour of the second bead may have been caused by the elevated concentration of manganese oxide of the glass which was 1.07%. Manganese, when added to other elements such as carbon and sulphur, is known to impart an amber hue. This, when added to a darker green glass, may have produced the more yellowish-green colour of this particular find. Unfortunately it is not possible to detect carbon using XRF analysis, but sulphur oxide was detected.

A total of five beads with polychrome or multi-coloured surfaces were analysed. These were found to be a mixture of potash-based, soda-based and mixed alkali-based glass with a wide range of colours. The analysis suggested tin oxide was used for white opaque glass, chromium oxide for green, manganese oxide and sulphur oxides for amber, lead oxide for yellow, cobalt oxide for blue and copper oxide for reds and blues.

There were twelve bracelet fragments analysed, ten of the fragments were a more translucent bright blue with white decoration while the other two were a lighter and more opaque greenish-blue. They exhibited some of the lowest amounts of corrosion of any of the finds analysed from this site, with low levels of aluminium oxide and high amounts of modifier substances remaining in their surface layers. It was most likely that a different glass production method and recipe was used for these objects,

resulting in an elemental composition more resistant to agents of corrosion. In particular, these bracelet fragments were more likely to have higher concentrations of soda. Soda glass typically survives better than potash-based glass which is more susceptible to weathering (Moran 2010, 17). It could also be due to the different relative-surface-area-to-volume ratio of the bracelet fragments when compared with that of the beads.

All twelve of the bracelet fragments contained traces of cobalt oxide which would have given a strong blue hue to glass even with such small amounts. All of the fragments bar one also contained varying amounts of copper oxide additives. This can also impart a blue colour to glass but as there was no visible difference between the fragment that did not contain copper and those that did, it was probably not added as a colourant in this case. Tin oxide was also found in all twelve finds and was likely used for the opaque white decoration which was present on all the blue bracelet fragments. Finally, the two greenish-blue examples had higher levels of lead oxide and this may have caused their more opaque appearance when compared to the other bracelet fragments.

There were four pieces of miscellaneous glass fragments analysed. The first was a clear vessel rim sherd with a slight hint of a green tinge. It was a mixed alkali glass, with a slight green colour caused by the presence of iron oxide in its structure. The second find was a flat sherd of blue glass which appeared to be some kind of window glass. It had signs of crizzling, which appear as small fine cracks on its surface. This was most likely caused by an imbalance of alkali in its surface, evident from the reduced amounts of modifier detected during the analysis, or by the humidity of the environment of the piece of glass changing suddenly (Bray 2001, 215). It was found to be soda-lime glass, with its blue colour coming from cobalt oxide. The third find was a small sherd of clear glass. Despite its very clear appearance, the visible air bubbles in its structure suggested that it was in fact ancient as these would be removed in the manufacturing process by the high heat which was attainable in modern furnaces. This is unsurprising given that the piece was found in a Period I context. The final find was a fragment of blue glass which

looked similar to an elongated toggle. Similarly to other blue beads from this site, this piece contained concentrations of cobalt oxide which were responsible for the bright blue hue it exhibited. While unstratified, the elemental analysis shows that this bead was most likely produced and utilised around the same time as the Early Medieval blue glass beads due to the similarities in their major and trace elements.

The Lagore glass assemblage contained a rich variety of glass colours and types which exhibited the broad types of raw materials and wide range of skills that ancient glassmakers possessed. Undoubtedly one of the most impressive collections of glass uncovered from Early Medieval Irish contexts, it highlights the high status nature of the site and much can be learned from the analysis. The elemental results show a range of potash-based, soda-based and mixed alkali-based glasses and can differentiate between beads which are visually quite similar, such as in the case of the undecorated blue beads where the lightest-coloured example was shown to have a different colourant than the others.

4.2.4 Kilteasheen, Knockvicar, Co. Roscommon. Early Medieval to Modern (Full Report, Appendix F)

The site which was excavated at Kilteasheen is known as the 'Bishop's Seat', a Late Medieval ecclesiastical site. Known to date to 1253 AD from records in the annals, excavations revealed a complex site with evidence of activity from the Neolithic, Bronze Age and Early and Late Medieval. The high status of this site is evident from the numerous times it is mentioned in annals from the thirteenth century, its strategic location alongside the Boyle River and its association with the O'Conor kings in Connacht (Read 2010, 41). The excavations were run for five seasons with as part of the Kilteasheen Archaeological Project which was led by Christopher Read from the Institute of Technology, Sligo and Dr. Thomas Finan from St. Louis University (Read 2010, 41, 45, 66). A total of twenty-seven glass pieces and eight stones with glaze on their surface were analysed.

Three narrow blue bead fragments were found associated with a juvenile burial. They were found to be potash-based glass with high levels of aluminium oxide which would suggest heavy leaching or corrosion of their surface layers. Their blue colour had been achieved by adding cobalt to the glass mixture. The three beads were undoubtedly from the same production as their concentrations of major elements were consistent with each other and they also contained the same trace contaminants including iron oxide, arsenic oxide, lead oxide and sulphur oxide. Two pieces of light-weight glassy material were also found in cuttings which contained burials, however these particular finds may have been introduced as part of dump layers associated with these particular burials. Like the three thin bead fragments, these were potash-based glass which had degraded after prolonged exposure in the ground and contained elevated levels of aluminium oxide and depleted amounts of modifer. They had high levels of iron oxide and manganese oxide which most likely reacted with carbon in the furnace during the production of the glass to cause their black colour.

Seven pieces of olive-green glass, most likely from Post-Medieval bottle glass, were also analysed. These pieces seemed to be mixed-alkali, containing detectable amounts of both potash and soda. All of these olive-green sherds showed significant concentrations of iron oxide which would have given a deep green colour. There are a few different possibilities as to what can cause an olive or yellow-green hue in glass. The first is the presence of trace amounts of sulphur oxides within the glass which, in conjunction with iron oxides will cause an olive colour (Freestone 2009, 81). None of these samples contained any detectable amount of sulphur however. Another factor is the oxidation state of the iron oxides. The presence of iron in the glass, whether intentional or as an accidental contaminant, causes a green colour. When the iron content is mainly Fe (II) the colour is green, but when the iron is present in predominately Fe (III) form, the glass will exhibit a more yellow-green colour (Fenzi *et al.* 2010, 331). This would suggest that there may have been an oxidising environment in the glass furnace at time of production which would have allowed the iron to oxidise into Fe (III). This would imply that the glass-makers either intentionally wanted to produce olive green glass, that there was little control

over the flow of air into the furnace or that this factor was not considered particularly important in this case.

Two more pieces of blue glass were analysed in the form of a blue glass bead which was found to be a heavily corroded potash-based example and a mixed-alkali blue glass fragment which may have formed part of a bead. Both were coloured using trace amounts of cobalt oxide. There was also a single corroded sherd analysed, which was typical of Post-Medieval bottle glass in both appearance and elemental composition. It was found to be potash-based with significant levels of iron oxide, which caused its dark green colour.

A total of eleven glass pieces were found during field-walking at the site and will be discussed briefly here. Four green sherds had compositions consistent with that of low-quality, high-iron Post-Medieval bottle glass. Five pieces of clear glass were found including a mixed-alkali Post-Medieval bottle neck sherd, three modern sherds of soda-lime silica window glass and a piece which was much too small for its function to be identified. There was also a clear sherd with a purplish tinge which appeared to have formed part of a rim, although the piece was too small to estimate a diameter. It had the highest concentration of manganese in any of the clear samples which may have caused its purplish hue. Manganese oxide was often used as a decolourant in ancient glass to counteract the green colour given by iron but adding to much to the mix would give a purple colour (Goffer 2007, 121). The use of a decolourant and the levels of corrosion in this piece would suggest that it was not modern and instead was most likely Post-Medieval in date.

A total of eight stones with glaze were analysed as part of this study (Plate 4.6). While the function of these pieces was not clear, it appears that they were formed when molten glass dropped on to stones. It could potentially be waste glass from glass production or pottery glazing. However, such material will generally be found in greatest concentration near the furnaces on sites where glass-working has taken place (Taylor and Hill 2008, 249). This makes it unlikely that they were made as part of glass-working on this site and instead may have been brought here from elsewhere. Dump layers, consisting of soil moved from elsewhere for the purpose of

covering graves were identified on the site, so the stones may have been transported there in this way also. Only five of the eight finds had detectable amounts of soda while all of them contained traces of potash. The results would suggest that the glaze came from both potash-based and mixed-alkali glass. However as the majority of the modifier which the surface layers would have contained when the glass was first produced has been leached away, it was impossible to say for sure. All eight of these glazed stones contain iron oxides which was likely an unintentionally contaminant added in with the raw materials used. The only evidence that the glassmakers attempted to manipulate the colour of this glass material was that seven of the eight glazes also contained trace concentrations of copper oxide potentially have acted as a colourant. However these traces were in such small concentrations that it is possible that this was added unintentionally as part of the raw materials of the glass. There was no detectable amount of lead in any of the glaze samples, a compound which was commonly found in pottery glazes (Henderson 2000b, 126). However, evidence from eleventh and twelfth century sites in the UK showed that glaze was sometimes 'splashed' onto the pot which would account for the spilling of glaze onto the stones at this site. Since the elemental composition and material characteristics are much the same for pottery glazes as they are for glasses, it is difficult to say with any certainty where the glaze on these stones came from.

Plate 4.6: Glazed stones

The finds from this site show a mixture of soda-lime, potash-based and mixed alkali-based glasses from a number of different time periods which have been subjected to varying degrees of corrosion over time. Only the three thin blue bead fragments appear to have been purposely placed, being associated with a burial. The majority of the glass uncovered seems to represent lower-quality bottle glass. The glazed stones could potentially be waste glass from glass production or from the production and application of glazes to pottery, and were most likely formed when molten glass or glaze fell on them.

4.2.5 Blackfriary, Trim, Co. Meath. Late Medieval to Post-Medieval (Full Report, Appendix G)

The site of Blackfriary situated in the townland of the same name in Trim, Co. Meath was a Dominican Friary which was founded in the thirteenth century. The first year of excavations, which took place in 2010, consisted of two cuttings adjacent and within what was thought to be the church. Remains of walls relating to the belfry tower of the church were uncovered in these cuttings. There was a copious amount of waste material from dumping interspersed throughout the layers which dated to both the modern period and the Post-Medieval. Excavations in the following three years focused on exposing other elements of the church and cloister, and included the excavation of human remains within the nave, cloister garth and ambulatory (O'Carroll 2014). A total of six glass pieces were analysed from this site.

The first fragment was a heavily corroded green glass piece found in burial 5 in context F335 and has a possibly medieval date. The piece was somewhat similar in appearance to the two fragments from context F708, however it had no sign of decoration on its surface. Burial 5 was a full adult inhumation which was orientated east to west. There were several other objects found alongside the glass piece including a piece of metal, a stone, a piece of lead and five shroud pins. Given that the context was situated within the nave of the church, it is likely that this piece came from a stained-glass window. The lead piece found alongside may have come

from a frame which once held the glass and may be indicative of the destruction of a window at an earlier stage (O'Carroll 2014, Appendix D).

This piece showed heavy signs of weathering with only minute traces of potash remaining in the structure. Medieval window glass in Ireland was predominantly potash-based and these types of glass are highly susceptible to weathering due to their high alkalinity (Moran 2010, 17). This find also contained traces of phosphorus oxide and chlorine in its structure. Medieval glass made using potash sourced from burnt tree ash, or 'forest glass', often has significant levels of both phosphorus and chlorine (Goffer 2007, 155-156). It can also often contain concentrations of magnesium oxide, although there was none detected in this particular piece. The presence of such levels of phosphorus oxide in a glass can also increase the separation of the phases in the glass, reducing its chemical resistance (Goffer 2007, 172). This would further account for the susceptibility of this piece to corrosion as was evident from the dark layers which had developed on its surface. The green colour of this piece was likely caused by the presence of iron oxide, however it also contained traces of both copper oxide and nickel oxide, which can act as green colourants in glass.

The second piece of glass was a small black sherd with no visible signs of corrosion which was found in context F401, a natural accumulation of topsoil (O'Carroll 2014, Appendix D). The levels of potash and soda indicated that it was either a soda-lime glass or a mixed alkali glass. The black colour may have been caused by several different factors such as an abundance of coal in the glass furnace, which adds carbon to the mixture (Varshneya 1994, 217). As XRF cannot detect elements lighter than sodium, carbon would not be detected in the elemental results. This particular dark piece of glass may have been produced in a similar way to seventeenth century black glass from Britain. Examples there were known to have been made by utilising iron, manganese and sulphur in the glass melt and coupling this with a smoky atmosphere in the furnace (Davidson 2008, 77). This find had iron oxide, manganese oxide and sulphur, so it is possible that such a reaction with carbon may have taken place during its production. In addition, there were also traces of chromium oxide in

this piece, a powerful green colourant which could well have darkened the colour of the glass even further. It seems likely from the relatively uncorroded nature of this piece that it was Post-Medieval or early modern in date.

A third find from context F101 was a fragment of blue translucent glass. This context was also a modern accumulation of soil and contained a wide range of finds including modern pottery, plaster, a perforated kiln brick, a nail and this piece of medieval glass (O'Carroll 2014, Appendix D). This piece, like the first fragment discussed, was likely potash-based. However many of the trace elements associated with the addition of potash from burnt wood such as magnesium oxide and phosphorus oxide were not detected. Significant levels of cobalt oxide in its composition would have caused its bright blue colours. This piece also had no detectable amounts of many of the trace elements found in the other pieces such as barium oxide, strontium oxide, sulphur oxide and lead oxide. This, coupled with its much higher levels of corrosion, as indicated by the elevated levels of aluminium oxide, would suggest that this piece was produced with significantly different raw materials or that the production method used was different than the other pieces. This could suggest that this piece was imported from a different area than the others or that it dates to a different time than some of the other pieces that were analysed. It is unfortunate that this piece was found in a modern layer as its context was disturbed, however its composition was typical of medieval potash-based glass.

Two fragments were uncovered in context F708 (Plate 4.7), a modern trampled clay-rich layer located beneath the rubble of F709 (O'Carroll 2014). The first was a glass piece with four-leaf decoration. The decoration was a brownish colour and appeared to have been painted onto the glass. The piece itself was flat and was similar in appearance to other stained-glass window fragments from this site and it too was potash-based. It also had significant levels of phosphorus oxide, chlorine and manganese oxide but had no detectable traces of magnesium oxide. The manganese concentration could have added to the brownish colour. This piece had a significant quantity of iron oxide which may also account for its brownish colour. Overall the composition of the piece seemed to fit with that of a piece of decorative medieval

potash-based glass. The second piece of glass from context F708 was a small reddish-brown fragmented piece. Like the larger decorated piece from this context, it was potash-based however it had retained much more of this substance than the previous piece. A high level of potash was unusual given that this type of glass does not survive as well as soda-glass. It is possible that the potash for this particular piece came from a different source because it had much lower amounts of manganese oxide and phosphorus oxide as well as a higher concentration of chlorine and a significant concentration of magnesium oxide. This piece also had far less iron oxide than the larger fragment. Its copper oxide level was quite high however and depending on the oxidation conditions of the furnace, this could have given it its reddish-brown colour (Pollard and Heron 2008, 163). Given the small size and fragmented nature of this piece, it was difficult to determine what its original function may have been but it may have been a fragment of medieval stained-glass.

Plate 4.7: Corroded green window sherd

The final glass piece from this assemblage was a translucent pale-green glass fragment discovered in context F709, a deposit of rubble collapse of the north range and cloister, dating to the early modern period (O'Carroll 2014, Appendix D). It was difficult to tell what the original function of this glass piece was given its small size. Visually, it exhibited no sign of corrosion or discoloration however the elemental

composition showed that this find had suffered a great deal of corrosion in its surface layers. This can most clearly be seen in the concentrations of modifier which were found to consist of only trace amounts of potash. This would suggest a potash-based glass. The green colour comes from the significant level of iron oxide it contained as well as trace amounts of other green colourants including copper oxide and nickel oxide.

It became apparent upon analysis that the majority of the glass from this site was potash-based glass which had been subjected to varying degrees of corrosion due to being exposed to groundwater over time. The sherds of green window glass had significant iron in their compositions which would have given a deep green colour, but additional colourants such as nickel, copper and manganese oxides had also been added.

4.2.6 Bective Abbey, Co. Meath (Appendix F)

Bective Abbey was the site of a Cistercian abbey in Co. Meath which was excavated by Matthew and Geraldine Stout between 2009 and 2012. In total, 101 glass fragments from the excavations were analysed, much of which had visible signs of corrosion. The majority of the glass was potash-based with some mixed-alkali examples. Most of the finds, sixty-five in total, were from green bottles which were made from low-quality sands and ranged from a pale-green to an almost black-green colour. No other green colourants were detected which is typical of bottle glass. The black-green glass fragments were found to contain iron, manganese and sulphur in their elemental composition (Plate 4.8). This is consistent with other examples of black Post-Medieval glass in Britain, which were produced by combining iron, manganese and sulphur in the glass melt (Davidson 2008, 77).

There were thirteen sherds of clear glass in total. Their elemental composition contained very few trace elements and only slight evidence of corrosion effects which would suggest that they were modern soda-lime glass fragments, most of which appeared to have come from bottles. Another modern find was an amber

Plate 4.8: Black-green glass sherd

coloured sherd which was also soda-lime based glass and found to have been coloured by relatively high levels of manganese oxide.

Possibly some of the oldest glass pieces on the site were two sherds of window glass which were found in post-Dissolution contexts. Elemental analysis revealed them to be corroded potash-based glass. This would be consistent with early Irish church window fragments which were always produced using potash-based glass which is much more susceptible to corrosion due to its highly alkaline nature. This is why window glass found in medieval Irish contexts often shows varying degrees of corrosion (Moran 2010, 17). Given their find context, they were most likely part of a medieval window pane which was smashed during the dissolution of the abbey.

The majority of the glass from this site appears to be degraded potash-based or mixed alkali-based glass which has been subjected to a great deal of ground-water corrosion. Elemental analysis reveals that the alkali in the surface of the glass fragments has been leached away, leaving a disproportionate amount of the heavier elements behind. Much of what was found was consistent with lower quality Late

Medieval and Post-Medieval bottle glass, although some of the bottle glass was modern soda-lime silica glass.

4.2.7 Moygara Castle, Co. Sligo. Post Medieval to Modern (Full Report, Appendix I)

A number of glass fragments and glaze-covered stones were excavated at Moygara Castle by Christopher Read of Institute of Technology, Sligo. This was one of the main residences of the O'Garas, who were a prominent Sligo family. There are records of the site being attacked in 1538 and again in 1581 by the O'Donnell family and Scottish mercenaries respectively (O'Rorke 1889, 364-365). The current structure consists of a curtain wall with a tower at each corner, a gate-tower in the middle of the west side and the lower courses of a rectangular structure along the inside of the north wall. With the exception of the rectangular structure in the north wall which was most likely the remains of a medieval tower house, the rest of the structure most likely dates to the late sixteenth or early seventeenth centuries (Egan *et al.* 2005, 479). The number of glass finds and glazed stones came to fourteen, however two of the four glazed stones were too large to be analysed with the XRF.

The main type of glass uncovered from Moygara was green bottle sherds which appeared in good condition with no signs of corrosion or flaking. One sherd was found to be a mixed-alkali glass which was coloured using iron oxide. Ten similar sherds were found in close proximity to each other. The composition of all these pieces, with elevated levels of aluminium oxide and reduced amounts of modifier substances would suggest typical low-quality bottle glass, quite possibly Post-Medieval as opposed to modern given that the surface layers have undergone a great deal of corrosion. However, the variable amounts of modifier and trace elements would suggest that they did not all come from the same object. For example, only two finds contained traces of sulphur oxide, three of the ten pieces contained lead oxide and four of the ten pieces contained strontium oxide. The bottle-green colour exhibited by these sherds was caused by their concentrations of

iron oxide. Other green colourants, such as chromium oxide and nickel oxide were not detected in any of the pieces suggesting that the levels of iron oxide were high enough to cause the green hue.

The single clear sherd from the site was found to be a typical soda-lime-silica glass. It contained only traces of iron oxide and contained no concentrations of any elements which would have acted as decolourants. It also had very few trace elements within its structure, containing no detectable levels of zinc oxide, zirconium oxide, copper oxide or barium oxide which were found in many of the other glass pieces from this site. This suggests that this particular sherd was modern, as a much wider and higher percentage of trace elements would be expected in the composition of glass produced in ancient furnaces where it was much harder to exclude impurities. It had likely been exposed to the elements for some amount of time given that there was some evidence of corrosion based on the aluminium oxide being slightly higher than would be expected. Although a small fragment, its flat shape would suggest that it came from a sheet of window glass.

Two stones with glaze were analysed as part of this study from a total of four which were uncovered during the excavations. The others were too large to be analysed by the XRF. While the function of these pieces was not clear, it appears that they were formed when molten glass was dropped onto stones. It could potentially be waste glass from glass production or pottery glazing. Only the second glaze example had detectable amounts of soda while both contained potash. This result suggests that different types of modifier were used to produce the glaze on each of these stones. Both contained iron oxides which may well have been added in unintentionally as part of the raw materials that were used. The two glazes differ in the trace elements that they contained, further supporting the suggestion that they were not produced in the same way. One of them also contained low amounts of copper oxide. The only evidence that the glassmakers attempted to manipulate the colour of the glassy material on the second stone was the fact that it contained trace concentrations of copper oxide which could potentially have acted as a colourant. However this amount of copper oxide was in such a low concentration that it is more likely that

this was added in unintentionally as part of the raw materials of the glass. The glaze on both stones appeared to have a slight green tinge, however this was most likely caused by the significant level of iron oxides found in both finds.

The majority of the glass found on this site were pieces of Post-Medieval bottle glass, consisting of either potash-based or mixed-alkali material and which obtained their colour from iron contaminants. All of the green glass pieces exhibited corrosion of the surface layers with elevated levels of aluminium oxide and reduced amounts of modifier substances. The exception was a clear glass sherd which was a modern soda-lime-silica glass that most likely came from a pane of window glass. The layers of glaze on the two stones appeared to have very different production methods. One obtained its colour solely from its concentrations of iron oxide while the second had copper oxide in addition to iron oxide. Furthermore, the first example seems to have been a potash-based glass while the second was more likely a mixed-alkali example.

4.2.8 Seagrange, Baldoyle, Co. Dublin. Post-Medieval to Modern (Full Report, Appendix G)

This site is located in a suburban estate in Baldoyle, North Dublin. It exhibits several features which are believed to be consistent with those of a medieval moated site. This, alongside the recovery of Leinster Cooking ware sherds from topsoil of a garden, prompted the Grassroots Archaeological Project to conduct targeted excavations in some of the green areas and gardens (Grassroots Archaeology Project 2014). Two main phases of activity were identified during excavations: Medieval and Post-Medieval (Grassroots Archaeology Project unpublished). All of the glass which was analysed, a total of five pieces as well as a piece of vitreous slag, appeared to be Post-Medieval or modern in date.

The first two pieces, a thick piece and thin piece of glass rod (Plate 4.9), were very similar in composition. Both contained only small amounts of modifier, although the thin piece appeared to be mixed-alkali while the thicker piece only contained potash. Both were coloured solely by iron oxides in their structure with no other green

colourants such as nickel or chromium detectable. Both pieces had similar concentrations of certain trace elements such as iron oxide, titanium oxide and barium oxide.

Plate 4.9: Thick (left) and thin (right) glass rod pieces

The third find was a melted glass piece which had either been partially molten in the past or improperly formed to begin with. It could potentially be waste glass from glass production. Like the thin rod, it was likely a mixed alkali glass; however it also contained traces of magnesium oxide. This substance is often introduced to the glass mix as part of the source of potash, which suggests that a different source of potash may have been used for this piece. Its colour was also caused solely by iron oxide but overall the trace elements it contained were not consistent with those found in the two glass rod fragments, suggesting that a different production method or raw materials were used.

A corroded fragment displayed significant visual corrosion in the form of a flaky iridescent layer. Its appearance was typical of Post-Medieval bottle glass and the elemental results corroborate this. The fifth piece was a clear bottle neck sherd with a greenish tinge which was found to be soda-based glass. It did not contain detectable amounts of many of the trace elements which are present in some of the other glass finds such as zinc, zirconium, magnesium and cobalt. Given this, as well as its less corroded elemental condition, it was likely a modern soda-lime glass piece.

The final find analysed was a piece of vitreous slag which was a dark colour with an angular lump-like shape. It was also lightweight and porous. Elemental analysis showed significant concentrations of silica, aluminium oxide and iron oxide, as well as many trace elements not present in the glass pieces such as chromium, nickel and copper. If these elements had been present in the glass finds they would have acted as powerful colouring agents and greatly altered their appearance. Given its composition it is likely that this piece was unrelated to the glass finds and most likely a side product of iron smelting given that it did not contain significant quantities of elements associated with other types of metal smelting.

The glass from this site proved interesting, particularly the glass rod fragments and melted piece, which may have been the product of small-scale production rather than large glass-making facilities. The only colourant that was found in any of these glass objects was iron oxide and this would have been present in the raw materials in the glass. There was no evidence that the producers of this glass attempted to add any other colouring agents or significant quantities of decolourants which would have counteracted the green colour caused by the iron contaminants. This would suggest that the glassmakers were either not particularly knowledgeable with regards the intricacies of glass production or else that the objects were intended as cheaply manufactured objects. It could also imply that there simply was not a demand for highly decorative glass objects.

4.2.9 Rothe Castle, Kilkenny. Post-Medieval. (Full Report, Appendix H)

Rothe House is an Early Modern townhouse located on Parliament Street, Kilkenny which is maintained by the Kilkenny Archaeological Society. The site is the best-preserved example of an urban mansion of the Irish Renaissance period. The archaeological excavations took place within the gardens of the house and were undertaken as part of a plan to recreate the original gardens to the rear of the house (Ó Drisceoil 2007). All glassware found on the site was of Post-Medieval origin

(Roche unpublished, 1). A total of sixteen glass finds from this site were analysed from a much larger assemblage.

The largest group of glass finds were twelve pieces from a German Stangenglas, or tall beer glass, which was of sixteenth or seventeenth century date (Plate 4.10). Three of the fragments formed part of the base while the rest were most likely body sherds. All were in good physical appearance although they displayed a light iridescent sheen on their surface. The pieces were from a mixed-alkali glass, with both soda and potash detected in their surface layers. The trace elements were quite low which is unsurprising given the high quality of the pieces. Many elements that are often found in ancient glasses were not detected including cobalt, nickel and chromium while iron oxide was only present in very small quantities. This suggests that fairly pure sands were used in the production of this piece and was undoubtedly the work of a very skilled glass-maker as the glass was completely clear with no colouration. The lack of variability in the composition of the pieces would also suggest skill on the part of the glass-maker in that they were able to produce a glass which had a homogenous composition.

Plate 4.10: German Stangenglas fragments

Two sherds of a possible 'porridge bowl' were analysed. The larger piece, which had white decoration, was analysed twice, once on the brown glass of its interior side and once on the white decoration of the exterior side. The smaller piece consisted of brown glass only with no visible white trail (Plate 4.11). A total of eight fragments from this artefact were uncovered and when reconstructed were found to form a portion of a small bowl with rounded shoulders and a flat, Y-shaped handle (Roche unpublished, 2). Potash concentrations were found in both samples with no detectable levels of soda. There are a number of different possible causes for the brown hue in these pieces. It is possible that the concentrations of iron oxide may have added to the hue. The concentrations of manganese oxide also seem elevated and may have imparted an amber or brown hue if in the presence of carbon in the furnace. The results from the analysis of the white decoration showed a high concentration of lead oxide. This is known to produce opaque white glass and was undoubtedly what was used to produce the white trail decoration (Henderson 2000b, 74). It also contained a high concentration of sulphur trioxide which was not present in the brown glass. Sulphur additives can react with other elements to form many different colours from yellow to brown and even black (Davidson 2008, 77), however it does not seem to have been added for the purpose of colouring in this case as sulphur is not known to produce a white hue. It is possible that they may have been added in as part of the source of lead, which as mentioned was added to provide the white colour. For example, galena, the main ore of lead, is composed of lead sulfide (Goffer 2007, 120).

It was suggested by Roche (unpublished, 2) that the object from which these fragments came could be a type of bowl used for eating porridge or gruel known as a porringer. Porringers of brown glass with white decoration were produced in late seventeenth century Germany. The report also mentions a comparable vessel in the form of a Roman patera dating from the second or third century AD (Roche unpublished, 2, 3). A Roman date for these fragments based on the elemental composition seems unlikely. Firstly, the level of corrosion based on the quantity of aluminium oxide seemed quite low if the object was ancient. Secondly, the items appeared to have been produced using a potash flux. This would be quite unusual

for a high quality Roman object, which would have been more likely produced using a high quality soda flux (Freestone 2009,83). If this bowl was indeed a replica of a Roman patera, it was likely produced much later.

Plate 4.11: 'Porridge-bowl' sherds

A single clear vessel shard was noted to be possibly part of the upper bowl and rim of a wide mouthed drinking glass. It had opaque white trails on its surface and a very slight greenish tint (Roche unpublished, 4). Its modifier levels were low but again seem to suggest a mixed-alkali based glass. The greenish colour of this find was due to iron oxide as other substances known to act as green colourants, such as oxides of copper, chromium and nickel, were absent. Manganese oxide was also detected in this piece, which could well have been an attempt to counteract the green colour caused by the iron oxide, an attempt that was not entirely successful. Roche (unpublished, 4) notes that this fragment was in the style of Venetian glass but it was not of high enough quality for Venetian ware as it displays a greenish tint. The results from the elemental analysis support the idea of a copy rather than the genuine Venetian. The results indicate that this fragment was most likely produced using a potash flux. This is in contrast to the true Venetian wares which were produced using a high quality source of silica and a soda-rich ash. The results were highly clear and transparent glassware. Tinges of green or brown in copies of

Venetian-style glassware were often caused by using a mixed alkali rather than a pure soda flux (Willmott 2004, 289).

A single Post-Medieval low-quality bottle fragment from this assemblage was analysed as the majority of the glass finds discovered during the Rothe House excavations were fragments of seventeenth to nineteenth century wine bottles (Roche unpublished, 1). The bottle fragments exhibited more visible corrosion than the higher quality glass fragments that have already been discussed and this single piece was taken as an example. The glass used for making bottles was almost always of a lower quality that that of other vessels and usually had a very dark green colour, caused by varying iron impurities (Roche 2007, 411). Its appearance was typical of bottle glass, which was cheaply manufactured and widely used during the Post-Medieval. It was found to be a potash-based example with its colour being caused by iron oxides in its structure.

The glass analysed from Rothe House includes a rich variety of high status Post-Medieval glassware. The results would suggest that overall the Stangenglas fragments survived the best out of the different groups of glass which make up this assemblage. This may have been due to the high quality of the glass used to produce this object, as it can be seen from the clear glass that pure sources of modifier and silica must have been used. The porridge bowl sherds were most likely potash-based and had decoration which was produced using lead oxide as a colourant and opacifier. The level of corrosion and type of modifier used would seem to suggest a Post-Medieval rather than Roman date for this find. The clear glass vessel fragment with a slight green tinge shows attempts by its maker to counteract its green colouring by adding manganese oxide to the glass mix. Finally, the corroded green sherd appears to be a fragment of typical low quality bottle glass, probably dating to the Post-Medieval period.

Chapter 5: Discussion

This section will discuss the findings from the research carried out as part of this thesis. Firstly, the information gleaned from compiling the database of glass from archaeological sites in Ireland will be discussed. In the following sections, correlations that were observed in the elemental analysis of the glass artefacts will be explored. Finally, the cultural and economic significance of these findings will be examined.

5.1 Database of archaeological glass finds

This section will discuss what further information can be gleaned by analysing the amounts and types of glass recovered from Irish archaeological sites. The purpose of compiling this information was not only to determine possible sources of glass for analysis but also to identify areas where elemental analysis could provide more information.

Figure 5.1 and Table 5.1 combine both the time period and function of the types of glass found on these archaeological sites showing the number of excavations, 487, where these glass types were found in relation to the period from which they come. There are two main trends that can be seen. Firstly, the majority of glass was both of unspecified type and comes from the Post-Medieval period. Secondly, the majority of the glass beads found on excavation sites are also of unknown date. The percentages and figures listed here are based on the number of sites at which certain types of glass were found, not the amount of individual artefacts, and will be discussed as such. This is because many of the excavations entries list the type of glass but do not specify how much was found. For example, several of those examined simply listed 'glass beads' and did not mention a quantity.

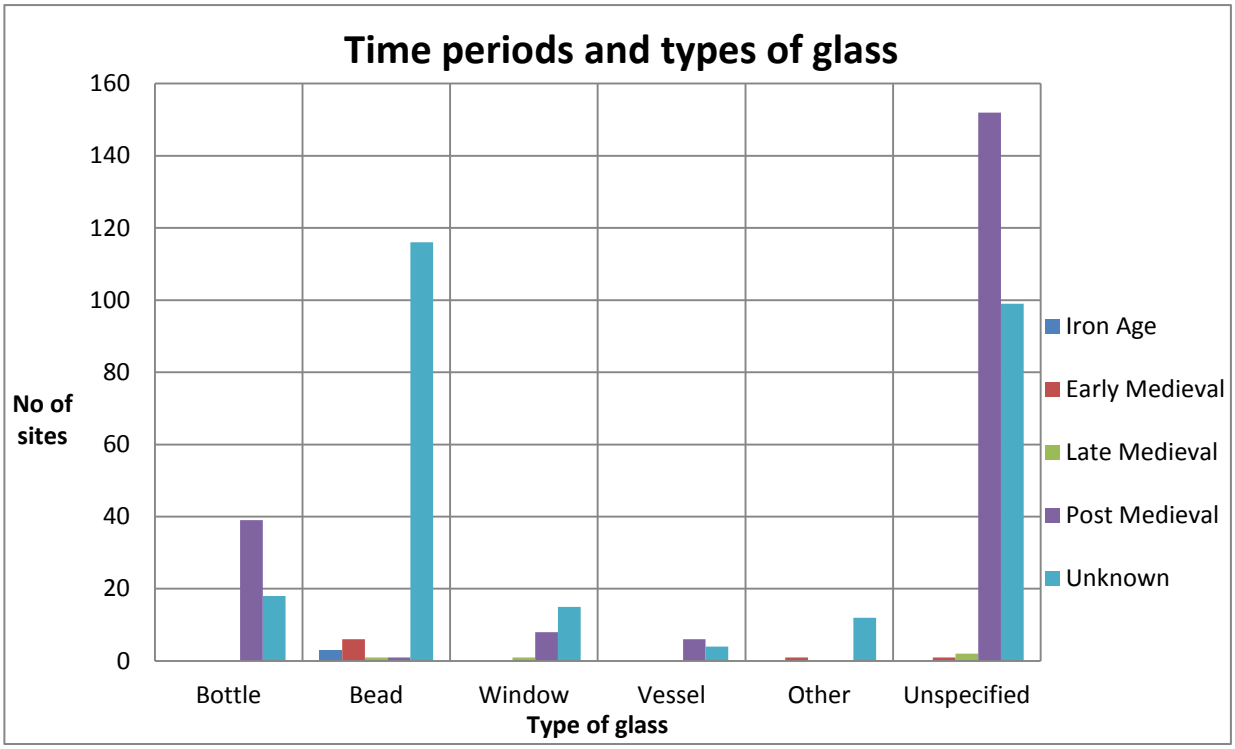

Figure 5.1 Dates and types of glass

	Iron Age	Early Medieval	Late Medieval	Post Medieval	Unknown (may include modern)
Bottle	0	0	0	8.04	3.71
Bead	0.62	1.24	0.21	0.21	23.92
Window	0	0	0.21	1.65	3.09
Vessel	0	0	0	1.24	0.82
Other	0	0.21	0	0	2.47
Unspecified	0	0.21	0.41	31.34	20.41

Table 5.1 Percentages of chronologies and types of glass

The data shows that 26% of the glass finds listed on archaeological sites were beads, the vast majority of which were undated. Of those that have a known date, most come from Iron Age or Early-Medieval contexts. Of those for which a description was given, the majority of them are simple blue glass beads which would suggest they could be as old as the late prehistoric (Bray 2001, 65). It has been suggested by some authors, including Edwards (1996) that antimony may have been used in increasing amounts as the Early Medieval period progressed. This would be

detectable with the elemental analysis carried out with the XRF and so may be a way to approximately date blue glass beads in relation to each other.

Most of the glass of unknown function for which a date is known comes from Post-Medieval contexts. The amount of unknown pieces could be lessened by carrying out elemental analysis which would potentially identify the type of glass and by extension, what it was used for. As was discussed in Section 2.2, different types of Post-Medieval glasses had varying compositions and would have been used for different purposes. Bottle glass, for example, was often mass produced and made with cheaply-sourced and easily-obtainable materials while flint glass is usually found to have a low iron content along with quantities of lead oxides, potash and manganese. Plate glass is a much higher quality type, containing finer materials with low iron content, costing more to produce and being physically thicker than other glasses (Rynne 2006, 184-185). Examining glass fragments with the naked eye can sometimes give an indication of what type of glass a fragment is, however elemental analysis provides much more detail and is far less ambiguous. Knowing the type of glass would help give an indication of what the object may have been, as different types of glass were generally used for different purposes. It could also help put the site where the glass was found into context.

Aside from unknown fragments and beads, bottle and window fragments make up the next largest groups of glass found, with 11% and 5% respectively. This figure may be considerably higher if the large body of unknown fragments could be classified. For example, cheap Post-Medieval bottle glass would likely have high iron-contaminants and a range of trace elements while medieval window glass is likely to be corroded potash-based glass. Like window glass, vessel glass is surprisingly rarely found (or perhaps, rarely identified) on archaeological sites, representing just 2% of the finds listed in the database. This may simply be attributed to the poor survivability of these objects in an archaeological context. As was discussed in Section 2.2, medieval stained-glass windows are rarely found due to their poor survivability. Their elemental composition makes them more prone to

corrosion as well as the destruction caused during the religious upheavals of the Late Medieval.

Other types of artefacts which have been uncovered, including the bracelet fragments and the glass inkpot, are rare in the archaeological record in Ireland. They are still worth analysis in their own right and could potentially be compared with results from similar objects abroad. Such rare items were likely to be indicative of high status and more than likely imported, therefore elemental analysis could provide much information on where they were produced and sourced.

The information gained by compiling this database of archaeological glass was invaluable not only because it identified sources of glass for the purpose of analysis but also as it highlighted the gaps in the knowledge of Irish archaeological glass. Namely, the difficulty in dating the relatively common blue glass beads, the lack of identification of the function of Post-Medieval glass and the inclusion of modern material in archaeological assemblages.

5.2 Elemental analysis of glass and the benefits of XRF without pre-treatments

This section will discuss the elemental results for the largest groups of glass from this study. Statistical analysis has been utilised to highlight trends within the groups of glass. The groups of glass that underwent statistical analysis are outlined in Table 5.2. This aided in the interpreting the results and adding to the information they could provide about their role in the economic and cultural background of the sites they were found in. All the results from the analysis are compiled in a database providing a basis for comparing results in the future. As this study has shown, glass which has been exposed to groundwater and soil becomes increasingly corroded over time. This greatly varies depending on the original composition of the piece as well as the environmental factors in question and the length of time it has been in the ground. However, employing destructive techniques to remove corroded layers is not particularly desirable for archaeological glass, particularly very small delicate items such as the beads recovered from Lagore crannog and the delicate Viking necklace beads which were found in Glencurran cave. In cases such as these it may be preferable to perform elemental analysis with no preparation techniques rather than risk greatly damaging the artefacts. While the results obtained are not necessarily a true representation of the exact original composition, they can give an indication of the original composition of the glass fragment as well as shedding light on the corrosion to which the object has been subjected. This can be useful in determining raw materials used as well as trace elements purposely added to affect the properties of the glass.

Site	Blue beads	Greenish-blue beads	Post-Medieval green glass	Post-Medieval clear glass	Post-Medieval clear glass with green tinge
Dún Ailinne	14	3	0	0	0
Glencurran	2	1	0	0	0
Lagore	25	2	0	0	0
Kilteasheen	2	0	13	2	4
Bective	0	0	65	14	10
Moygara	0	0	10	2	1
Seagrange	0	0	1	0	4
Total	43	6	89	18	19

Table 5.2 List of finds by type and site

Even without destructive techniques, different types of glass can be distinguished, such as potash-based and soda-based examples. In fact, the analysis of glass during this study highlighted how much more susceptible to corrosion and weathering potash-based glass was compared to soda-lime glass, with most soda glass fragments maintaining elements in their outer surfaces layers to a greater extent than potash glass found in the same environment. Elements added in as part of the raw materials were also identified, such as manganese which would have been added in as part of the potash source and osmium which may have come from the sand or silica used in certain glass artefacts. Colourants were also easily identified in most cases, such as cobalt in the majority of blue glass, iron in green bottle glass and tin and lead oxides in white and yellow beads respectively. A single type of colourant used across material from a wide range of sources would indicate a well-established method of producing a particular type of glass. Decolourants and opacifiers, such as antimony and tin oxides respectively, were also identified despite any corrosion in surface layers.

The elemental results from individual objects and sites can be applied to further knowledge about glass traditions as a whole as well as their role in the economy and social interactions of ancient peoples. For example, it is likely that Early Medieval communities may well have been importing ingots from elsewhere in order to rework the glass and produce their own artefacts. Red glass in toggle form, which is more or less unique to Ireland, was found to have a composition fairly consistent with red glass ingots found both in Ireland and in Britain which would support this. The glass-making techniques that were used in Britain appear to be in use in the Irish glass-making industry based on the elemental analysis, which fits what we know about the Irish Post-Medieval glass industry based on documentary and archaeological evidence.

5.2.1 Blue glass beads

Simple blue glass beads are some of the most common glass artefacts found in the Irish archaeological record and in particular are known from Iron Age and Early Medieval contexts. A total of forty-three plain blue glass beads were analysed from the nine sites in this study, with most coming from Lagore Crannog and Dún Ailinne, which date mainly to the Early Medieval and Late Iron Age respectively (Hencken *et al.* 1950, Johnston 2007) (Table 5.2). Beads are often indicative of a high status site. For example, in the Iron Age they are most often associated with burials, such as those at Knowth, Co. Meath (Bray 2001, 65). Bright blues are common colours in ancient glass, often achieved by adding cobalt to the glass during its production. Blues which can range from a very pale hue to a bluish-green can also be achieved by adding copper oxides to the glass (Bhardwaj 1979, 42-43). Despite their frequency, they are very difficult to date if they are not found in a defined context.

A number of interesting correlations were evident when statistical analysis was applied to the results of these blue beads. As no preparation techniques were used on the samples prior to analysis with the exception of washing, the outermost layers that were analysed by the instrument may have been corroded. Unfortunately, it is not possible to analyse the centre of the glass without utilising more destructive methods such as grinding and polishing the surface of the pieces and even in this case there is no guarantee that the inner layers have not been affected by corrosion or weathering agents (Zucchiatti 2004, Pollard and Heron 2008, 166). However, a lot of information was still gathered by examining the outermost layers.

A plot of silica versus aluminium oxide concentrations for blue glass beads demonstrates a significant inverse relationship between the two variables with an r value of -0.925 ($p = <0.001$) (Figure 5.2). Based on the criteria outlined in the methodology (Section 3.6) an r above 0.7 indicates a strong correlation. This is a trend observed in many of the glass fragments within this study but the correlation is particularly strong in this group. Elevated levels of aluminium were observed in many of the glass pieces which had undergone corrosion and were often found alongside depleted levels of lighter elements, in particular modifier substances.

Based on the results from this study, high levels of aluminium appear to be a strong indicator for corrosion. Aluminium would most likely have existed in the structure of the beads prior to any corrosion taking place. This may have been preferentially held in the structure compared to other elements. There is also the possibility that aluminium from the soil and surrounding environment were absorbed into the glass structure. Glass is particularly prone to corrosion when buried due to reactions with ground water. The process is complex and not well understood but it is known that the process begins at the outermost layers of the glass and gradually spreads inwards (Varshneya 1994, 398). Visually this often appears as a corroded, iridescent, flaky layer on the surface of the glass which eventually falls away, exposing lower layers to the same process. However this is not always the case, with the majority of the blue beads analysed showing no visible sign of corrosion prior to analysis.

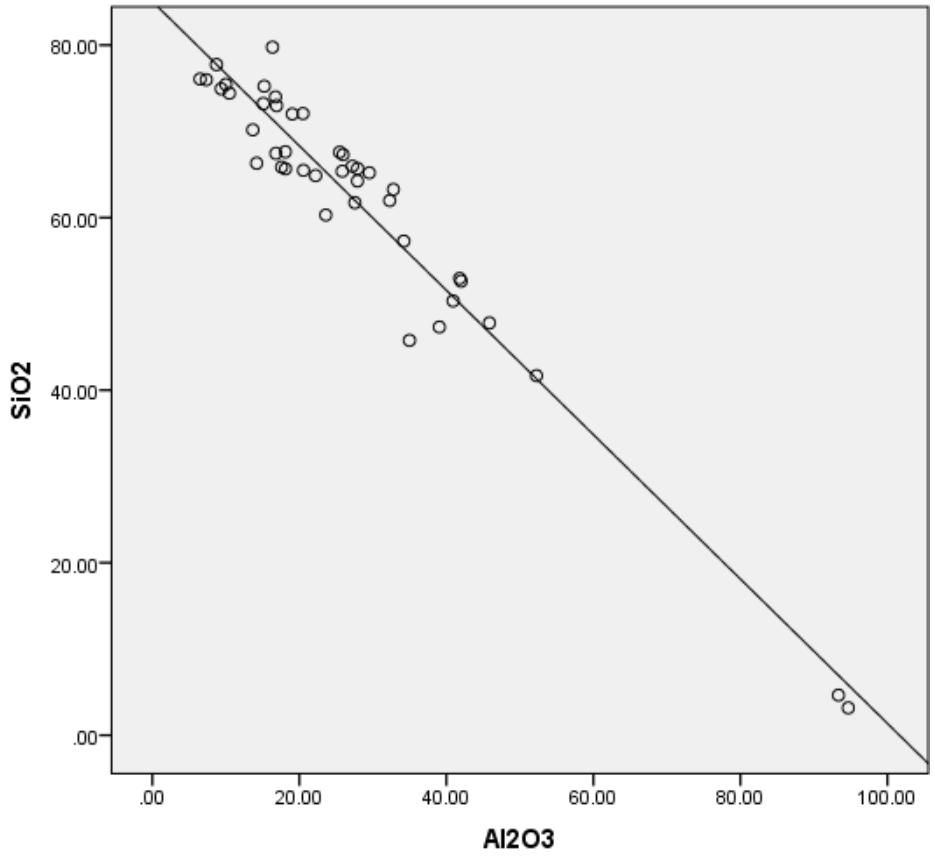

Figure 5.2 Silica (SiO_2) vs aluminium oxide (Al_2O_3) in plain blue beads (n=43)

A similar trend can be observed in the aluminium oxide vs calcium oxide concentrations although this is a much weaker correlation with an r value of -0.714 (p= <0.001) (Figure 5.3). This would indicate that both silica and calcium oxide are affected by the process of corrosion of the surface layers. Both of these elements are relatively light which seems to make them more susceptible to leaching. Other elements, particularly heavy metals, do not seem to have been affected to as great an extent as these, if at all. For example, with few exceptions, the concentration of copper oxide in these beads remains consistent despite varying amounts of corrosion. This can be seen most clearly by looking at the concentration of copper oxides versus aluminium oxides concentrations in this glass (Figure 5.4).

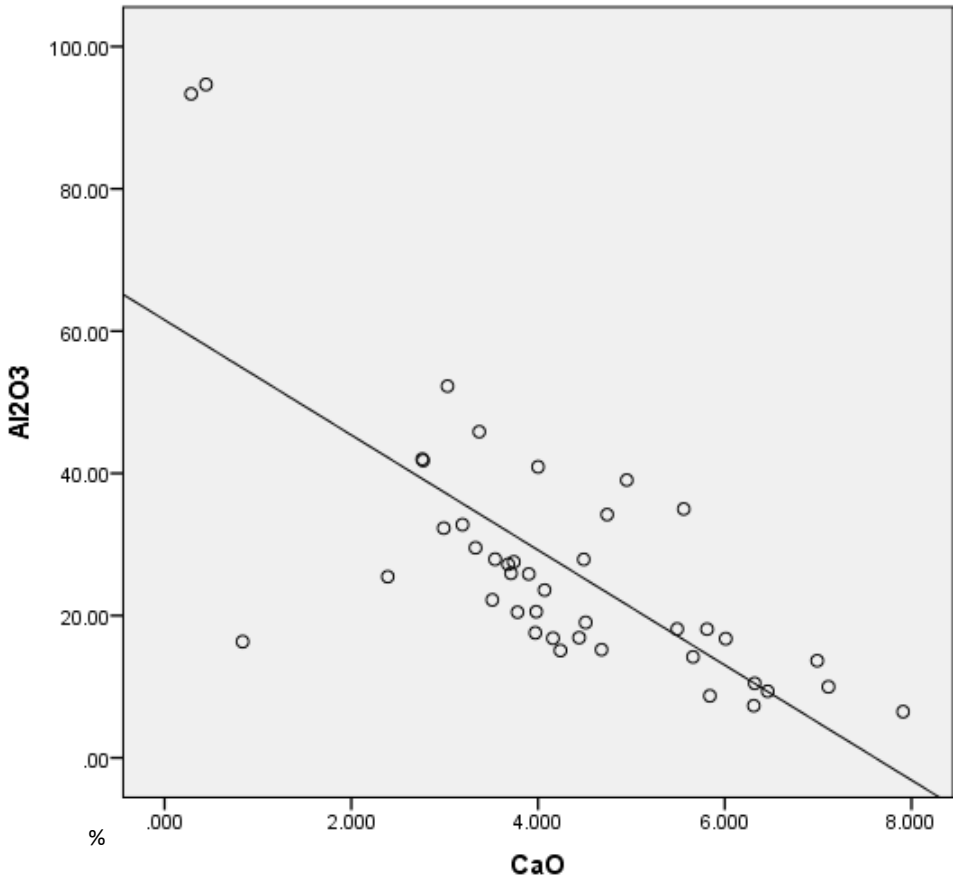

Figure 5.3 Aluminium oxide (Al_2O_3) vs calcium oxide (CaO) in plain blue beads (n=43)

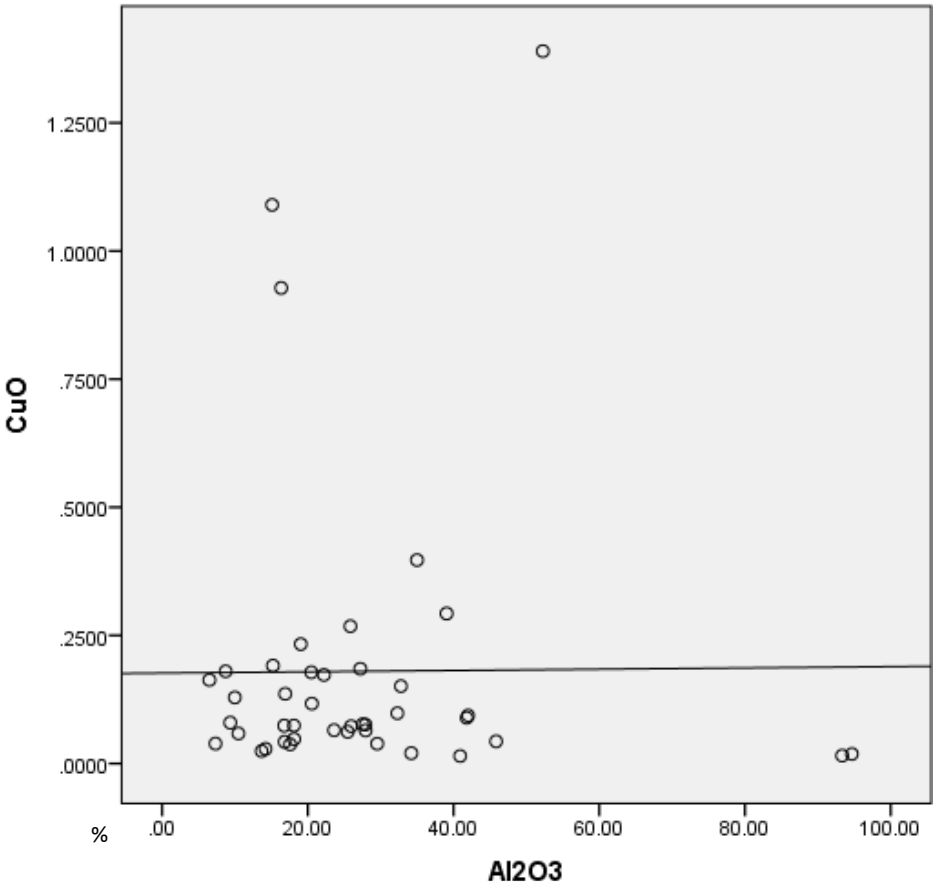

Figure 5.4 Copper oxide (CuO) vs aluminium oxide (Al_2O_3) concentrations in plain blue beads (n=43)

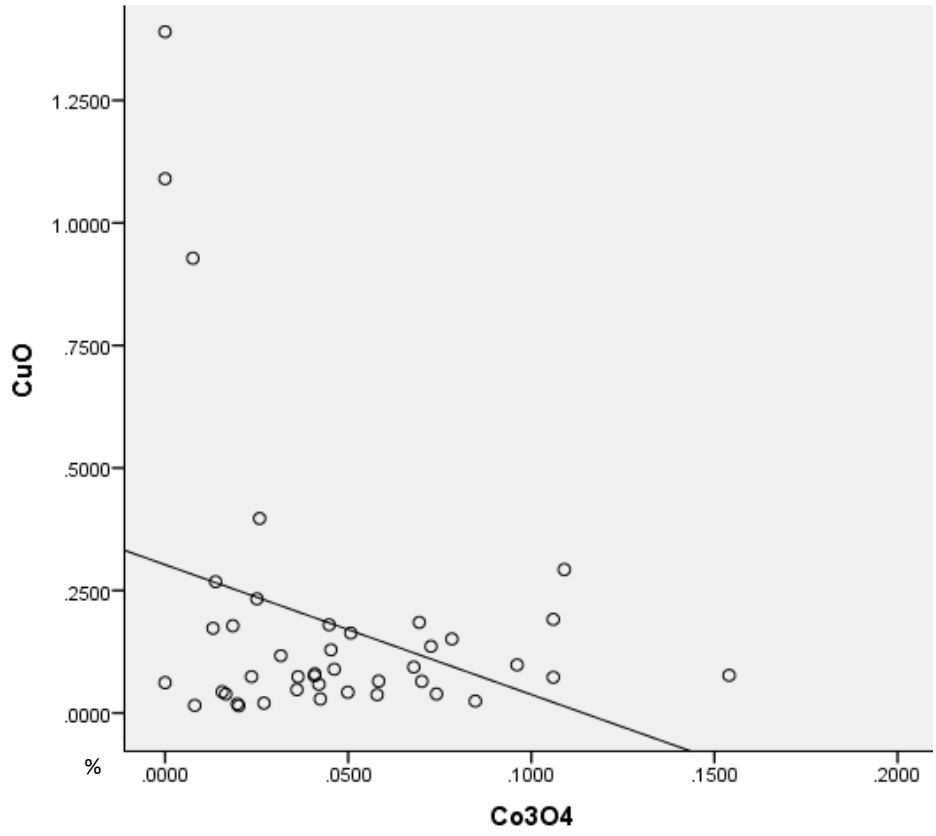

Figure 5.5 Copper oxide (CuO) versus cobalt oxide (Co_3O_4) concentration in plain blue beads (n=40)

As mentioned, the copper present in these beads appears to remain consistent with a few exceptions. Three of the beads had considerably higher concentrations of copper than the rest. However, of these, two had no detectable cobalt and the other had only a very low amount of 0.0026%, therefore it seems that copper would have been deliberately added to these in order to give a blue colour (Figure 5.5). Two of the beads came from Lagore while the other was found during the excavations at Glencurran. In the rest of the beads where cobalt was used as a blue colourant, copper would have been added unintentionally.

Antimony concentrations seem to vary quite widely in these beads as can be seen by examining the levels of antimony oxide versus copper oxide in Figure 5.6. It has been noted by several authors that a rising antimony content may be seen in glass as the medieval period progresses (Warner and Meighan 1994, Edwards 1996, 93). Blue beads recovered from Dún Ailinne, many from earlier Iron Age contexts, contained much lower concentrations of antimony than later medieval examples with an average amount of 0.11% for those that contained antimony, with a larger number having no detectable amounts at all. In general, blue beads from the site of Lagore, which dated to the Early Medieval, contained higher concentrations of antimony, with an average concentration of 0.58%. This would suggest that sources containing antimony were utilised to a much greater extent in the later site of Lagore.

Many of these blue beads also contained trace amounts of osmium oxide in their structure. Osmium is one of the rare metals and was not an intentional additive to ancient glass, instead being an accidental inclusion due to its presence in some of the raw materials. It is most often found either in natural alloys such as those containing nickel, platinum and copper or as an uncombined element, in which case it is generally found in igneous rock or soils with meteorite or comet residue (Emsley 2003, 199-200). A number of possible variables were examined and the only correlation that osmium has with another substance is with lead. The level of osmium oxide increases along with the level of lead oxide, a significant relationship with an r value of 0.891 ($p=<0.001$). Therefore, it seems likely that it was added in as

part of the lead oxide source which was used (Figure 5.7). Lead oxide was used in many of these blue beads for the purpose of giving the blue a more opaque colour.

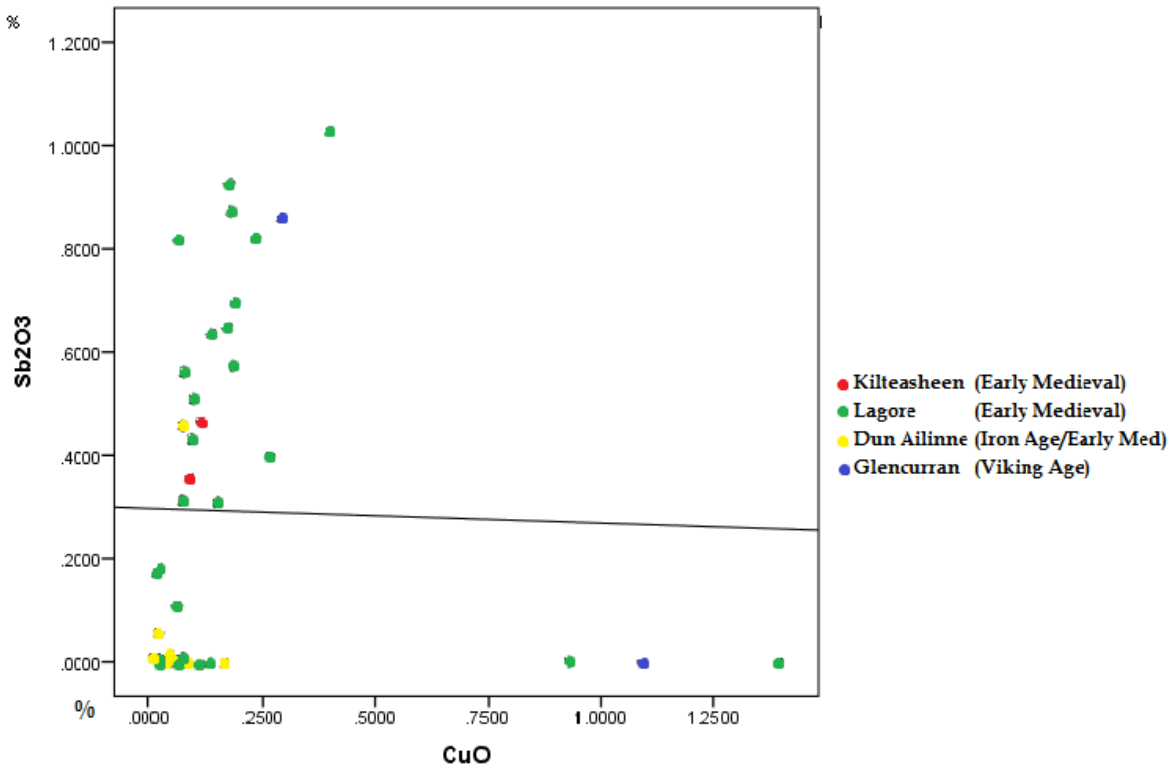

Figure 5.6 Antimony (Sb_2O_3) versus copper oxide (CuO) in blue glass beads (n=43)

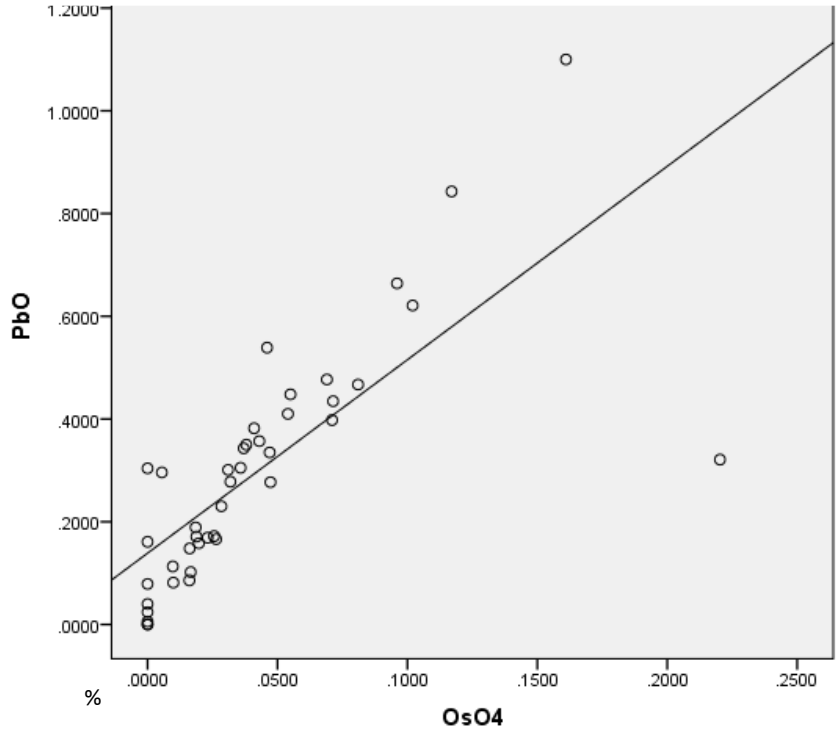

Figure 5.7 Lead oxide (PbO) versus osmium oxide (OsO_4) in blue glass beads (n=43)

5.2.2 Bluish-green beads

Bluish-green beads are very similar to simple blue glass beads in elemental composition and appearance; and are found in the same type of contexts such as burials and high status sites, albeit not as frequently. A total of six were analysed as part of this study (Table 5.2). Several authors have suggested that blue-green glass was a very common colour found in Bronze Age glass (Barber 1991, 235, Bellintani 2013, 283, Henderson 2013, 75). However, given the contexts that the blue-green beads were found in dated to the Iron Age and Early Medieval makes it seem more unlikely that they are indeed Bronze Age. By examining the elemental composition, it is possible to speculate further on the possible date for these objects. Magnesium oxide (MgO) was a characteristic component found in blue-green Bronze Age glasses which were made using plant ash alkali sources, both in Ireland and throughout Europe (Henderson 2013, 75). However there was no detectable level of magnesium oxide in most of these beads, with a single exception from Lagore, suggesting that most of them did not have a composition typical of that of Bronze Age glass.

None of these beads contained detectable amounts of cobalt and, like the three blue beads which were discussed as part of Section 5.2.2, most likely get their hue from the copper in their structure. There was no noticeable elemental difference in the concentrations of copper between the blue copper beads and bluish-green copper beads which would cause a more greenish hue, but it was possibly due to oxidation conditions in the furnace environment. Copper can provide many different colours when added to glass depending on its oxidation state, with blues ranging from pale shades to greenish-blues to bright blues (Bhardwaj 1979, 42-43). Detailed knowledge and careful addition of colourants would have been required to purposely achieve any given colour.

The trends evident in the blue glass beads were not evident in the blue-green examples with the exception of the correlation between silica and aluminium oxide. This may be due to the small sample size. Like the blue glass beads, an inversely proportional trend was observed when looking at the relationship between silica oxide and aluminium oxide (Figure 5.8). An r value of -0.962 ($p=0.002$) is observed

which indicates a strong correlation between the two. This value is nearly identical to that observed in the blue beads, although there is a much lower sample size than in the case of the blue beads. Like the blue beads, elevated levels of aluminium oxide are indicative of corrosion in the surface layers of the objects. The higher the level of aluminium oxide, the lower the level of silica, indicating that aluminium was being held preferentially in the surface layers when corrosion took place. Other elements had a similar relationship to aluminium oxide as silica. Such trends were not observed in the blue beads. While these figures would indicate a much weaker correlation than that between silica and aluminium, it highlights how elements are consistently removed from the surface layers of the glass objects while aluminium oxide is preferentially held or enters the surface layers from the surrounding environment. In the case of these bluish-green beads, it seems that as corrosion takes place, zinc oxides were also held preferentially compared to other elements. By examining the concentrations of aluminium oxide versus zinc oxides, it can be seen that as the level of aluminium oxide rises with corrosion, so too does the level of zinc oxide ($r = 0.492$, $p = 0.031$) (Figure 5.9).

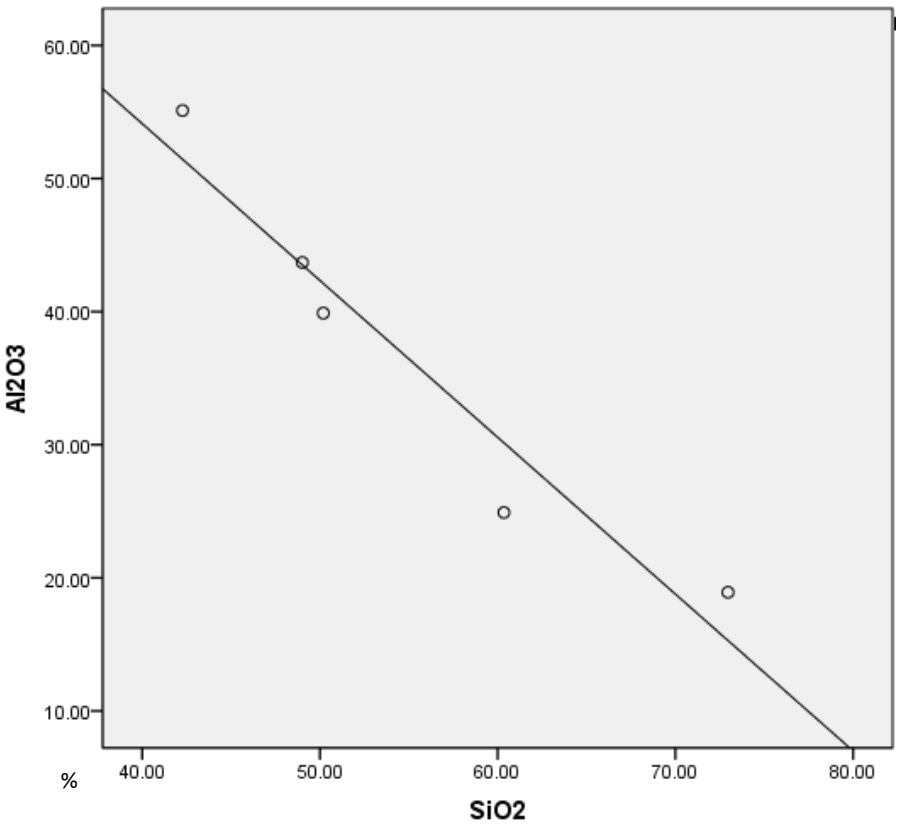

Figure 5.8 Aluminium oxide (Al_2O_3) vs silica (SiO_2) in bluish-green beads (n=6)

Antimony was only detected in trace quantities in one bead from Dún Ailinne, with the rest containing no detectable amounts. This may suggest that they may have been earlier in date compared to the high level of antimony which was found in some of the later blue bead material analysed from Lagore. The bluish-green beads also differed from the majority of the blue beads in that most of them contained no detectable levels of lead oxide or osmium oxide. This would further strengthen the suggestion that osmium oxide was an unintentionally added to the blue beads as part of the lead ore that was utilised. The absence of lead in many of these beads would account for their more transparent appearance compared to many of the plain blue beads which looked more opaque.

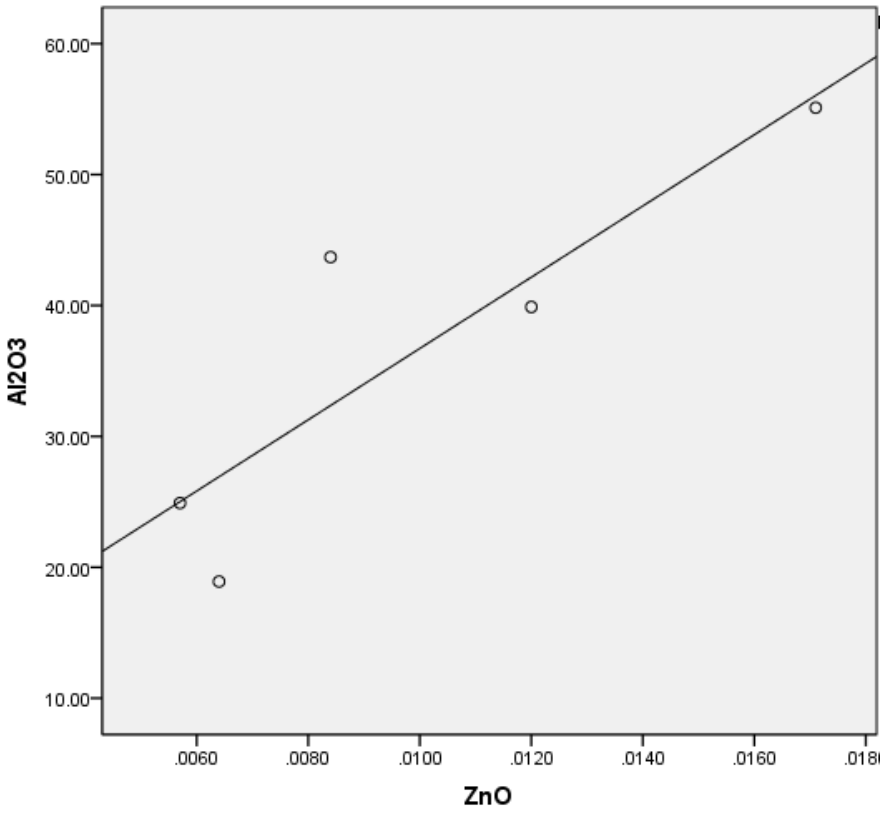

Figure 5.9: Aluminium oxide (Al_2O_3) vs zinc oxide (ZnO) in bluish-green beads (n=5)

5.2.3 Blue glass bracelet fragments

Blue glass bracelet fragments accounted for eighteen of the glass finds analysed and came solely from two high profile sites. Six of the eighteen fragments came from Dún Ailinne with the remaining twelve coming from the Lagore assemblages. All of the bracelet finds were fragmented pieces which, upon analysis, were found to generally have far less corrosion in their surface layers than beads. This was evident in the higher amounts of modifier that they contained. Given that the elemental analysis would suggest a similar original composition for both blue bracelet fragments and blue beads, it seems likely that this is due to the different relative surface area of these objects. Unlike the blue bead group which had a mixture of cobalt-coloured and copper-coloured examples, all of the bracelet fragments were coloured with cobalt. Some of these bracelet fragments had white decoration on their surface which was produced using tin oxide to produce an opaque white glass. These types of artefacts would have been indicative of considerable wealth and prestige, given their presence on two very high status sites.

Comparing the silica and aluminium oxide concentrations for these fragments showed that while there was only a moderate correlation between them, with an r value of -0.721 ($p=<0.001$) (Figure 5.10). However, this is most likely due to the fact that most of these bracelet fragments had much lower levels of corrosion than that found in the beads. In addition, there was no significant correlation between calcium oxide concentrations and aluminium oxide concentrations with an r value of only -0.843($p=0.038$) (Figure 5.11). The fact that there was no correlation between the two indicates that aluminium concentrations are useful when implying corrosion.

Like the majority of the blue beads, all of the blue bracelet fragments contained traces of osmium oxide. Once again, by comparing the concentrations of osmium oxide and lead oxide, it is apparent that it was also added in as part of the lead oxide source in the blue bracelet fragments. A strong correlation with an r value of 0.740 ($p=<0.001$) can be observed (Figure 5.12). Like many of the blue beads, the bracelets had an opaque appearance which would have been caused by the addition of this lead oxide

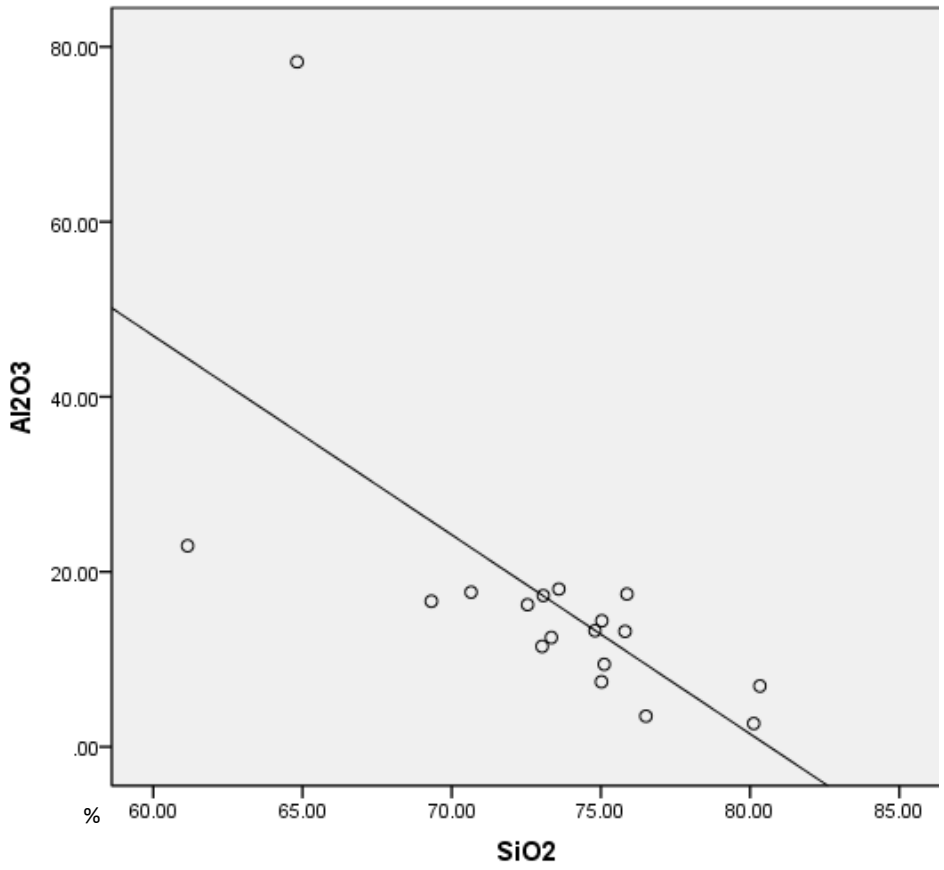

Figure 5.10 Aluminium oxide (Al_2O_3) vs silica (SiO_2) in blue bracelet fragments (n=18)

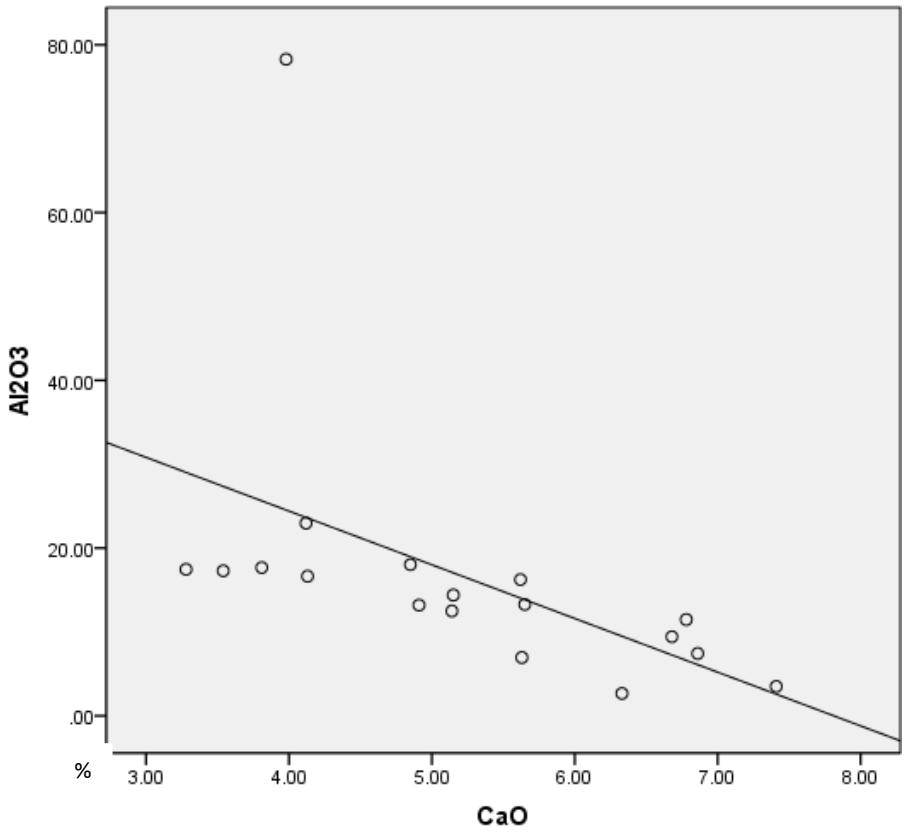

Figure 5.11 Aluminium oxide (Al_2O_3) vs calcium oxide (CaO) in blue bracelet fragments (n=18)

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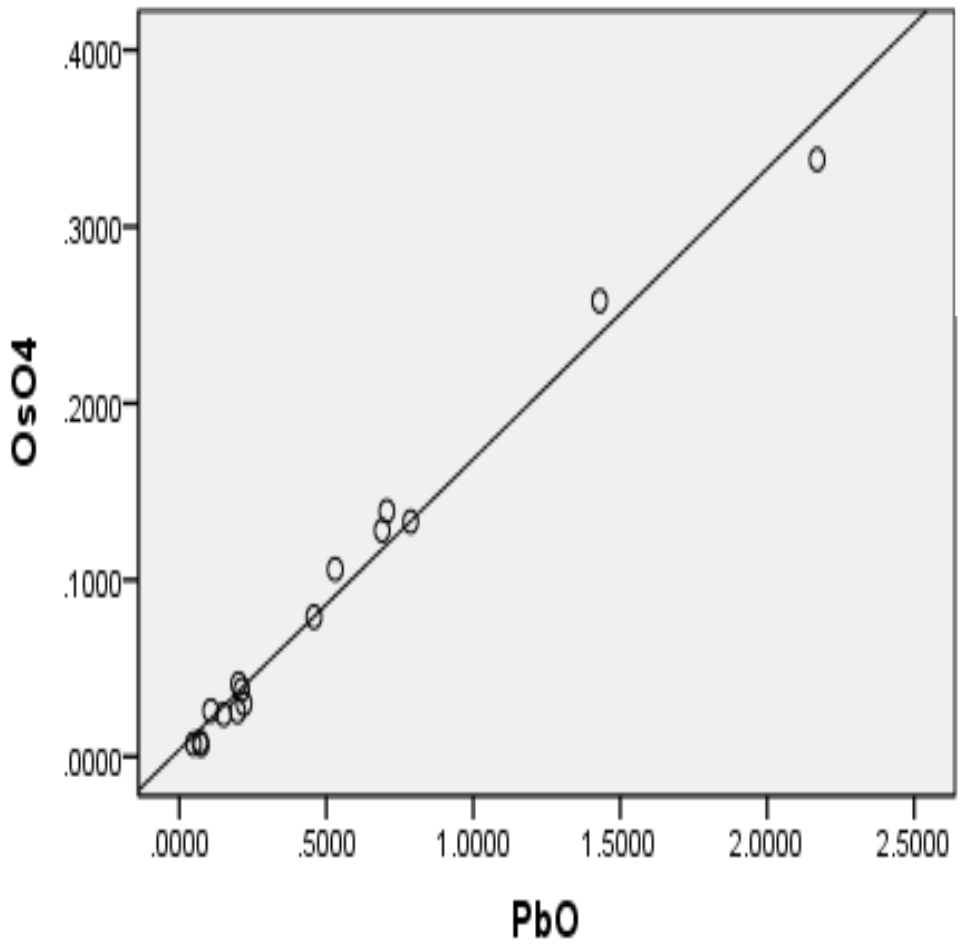

Figure 5.12: Osmium oxide (OsO_4) vs lead oxide (PbO) (n=16)

5.2.4 Green Post-Medieval bottle glass

The largest group of glass analysed comprised of iron-rich green Post-Medieval bottle fragments. The majority of glass found on Irish archaeological contexts is post seventeenth century material and it is unsurprising that bottle glass is the most common find given that is was cheaply produced and widely utilised. Bottle glass fragments are almost always of a lower quality than other Post-Medieval glass objects which are produced using flint glass, plate glass or crown glass. Readily available sand sources, often high in various trace contaminants including iron, were utilised for producing these objects and they were commonly made with potash-based glass. Bottle fragments are also usually a very dark green colour, caused by

differing amounts of iron impurities (Rynne 2006, 184 , Roche 2007, 411). A total of ninety fragments were analysed as part of this study, with the majority coming from the site of Bective Abbey, a Cistercian abbey site (Table 5.2)

The relationship between silica and aluminium oxide appears considerably different for Post-Medieval bottle glass than the earlier blue glass samples. While the blue beads and bracelets, as well as the blue-green beads, exhibited a very strong inverse relationship between the two, the amount of silica appears much more stable in the Post-Medieval glass. Heightened levels of aluminium oxide are still indicative of corrosion in the bottle glass fragments, however the amount of corrosion taking place is much lower. This is supported by the fact that silica and aluminium oxide have little to no correlation. The amount of silica appears to remain relatively constant despite varying levels of aluminium in the surface layers. This can be seen most clearly when the levels of silica are plotted against the levels of aluminium oxide (Figure 5.13). The most likely reason for this apparent discrepancy is simply that the Post-Medieval glass has not had as much time to corrode as the earlier glass artefacts. It is likely that a much stronger trend, akin to that seen in the blue beads and bracelets, would become apparent if the Post-Medieval fragments had more time to undergo corrosion.

The corrosion process may also affect different types of glass in different ways, given that corrosion is complex and the way it occurs is heavily dependent on the original composition of the glass. It is clear that bottle glass is affected differently by corrosion in some respects. Corrosion manifests in the form of a heavy iridescent crust in many cases, something which is not seen nearly as frequently on earlier bead artefacts. Given that these iridescent layers eventually flake off and the process starts again on the lower layers of the glass, it is clear that the iridescence is merely a transitional phase as the glass undergoes corrosion.

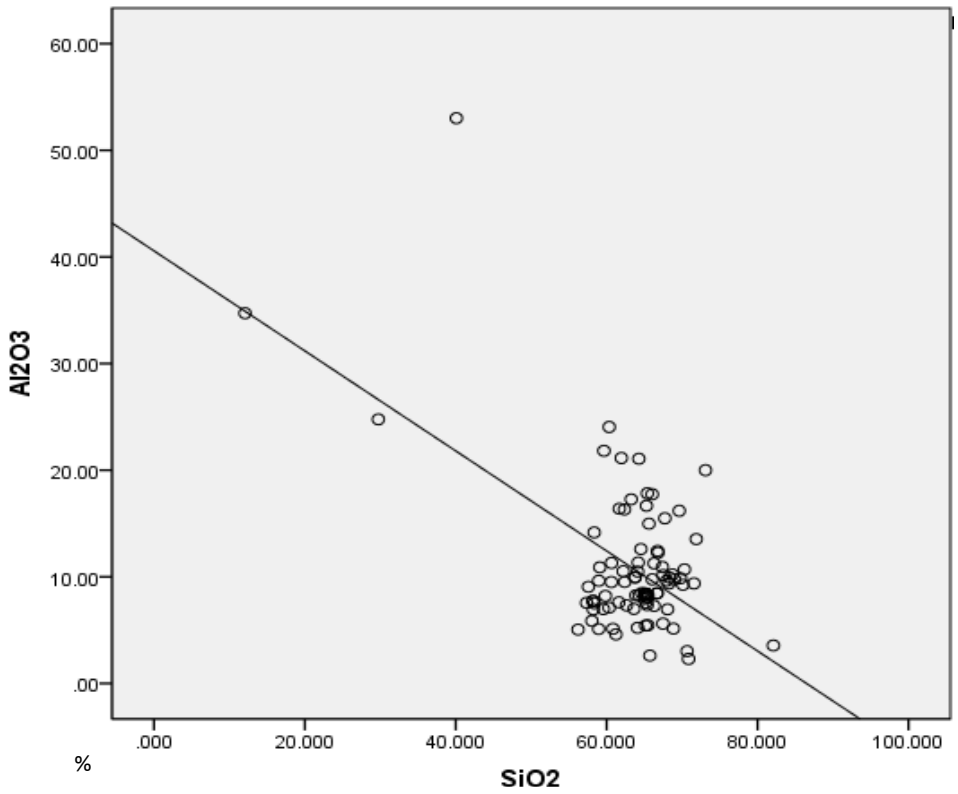

Figure 5.13 Aluminium oxide (Al_2O_3) vs silica (SiO) in green Post-Medieval bottle glass (n=90)

Many of these bottle sherds contain concentrations of cobalt oxide in their structure. Cobalt is one of the most powerful colouring agents used in ancient glass, capable of imparting a rich blue colour even in trace quantities. No blue colour is evident in these glass pieces however the deep green of the significant iron contaminants is likely the reason why there is no visible effect from the presence of cobalt in the glass structure. When the concentrations of iron were plotted against the concentrations of cobalt for these pieces, it was found there a moderate correlation between the two, with an r value of 0.667 ($p=<0.001$) (Figure 5.14). When two outliers were identified using a stem and leaf plot, and removed from this graph, the r value increased to 0.780, indicating a stronger correlation between the iron and cobalt oxides. Given that the iron was certainly added in as contaminants in the sand, it is likely that the cobalt was also added accidentally in this way.

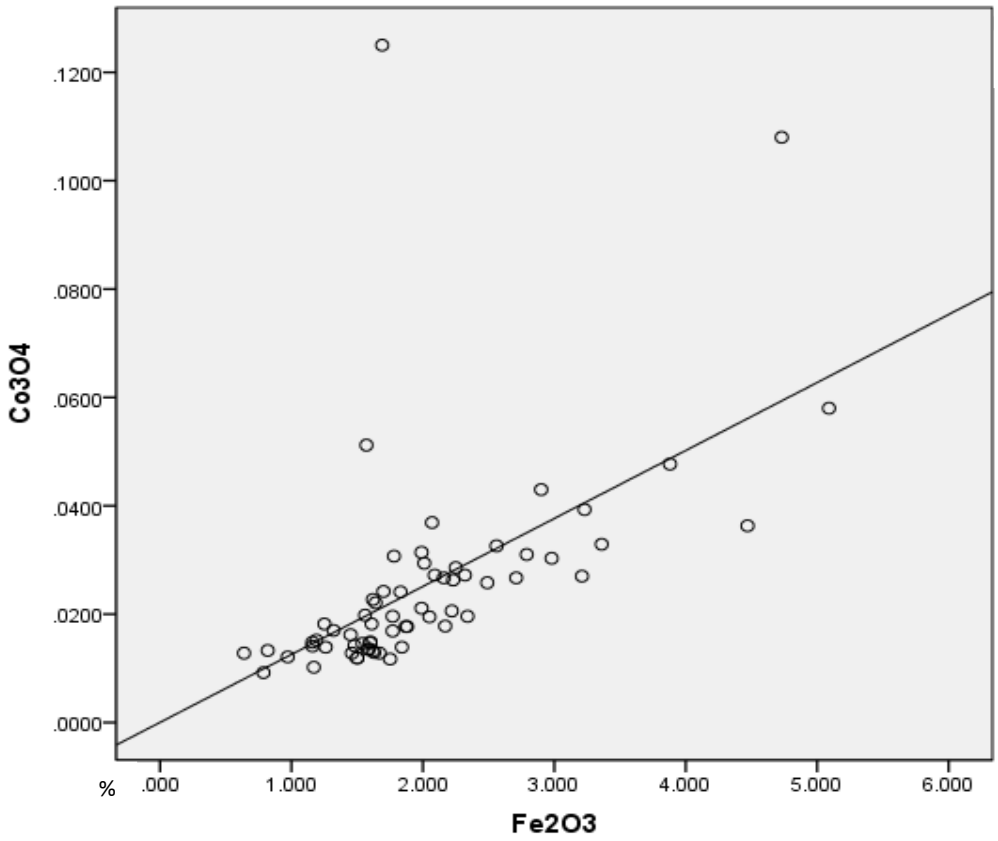

Figure 5.14 Cobalt oxide (Co_3O_4) vs iron oxide (Fe_2O_3) in green Post-Medieval bottle glass (n=65)

5.2.5 Clear Post-Medieval bottle glass

A number of clear Post-Medieval bottle glass sherds were also analysed. Unlike the green glass sherds however, the majority of these were soda-based as opposed to potash-based. Many clear glass sherds which were analysed were found to be modern examples based on the levels of corrosion and types and quantities of trace elements found in their structure. Modern glass has fewer trace elements and in smaller quantities, the result of using finer materials and being able to reach much higher temperatures in the furnace. A total of eighteen clear bottle sherds were found to have compositions consistent with that of Post-Medieval bottle glass and these will be discussed in this section. Fourteen of these came from Bective Abbey, with the rest coming from Kilteasheen and Moygara (Table 5.2).

In contrast to the earlier blue glass, and to a lesser extent the Post-Medieval green glass, the elemental composition of these clear sherds had much weaker correlations between the elements they contained. There was no significant correlation between the aluminium oxide and silica in these pieces, however there was very little elemental corrosion in these pieces compared to some of the earlier glass. A weak correlation was observed between potash and manganese, with an r of 0.412 (p=0.049) (Figure 5.15).. Given that the majority of these glass sherds are clearly soda-lime glass, based on the concentration of soda they contain, potash would not have been added to them in any quantity. However, manganese is a common contaminant when potash is used as a modifier. This would suggest that manganese and potash contaminants were being added from the same source to the glass. It is possible that both of these trace elements were added to the mix in the form of cullet. This is broken glass added to the glass mix for the purpose of lowering the overall melting point of the silica as well as to recycle broken glass. Cullet was commonly used in the Post-Medieval period and complicates the elemental composition of the pieces (Pollard and Heron 2008, 183).

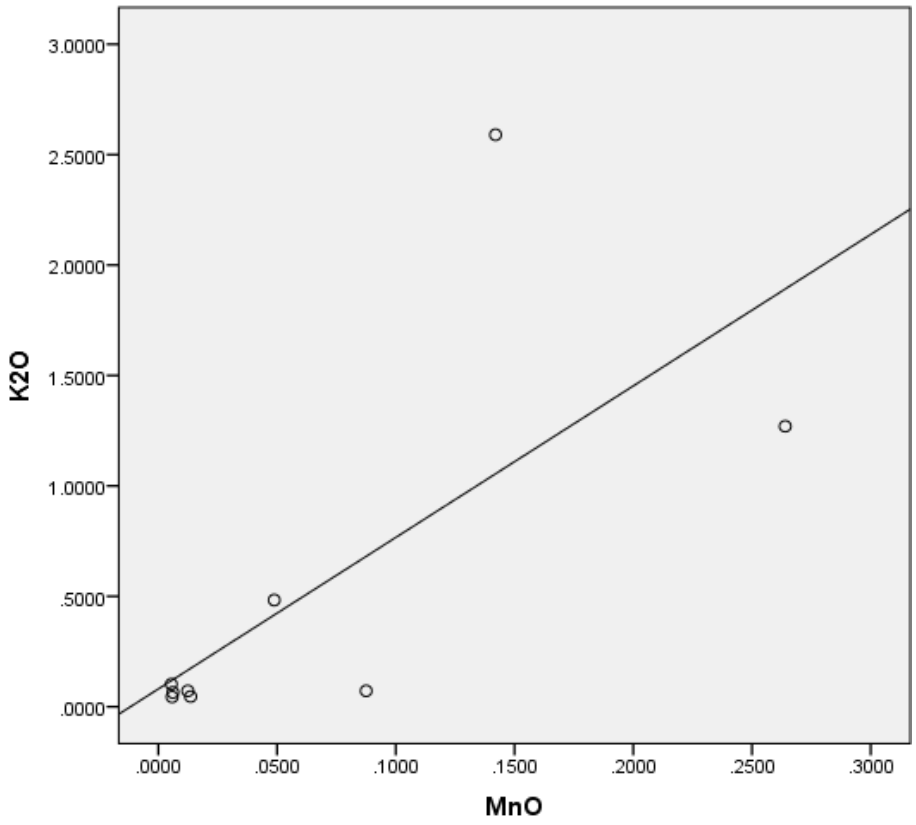

Figure 5.15 Potash (K_2O) vs manganese oxide (MnO) in clear Post-Medieval bottle glass (n=11)

5.2.6 Clear Post-Medieval glass with green tinge

The last large group of Post-Medieval bottle glass consisted of clear sherds with a slight green tinge. Like the green examples, this colour was caused by iron impurities in the glass mix, albeit in much smaller quantities with most containing less that 0.4% iron oxide. The majority of these were soda-lime glass like the clear sherds, as opposed to potash-based glass like most of the green bottle sherds. A total of nineteen clear bottle sherds with a green tinge were analysed. Most of this group came from the Bective excavations with ten finds. The rest of the finds came from Kilteasheen, Grassroots and Moygara excavations (Table 5.2).

There is not as much evidence of corrosion in these glass pieces compared to glass from earlier periods and as such there is no correlation evident between the silica and aluminium oxide levels for these pieces. However, there are certain trends evident when comparing the concentrations of traces element.

The strongest relationship between any of these trace elements and the main materials of the glass is observed when the concentrations of strontium oxide are plotted against the concentrations of potash (Figure 5.16). This shows an r value of 0.683 ($p=0.002$). As most of the glass appears to be mixed-alkali based, this could suggest that these trace elements were added in as part of the potash source. Potash sources can have widely varying elemental compositions and can add many different trace elements into the composition of the glass.

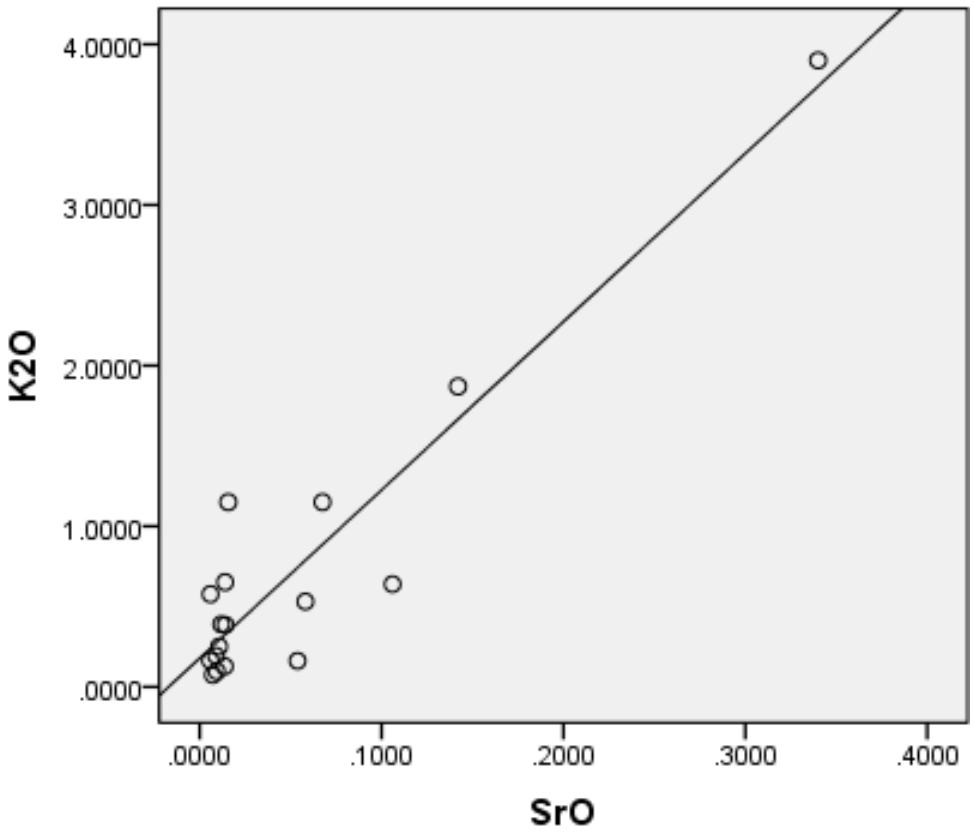

Figure 5.16 Potash (K_2O) vs strontium oxide (SrO) in clear Post-Medieval bottle glass with a green tinge (n=17)

5.2.7 Conclusions of elemental analysis

Some interesting relationships are apparent on looking at the statistics carried out on these finds. Firstly, aluminium oxide is very useful as an indicator of corrosion on the outer layers of the glass objects where the elemental composition has been altered over time. As can be seen by the results, the late-prehistoric/Early Medieval glass has much higher levels of aluminium oxide in their structures than the Post-Medieval glass. This is to be expected given that they have been exposed in the ground over a much longer period of time. Other trends also become apparent such as a rise in the concentration of antimony in the blue glass over the course of the Early and Late Medieval periods.

5.3 Cultural and economic significance

5.3.1 Iron Age and Early Medieval beads

It is perhaps unsurprising that the earliest forms of glass were small, simple objects such as beads and bracelets. These objects were easily transportable and had the capacity to be highly ornate depending on the skill of the maker. Glass jewellery was an important part of the material culture which would have been a powerful symbol of status and wealth when worn. It has been suggested that ancient people may have been trying to emulate precious metals and stones when manufacturing these early glass creations (Henderson 2013, 9). They may also have had a spiritual or ritual significance ascribed to them, given that they are often found as inclusions in high status burials such as at Knowth (Bray 2001, 65). Such items, found right across the country in many of the same types of contexts, may also reflect the complex trade and cultural links that existed between ancient communities.

The most common type of Iron Age and Early Medieval beads would have been simple blue ones and this is reflected in the artefacts which were analysed as part of this study. Blue beads made up the largest group of glass that were analysed from the Iron Age and Early Medieval periods. The majority were found from high status sites such as Lagore or Dún Ailinne, or else associated with other high status objects such as the Viking necklace at Glencurran cave. As such, they indicate the wealth and prestige that would have been associated with these places. In later periods, functionality became more important when producing glass, such as in the use of stained-glass windows in the Late Medieval. These glass beads, however, represent the typical function of most glass objects from these earlier periods; personal adornment as a show of status and wealth. The main raw materials appear similar in all of them and there was a good deal of uniformity with regard to the trace elements that they contained, with the exception of a small minority which were produced using copper as a colourant instead of cobalt. This would indicate that similar production methods and materials were utilised for all the cobalt-blue beads, something which would have been a closely-guarded trade secret in those times. The main differences would have been the varying types of modifier, potash and soda,

which were used. However this could simply be glass-makers using what was most readily available to them.

The blue colour in the vast majority of the blue glass beads which were analysed was caused by the presence of highly oxidised cobalt. Cobalt is the most powerful transition metal when used as a colourant in glass and typical levels in ancient soda-lime-silica glass are often around 0.05% (Henderson 2000b, 29). This proved true for the vast majority of the cobalt beads that were analysed. Most had cobalt oxide concentrations of between 0.01 and 0.07%, with only a few examples containing larger quantities. Blue beads that did not contain cobalt were something of an anomaly in this study. A single blue bead from the Dún Ailinne sample was found to be coloured solely with elevated levels of cupric oxide. This distinguished this single example as unique amongst the large amount of blue glass beads from this site and suggests that the finds at this site were sourced from many different places.

In ancient glass, it is often possible to suggest what type of cobalt ore was used based on other trace elements that the glass objects contain. In modern glass, this would not be apparent due to the fact that refined cobalt would be used. The different trace elements from the cobalt-bearing ores used in archaeological glass however, can sometimes be traced on the source. For example, trianite ($2Co_2O.CuO.6H_2O$) would add trace amounts of copper (Cu) to the glass mix while skutterudite ($(Co.Ni.Fe)As_2$) would add nickel and arsenic (Henderson 2000b, 30). This was apparent in the Lagore blue beads in which eight of the plain blue beads containing cobalt also contained traces of arsenic oxide, with seven of these also containing detectable amounts of nickel oxide. This would suggest that these beads were produced using the same type of cobalt ore, which is consistent with the elemental composition of skutterudite. While this ore is known to occur in Ireland, such as at Muckross Mine, Killarney and Gortdrum Mine in Monard, it was also a widely-used source of cobalt throughout Europe, including Italy where elemental analysis of blue beads suggested that it had been used (Henderson *et al.* 2015, 2)

Many of the Irish blue beads analysed also had tin oxide in their structure. This would have been utilised for the purpose of white decoration in the decorated blue

beads or else to add a more opaque appearance to the plain blue beads. A selection of unusual white and yellow opaque beads were analysed from the Lagore assemblage. The colour for the majority of the white finds was found to be caused by the presence of tin oxides in their structure. Meanwhile, the opaque yellow beads from the Lagore assemblage were of similar appearance to contemporary finds from Britain. The yellow hue of these beads was achieved by using tin and lead oxides, as these elements together are known to produce opaque whites and yellows (Henderson 2000b, 74). Major sources of tin during this time included Cornwall and Brittany which could well have been where the tin for these pieces was obtained (Comber 2001, 83). Sources of tin would have been available to Irish populations, either through trade with these areas, or possibly from an indigenous source, such as at the Mourne Mountains in Co. Down (Warner *et al.* 2010, 18).

Toggles represent some of the most convincing evidence for some form of early indigenous glass manufacturing, or at the very least glass re-working, in Ireland. The form of the toggle is unique to Ireland, with the exception of some finds such as those at Kildalloig, Scotland and the Isle of Man (Gelling 1958, 95-96, Ritchie 1991, 153) which may have been exported from Ireland. Glass was certainly being imported to Ireland from mainland Europe and quite likely Britain as well; however, the influx of this technology and material may have served as a model for the development of small-scale indigenous production of glass material or glass-working in Ireland. This in turn may have led to unique forms and styles such as the toggles. The red toggle from Dún Ailinne in particular is a highly interesting example. While opaque red beads are common Germanic types and appear in Anglo-Saxon graves, red glass is very rare in Ireland particularly for this period (Laing 1975, 337). While heavily corroded, the analysis of the red toggle from Dún Ailinne showed significant concentrations of lead and copper oxides, similar to the block of red enamel found near Tara.

Overall it seems very likely that Irish artisans were importing glass slabs through trade links with the Roman world and elsewhere and then using these to produce their own types of artefacts. There is plenty of evidence that Roman glass slabs were

a traded commodity elsewhere, such as an opaque glass rod found in Culduthel, Scotland which was reworked locally. Indeed, finished red glass beads with similar elemental compositions as the Irish red slab and toggle were found in north-eastern Scotland (Bertini *et al.* 2011, 2765).

5.3.2 Late Medieval window glass

Very little evidence for medieval stained-glass windows exists in Ireland. Archaeological evidence for the use of stained glass windows is very limited, particularly prior to 1000AD, but literary sources document the production of glass for use in European churches from after the fourth century AD with production of stained glass windows becoming very common throughout Europe from around the twelfth century onwards (Kemp 2000, 108). Stained glass created a unique kind of lighting, one which was believed to have special significance in a religious context as well as mystical and mysterious qualities. Physical light was often considered to represent divine light, and many windows depicted Jesus as 'the true light' (Rebold-Benton 2009, 174). The technology took many different forms over the centuries as glass-makers experimented with ways of improving their art. For example, while thirteenth century windows on the whole could be considered flawed in the sense that the glass pieces differed much more widely in size and shape than earlier examples, this caused the light which passed through to be affected in different ways and produced a glittering effect, altering the visual impact of the window. The leads which held the glass together were also highly skilfully crafted, forming the outline of people and other objects in the design while later windows such as in the 16th century had large plates of glass held together by squares of lead which could cut down in a straight line through the picture (Thorndike 2005, 427).

Unfortunately, Irish medieval window glass is particularly problematic for two reasons. Firstly, the window glass found in Ireland was produced using potash-based glass as opposed to soda-lime glass. Potash glass is much more prone to weathering and corrosion than soda-lime or mixed-alkali glasses due to its high

alkalinity and in general does not survive well in an archaeological context (Moran 2010, 17). Secondly, many stained glass windows were destroyed during the Reformation and Cromwellian eras by religious fanatics. Finally, some were destroyed in the eighteenth and nineteenth centuries as old glass was removed and replaced by modern glass (Ditchfield 2010, 188). These factors contribute to the relatively low amounts of window glass found in Irish archaeological contexts compared to other glass types.

Only four pieces of Late Medieval glass were analysed as part of this study. Several other window sherds were analysed but were determined on analysis to be of later date due to their elemental composition. Three of the four pieces came from Bective Abbey while the fourth came from the site of Blackfriary in Co. Meath. The three window sherds from Bective had compositions typical of those found in Irish medieval window glass, namely heavily corroded potash-based glass. Much of the elemental composition in their surface layers had been leached away. The three also exhibited remarkable uniformity to each other with regard to the trace elements they contained, suggesting they may have come from the same window. All three had a clear appearance, yet exhibited signs of a flaky iridescent layer forming on their surface. They were uncovered in Post-Dissolution contexts and it is probable that they represent the last remains of medieval windows that were broken during the Dissolution period. The window sherd at Blackfriary was also found to be potash-based on analysis and had heavily leached surface layers. This was found within the fill of a burial situated within the nave of the church. A piece of lead found in close proximity to the sherd may indicate that the window was deliberately smashed. Many Irish stained-glass windows met a similar fate. Accounts of the destruction caused by Cromwell's soldiers, for example, note how they tore down the windows and attempted to melt down the lead for their own purposes (Graves 1850, 210).

5.3.3 Post-Medieval and modern glass assemblages

Even a brief examination of the database of archaeological glass in Ireland in Appendix A will show that the majority of glass found in archaeological contexts was Post-Medieval in date. The Post-Medieval saw the expansion of the glass-making trade throughout Ireland and Europe. Specialised glass-making areas started diversifying from simple vessels and window glass to a broad range of elaborate and decorative table-wares. These changes began in Europe in the early sixteenth century, leaving the British Isles relatively unaffected until an influx of Huguenot and Dutch Protestant immigrants brought with them their knowledge of glass production in the latest part of the sixteenth century. As the industrial revolution took hold in England, the increased efficiency of agricultural methods ensured enough food and resources that the population rapidly expanded and furthermore allowed urbanisation. For the first time, significant labour and time could go towards the production of products other than food and many forms of advanced technology were improved upon and expanded (Wrigley 2010, 33).

The form of glass furnaces greatly changed from the late sixteenth century, from simple structures to multi-winged forms to accommodate larger quantities of glass. 'Bottle-houses' were established to supply the new demand for wine bottles (Willmott 2011, 8). Of the four main types; bottle glass, flint glass, crown glass and plate glass, the vast majority sourced for this study was bottle glass, demonstrating the high demand for this every day object. Most of the bottle glass is a characteristic dark-green colour, caused by varying amounts of iron impurities in their structure, but other colours such as brown, black, clear and pale green were also included in this study. Most of the Post-Medieval bottle glass analysed in the course of this study came from the sites of Bective, Grassroots, Kilteasheen, Moygara and Rothe House.

Bective Abbey contained a rich variety of Post-Medieval bottle glass. Different colours and thicknesses of glass were apparent in the finds which ranged from olive-green to dark green as well as clear, brown and black fragments. Elemental analysis indicates that some of the glass was either imported from England, or at least was

manufactured using English techniques. Most notably, analysis of some of the black glass sherds indicated that they had been produced using iron, manganese and sulphur. Studies of similar black glass in parts of Britain have demonstrated that glass-makers there were making such bottles by combining these three elements with a smoky carbon atmosphere (Davidson 2008, 77). This supports much of what is known about the Irish Post-Medieval glass industry being heavily influenced by the British tradition. Glass-makers who relocated from Britain to work in the Irish glassworks would have continued producing wares that they had been produced in their home country. Records show that a patent to produce glass in Ireland were granted to, among others, George Longe, a glassmaker from the Weald, in 1589. Another was granted in 1613 to William Robson, a glass-maker who held a monopoly of glass-making in England (Farrelly 2011, 39-40).

Most of the Bective bottle glass was dark green in colour and heavily corroded, as is typical of Post-Medieval bottle glass. Several pieces of thin green glass were identified as modern however. Other finds which were also determined to have elemental compositions consistent with modern soda-lime-silica glass including an amber-coloured sherd and several pieces of clear glass. As most of the glass was found in Post-Dissolution contexts, it is useful to be able to verify whether or not they are actually of Post-Medieval date by using elemental analysis.

The Post-Medieval finds from Seagrange, Co. Dublin were much different from any of the other objects discussed as they may represent small scale production of glass. The two glass rods and single glass piece, either partially melted or else never properly formed, are similar to the types of glass produced in the so-called 'forest glass' tradition. This refers to small local glass-works which were set up in rural locations that produced glass on a small scale using easily-sourced local materials. Such work was carried out throughout central and northern Europe. Potash from local timber was used as a flux with the lime that was needed to stabilise the glass being added in as a natural impurity in the raw materials (Hess 2005, 70).

The finest examples of Post-Medieval glassware in this analysis came from Rothe House in Co. Kilkenny. Two sherds of a possible 'porridge bowl', consisting of a

brown glass with white decoration on the exterior side of the pieces were analysed. It was similar in shape to a comparable vessel; a Roman patera dating from the second or third century AD (Roche unpublished, 2, 3). However the analysis indicated that a Roman date for these fragments was highly unlikely. Firstly, the level of corrosion based on the quantity of aluminium oxide seems quite low if the object is ancient. The glass was also produced using a potash flux, which would not have been used for a high quality Roman vessel (Freestone 2009,83). If this bowl was indeed a replica of a Roman patera, it was produced much later.

Other finds analysed from this site included twelve fragments of a sixteenth or seventeenth century German Stangenglas, which were thin, clear, good quality glass albeit with some iridescence on their surface. The elemental analysis showed a very similar composition for all of the fragments and they all most likely came from the same artefact.

A fragment thought to have been produced in the style of Venetian glass was also analysed. It was not thought to be of high enough quality for true Venetian ware as it displayed a greenish tint and this assessment was supported by the elemental composition. The results indicated that this fragment was most likely produced using a potash flux. This is in contrast to the true Venetian wares which were produced using a high-quality source of silica and a soda-rich ash. As such, true Venetian ware was highly clear and transparent. Tinges of green or brown in lower quality Venetian style glassware were often caused by using a mixed alkali rather than a pure soda flux (Willmott 2004, 289). This fragment of glass, alongside the 'porridge-bowl sherds' mentioned earlier, found at such a high status site, point to a thriving industry which sought to emulate high quality glassworks from elsewhere.

5.3.4 Conclusions of economic and cultural significance

A common factor in the use and production of glass in Ireland from the earliest times to the Post-Medieval is the heavy influence that glass-making techniques from England and elsewhere had on it. From the importation of glass slabs in the Early

Medieval period to the movement of skilled glass-workers into Ireland in the Post-Medieval, such influences have had an important impact on the types of glass found in Irish archaeological contexts. However, many aspects unique to Ireland are also evident. Toggles, for example, are almost unique to Ireland. With regards to Late Medieval window glass, examples found in Ireland are exclusively potash-based, unlike examples found in England, some of which are soda-lime. The Post-Medieval saw the pinnacle of Irish glass-making as skilled English glass-makers took advantage of the lack of excise taxes on glass from Ireland prior to 1825 (Roche 2007, 405).

6. Conclusions and Recommendations

6.1 Findings of the study

The main objective of this study was to examine the raw materials and trace elements present in Irish archaeological glass. Furthermore, this thesis examined how elemental analysis of such artefacts could aid in our understanding of this material and how it was viewed and used by people in the past. To this end, a database of glass found during excavations on Irish archaeological sites was compiled, glass artefacts from numerous different sites were analysed and the results interpreted. The study utilised X-ray fluorescence which is a non-destructive analytical technique.

XRF is a useful technique given the limitations of the surface depth it can analyse, about 30μm. The results obtained gave an accurate quantitative composition for the surface layers although these may not have been representative of the whole glass object depending on corrosion. The analysis allowed the different modifiers used to produce the objects; potash, soda or a mixture of the two, to be identified. It was also possible to identify decolourants and colourants used such as manganese, iron, cobalt, copper and lead. In some cases, this could provide clues about the possible origin of the piece or the materials sourced to produce it, such as in the case of cobalt-coloured glass where a trace elemental composition consistent with the use of a skutteridite ore was identified. Analysing the glass without any preparation methods apart from washing also highlighted an interesting inverse relationship between silica and aluminium oxide in many of the samples. High aluminium oxide concentrations were found in many of the samples and this was found to be a useful indicator of corrosion in the surface layers.

Prehistoric blue glass as a whole made up a large proportion of the glass finds analysed as part of this study. The majority of these were cobalt-based examples but it was possible to identify a few that were coloured with copper by looking at the analytical results. There appeared to be a rise in the level of antimony used in the blue glass throughout the Early Medieval period, reflecting changes in the

production of this type of glass that was occurring elsewhere in Europe. Other authors including Edwards (1996) and Warner and Meighan (1994. 53-54, 60-65) have already noted such a trend. Further analytical work would be beneficial in determining if this is characteristic of Early Medieval blue glass in Ireland as a whole. It is very difficult to prove that glass-making was taking place in Ireland during the Early Medieval. There is, however some evidence of glass-working from this study; the red glass toggle uncovered at Dún Ailinne. Toggles, with few exceptions, are unique to Ireland, yet this piece had an elemental composition similar to red glass found elsewhere, including Scotland. It is known that glass ingots were imported throughout Europe and the find of a red glass ingot near Tara would suggest that Ireland was no exception. It would seem from the evidence that Irish glassmakers were importing glass slabs from elsewhere and creating their own objects from them. Late Medieval glass was mainly represented by window-glass and stained-glass window glass. All of these finds were found to be produced using potash-based glass, which is what would be expected from window-glass for this period.

A wide variety of Post-Medieval glass, mainly bottle glass, was also analysed. The elemental analysis proved useful in distinguishing between modern and Post-Medieval glass, given that modern glass did not contain as many trace elements or show as much evidence of corrosion. Other factors which distinguish the two include the use of decolourants in Post-Medieval glass such as manganese to counteract the green colouring effect of iron contaminants. In the case of modern glass, decolourants are unnecessary as it is possible to use refined raw materials. The analysis also made it possible to characterise certain glass based on the elemental composition. For example, a sherd of what was believed to be imitation Venetian glassware was confirmed as such upon analysis as it had modifier substances and trace elements inconsistent with real Venetian ware. As well as that, a Roman origin was ruled out for the sherds of 'porridge bowl' from the same site as, again, the elemental composition was inconsistent with what would be expected. Both of these examples highlight the usefulness of elemental analysis in certain cases to look at

authenticity and provenance of glass objects, particular objects which are known to have particular compositions.

6.2 Recommendations and further research

XRF is used in this study as it is non-destructive. However it can only analyse to a depth of 30μm, which in essence is the surface layer of the glass. This means that if corrosion has taken place to any significant degree then the analytical results obtained will not be representative of the whole glass object or of the original composition of the glass. While preparation techniques could be used to minimise the effect of corrosion on the results, this would require using destructive processes on delicate archaeological artefacts. This is not ideal, particularly in the case of smaller and more delicate objects such as the Lagore and Glencurran beads. For relatively common glass artefacts, such as Post-Medieval bottle glass, destructive techniques, such as inductively coupled plasma mass spectrometry (ICP-MS) may be more suitable. The need to analyse all layers of the glass must be weighed against the damage it will cause to the artefact in question. In the case of small, fragile items the extra information gained from a destructive technique may not be enough to warrant destroying the glass or part of the glass. In these cases, non-destructive analysis, while may not be entirely representative, can be beneficial without the need to damage the object.

This timescale of the project limited the number of samples which could be analysed given the requirement to analyse all samples in triplicate. Irish archaeological glass varies widely and 328 glass pieces were analysed which were representative of the range of chronological periods, geographical regions and artefact types available. Analysis of larger numbers of samples would be required in order to further investigate how these factors affect the elemental composition. The results of this study provide a very good baseline upon which further research can be built upon and analysing a larger number of samples will give a greater understanding of the elemental composition of the glass and the presence of trends within the glass.

There is much more work that could be achieved by analysing archaeological glass using scientific techniques. Very little elemental analysis is carried out on archaeological material in general in Ireland but particularly on glass. It is often seen as a problematic material to analyse, given the wide variability in its composition, but as this study has shown, valuable results can be obtained even with non-destructive elemental analysis. Further work would be most beneficial to better our understanding of Irish glass, its importance in the economic and social aspects of individual sites and how it fits into a wider European context. The more material which is analysed, the easier it will be to identify trends in glass over time as well as potentially define sources of Irish glass. It may also be possible to identify imported glass as opposed to indigenous Irish glass and to examine how glass was traded in past societies. Elemental analysis focused on the study of toggles, a distinctly Irish form of bead, may well be extremely beneficial in this case. By analysing a large volume of these artefacts it may be possible to identify elemental signatures of Irish glass-makers or glass-workers. Certain trends in Irish archaeological glass have already been noted in this study but further elemental analysis of glass from other sites could serve to strengthen or disprove these suggestions. For example a rise in antimony from the Late Iron Age and throughout the Early Medieval was tentatively supported by the data gathered as part of this study; however a larger sample size could indicate whether or not this is actually representative of Early-Medieval glass production as a whole.

The above research has shown that valuable information about the elemental composition of archaeological glass can be obtained purely by using non-destructive techniques. Furthermore, the information gleaned from elemental analysis can aid our understanding of glass objects from Irish archaeological sites and how they fit into the economic and social culture of past peoples. The results from this study can serve as a baseline against which any results from future analysis can be compared.

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The classification and characterisation of archaeological glass using multi-elemental analysis

Volume 2 of 2

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Submitted for the Degree of Master of Science (Research)

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Submitted to Institute of Technology, Sligo, May 2015

Appendices

Appendix A: Database of Glass found on Archaeological Sites (1997-2008)

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Appendix A: Database of glass found on archaeological sites (1997-2008)

	County	Location	Excavation no.	Description	Source
1	Antrim	Duncan's Road, Magheralave	AE/08/24	Post-Medieval glass bottles	(Stirland 2008)
2	Antrim	26-28 Waring Street, Belfast	J34087455	Glass	(Ó Baoill 2002)
3	Antrim	Castle Upton, Templepatrick	J225859	A small blue glass bead	(Gahan 1997)
4	Antrim	Drumnahoe	D375014	Post-Medieval glass	(Gahan 2000)
5	Antrim	Lisburn Castle Gardens, Lisburn	ANT068-002	17th/18th century glass fragments and 17th fine glassware	(McMullen 2006)
6	Antrim	Rectory Gardens, Raceview Road, Broughshane	D14800630	19th and 20th century glass	(O'Rourke 2007)
7	Antrim	Sites 1 and 2, Cotton Court, Waring Street, Belfast	J34087455	Post-Medieval glass	(Ó Baoill and McQuaid 2002)
8	Antrim	Antrim Branch Library, Railway Street, Antrim	AE/08/53	19th century broken glass	(Kilner and Bailie 2008a)
9	Antrim	Crebilly	AE/07/159	19th century bottle glass	(Kilner and Bailie 2008b)
10	Antrim	Lisburn Castle Gardens, Lisburn	J26946433	Window and flowerpot glass	(Ó Baoill 2003)
11	Antrim	Former Woolworth's Store, High Street/Anne Street/Cornmarket/Crown Entry, Belfast	3343 3725	Quantity of glass	(Moore 2003)
12	Antrim	Carravinally, Rathlin Island	AE/05/72	19th century glass	(Forsythe 2004)
13	Antrim	Victoria Towers Development, Belfast	AE/07/231	Post-Medieval glass	(Mac Manus 2008)
14	Antrim	156-158 Main Street, Bushmills	AE/05/99	Post-Medieval glass	(Reilly 2006)
15	Antrim	Carnalbanagh West to Magheramesk (Moira Trunk Mains)	J15576130	Glass beads, lumps of blue glass	(Devlin 2007)
16	Antrim	Kilbegs Road, Dunsilly	T990226	19th and 20th century glass	(Chapple 2002)
17	Antrim	Sirocco Works, Ballymacarrett, Belfast	J34887432	19th and 20th century glass	(Lyall 2000)
18	Antrim	Lissue and Knockmore	AE/06/199	Glass beads, including a yellow and blue Early Medieval example	(Nicol 2006)
19	Antrim	Goodland	D19084180	Glass bead	(Horning and Brannon 2007)
20	Armagh	A1 Scheme 1, Newry, Derrybeg – Site 14	J07102765, AE/08/06	Sherd of green glass	(Bailie 2008)
21	Armagh	Market St., Armagh	H87564524	18th century glass remains found in rubbish pits	(Gilmore 2000, 2)

	County	Location	Excavation no.	Description	Source
22	Carlow	Powerstown	E2601	Post-Medieval glass	(Hackett 2006)
23	Carlow	Swellan Lower	03E0567	Post-Medieval bottle glass	(Read 2003d)
24	Carlow	Cox's Lane, Carlow	04E1716	19th century glass	(Keeley 2005)
25	Cavan	Main Street, Cavan	01E0896	Glass	(Shanahan 2001)
26	Clare	Ballycasey More	02E1045	Two glass beads	(O'Neill 2002)
27	Clare	Clonmoney West	01E0024	Post-Medieval glass	(Murphy 2001a)
28	Clare	Coolnatullagh	97E0204	Green glass bead	(Eogan 1997)
29	Clare	Clonmoney West	99E0640	Post-Medieval glass	(Jones 2000)
30	Clare	4-5 Carmody Street, Ennis	02E1180	Possible sherd of early glass	(Grant 2002a)
31	Clare	Cahermackirilla	02E1041	One glass bead and three fragments of glass beads	(Grant 2002b)
32	Clare	Leamaneh Castle, Leamaneh North	02E0886	Fragments of medieval glass	(Grant 2002c)
33	Clare	Carrigaholt, Castle, Carrigaholt	02E1579	Post-Medieval glass assemblage	(Dunne 2002b)
34	Clare	Ballaghfadda East	02E1193	19th and 20th century glass	(Hull 2002a)
35	Clare	Mount	02E1149	Over 800 fragments of glass	(Taylor 2002c)
36	Clare	Glencurran Cave, Tullycommon	04E0432	50+ glass beads	(Dowd 2004b)
37	Clare	Glencurran Cave, Tullycommon	05E0379	Glass beads	(Dowd 2005)
38	Clare	Kilfenora Cathedral, Kilfenora	02E0334	Glass	(Rogers 2002a)
39	Clare	Clare Abbey, Clareabbey	C020	High quality glass vessel, poss 17th c	(Hull 2005)
40	Clare	Cratloemoyle	151152 159479 TO 151623 189327	Glass bottles	(Reilly 2005)
41	Clare	Site AR129, Keelty	04E0025	Glass inkpot	(Hull 2004a)
42	Clare	Site AR130	04E0030	Window glass	(Taylor 2004)
43	Clare	Site AR131, Claureen	04E0026	Glass beads	(Hull 2004b)

	County	Location	Excavation no.	Description	Source
44	Clare	Ballyconneely	00E0297	Glass bead	(Breen 2000a)
45	Clare	Ballyconneely/Ballygirreen	00E0284	Glass beads	(Breen 2000b)
46	Clare	Carrigoran	98E0338	Blue glass beads and Post-Medieval glass	(Reilly 2000a)
47	Clare	Carrowlagan/Finnor More/Rineroe/Tromracastle	08E0548	Post-Medieval glass	(Barker and Keeley 2008)
48	Cork	Curraheen 1	01E1209	A glass bead	(Danaher 2002)
49	Cork	Ballynacarriga 1	01E0567	2 decorative glass beads	(Noonan 2001a)
50	Cork	Greenfield	01E0732	Mid-18th century glassware	(Murphy 2001b)
51	Cork	Lisnagar Demesne 1	03E1510	Post-Medieval glass	(Murphy 2003a)
52	Cork	Muckridge 1	01E0429	Iron Age blue glass bead	(Noonan 2001b)
53	Cork	James Fort, Old-Fort, Kinsale	98E0279	Post-Medieval bottle glass	(O'Donnell 2000, 21-22)
54	Cork	St. Anne's Graveyard, Shandon, Cork	01E0529	19th century glass	(McCarthy 2001)
55	Cork	Cork	01E0984	Post-Medieval glass	(Kellerher 2002)
56	Cork	St Peter's Avenue, Cork	97E079	Window glass	(Hurley 1997)
57	Cork	Barrees	02E0914	Dumb-bell shaped glass beads	(O'Brien 2002)
58	Cork	Barrees	02E0914	Early Medieval beads	(O'Brien 2003)
59	Cork	20 and 22 Hanover Street, Cork	05E0808 05E0809	Glass	(Ó Faoláin 2005a)
60	Cork	Crosse's Green, Cork	04E1616	Post-Medieval glass	(O'Rourke 2007)
61	Cork	Gortnahown 2	00E2426	Post-Medieval glass bottles	(O'Donoghue 2007)
62	Cork	Kilshanny 1	E2430	Post-Medieval glass	(Lyttleton 2007)
63	Cork	Castledonovan	E1569	Glass, including window glass	(Hegarty 2008b)
64	Cork	Ashe Street, Youghal	01E0876	Post-Medieval glass	(Hurley 2001)
65	Cork	Curraheen	08E0802	Coloured glass beads	(Hurley 2008d)
66	Cork	7 Coach St., Cork	00E0279	17th c. glass vessel fragment	(Kielty 2000a, 18)
67	Cork	Mill Business Centre, Crosse's Green, Cork	04E1616	18th/19th century glass	(Loingsigh 2004)

	County	Location	Excavation no.	Description	Source
68	Derry	20 Castle St., Bellaghy	H953966	Bottle glass	(O'Baoill 2000b, 24)
69	Derry	Bishop's St. Without, Derry	C43211645	Post-Medieval glass	(Logue 2000, 38)
70	Derry	Ballynashallog	C45942130	Post-Medieval glass	(Schulting and Ó Neill 2002)
71	Derry	Crossreagh West	C82123647	Glass	(Macdonald 2002a)
72	Derry	Abbey Street, Coleraine	C84803220	Red and blue glass decoration on a brooch	(Logue 2001)
73	Donegal	Glenveagh Cottage, Glenveagh National Park	06E0315	Post-Medieval glass	(Orser 2006)
74	Donegal	Sheep Lane, Raphoe	07E0187	18th/19th century hand-blown glass wine bottle fragments	(Hurley 2008c)
75	Donegal	Grainán of Aileach, Carrowreagh	04E1281	19th century glass sherds	(Moore 2007)
76	Donegal	Grian.n of Aileach	03E0996	19th century glass	(Read 2003c)
77	Donegal	Magheracar	01E0683	Two small blue glass beads	(Read 2001b)
78	Down	2 Union Street, Donaghadee	Not listed	19th and 20th century glass	(Kilner and Bailie 2008c)
79	Down	A1 Scheme 1, Newry, Carnmeen – Site 3	J094003132	Blue glass beads	(Ryan 2008)
80	Down	Bagenal's Castle, Newry	J08732615	Post-Medieval glass	(McQuillan 1999)
81	Down	Edenderry Road, Banbridge	J11854590	Post-Medieval glass	(Kovacik 2005)
82	Down	Lisnagade	AE/06/47	Post-Medieval glass	(Crothers 2006)
83	Down	Belfast Road, Downpatrick	J47204645	2 blue glass beads	(Mac Manus 2000a, 33)
84	Down	Edenderry Road, Banbridge	J11654532	19th century glass	(McKee and Kovacik 2006)
85	Down	Mahee Castle, Mahee Island	J52396394	Glass	(Macdonald 2002b)
86	Down	Portaferry	Not listed	Dark-green glass fragments, possibly from 17th/18th century "onion" bottles	(Hurl 2008)
87	Dublin	Docklands, Sheriff Street, Dublin	06E0682	Post-Medieval glass	(Ronayne 2006b)
88	Dublin	Newtown	01E1214	Glass fragments	(Fitzpatrick 2002b)
89	Dublin	Morgan Hotel, 1-2 Aston Place, Dublin	04E0707	18th century glass	(O'Hara 2004)

	County	Location	Excavation no.	Description	Source
90	Dublin	43-44 Hill Street, Dublin	04E0649	Glass	(Turrell and Lynch 2004)
91	Dublin	Augustine Street/16-17 John Street West, Dublin	97E0343	Glass sherds	(Cosgrave 1997a)
92	Dublin	St Clare's Fold, Griffith Avenue, Dublin	05E1194	Post-Medieval glass	(McConway 2005)
93	Dublin	2-5 Meath Market, South Earl Street, Dublin	96E0357	Window glass	(Walsh 1997)
94	Dublin	15 Capel Street, Dublin	97E103	Glass	(Sullivan 1997)
95	Dublin	3 Meeting House Lane, Dublin	02E0127	Post-Medieval glass	(McCabe 2002)
96	Dublin	32 Dame Street, Dublin	07E0582	17th century glass vessels	(Giacometti 2007)
97	Dublin	6 Main Street, Raheny	04E0967	Glass	(Dehaene 2004)
98	Dublin	60-62 The Lotts, Liffey Street, Dublin	03E0035	Post-Medieval bottle glass	(Larsson 2003)
99	Dublin	Collins Square (Royal Square), Collins Barracks, Dublin	94E0125	Glass	(Baker 2001)
100	Dublin	St Michael's Christian Brothers' School (former), Inchicore	08E736	Window glass	(Giacometti 2008a)
101	Dublin	Templeogue House, Templeogue	04E1111	Large amount of late medieval and post-medieval glass	(Giacometti 2005)
102	Dublin	Templeogue House, Templeogue	04E1111	Post-medieval glass vessels, bottles, wine-glass fragments, table glasses	(Giacometti 2006)
103	Dublin	Templeogue House, Templeogue	04E1111	18th century glass wine bottles	(Giacometti 2008b)
104	Dublin	Corke Great	04E0354	Fragment of 18th/19th century glass	(Byrne 2004)
105	Dublin	Callaghstown Lower	03E1693	Bottom of an 18th century glass vessel	(O'Connor 2003)
106	Dublin	Murphystown	06E0227	Post-Medieval glass	(Johnston 2006)
107	Dublin	Temple Street West, Dublin	03E1766	1927 glass bottle	(Clutterbuck 2003)
108	Dublin	Cope Street/ Crown Alley, Dublin	98E0161	18th – early 20th century green glass	(Clutterbuck 2008)
109	Dublin	Church Lane, Swords	98E0082	Glass, including bottle glass found in urban Medieval context	(O'Carroll 2000, 67)

	County	Location	Excavation no.	Description	Source
110	Dublin	10 Exchange Street Upper/1 Essex Street, Dublin	96E040	Glass	(Scally 1997)
111	Dublin	9 Merchant's Quay, Dublin	00E0558	18th/19th century glass fragments	(Kehoe 2000)
112	Dublin	189-194 King Street North, Dublin	98E0088	Post-Medieval glass	(Nelis 2000, 72)
113	Dublin	62 Castle Street, Dalkey	02E1871	Post-Medieval glass	(Kavanagh 2003)
114	Dublin	Balgriffin Park, Dublin	04E1371	Early Medieval bead	(McLoughlin 2004)
115	Dublin	Folkstown Great, Areas 2 and 3	08E0054	Post-Medieval glass	(Kavanagh 2008)
116	Dublin	Deputy Master's House, Royal Hospital, Kilmainham	98E0365	Post-Medieval glass	(Desmond 1999)
117	Dublin	Corcagh Demesne, Clondalkin	01E0911	Glass beads	(Carroll 2001a)
118	Dublin	Rosepark, Balrothery	99E0155	Glass beads	(Carroll 2000b)
119	Dublin	Rosepark, Balrothery	99E0155	Glass beads	(Carroll 2001b)
120	Dublin	124-127 St. Stephen's Green, Dublin	01E0850	Glass	(Bolger 2002)
121	Dublin	2-6 Longford Street Little/Dawson Court, Dublin	00E0137	Small glass bead	(Ó Neill 2001b)
122	Dublin	3-6 Palace Street, Dublin	02E0244	Glass fragments	(Simpson 2005)
123	Dublin	48-50 Newmarket/14-16 Newmarket Street, Dublin	02E1692	Glass	(Frazer 2003)
124	Dublin	Ballycoolin Road, Cappoge	99E0724	Post-Medieval glass	(Myles 2000a)
125	Dublin	Cherrywood and Laughanstown	03E0839	Post-Medieval glass	(McQuade 2003)
126	Dublin	Cherrywood/Lehaunstown/Loughlinstown	97E0279	Post-Medieval glass	(O'Donovan 1997)
127	Dublin	Cherrywood Science and Technology Park, Cherrywood	99E0523	Blue glass beads	(O'Neill 2000, 54-56)
128	Dublin	Corballis House, Corballis	05E0440	Glass	(O'Donovan 2006)
129	Dublin	Fitzwilliam Point Apartment Scheme, Fitzwilliam Street, Ringsend	06E0375	18th/19th century bottle glass	(Myles 2006a)
130	Dublin	Gracedieu	99E0217	Post-Medieval bottle and window glass	(Conway 1999)
131	Dublin	Kildare Rail Route Project, Section 2, Cappagh to Stacumny Cottege	07E0749	Post-Medieval glass	(Moriarty 2007)
132	Dublin	Molyneaus House, Bride Street, Dublin	02E0163	Post-Medieval glass fragments	(Simpson 2002a)

	County	Location	Excavation no.	Description	Source
133	Dublin	Mother Redcap's Market, Back Lane, Dublin	06E0048	19th century glass bottles	(Myles 2008)
134	Dublin	Newtown Little	02E1104	Glass	(Hagen 2002)
135	Dublin	Pearse College, Clogher Road, Crumlin	00E0748	Early 20th century glass	(Myles 2000b)
136	Dublin	RDS Simmonscourt, Ballsbridge	05E1362	Broken glass tubes and glass bottles	(Molloy 2006a)
137	Dublin	Santry Demesne, Santry	05E0894	Clear window glass	(Sullivan 2005)
138	Dublin	Ship Street Great, Dublin	01E0772	Glass bead	(Simpson 2002b)
139	Dublin	Sick and Indigent Roomkeepers' Society, 2 Palace Street, Dublin	05E1362	17th – 19th century bottle glass	(Myles 2006b)
140	Dublin	Smithfield, Dublin	00E0272	Glass cullet and frit	(Myles 2003)
141	Dublin	The Monument of Light, Nelson's Pillar, O'Connell Street, Dublin	01E0871	Post-Medieval bottle glass	(Myles 2001a)
142	Dublin	Trinity College (Library Extension Site), Dublin	98E0361	Post-Medieval glass	(Kehoe 2000b, 76)
143	Dublin	St. Stephen's Green, Dublin	E3963	Glass fragments	(Dennehy 2008)
144	Dublin	Glebe	00E0758	Two glass beads	(Seaver and Keeley 2000a)
145	Dublin	Glebe	00E0758	Blue glass beads	(Seaver 2002a)
146	Dublin	Kingstown	00E0147	A piece of green glass	(Clinton 2000)
147	Dublin	Laughanstown	00E0283	A blue glass intaglio	(Seaver and Keeley 2000b)
148	Dublin	Laughanstown	00E0283	Glass fragment	(Seaver 2002b)
149	Dublin	Murphystown Site 6, Murphystown/Carmanhall and Leopardstown	02E0153	Bottom sherd of bottle glass	(Breen, 2002a)
150	Dublin	Site 43, Glebe	00E0758	Blue glass beads	(Seaver and Keeley 2001)
151	Dublin	Site 70, Ballyogan	02E0481	Post-Medieval glass	(Breen 2002b)
152	Dublin	Kilgobbin Lane/Enniskerry Road, Stepaside	04E0501	Glass beads	(Larsson 2004)
153	Dublin	Golden Lane, Dublin	04E1030	Fragmented drinking glass and wine bottle, 17th century	(O'Donovan 2005)
154	Dublin	Mount Offaly, Cabinteely	98E0035	Glass fragments from Early Medieval cemetery	(Conway 2000, 36)

	County	Location	Excavation no.	Description	Source
155	Dublin	Tram Street/ Phoenix Street, Dublin	01E0229	Fine glassware	(Myles 2001b)
156	Dublin	Wolfe Tone Park, Jervis Street, Dublin	01E0080	Post-Medieval glass sherds	(Myles 2001c)
157	Dublin	Dunnyneill Island, Strangford Lough	35474 35384	Imported glass	(McCormick and Macdonald 2003)
158	Fermanagh	Aghnavea Church, Aghavea	H37063883	Glass beads	(Ó Baoill 2000a)
159	Fermanagh	Reyfad	H112461	Stem from glass drinking goblet	(Donnelly and Murphy, 1999)
160	Galway	Court Lane, Athenry	06E0086	19th century glass fragments	(Rooney 2006)
161	Galway	Newtownsmith	07E0890	19th century glass	(Fitzpatrick, 2008)
162	Galway	Ardamullivan	01E0770	20th century glass	(Rooney 2002a)
163	Galway	Merlin Park, Galway	02E1364	Glass fragments	(Fitzpatrick 2002a)
164	Galway	Raheen	02E0246	Glass	(Fitzpatrick 2002c)
165	Galway	Rahally	E2006	Blue glass bead	(Mullins 2006)
166	Galway	Treanbaun	E2123	1 green glass and 1 blue glass bead	(Muniz Perez 2006)
167	Galway	Doonloughan	97E0197	Broken blue glass bead	(McCormick and Murray 1997)
168	Galway	10 High Street, Galway	06E0457	Glass fragments	(Delaney 2008)
169	Galway	26 Prospect Hill, Galway	99E0424	Green glass wine bottle fragments	(Delaney 2000d, 102)
170	Galway	Annaghdown Castle	00E0648	Three Post-Medieval green glass bottle fragments	(Delaney 2000a)
171	Galway	Custom House, Court House Lane/Flood Street, Galway	97E0082	Various glass; fragments, beads, goblets	(Delany 1997)
172	Galway	Custom House, Flood Street/ Courthouse lane, Galway	97E0082	18th century glass fragments	(Delaney 1999a)
173	Galway	Naughton's Carpark, Market St., Galway	98E0428	Glass fragments from urban medieval context	(Delaney 2000c, 81)
174	Galway	Mackney	E2444	Glass fragments	(Delaney 2006)
175	Galway	Moyveela 3	E3907	Glass fragments	(Hegarty 2008a)
176	Galway	High Island	95E0124	One piece of glass and one blue glass bead	(Scally 2000)

	County	Location	Excavation no.	Description	Source
177	Galway	Moyode	E2353	18th/19th century vessels and window glass	(Janes 2006)
178	Galway	Ballyboy 1	E3719	7 glass beads	(McNamara 2007a)
179	Galway	Ballyboy 2	E3718	Fragment of blue glass	(McNamara 2007b)
180	Galway	50 Abbeygate Street Upper, Galway	98E0045	Green glass wine bottle (approx 16th-18th c.)	(Higgins 2000a, 76)
181	Galway	Barracks Street, Loughrea	97E0342	18th - 20th century	(Higgins 1997a)
182	Galway	Convent of Mercy, Francis St., Galway	98E0192	Stained glass from a window bearing a floral design, bottle glass (18th – 19th c.)	(Higgins 2000c, 80).
183	Galway	St. Nicholas' Scollegiate Church, Galway	98E0428	18th/ 19th c. glass fragments	(Higgins 2000e, 82)
184	Kerry	Cloghermore Cave, Cloghermore	99E0431	Blue glass bead	(Connolly 2000)
185	Kerry	14 Castle Street Lower, Tralee	08E0966	19th century bottle glass shards, window-glass shards, a shard of mirror glass	(Bartlett 2008)
186	Kerry	Abbey Street, Tralee	03E1878	Glass shards	(Dunne and Bartlett 2007a)
187	Kerry	Clahane, Tralee	00E0667	19th/early 20th century glass	(Dunne 2000a)
188	Kerry	Clahane, Tralee	05E1326	Blue glass beads	(Dunne and Bartlett)
189	Kerry	Dominic Street, Tralee	03E1878	17th century glass shards	(Dunne and Bartlett 2006)
190	Kerry	Main Street, Dingle	97E104	Post-Medieval glass	(Dunne 1997)
191	Kerry	Meadowlands Hotel, Cloonadour, Tralee	01E1119	Glass	(Ó Faoláin 2002)
192	Kerry	Cathair Fionnurach (Cathair A Bhoghasin), Ballynavenooragh	94E005	Blue glass bead	(Gibbons 1997)
193	Kerry	Ashe Street, Tralee	05E1438	Glass	(Hegarty 2006)
194	Kerry	Caherweesheen	08E0521	19th century glass	(Hurley, 2008a)
195	Kerry	Carrigeendaniel	00E0265	Blue glass bead	(Brady 2000)
196	Kildare	6 The Mall, Leixlip	01E0643	Post-Medieval glass	(Elliot 2001)

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197	Kildare	Mooreabbey Demesne	03E0691; 03R051	20th century glass	(Murphy 2003c)
198	Kildare	St Bridget's Cathedral Carpark, Kildare	04E1569	Remains of a glass bottle	(Clarke 2004)
199	Kildare	Stacummy House, Celbridge	97E0119	Glass beads	(Cosgrave 1997b)
200	Kildare	Moneycooly, Maynooth	04E0644	Post-Medieval glass piece	(Duffy 2004c)
201	Kildare	Ballynakill/ Calf Field/ Boolykeagh	02E0292	Post-Medieval glass	(O'Connor 2007)
202	Kildare	Ballynakill/ Calf Field/ Boolykeagh	02E0292	Glass	(O'Connor 2002)
203	Kildare	Ballymount	E2876	Half a glass bead	(McCarthy 2007)
204	Kildare	Blackchurch	03E1607	Blue glass bead	(Duffy 2003)
205	Kildare	Blackchurch	03E1607	2 blue glass beads	(Duffy 2004a)
206	Kildare	Killickaweeny	02E1002	Several glass beads	(Walsh 2002)
207	Kildare	Site AE23, Killickaweeny	02E0135	Blue glass bead	(Delaney 2002b)
208	Kildare	St. Mary's Church, Leixlip	07E1081	Post-Medieval glass	(Kavanagh and Quinn 2007)
209	Kildare	Kill Hill	03E1570	Piece of burnt misshapen glass	(Connolly 2003)
210	Kildare	Main Street, Celbridge	03E1829	18th century glass bottle	(Wiggins 2004)
211	Kildare	Backweston State Agriculture Laboratory Campus Ballymadeer	02E0531, 02E0680	Indigo, apple-shaped glass bead	(Frazer 2002)
212	Kildare	Claregate Street, Kildare	03E1627	Post-Medieval base of a glass bottle	(Seaver 2004a)
213	Kildare	Site 16/17, Collinstown	01E0893	Post-Medieval glass	(Reilly 2001)
214	Kilkenny	Blanchfieldsland	04E0661	Blue glass bead	(Lennon 2004)
215	Kilkenny	Site 8, Dunkitt	03E0911	19th century glass	(Gregory 2003)
216	Kilkenny	Site B, Neworchard	03E1721	19th and 20th century glass	(O'Hara 2003c)
217	Kilkenny	St Lachtan's Church, Freshford	01E0815	Window glass	(Murtagh 2001)
218	Kilkenny	11 Patrick Street, Kilkenny	06E0230	19th and 20th century glass	(Kielty 2007)
219	Kilkenny	New Street Lower, Kilkenny	98E0382	Broken post-medieval glass	(Kielty 2000b, 118).
220	Kilkenny	Granny	04E0200	Glass	(Gleeson 2004)

	County	Location	Excavation no.	Description	Source
221	Kilkenny	Tinvaun	E3678	Glass bead	(Lyne 2007b)
222	Kilkenny	17 High Street ('The Hole in the Wall'), Kilkenny	07E0684	19th century glass fragments	(Ó Drisceoil, 2008a)
223	Kilkenny	18, 19 and 21 High Street (rear of), Kilkenny	07E0910	Bottle glass	(Ó Drisceoil, 2007a)
224	Kilkenny	Kells Priory, Rathduff	05E0516	Bottle glass	(Devine 2005)
225	Kilkenny	Rothe House Garden, Rothe House, Parliament Street, Kilkenny	05E0598	German table glass	(Ó Drisceoil 2007b)
226	Kilkenny	Rothe House, Parliament Street, Kilkenny	05E0598	17th century glass	(Ó Drisceoil, 2008b)
227	Kilkenny	The Deanery Orchard, St. Canice's Cathedral, Kilkenny	06E0306	Post-Medieval glass	(Ó Drisceoil 2006)
228	Kilkenny	Kilkenny Castle, The Parade, Kilkenny	E627	17th - 18th century glass	(Murtagh 1997a)
229	Kilkenny	Banks of the River Nore, Kilkenny	01E0821	18th to 20th century glass	(Doyle 2003)
230	Kilkenny	Black Abbey/ Breagagh River, Kilkenny	04E0944	Glass	(Lohan 2004a)
231	Kilkenny	Dean's Court, Irishtown, Kilkenny	02E1370	Post-Medieval bottle glass	(Stevens and Slater 2002)
232	Kilkenny	Former Union Workhouse, John Street/Dublin Road, Kilkenny	05E0435	19th century glass	(O'Meara 2006)
233	Kilkenny	Irishtown, Kilkenny	04E05615	76 sherds of 18th and 19th century glass	(Lohan 2004b)
234	Kilkenny	John's Bridge, Kilkenny	01E0980	Post-Medieval glass	(Doyle 2001a)
235	Kilkenny	Mill Island and Green's Bridge Weir, Kilkenny	01E0608	Glass	(Stevens and O'Meara 2002)
236	Kilkenny	River Nore, Kilkenny	01E0909	Glass from river gravels	(Doyle 2001b)
237	Kilkenny	River Nore, Kilkenny	01E0909	Post-Medieval glass	(Doyle 2002)
238	Kilkenny	Dunmore Cave, Mohil	04E1517	Blue glass beads	(Dowd 2004a)
239	Kilkenny	Rathculliheen	08E0675	19th and 20th century glass	(Hurley 2008b)
240	Kilkenny	Ardclone	00E0401	Piece of blue glass	(Neary 2000)
241	Kilkenny	Evans Lane, Kilkenny	02E1107	Post-Medieval glass	(Neary 2002)
242	Kilkenny	Kilkenny Main Drainage	97E0481	Medieval/Post-Medieval glass	(Neary 1997)
243	Kilkenny	Tullaroan	E2403	Glass bottles	(Neary 2006b)
244	Kilkenny	26-29 Patrick Street, Kilkenny	98E0092	17th c. glassware	(Carroll, 2000a, 118-120)

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245	Kilkenny	Glendonnell	E3386	19th century glass fragments	(Monteith 2007)
246	Laois	Lismore 1	228754 185517	A green glass ring bead	(Wiggins 2005)
247	Laois	Derryvorrigan 1	E2193	Glass bead	(Lennon 2006)
248	Laois	Parknahown 5	234214 173827	Glass beads	(O'Neill 2005)
249	Laois	Parknahown 5	E2170	Glass beads	(O Neill 2006)
250	Laois	Old County Infirmary, Portlaoise	02E1743	19th and 20th century glass	(Carroll 2002)
251	Laois	French Church Street, Portarlington	99E0281	Post-Medieval glass fragments	(Delany 2001)
252	Laois	Redcastle	03E0087	Post-Medieval glass	(Delany 2003)
253	Laois	Portlaois Gaol and Courthouse, Portlaois	96E365	Post-Medieval glass	(Reilly 2000b, 125)
254	Laois	Ballydavis	03E0151	A piece of a composite glass bracelet	(Fegan 2003)
255	Laois	Ballyshaneduff or the Derries	03E0149	Bottle glass	(Seaver 2003)
256	Leitrim	Our Lady's Hospital, Manorhamilton	01E0720	Twenty blue glass beads	(Rogers 2002b)
257	Leitrim	Bridge Street, Townparks, Carrick-on-Shannon	01E0332	19th century glass	(Read 2001a)
258	Leitrim	Commons, Fenagh	01E0159	Post-Medieval glass	(Read 2003a)
259	Limerick	Ballyclough	99E0040	Glass fragment	(Coyne 1999)
260	Limerick	Ballysimon II	98E0485	2 sherds clear bottle glass	(Collins 2000, 130)
261	Limerick	Gortnascarry	98E0196	Iron Age blue glass bead	(Mac Manus 2000b, 133)
262	Limerick	Gardenhill	E2320	Thin green glass	(Harte 2006)
263	Limerick	Jamestown	E2895	Post-Medieval glass fragments	(Delaney 2007)
264	Limerick	Newtown A	00E0853	Fragment of an Early Christian glass armlet	(Hayes 2001)
265	Limerick	Newtown (A and E), Limerick	01E0214	Fragment of a blue glass armlet and two glass beads	(Coyne 2001)
266	Limerick	St Mary's Cathedral, Limerick	92E0075	Post-Medieval glass	(Hodkinson 1997)

	County	Location	Excavation no.	Description	Source
267	Limerick	Adare Castle, Adare	01E1153	Sherds of medieval coloured window glass, two glass beads	(Dunne 2002a)
268	Limerick	Adare Castle, Adare	01E1153	Glass	(Kiely 2003)
269	Limerick	Church Street, Askeaton	05E0778	Glass	(Ó Faoláin 2005b)
270	Limerick	Clonmacken	08E0288	18th – 20th century glass bottles	(Tierney 2008b)
271	Limerick	Desmond Castle Complex, Newcastle West	01E0079	Window and bottle glass	(Dunne 2001)
272	Limerick	Desmond Castle Complex, Newcastle West	01E0079	Post-Medieval bottle and window glass	(Dunne and Bartlett 2007b)
273	Limerick	Fish Lane/Sir Harry's Mall, King's Island, Limerick	96E0334	Post-Medieval glass	(Hanley 1997)
274	Limerick	Carrow	02E0690	Post-Medieval glass	(Hull 2002b)
275	Limerick	Dollas Lower	02E0632	Post-Medieval bottle glass	(Taylor 2002a)
276	Limerick	Inchagreenoge	02E0899	Post-Medieval glass	(Taylor 2002b)
277	Limerick	Kilfinny	02E0581	A piece of bottle glass	(Hull 2002c)
278	Limerick	Site 47001B, Knockcommane	E2342	Blue glass bead	(Molloy 2006b)
279	Limerick	Ballycummin	98E0433	Post-Medieval glass	(Dunne 1999)
280	Longford	Granardkill	02E0795	Blue glass bracelet fragment	(O'Conor 2003)
281	Longford	Edgeworthstown	05E0762 05£0762	Fragment of a glass bead	(Carroll 2005)
282	Louth	Chord Road, Drogheda	02E0736	Post-Medieval glass	(Murphy 2002)
283	Louth	9/10 Mill Lane, Drogheda	98E0404	Post Medieval glass fragments	(Murphy 2000a, 144)
284	Louth	Battsland, Dunleer	00E0188	Broken post-medieval glass	(Murphy 2000b)
285	Louth	Former Dundalk Gasworks, Bridge Street, Dundalk	03E0244	19th and 20th century glass	(O'Hara 2003a)
286	Louth	Millmount, Drogheda	98E0194	Post-Medieval glass fragments	(Murphy 2000d, 144)
287	Louth	Moneymore, Drogheda	02E1695	Post-Medieval glass	(Murphy 2003b)
288	Louth	Moneymore, Drogheda	02E1695	Glass	(Murphy 2004)

	County	Location	Excavation no.	Description	Source
289	Louth	Site 2, Whiterath	99E0485	Half of a broken blue glass armlet	(Ó Drisceoil 2000)
290	Louth	St. Peter's Church of Ireland church, Drogheda	01E1065	Post-Medieval glass	(Clarke and Coldrick 2001)
291	Louth	The Gate Lodge, Sienna Convent, Chord Road, Drogheda	97E0149	Post-Medieval glass	(Murphy 1999)
292	Louth	Aghnaskeagh 4	E3796	Glass fragments	(Ronayne 2008)
293	Louth	Faughart Lower 10	E3801	Blue glass beads	(Bowen and Dawkes 2008)
294	Louth	Old Mart Site, Green Lane and Magdalene Street, Drogheda	03E1498	Glass	(Lynch 2004)
295	Louth	Donaghmore 5	02E1333	A blue glass bead	(O'Donnchadha 2002)
296	Louth	Market Street, Ardee	02E0193	Post-Medieval glass	(Clutterbuck, 2002)
297	Louth	Balriggan	02E1325	Blue glass beads	(Delaney 2002)
298	Louth	Newtownbalregan	03E0115	3 decorated glass beads	(Bayley 2003)
299	Louth	Site 13, Haggardstown	06E0485	Glass bead	(McLoughlin 2006)
300	Louth	St Malachy's Church and Priory, Anne Street, Dundalk	02E1007	18th and 19th century glass	(Campbell 2002)
301	Louth	Balgatheran 1	00E0477	2 blue glass beads	(Chapple 2000)
302	Louth	John Street, Drogheda	98E0250	Post-Medieval glass fragments	(Conway 1999b)
303	Louth	Mell 2	00E0430	Decorated glass bead	(Chapple 2001)
304	Louth	Mell 3	00E0631	Blue glass bead, piece of green glass	(Breen, 2000c)
305	Mayo	Slievemore, Achill Island	05E0599	Glass	(Horning 2005)
306	Mayo	Slievemore Deserted Village, Slievemore, Achill Island	08E0578	19th century glass fragments	(Rathbone 2008)
307	Mayo	The Deserted Village, Slievemore	91E0047	18th and 19th century glass	(McDonald 2001)
308	Mayo	The Deserted Village, Slievemore	91E0047	Glass fragments and beads	(McDonald 2003)
309	Mayo	The Deserted Village, Slievemore	91E0047	Glass	(McDonald 2004)
310	Mayo	Quignalecka	07E0627	Glass fragments	(Fitzpatrick 2007)
311	Mayo	Lecarrowkilleen	05E1297	Glass fragments	(Guinan 2006b)
312	Mayo	Lecarrowkilleen	05E1297	6 glass beads	(Guinan 2007)

	County	Location	Excavation no.	Description	Source
313	Mayo	Testing Area 17, Baltrasna	03E1354	17th/18th century glass bottle fragment	(Halliday 2003b)
314	Mayo	Cranmore	E3520	A blue glass bead	(Kerrigan 2006)
315	Mayo	Gortaroe	04E1130	Glass beads	(Quinn 2004)
316	Mayo	Slievemore Deserted Village, Slievemore, Achill Island	07E0191	Blue glass bead, window glass	(McDonald and Brannon 2007)
317	Mayo	Rockfield	01E0659	Glass bead	(King 2001)
318	Mayo	Drumshinnagh	05E0733	Glass sherds	(Guinan 2006a)
319	Mayo	Gortaroe III	01E1042	Perforated black glass bead	(Gillespie 2001)
320	Mayo	Slievemore, Achill	06E0428	Glass fragments and beads	(Ó Faoláin 2006)
321	Mayo	Castlegar	99E0037	Glass beads, fragment of glass bracelet	(Zajac 1999)
322	Mayo	Deserted Village, Slievemore, Achill	91E0047	Glass fragments	(McDonald 2000, 158)
323	Meath	Johnstown 1	02E0462	Glass	(Clarke 2002)
324	Meath	11F02 Platin	06E0246	Post-Medieval glass	(Ronayne 2006a)
325	Meath	Abbeyland and Prioryland, Duleek	08E0536	Four glass fragments	(Ó Maoldúin, 2008)
326	Meath	Mercy Convent, Athboy	02E1047	Post-Medieval glass	(Elliot 2002)
327	Meath	Ninch, Laytown	98E0501	Glass beads and slag	(McConway 2001)
328	Meath	Stagrennan	99E0535	Post-Medieval glass	(Whitaker 1999)
329	Meath	Townparks, Kells	05E046	Blue glass bead	(Rohan 2007)
330	Meath	Knockharley	04E0778	A fragment of dark-green glass	(Fitzpatrick 2004)
331	Meath	Ardsallagh 5, Ardsallagh	288095 263919	Blue glass bead	(Clarke 2005)
332	Meath	Castlefarm 1, Castlefarm	300375 241599	Early Medieval glass beads	(O'Connell 2005)
333	Meath	Colp West	99E0472	Decorated glass bead	(Murphy 2000c)
334	Meath	Colp West	99E0472	Glass bead fragment	(Clarke and Murphy 2001)
335	Meath	Dowdstown 1, Dowdstown	290435 262077	Sherds of glass including window glass	(Linnane 2005)

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336	Meath	Moathill, Navan	99E0653	Glass	(Conway 1999a)
337	Meath	Mill Lane, Navan	03E0004	Glass	(Russell 2003a)
338	Meath	Roestown 2	E3055	Glass	(O'Hara 2006)
339	Meath	Site M, Knowth	02E0726	Glass beads	(Stout 2002)
340	Meath	Site M, Knowth	02E0726	Glass beads	(Stout 2003)
341	Meath	Clonee, Meath	08E0840	Post-Medieval glass	(McCarthy 2008)
342	Meath	Commons of Lloyd, Kells	03E0020	Broken glass	(Wallace 2003)
343	Meath	Ratoath	03E1781	Blue glass beads	(Wallace 2004)
344	Meath	Ida Business Park, Kilkarn, Athlumney, Navan	98E0596	Glass bead	(Jones 1999)
345	Meath	27 High Street	06E0148	Glass	(Duffy 2006)
346	Meath	Market Street, Trim	04E1164	Glass	(Duffy 2004b)
347	Meath	Dowdstown	05E1138	19th century glass	(McGowan 2005)
348	Meath	Dunboyne	03E1112	Post-Medieval glass	(O'Carroll 2003)
349	Meath	Nobber	07E0345	Glass bottle (18th century type)	(Seaver 2007)
350	Meath	Site 10, Garadice	07E0296	Medieval glass beads	(Larsson 2007)
351	Meath	Ardsallagh 2	E3087	Blue glass bead	(Clarke 2006)
352	Meath	Balgeen	01E0411	18th and 19th century glass	(O'Carroll 2001a)
353	Meath	Cookstown	03E1252	Glass, including part of a brown glass bracelet	(Clutterbuck 2004)
354	Meath	Possackstown, Rathcore, Enfield	02E1526	Green glass	(Shanahan 2002)
355	Meath	Ratoath	01E1173	Post-Medieval glass	(O'Carroll 2001b)
356	Meath	Raystown	03E1229	Blue glass beads	(Seaver 2004b)
357	Meath	The Knockans, Teltown, Oristown	97E0301	Sherd of glass	(Waddell and O'Brien 2000, 165)
358	Meath	Moynagh Lough, Brittas	E337	Glass bead	(Bradley 1997)

	County	Location	Excavation no.	Description	Source
359	Meath	Rath na Ríogh (Tara), Castleboy	97E0300	Blue glass fragments and fragment of a glass bracelet	(Roche 1997)
360	Meath	Killegland, Ashbourne	05E0423	Post-Medieval glass	(Kavanagh 2006)
361	Meath	Duleek Road, Platin	01E0822	Glass beads, possible other glass material	(Lynch 2001)
362	Meath	Grange 2	E3124	Glass bead	(Kelly 2007)
363	Meath	Kiltrough	08E0297	Glass beads	(Gallagher 2008)
364	Meath	Nugentstown 1	E3136	Glass bead	(Lynch 2007)
365	Meath	Platin	00E0822	Glass beads	(Lynch 2000)
366	Meath	Phoenixtown 4	E3131	Glass tubing	(Lyne 2007a)
367	Meath	Townparks 3	E3149	Glass	(Gleeson 2007)
368	Meath	Randalstown	04E1351	Post-Medieval glass	(Murray 2004)
369	Meath	Site 21, Raystown	03E1229	Glass beads	(Halliday 2003a)
370	Meath	Glebe	05E0714	19th/20th century glass	(Campbell 2005a)
371	Meath	Augherskea	02E1229	A blue glass bead	(Baker 2002)
372	Meath	Site A, Killeen Castle, Killeen	05E0303	Glass	(Baker 2005)
373	Meath	Gernonstown	06E0606	18th century glass bottle fragments	(Reid 2006)
374	Meath	Trimgate Street, Navan	98E0162	Post Medieval bottle glass	(Meenan 2000b, 165)
375	Meath	Site 2, Flower Hill, Navan	03E1352	Glass fragments	(O'Carroll 2004)
376	Monaghan	84 Glaslough Street, Monaghan	01E0527	18th and 19th century bottle glass	(Halpin 2001b)
377	Monaghan	The Crosses	00E0011	Post-Medieval glass	(McLoughlin 2000)
378	Monaghan	Carrickmacross Sewerage Scheme, Drummond Outra, Carricknacross	00E0108	19th and 20th century glass	(Bermingham 2000)
379	Monaghan	19-20 Park Street, Monaghan	04E1566	Glass phial and a glass button	(Duffy 2004d)
380	Monaghan	Mullanrockan	06E0640	Glass	(Duffy 2007)

	County	Location	Excavation no.	Description	Source
381	Monaghan	Maghernacloy	04E0513	19th or 20th century glass	(Campbell 2004b)
382	Monaghan	Fermanagh Street, Clones	04E0531	20th century coloured bottle glass	(O'Connell 2004)
383	Monaghan	Drumirril	03E1231	Blue glass beads	(O'Connor 2003)
384	Monaghan	Monanny 1	03E0888	19th century glass	(Walsh 2003)
385	Monaghan	Site 104, Lismagunshin	05E0785	Blue glass bead	(Sutton 2005)
386	Offaly	Birr	07E0855	Bottle glass	(Petérváry, 2008)
387	Offaly	Cuba	00E0677	Green glass bottle piece	(Delaney 2000b)
388	Offaly	Killeigh	99E0348	Green glass bottle fragments	(Delaney 1999b)
389	Offaly	Church Street, Banagher	04E0854	Window glass	(Campbell 2004a)
390	Offaly	Main Street, Banagher	05E1212	19th/20th century glass	(Campbell 2005)
391	Offaly	New Graveyard, Clonmacnoise	E558	A blue glass bead	(King 1997)
392	Offaly	Glasshouse	99E0191	Window and vessel glass	(Farrelly 2001)
393	Offaly	28 Main Street, Birr	08E0198	Post-Medieval glass	(Tierney 2008a)
394	Roscommon	Boyle	04E0945	Post-Medieval glass	(Rooney 2004)
395	Roscommon	Castle Street, Roscommon	02E1830	20th century glass	(Rooney 2002b)
396	Roscommon	Former Gaol, Roscommon	03E1245	Early 20th century glass	(O'Hara 2003b)
397	Roscommon	Ballykilcline	98E0297	Glass fragments and beads	(Hull and Orser 2002)
398	Roscommon	Tulsk	04E0850	Glass beads	(Brady 2007)
399	Roscommon	Tulsk	04E0850	Blue glass beads	(Brady 2008)
400	Roscommon	Aughamore Village, Ballykilcline	98E0297	Curved and flat glass fragments	(Orser 2000a, 177-178)
401	Roscommon	Ballykilcline	98E0297	19th century glass sherds	(Orser 2000b)
402	Roscommon	Ballykilcline	98E0297	Post-medieval window glass and glass beads	(Orser 2001)
403	Roscommon	Mulliviltrin	97E0164	9.70E+165	(Orser 1997)
404	Roscommon	Carns	06E0655	Blue glass bead	(Shanahan 2007a)

	County	Location	Excavation no.	Description	Source
405	Roscommon	Carns	07E0688	Glass-bead necklace	(Shanahan 2007b)
406	Roscommon	Elphin	01E0704	18th and 19th century glass	(Read 2003b)
407	Roscommon	Killtullagh Hill, Killtullagh	96E0179	Blue glass bead found in barrow	(Robinson and Coomb 2000, 179)
408	Roscommon	Rathpeak 2	E2834	Post-Medieval glass	(Jackman 2007)
409	Roscommon	Roscommon Jail. The Market/Castle Street/ Main Street, Roscommon	97E0419	Post-Medieval glass	(Higgins 1997)
410	Sligo	5 High Street, Sligo	02E1164	Post-Medieval glass	(Halpin 2002)
411	Sligo	Carrowmore	03E1516	Glass fragment	(Fitzpatrick 2006)
412	Sligo	Rathbraghan	01E1070	Glass fragments	(Fitzpatrick 2001)
413	Sligo	Listoghil, Carrowmore	03E1050	20th century glass fragments	(Fitpatrick 2003)
414	Sligo	1-2 John Street, Sligo	06E0920	Glass piece	(Turrell 2006)
415	Sligo	Barlow's Field, Carrowcashel	03E0925	Glass fragments	(Orser 2005)
416	Sligo	First Coopershill House, Riverstown	03E0925	Olive green glass	(Orser 2004)
417	Sligo	Derroon	06E0720	Ten glass beads/ bead fragments, 2 unperforated beads	(Keane 2006)
418	Sligo	Trahaun O Riain, Inishmurray	97E0256	Sherd of green glass vessel - possible Mediterranean	(O'Sullivan 1997)
419	Sligo	11 Market Street, Abbeyquarter South, Sligo	04E1013	Glass	(Timoney 2005)
420	Sligo	12 Market Street, Abbeyquarter South, Sligo	07E0233	Glass pieces	(Timoney 2007b)
421	Sligo	9-10 Castle Street, Abbeyquarter South, Sligo	06E1173	Glass fragments	(Timoney 2007a)
422	Sligo	Grange North	01E0504	Post-Medieval glass	(Timoney 2001)
423	Sligo	22 John Street, Sligo	01E0207	Post-Medieval glass sherds	(Ryan 2001)
424	Sligo	Cornageeha	01E1130	Post-Medieval glass	(Haplin 2001a)
425	Tipperary	Sites 11-13, Killalane	E3534	Glass bead, possibly Early Medieval	(Sutton 2007)
426	Tipperary	36-37 Parnell Street, Clonmel	99E0649	Post-Medieval bottle glass	(Moran 1999a)

	County	Location	Excavation no.	Description	Source
427	Tipperary	Rocklow Road, Fethard	99E0632	Sherd of Post-Medieval bottle glass	(Moran 1999b)
428	Tipperary	29 Main Street, Cashel	00E0871	Post-Medieval bottle glass	(Pollock 2001)
429	Tipperary	Burncourt Castle, Burncourt	03E1909	Pre-1830 glass	(Cleary 2005)
430	Tipperary	51-53 Grove Street/ The Crescent, Roscrea	08E0289	Glass fragments	(Sullivan 2008)
431	Tipperary	Knockgraffon	E2272	2 blue glass beads	(Moriarty 2006)
432	Tipperary	Loughfeedora	E2291	Post-Medieval glass	(Doody 2006)
433	Tipperary	Marlhill	E2124	Blue glass beads	(Molloy 2007)
434	Tipperary	The Munster Hotel, Cathedral Street, Thurles	98E0598	Post-Medieval glass	(Stevens 1999)
435	Tipperary	5, 6, 7-8 Castle Street, Abbeyquarter South, Sligo	07E0096	59 pieces of glass, including from bottles and one from window glass	(Timoney 2008)
436	Tipperary	Clonmel town and environs	06E0651	Bottle glass	(Henry 2006)
437	Tipperary	Morton Street, Clonmel	07E0133	Glass sherds	(Henry 2007)
438	Tipperary	Hazelwood Demesne	08D086	19th century glass	(Pollard 2008)
439	Tipperary	Annaholty	E3326	Post-Medieval glass bottle	(McNamara 2007a)
440	Tipperary	Carrigatogher (Harding)	E2286	2 blue glass beads	(Casey 2007)
441	Tipperary	Cooleen	E3370	Post-Medieval glass	(McNamara 2007b)
442	Tipperary	Camlin 3	E3580	4 blue glass beads	(Flynn 2007)
443	Tipperary	Site AR33, Borris	E2376	Glass bead	(Ó Droma 2007)
444	Tyrone	Farriter, areas 34-36	Not listed	Post-Medieval glass	(Mossop 2008)
445	Tyrone	Ranfurly House, Castle Hill, Dungannon	H79806250	Post-Medieval glass	(Vuolteenaho 2008)
446	Tyrone	Newtownsteward Castle, Newtownsteward	H40208583	17th century window glass	(Ó Baoill 1999)
447	Tyrone	Castle Hill, Dungannon	H79906262	Glass	(Environment and Heritage Service 2007)
448	Tyrone	Relough	H76126586	Blue glass bead	(McQuillan 2001)

	County	Location	Excavation no.	Description	Source
449	Tyrone	Castle Hill, Dungannon	07990 6262	Stem of a wine glass	(Chapple 2003)
450	Waterford	Adamstown 1	03E1215	Fragment of a glass bead	(Russell 2003a)
451	Waterford	Knockhouse Lower 3	03E0335	Small glass bead	(Clarke 2003a)
452	Waterford	Knockhouse Upper 2	03E0339	Sherds of glass	(Clarke 2003b)
453	Waterford	Woodstown 6	E2964	Glass beads	(Russell 2007)
454	Waterford	Reginald's Tower, The Quay, Waterford	97E0246	Post-Medieval window glass	(Murtagh 1997b)
455	Waterford	Waterford	06E0325	16th to 18th century glass	(Hurley 2006)
456	Waterford	Kill St Lawrence	03E0883	Glass	(Scully 2003)
457	Waterford	St John's Priory, Waterford	03E1830	Broken glass	(Scully 2005)
458	Waterford	Lifetime Day Care Centre, Lady Lane, Waterford	95E0098	Post-Medieval bottle glass	(Tobin 2001)
459	Westmeath	Blackhall Street, Mullingar	00E0781	20th century glass	(Fitzpatrick 2000)
460	Westmeath	Newtown 2	04E0690	19th century glass	(Stevens 2004)
461	Westmeath	Old Relic Road, Kilbeggan	04E1327	A coloured glass bead	(Corcoran 2005)
462	Westmeath	Boreen Bradach, Kinnegad	06E0448	Glass slag	(Whitty 2006)
463	Westmeath	Stonehousefarm 1	233910 234065	Post-Medieval glass	(McDermott 2004)
464	Westmeath	Dominick Place, Mullingar	00E0622	Glass	(Meenan 2000a)
465	Westmeath	Piercefield or Templeoran	04E1176	19th century bottle glass	(Meenan 2004)
466	Westmeath	Church Avenue/ Pearse St	98E0209	Bulbous Post-Medieval glass bottles	(Higgins 2000b, 212)
467	Westmeath	Friars Hill Road, Mullingar	98E0153	Post-Medieval bottle glass	(Higgins 2000d, 212-213
468	Westmeath	Area 1C, Blackhall Street Carpark, Mullingar	03E1545	Post-Medieval glass and stained glass fragments	(Hardy 2003a)
469	Westmeath	Blackhall Street, Mullingar	E2497	Stained glass window fragments, Post-Medieval glass	(Breen 2006)
470	Westmeath	Country Buildings, Mullingar	03E1544	19th century glass fragments	(Hardy 2003b)
471	Westmeath	Country Buildings, Mullingar	03E1544	19th century glass	(Hardy 2004)

	County	Location	Excavation no.	Description	Source
472	Westmeath	Country Buildings, Mullingar	03E1544	19th/20th century glass	(Hardy 2005)
473	Westmeath	Sites 42-44, ASK	317645 163279 TO 317741 163451	Blue glass beads	(Stevens 2005)
474	Wexford	Talbot Hotel, King Street Lower/ Trinity Street, Wexford	02E1652	Post-Medieval glass	(Larsson 2002)
475	Wexford	Rathaspick	01E0250; 01E0345	Blue glass bead	(Mullins 2001)
476	Wexford	1a Main Street North, Wexford	01E0074	Clear window glass	(Tierney and Frazer 2001)
477	Wexford	Whiterock South	00E0805	Glass	(O'Neill 2001c)
478	Wexford	Ferns Lower, Ferns	99E0450	50+ glass beads	(Ryan 1999)
479	Wexford	Ballyhack	03E1630	17th and 18th century glass	(Reid 2003)
480	Wexford	Brideswell Big	01E0801	Post-Medieval glass	(Gregory 2001)
481	Wexford	Dunbrody Abbey	E2815	Glass	(Neary 2006a)
482	Wexford	River Barrow, New Ross	07E056	20th century glass bottles	(Bangerter 2007)
483	Wexford	Moneytucker	04E0329	Post-Medieval glass	(Maoldoein 2004)
484	Wexford	Site 27, Raheenagurren West	316478 158079	A blue glass bead	(Breen 2005)
485	Wexford	Site 37, ASK	317511 162248	Glass fragments and beads	(Martin 2005)
486	Wicklow	Coolbeg	E3253	Post-Medieval glass	(Dehaene 2006)
487	Wicklow	Kilmurry North	01E0572	Green glass bead (possibly Iron Age)	(O'Neill 2001a)

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Appendix B: Glass Reference Material Data Sheets

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Standardglas I der DGG

(Kalk-Natron-Glas)

Das Standardglas I der DGG ist ein Kalk-Natron-Silicatglas (Flachglas). Für das Glas liegen Daten über die chemische Zusammensetzung, die Viskosität im Temperaturbereich zwischen 500 und 1400 °C, die Transformationstemperatur und den thermischen Ausdehnungskoeffizienten vor.

1. Chemische Zusammensetzung

Bestandteil	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	SO_3
Anteil in Gew.-%	71,72	1,23	0,191	0,137	0,436
Bestandteil	CaO	MgO	Na_2O	K_2O	
Anteil in Gew.-%	6,73	4,18	14,95	0,38	

Die chemische Zusammensetzung wurde im Rahmen eines Ringversuches des Unterausschusses Glasanalyse des Fachausschusses I der DGG bestimmt.

2. Viskosität

Temperatur in °C	500	600	700	800	900
Viskosität in d Pa s	$1.02 \cdot 10^{15}$	$5.66 \cdot 10^{10}$	$9.88 \cdot 10^{7}$	$1.76 \cdot 10^{6}$	$1.12 \cdot 10^{5}$
Temperatur in °C	1000	1100	1200	1300	1400
Viskosität in d Pa s	$1.49 \cdot 10^{4}$	$3.19 \cdot 10^{3}$	$9.32 \cdot 10^{2}$	$3.41 \cdot 10^{2}$	$1.48 \cdot 10^{2}$

Die Viskositätsmessung wurde durch die Physikalisch-Technische Bundesanstalt (PTB) in Braunschweig durchgeführt.

Literatur: Meerlender, G.: Viskositäts-Temperaturverhalten des Standardglases I der DGG. Glastechn. Ber. 47 (1974) Nr. 1, S. 1-3.

Standardglas II der DGG

(Kalk-Natron-Glas)

Das Standardglas II der DGG entspricht in seiner Zusammensetzung einem Floatglas. Für dieses Glas liegt die in einem Ringversuch mit acht beteiligten Glaslabors ermittelte chemische Zusammensetzung vor.

Chemische Zusammensetzung

Bestandteil	SiO_2	Al_2O_3	Fe_2O_3	TiO_2
Anteil in Gew.-%	72,26	0,10	0,021	0,033
Bestandteil	CaO	MgO	Na_2O	SO_3
Anteil in Gew.-%	10,05	3,40	13,78	0,27

Die Lieferung erfolgt in Scheiben (80 mm x 50 mm x 5 mm) zu je 50 g.
Preis: € 100,-/100 g Standardglas plus Versandkosten.

Bestellungen sind zu richten an:

Hüttentechnische Vereinigung der Deutschen Glasindustrie (HVG),
Siemensstraße 45, D-63071 Offenbach,
Tel.: +49(0)69-97 58 61-0, Fax: +49(0)69-97 58 61-99,
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Appendix C: Analysis of glass from Dun Ailinne

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Appendix C: Dún Ailinne, Co. Kildare

1. Introduction

This report details the analysis of a number of glass artefacts which were uncovered during the excavations at Dun Ailinne. The multi-elemental analysis was carried out using X-ray Fluorescence at I.T. Sligo. The aim of this analysis was to determine trace elements within the glass beads which could potentially answer questions about their origin or production. The report will cover the interpretation of the results obtained from the Dun Ailinne assemblage. More work will be necessary to examine how the artefacts differ based on what phase they were associated with and their artefact type.

The samples in this analysis included a range of glass beads and bracelet fragments. The site of Dun Ailinne includes around 34 acres on a hilltop, which is enclosed by a ditch and bank. Although the site is often referred to as a hill-fort, the position of the bank downhill and outside of the ditch would indicate that its primary purpose was not defensive. Excavations noted four major stages of construction on the summit; a Neolithic structure and three subsequent Iron Age timber structures. Artefacts uncovered during excavations indicated heavy use of the site during the Iron Age and Early Medieval (Wailes 2007b, xxv-xxix). The most prominent features dating to the Iron Age were the three successive construction phases which were, dating from early to late, the White, Rose and Mauve phases. Each of these was shown to contain circular palisade trenches which would have held upright timbers. A low mound, roughly 20m diameter and barely 1m above ground level, was completely excavated. This included a series of complex layers which were likely accumulated while the timber structure of the Mauve phase was still standing, however its uppermost level, which shows evidence of feasting, post-dates the deconstruction of all of the structures associated with the Mauve phase and is classified as the Flame phase (Wailes 2007a, 22). Many of the glass artefacts are associated with these various layers as will be discussed in Section 2.1.

2. Methodology

2.1. Sample collection and selection

A selection of glass beads and bracelet fragments from the Dun Ailinne excavations were obtained from the National Museum of Ireland for the purpose of this study. The samples were chosen from the Dun Ailinne glass assemblage with a number of objects being excluded due to their fragmented nature or small size. In total, 43 artefacts from a total of 50 in the assemblage were analysed using XRF analysis, as seven of the artefacts were either too small or too fragmented for analysis. This included 20 beads, 11 bracelet fragments, 8 toggles and 4 unidentified fragments. Of the 50 glass artefacts which were discovered during the Dun Ailinne excavations, 18 come from unknown phases. Of the remaining 32, 17 come from the Flame phase contexts, which represent the latest Iron Age deposits on the site, and it has been suggested that they represent lost personal adornment that was deposited during feasting activities which are well represented in this phase. The Mauve and Rose phases, which also date to the Iron Age although earlier than the Flame phase, contained three and four glass artefacts respectively. The remaining eight glass artefacts were uncovered from complex levels layering the low mound superimposed under the Flame phase deposits (Johnston 2007, 115).

2.2. Calibration/Quality Control

The XRF was calibrated monthly using the standard procedure for this instrument. The accuracy of the instrument is also tested regularly using glass reference material. Table 1 below illustrates the accuracy and precision of the XRF using a reference sample. The sample was run five times and an average taken of the results. The percentage difference and relative standard deviation was then calculated from the results.

	Stated concentration (%w/w)	**Average obtained (%w/w)**	**Relative Standard Deviation%**	**%Error**
SiO_2	72.26	72.62	0.360	0.503
Na_2O	13.78	12.88	1.399	-6.516
CaO	10.05	10.71	0.598	7.000
MgO	3.40	3.64	2.423	-0.0549
SO_3	0.270	0.027	9.658	-90.074
TiO_2	0.033	0.0237	7.413	-28.121
Fe_2O_3	0.021	0.0177	4.058	-15.619

Table 1: Reference sample results obtained

2.3. Sample washing and preparation

No washing or other preparation was carried out on these samples prior to their analysis in the XRF. It is desirable to gently clean the surface of archaeological samples using a 1:1 ratio solution of deionised water and 99% ethanol solution prior to elemental analysis to remove surface contamination on the glass. However, due to the highly delicate nature of these samples, it was considered safer to analyse them as they were. All samples were handled using gloves to avoid adding any further surface contamination.

2.4. Testing of samples

Each sample was analysed by XRF in triplicate and the results averaged. Samples were analysed in the condition they were received with no preparation. XRF was chosen for this analysis as it provides a highly sensitive, multi-elemental analysis and is completely non-destructive. XRF is a surface technique, therefore the elemental composition it gives is indicative of the surface layers only and this may not be an accurate representation of the whole sample.

3. Results

The results of the analysis (given in percentage w/w) can be seen in the Appendix 1 at the end of this report. It shows the results that were obtained from the 43 samples during this study as well as a description of each object.

4. Discussion

4.1 Condition of samples

Some of the artefacts were in a fragmented condition. This mainly applied to the bracelet fragments, although several beads were in a broken state. The majority of the glass exhibited no visible sign of corrosion, pitting, crusting or an iridescent sheen which are common aspects of many ancient glass artefacts. Two notable exceptions were find Nos. E79.2209 and E79.50 (Plates 1 and 2 respectively). A discoloured layer had formed on the surface of find No. E79.50, a red toggle, while the composition of the latter was unusual and would suggest that it may have been subjected to some kind of stress, possibly intense heat. Find No. E79.2209 appeared slightly malformed, with visible striations through the glass and a crumbling appearance. The poor structure of bead E79.2209 may have been due to poor production conditions in the furnace, such as inconsistent or inadequate temperatures. A third example, find No. E79.1603, a blue glass bead, exhibited some signs of devitrification on its surface.

4.2 Elemental Composition

From ancient times, glass has been consistently made up of a glass former, such as sand or quartz pebbles (SiO_2), a modifier, such as soda (Na_2O) or potash (K_2O), and a stabilizer such as lime ($CaCO_3$). As well as this, glass may contain a variety of colouring agents, opacifiers and other trace elements, added either intentionally or

unintentionally (Goffer 2007, 124). From an analytical point of view, the composition of ancient soda-lime glass is typically 73% SiO_2 (silica), 23% Na_2O (soda) and 5% CaO (calcium oxide) (Gratuze and Janssens 2004, 665).

4.2.1 Beads

A total of 20 beads were analysed from this assemblage. A range of colours and sizes were represented. The majority of the beads, 14, were blue in colour, but there was also one green, two orange/amber, one blue-green, one colourless and one purple. A range of the beads found can be seen in Plate 1.

The main component of the 20 beads was found to be silica (SiO_2), which accounted for between 41.68% and 80.13% of their elemental composition. The low levels of silica in some of the beads, such as the 41.68% which was found in find No. E79.1603, highlights how these objects have suffered corrosion of the surface layers to some extent. Ground water can interact with buried glass material affecting the stability of the object. Signs that a glass fragment may have been affected by this include a flaky coating and iridescence on the surface of the object (Pollard and Heron 2008, 119, 178). Glass corrosion is a complex process which is not well understood, affected by many different factors. However it is thought that it occurs due to the preferential leaching of alkali ions to be replaced by hydrogen ions (Wayne Smith 2003, 94). The reaction begins at the surface of the object and spreads inwards (Varshneya 1994, 398). Cox and Ford (1993, 5639-43) conducted a detailed elemental study of multiple layers of medieval glass and concluded that corroded surface layers can be depleted of most oxides except silica (Si), aluminium (Al) and iron (Fe), and what is left behind is poorly crystalline hydrated silicates and aluminosilicates with varying amounts of calcium (Ca), phosphate (P) and manganiferous (Mn) minerals. The low percentage of silica, coupled with unusually high levels of aluminium oxide (Al_2O_3) in a number of samples, would suggest that the surface layers had lost some of their original composition. Aluminium may have existed in the structure of glass originally in smaller amounts and was held preferentially compared to other

elements. There is also the possibility that the surface layers contained aluminium which had entered from the environment. Low levels of silica in the samples were found to be associated with high levels of aluminium oxide (Al_2O_3), and an inversely proportional trend can be observed when the two results are plotted against each other (see Figure 1). An r^2 value of 0.8622 is observed for this graph. On a scale of 0 to 1, where 0 represents no correlation and 1 shows a very strong correlation, it can be seen that the result here does indeed indicate a strong correlation between the two.

Low levels of both potash (K_2O) and soda (Na_2O) were immediately apparent from the results obtained from the beads. As mentioned, the level of soda and potash can be up to around 23% for ancient glass. Generally, the lowest concentrations which would have been added would have been at least 15%. However some of the material contained only trace amounts of these substances. Of the 20 beads analysed, only 13 contained detectable levels of soda, at levels of between 1.28% and 8.86%. All 20 contained traces of potash, between 0.179% and 3.04%. These low levels further highlight the corroded nature of the surface layers of the glass, despite their appearance. Visually, these beads were in good condition and showed no sign of crusting or iridescence yet the elemental analysis reveals their degraded nature.

Soda, potash or a mixture of the two was an essential component when producing glass in ancient times. It acted as a flux, lowering the melting point of silica from 1700^{o}C to 1000^{o}C, a temperature which was obtainable in ancient furnaces (Goffer 2007, 115). Some of the beads analysed are almost certainly a soda-lime type glass. Find No. E79.2910, for example, contained 8.86% soda and 0.611% potash. While this is still well below the minimum 15% concentration which would be expected, it is clear that this bead had maintained its structural integrity better than many of the other samples.

As mentioned already, seven of the beads contained no detectable amounts of soda. Their potash level was also quite low. Find Nos. E79.71 and E79.134, for example, contained only 0.52% and 0.44% potash respectively. These figures are an average of the three sets of results that were obtained from analysing each sample in triplicate.

The %RSD for these results were found to be quite low, 0.938 and 1.216 respectively, highlighting that the figures achieved do not show a great degree of variability when the analysis is repeated and are is therefore an indication of the precision of the technique. Potash would have been sourced from wood ash as opposed to soda which was generally retrieved from marine plants. Potash glass became increasingly popular during the medieval period when demand for glass was growing and there was incentive to search for a more readily accessible alkali source. While corrosion may affect glass for a number of reasons, such as environmental factors, the most important factor in most cases is the original elemental composition of the glass. This determines the resistance of the glass to agents which can cause corrosion such as water, acidic and basic solutions and other atmospheric substances (Pollard and Heron 2008, 166). With regards to medieval window glass for example, it has been noted that potash based examples were more susceptible to weathering due to the high alkalinity of the glass (Moran 2010, 17). The small amounts of modifier found in these seven samples, along with a lack of soda detected would suggest that they were possibly potash-based. This suggestion is strengthened when it is considered that soda has survived to a greater extent in samples such as find No. E79.2910, which was mentioned already.

The beads which contained smaller amounts of both soda and potash may well have been formed from a mixed alkali glass type. A mix of potash and soda could have been added intentionally or it may have been accidental. For example, potash sources may occasionally contain traces of soda. It is also possible that cullet (broken pieces of glass) may have been used when producing the glass, and this would further complicate the elemental composition of the mixture.

Of the 14 blue glass beads, 13 were found to contain cobalt oxide (Co_3O_4). One lone exception to this was find No. E79.1603. Cobalt is a powerful blue colourant used in glass production, producing a bright blue hue even with very small amounts. It was extensively used in ancient glass production (Goffer 2007, 121-122). Find No. E79.1603 most likely gets its hue from copper. Blue tones ranging from bluish green to a very pale blue could also be achieved by adding cupric oxide to the glass melt

(CuO) (Bhardwaj 1979, 42-43). It contains 1.39% copper oxide (CuO), considerably more than the other blue beads. This would suggest that find No. E79.1603 had a different production method and therefore, likely a different origin than the other blue glass beads. This bead has a much higher level of aluminium oxide (Al_2O_3) than the other blue glass beads, most likely caused by corrosion as was discussed in Section 4.1. It also had the lowest amounts of silica and potash in any of the beads with 41.68% and 0.179% respectively. This again would suggest that the bead had a different original elemental composition than the other blue glass beads, as the susceptibility of glass to corrosion is influenced most by its original elemental composition. Johnston notes that this bead is of unknown date. She states that it may be modern but that its condition, with surface etching, may suggest an ancient origin (Johnston 2007, 119). Given the elemental corrosion it has suffered, it is highly unlikely to be modern and indeed may be one of the oldest blue beads from the assemblage.

Find No. E79.115, the single green-blue example, was uncovered from topsoil layers in an unstratified context. Johnston does note, however, that the colour of this bead is typical of Bronze Age glass (Johnston 2007, 116). Several other authors have suggested that blue-green glass was a typical colour found in Bronze Age glass (Henderson 2013, 75, Barber 1991, 235, Bellintani 2013, 283). It is also suggested that magnesium oxide (MgO) was a characteristic component found in blue-green Bronze Age glasses which were made using plant ash alkali sources (Henderson 2013, 75). However there was no detectable level of magnesium oxide (MgO) found in this bead. This makes it difficult to ascertain whether this bead is truly a Bronze Age example. E79.115 was also found not to contain cobalt and again, most likely gets its hue from the copper in its structure. E79.1603 is another bead which appears to have been coloured with copper, however it is both darker in shade and does not contain any hint of green. The lesser concentration of copper oxide in E79.115, 0.644% compared to the 1.39% found in E79.1603, would account for its lighter colour. There was no definitive element in the elemental analysis which would cause it to have a more greenish hue than E79.1603, but it was possibly due to oxidation conditions in the furnace environment. Copper has been found to impart a wide range of colours

in glass (Bhardwaj 1979, 42-43). This includes blue tones ranging from bluish green to a very pale blue that could also be achieved by adding cupric oxide (CuO) to the glass. Adding cuprous oxide (Cu_2O), meanwhile, resulted in a reddish brown colour (Bhardwaj 1979, 42-43). Detailed knowledge and careful addition of colourants would have been required to purposely achieve any given colour.

Find Nos. E79.723 and E79.111 were amber-coloured beads, with the latter being a ring bead. Johnston mentions that these may be amber as opposed to glass (Johnston 2007, 116) however the XRF analysis confirms that they are glass. Both appear to have lost a great amount of their original soda or potash content and contain relatively small amounts of trace elements compared to the other beads. It was not immediately apparent what was causing the amber hue of these beads. They contained 0.041% and 0.0243% manganese oxide (MnO) respectively. Manganese, when added to other elements such as carbon and sulphur, is known to impart an amber hue, but the content of manganese was comparable or even lower than many of the other bead samples. It is possible that the amber colour was caused by the addition of a reducing agent, such as carbon, to the glass furnace. When carbon is added to a glass mix containing iron and sulphur for example, it can result in varying shades of amber (Bray 2001, 65). Find Nos. E79.723 and E79.111 contained iron levels of 0.197% and 0.537% respectively. Unfortunately, carbon is too light an element to be detected by the XRF, so further investigation would be required in order to determine the level of carbon present.

The purple bead (E79.2209) was most likely coloured by the relatively high level of manganese oxide (MnO) it contains. Manganese oxide was found in trace quantities in all of the beads, however the purple bead had the highest concentration at 2.24%. The rest of the beads contained less than half the concentration of manganese oxide as the purple bead E79.2209. In many cases, manganese can be added unintentionally to the glass mix as impurities found in raw materials that were sourced (Wilson 1855, 261). It was sometimes added intentionally as a decolourant in glass production as it masks the green colour caused by iron. When used on its own without significant levels of iron, it gives a purple colour (Goffer 2007, 121). Find No.

E79.2209 seemed to be one of only two examples in this assemblage were it was purposely added in any quantity. The iron content of this bead was 0.477%, enough to impart a colour but not enough to need this amount of manganese added as a decolourant. The other, a bracelet fragment, will be discussed in Section 4.2.2.

Find No. E79.449, the most elaborately decorated Dun Ailinne bead, consisted of a light green glass with a yellowish-white decoration (Plate 1). It was found to contain concentrations of 0.573% tin oxide (SnO_2) and 1.41% lead oxide (PbO). This could account for the yellow-white hue of the decoration overlaid on the green glass, as these elements together are known to produce opaque whites and yellows (Henderson 2000, 74). The green colour of the bead was most likely due to iron oxide contaminants in the glass melt, as other substances known to act as green colourants, such as oxides of copper, chromium and nickel, were absent. In addition to this, the levels of iron oxide were found to be quite high, at 1.53%. Three other beads which had patterned decoration were analysed; E79.17, E79.907 and E79.1002, all of which were blue glass examples. The decoration on find No. E79.907 was a very faint white. This example only had a low quantity of tin oxide detected, 0.0066%. Find Nos. E79.17 and E79.1002 had stronger white trails visible and elemental analysis revealed higher amounts of tin oxide with 0.472% and 0.347% respectively. This would support the argument that tin oxide was being utilised for the purpose of decoration in these beads.

Chlorine (Cl) was found in fairly significant quantities in the majority of the glass samples from Dun Ailinne. This ranges from 0.06935% to 0.965% Cl. Chlorine can be transferred onto the surface of glass from handling objects with bare hands and generally this contamination would be greatly reduced by washing techniques. However, as these beads were not submitted to any washing technique due to the fragile nature of some of the artefacts, it is not surprising to see levels of chlorine in the results. As gloves were used when handling the samples at all times during their analysis, the contamination was not added immediately prior to analysis and would have been present on the surface of the glass for some time. It is possible for glass to contain some chlorine as part of its original structure due to it being added as part of

the source of soda or potash, however the concentrations here were large enough that the possibility of contamination should be considered (Henderson 2000, 94).

4.2.2 Bracelets

A total of 11 glass bracelet fragments were examined in the course of this analysis. A selection of these can be seen in Plate 2. Compared to the beads the silica (SiO_2) levels in the bracelet fragments were much more in line with the levels expected. With the exceptions of find Nos. E79.377 and E79.1927, which had silica concentrations of 64.82% and 64.595%, all of the bracelet fragments contained silica levels of between 70.34% and 75.06%. Many also contained low levels of aluminium oxide (Al_2O_3), such as E79.1034 and E79.1333 containing 2.67% and 3.56% respectively, an amount which could be reasonably expected in archaeological glass which has not undergone extensive corrosion. Examining the content of aluminium oxide versus silica shows that the correlation between them is far weaker than that found in the glass beads, with a correlation coefficient of only 0.2475 (Figure 2). This may be due to the less corroded nature of these objects. It is unclear what caused the bracelet fragments to survive better than the other glass objects. It is possible that a different glass production method was used for these objects, resulting in an elemental composition more resistant to agents of corrosion. It could also be due to the different surface area of the bracelet fragments when compared with the beads and the toggles.

In several examples, the bracelet fragments contained higher concentrations of soda than other glass objects in this assemblage. Bracelet fragments E79.1034, E79.1927 and E79.133 in particular had relatively high soda levels compared to the other glass objects, containing 11.82%, 11.94% and 9.22% soda (Na_2O) respectively, along with low amounts of potash. Of the remaining eight fragments, six contained soda concentrations of between 1.95% and 5.73% and two contained no detectable amount of soda. Potash (K_2O) concentrations ranged from 0.675% to 1.086% for all 11 samples. It seems to be the case that the glass artefacts in these contexts were losing

the potash in their surface layers, while soda was surviving to a greater extent, at least in these bracelet fragments. As already discussed, corrosion occurs as preferential leaching of alkali ions to be replace by hydrogen ions, and potash based glasses are more susceptible to this than soda-lime based ones (Wayne Smith 2003, 94).

Six of the bracelet fragments were blue in colour (E79.451, E79.625, E79.377, E79.427, E79.2869 and E79.2303). These six fragments contained traces of cobalt oxide (Co_3O_4), ranging from 0.035% to 0.0883%, while none of the other bracelet fragments contained detectable levels. This would account for their colour as cobalt is known to impart a strong blue hue to glass. They also contained varying amounts of copper oxide (CuO) additives, between 0.024% and 0.0713%, which may have further enhanced their blue hue. The other elements they contained, such as soda, silica, potash, lead oxide (PbO) and calcium oxide (CaO), had concentrations comparable to each other, which would suggest they had a similar production method.

Find No. E79.1333 was the only example of a colourless glass bracelet fragment. Find No. E79.1927 was found to have a similar elemental composition to it, however it had almost double the amount of iron oxide (Fe_2O_3) that the former does and this manifests as a slight green tinge in the glass (see Plate 2). Both samples have relatively high levels of soda, 9.22% and 11.94% respectively, alongside a lack of many trace elements found in the other glass bracelet fragments, such as sulphur (SO_3), cobalt oxide, tin oxide (SnO_2), lead oxide and copper oxide. Manganese oxide (MnO) was found in both, as with all the other glass samples, but, at 1.715%, the concentration was particularly high in find No. E79.1927. As mentioned already, manganese was sometimes used as a decolourant and this was likely an attempt to counteract the green colour caused by the iron oxide, an attempt that was not entirely successful.

Find No. E79.1034 was a purple bracelet fragment. Like the purple bead discussed in Section 4.2.3, this bracelet also contained manganese oxide (MnO), however it was considerably less with only 1.28% as opposed to the 2.24% found in the purple bead, find No. E79.2209. It was also one of the best preserved artefacts within this

assemblage from an elemental point of view, containing a relatively high level of soda, 11.82% and an aluminium oxide concentration of only 2.67%, showing that the surface layers had not been corroded to as great an extent as some of the other glass in the assemblage. Visually, it did not appear better preserved than any of the other bracelet fragments, none of which showed any signs of corrosion.

The final two bracelet fragments; find Nos. E79.2274 and E79.1020, are listed as amber coloured (Johnston 2007, 120), although they appeared a very dark colour with almost a greenish tinge prior to analysis (see E79.1020 in Plate 3). While having a similar appearance to each other, some clear differences in their elemental composition became apparent. Find No. E79.1020 contained 5.73% soda while the analysis of find No. E79.2274 detected no traces of soda whatsoever. With regards to trace elements, they appear more consistent with each other. Both contain low levels of iron oxide and manganese oxide compared to the other bracelet fragments. They also lack any obvious colouring agent, suggesting the elements they do contain may have reacted with elements such as carbon in the furnace environment to produce their dark colour. As XRF cannot detect elements lighter than sodium, carbon would not be detected.

4.2.3 Toggles

A total of eight toggles, which can be seen in Plate 3, were analysed. Six of these contained silica (SiO_2) concentrations of between 64.79% and 75.78%. The remaining two, find Nos. E79.1616 and E79.1674, contained concentrations of 50.19% and 43.87% respectively. A graph showing the silica and aluminium content for these samples also showed a high correlation between the two, much like the beads (Figure 3). In fact, with an r^2 value of 0.9265, the toggles exhibit the strongest correlation of any of the four groups of glass in this assemblage.

It can be seen from analysing the results that four of the eight toggles showed no detectable amounts of soda (Na_2O). Three of the remaining four had levels of 2.08%, 2.31% and 3.34%. Toggle E79.2755 was the anomaly here, containing 9.51% soda and

0.591% potash, which would suggest it was a soda-lime silica glass. The levels of potash (K_2O) in the other seven toggles varied from 0.383% to 1.68%, a range comparable with the results from both the glass beads and bracelets discussed so far. The low levels of both soda and potash make it impossible to suggest whether they were soda-based, potash-based or a mixture of the two.

Johnston 2007, (115-116) has noted that, with the exception of a red example (E79.50), all the glass toggles had colours typical of Iron Age glass: blue, amber and green. The red example was made even more interesting by the fact that it was a toggle. While opaque red beads are common Germanic types and are found in Anglo-Saxon graves, red glass is very rare in Ireland particularly for this period (Laing 1975, 337). There was a block of red enamel reputedly found at the Hill of Tara, however whether the artefact was truly discovered there is widely disputed. When analysed, the undated and unprovenanced red ingot was found to be comprised of a typical soda-lime-silica glass with 27% lead oxide (PbO) and 9% copper oxide (CuO) added to it (Stapleton *et al*. 1999, 913-915). By comparison, the red toggle from Dun Ailinne has a much lower concentration of lead oxide and copper oxide with 5.16% and 1.5% respectively. It must be borne in mind that the surface of the red toggle from Dun Ailinne has most definitely undergone corrosion and as such the results were not entirely representative of its original composition. This can be seen in the elevated level of aluminium oxide (Al_2O_3), 22.73% and slightly decreased level of silica, 64.79%. There was also a low level of potash, 1.1% and no soda detected, indicating that much of the modifier has been leached away. The red toggle was also the only toggle to contain tin oxide (SnO_2), which may have caused its opaqueness. The copper oxide which was detected from this toggle is somewhat similar to results obtained from red glass beads from north-eastern Scotland. Here it was found that opaque red glass was achieved with 6.1% copper oxide (CuO), 1.5% antimony (SbO) and 31% lead oxide (PbO) (Bertini *et al*. 2011, 2763, 2765). While the levels of such elements were much lower in the red toggle from Dun Ailinne, this may be due to corrosion on the surface which is apparent from the discoloured layer it possesses. It was known that coloured Roman glass was being traded in the form of blocks or slabs and then reworked in areas of Scotland which may provide an explanation as

to the source of these unusual red beads, such as the opaque glass rod found in Culduthel which was reworked locally (Bertini *et al*. 2011, 2765). It is possible that similar secondary reworking of imported glass slabs was going on in Ireland through trade links with the Roman world or elsewhere.

With regards the other toggles, the blue were coloured with cobalt oxide (Co_3O_4), much like most of the other blue glass samples. Find No. E79.1247, a deep green colour, had a high iron oxide (Fe_2O_3) content at 4.55%, which was responsible for its dark colour. A light greenish toggle, E79.52, had a much lower concentration of iron oxide, 0.597%, which imparted a much lighter tinge of green than that of E79.1247.

4.2.4 Miscellaneous fragments

Johnston notes four unidentified glass fragments of varying shades of blue (Johnston 2007, 116) and these samples were also analysed. Three of the four samples were small sherds and the fourth was a thin rod fragment. The silica levels were found to be between 58.31% and 71.35%. The aluminium (Al_2O_3) and silica (SiO_2) contents were also graphed for these samples and found to show some correlation, although with an r^2 value of 0.5037, this was nowhere near as close as what was found in both the beads and the toggles. However, with such a small sample size in this group, definitive conclusions should not be drawn from this. With the exception of E79.2075, the thin glass rod, the remaining three had detectable levels of soda (Na_2O) remaining. Fragment E79.2325 in particular had a relatively high soda concentration, with 8.82% and was most likely a soda-lime silica glass. The low amount of modifier found in E79.2075 was matched by the lowest levels of cobalt oxide (Co_3O_4) and copper oxide (CuO) out of the four samples. These results, coupled with a higher level of aluminium, 28.75%, would indicate a higher level of corrosion in this sample. All four were found to contain traces of both cobalt oxide, between 0.0291% and 0.077% and copper oxide, between 0.0236% and 0.071%, both of which could be responsible for the blue hues they exhibit. Find Nos. E79.1829 and E79.2325 had

slightly lighter shades of blue than samples E79.663 and E79.2075, corresponding with their lower levels of cobalt.

Conclusion

XRF analysis suggests that these glass samples were a mixture of potash-based, mixed alkali-based and soda-lime-based glasses which have undergone varying degrees of corrosion during their time exposed to groundwater. This has caused alkalis such as potash and soda in the surface to leach away, leaving a disproportionate amount of heavier elements such as aluminium behind. Some of the samples were in surprisingly good condition, with much of what would have been their original composition still intact. The results obtained from the elemental analysis of these beads when compared to their physical appearance, does highlight the corrosion which they were subjected to over the years. Even in cases where corrosion is not physically evident, it may still have occurred to a great extent. Unfortunately it is impossible to know what the original composition of these beads would have been without utilising more destructive methods in order to expose non-corroded layers deeper in the samples. The results would suggest that overall the bracelet fragments survived the best out of the four groups of glass which make up this assemblage. This may have been due to their surface area to volume ratio or possibly as a result of dating to a later time than the other material.

Many of the Dun Ailinne beads show a great uniformity in the types of trace elements they contain. For example, the vast majority of the blue glass beads show levels of cobalt when subjected to elemental analysis. This emphasises the similar production method and therefore most likely similar origin for many of these beads. Likewise, some anomalies amongst the assemblage are also highlighted. Only one blue example and the single blue-green example contain no cobalt, instead being coloured with copper. In addition, the inclusion of a highly unusual red opaque toggle poses more questions as to the ability that existed to source such rare and most likely greatly prized personal objects.

The discussion in this report is only a preliminary interpretation of the results obtained. The results so far are already suggesting strong differences in composition based on the different artefact types, so more work will be undertaken to further analysis the data by phase and artefact type. It is hoped that this will reveal further trends within the assemblage relating to the phases in which they were found. These results will then be compared to Johnston's analysis (2007) of the Dun Ailinne glass with the hope of addressing some of the issues that she raises.

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Plate 1: Glass beads (Clockwise from top; E79.17, E79.111, E79.115, E79.158, E79.449 and E79.2209)

Plate 2: Glass bracelet fragments (Clockwise from top; E79.427, E79.451, E79.1020, E79.1927, E79.1333 and E79.1034)

Plate 3: Glass toggles (Clockwise from top; E79.50, E79.52, E79.840, E79.1093, E79.1616, E79.2755, E79.1674 and E79.1247)

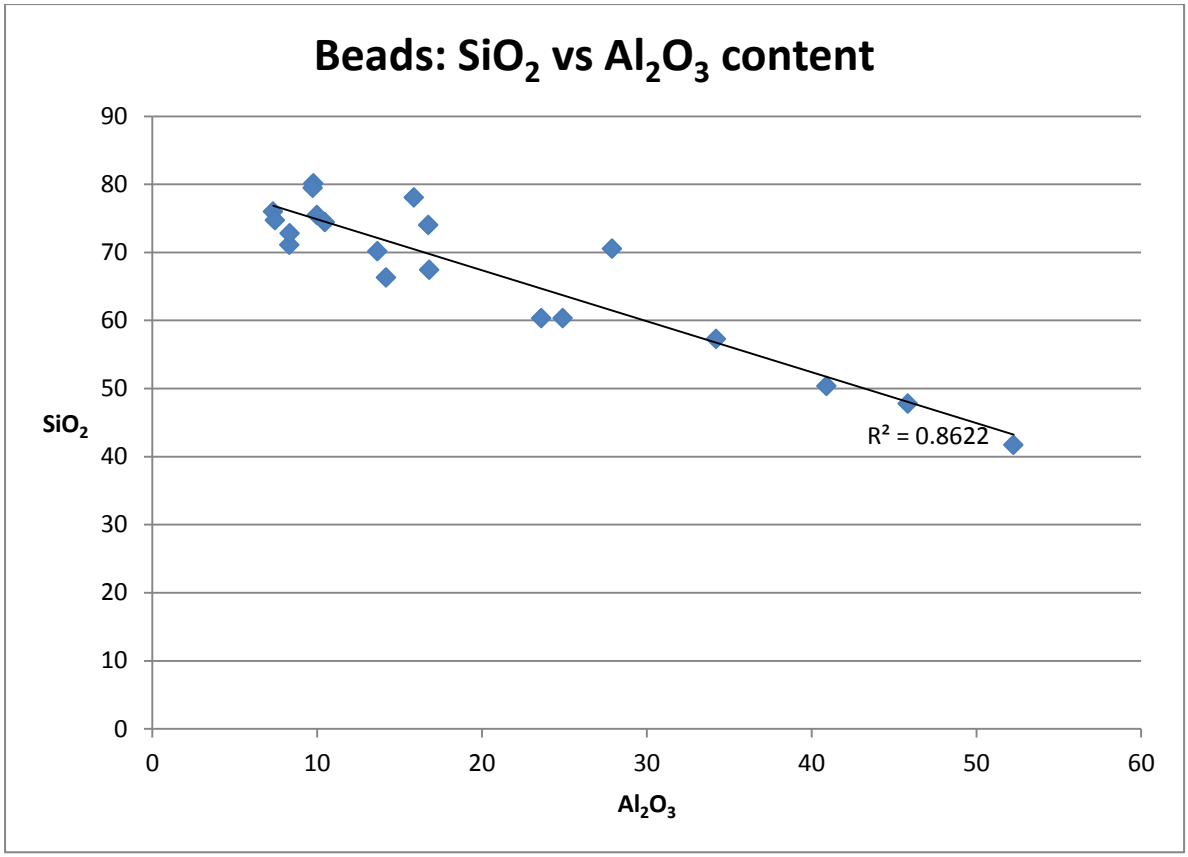

Figure 1: SiO_2 vs Al_2O_3 content in beads

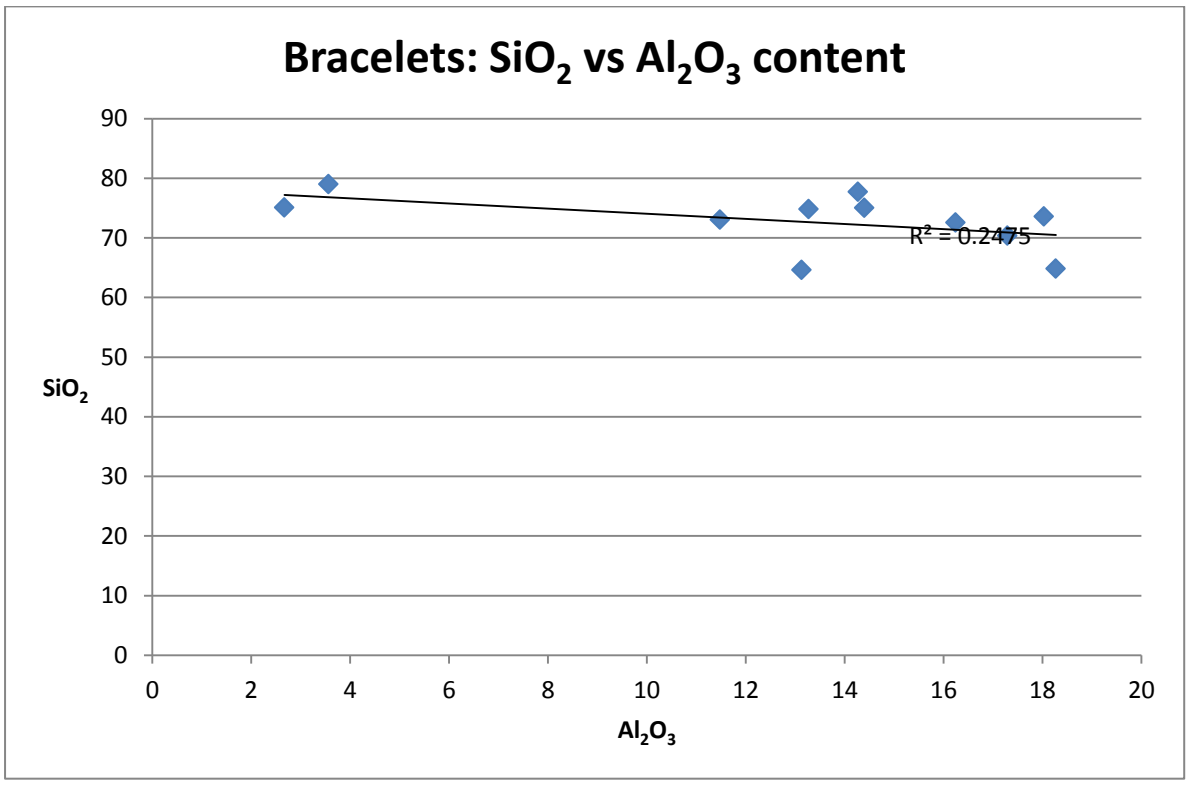

Figure 2: SiO_2 vs Al_2O_3 content in bracelet fragments

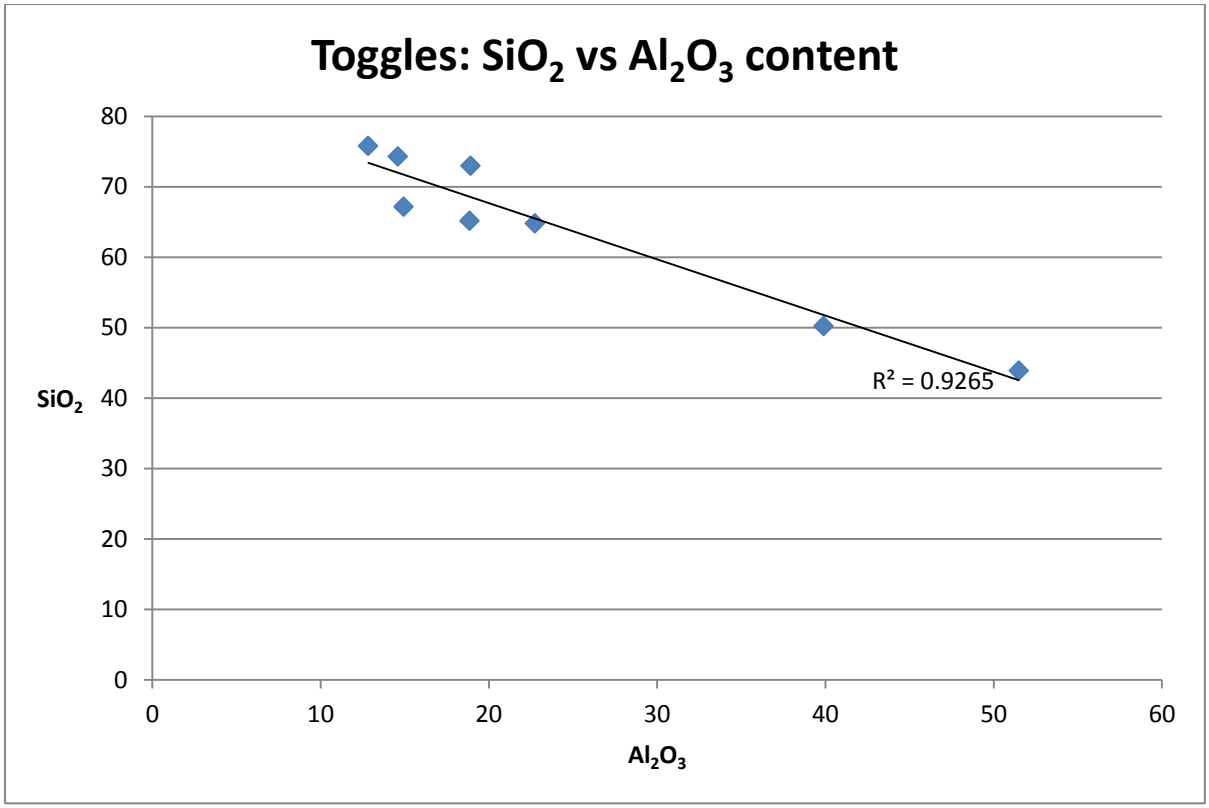

Figure 3: SiO_2 vs Al_2O_3 content in toggles

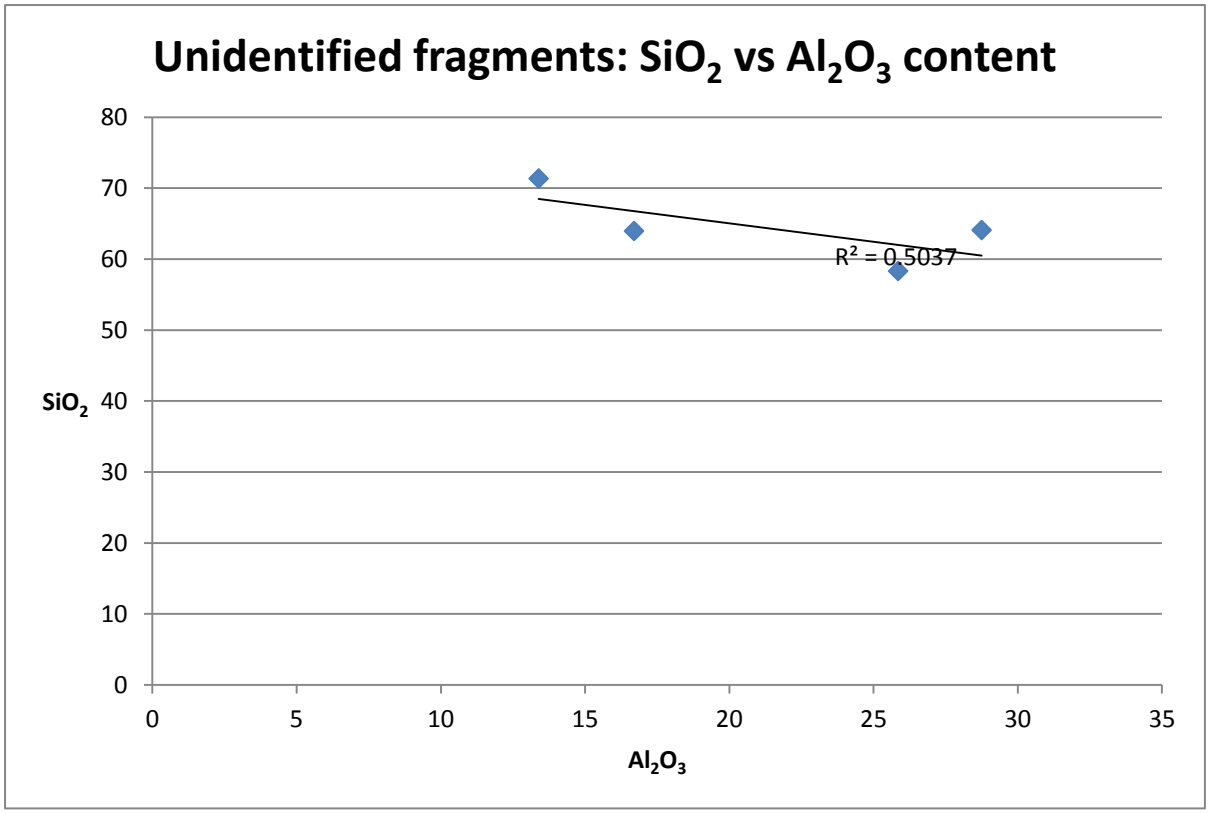

Figure 4: SiO_2 vs Al_2O_3 content in unidentified fragments

Appendix 1: Glass results (Results given in percentage w/w) (nd = not detected)

Beads										
Sample No.	E79.17	E79.71	E79.111	E79.115	E79.134	E79.136	E79.158	E79.225	E79.242	E79.428
Description:	*Blue bead with decoration*	*Blue bead*	*Flat ring amber bead*	*Greenish blue bead*	*Blue bead*	*Half a blue bead*	*Half a colour-less bead*	*Half a bluish grey bead*	*Blue bead*	*Blue bead*
Al_2O_3	16.81	45.85	9.77	24.91	16.75	7.33	7.44	8.31	34.2	9.98
As_2O_3	nd	nd	nd	0.0061	nd	nd	nd	nd	nd	nd
BaO	0.0144	0.0075	0.01	0.0052	nd	0.0177	0.0229	0.0122	0.0062	0.02
CaO	4.16	3.37	6.36	4.74	6.01	6.31	3.72	4.985	4.74	7.11
Cl	0.724	0.378	0.965	0.532	0.767	0.655	0.727	0.67	0.315	0.51
Co_3O_4	0.0499	0.0156	nd	nd	0.0363	0.0741	0.115	0.034	0.027	0.0453
CuO	0.0425	0.0433	nd	0.644	0.074	0.0389	nd	1.78	0.0202	0.129
Fe_2O_3	1.11	0.669	0.537	0.35	0.59	1.43	10.14	2.87	0.86	0.81
K_2O	3.04	0.52	1.08	0.496	0.44	1.18	0.617	1.01	0.601	1.61
MnO	0.535	0.244	0.0243	0.0079	0.0066	1.29	0.848	0.061	0.152	0.076
Na_2O	4.93	nd	1.43	5.42	nd	3.03	1.28	6.97	1.65	3.72
OsO_4	0.071	nd	nd	0.17	0.102	0.0161	nd	0.256	nd	0.031
PbO	0.398	0.0058	nd	1.45	0.621	0.0859	nd	1.7	nd	0.301
Sb_2O_3	0.01	0.0224	nd	nd	0.457	nd	0.202	0.022	0.057	nd
SiO_2	67.45	47.79	80.13	60.35	74	75.99	74.74	71.12	57.28	75.45
SnO2	0.472	nd	nd	0.0149	0.008	0.04	nd	0.0555	nd	0.0661
SO_3	nd	nd	nd	0.77	nd	2.08	nd	nd	nd	nd
SrO	0.0411	0.0262	0.0562	0.02	0.025	0.0603	0.0427	0.0456	0.0304	0.0534
TiO_2	0.136	1.02	0.113	0.119	0.0663	0.373	0.0843	0.118	0.0389	0.0689
V_2O_5	nd	nd	nd	nd	nd	nd	nd	nd	0.0096	nd
ZnO	0.0108	0.0196	nd	0.0057	0.0173	0.0152	0.0063	nd	nd	nd
ZrO_2	nd	nd	0.0072	nd	0.016	0.0063	0.0086	0.0052	nd	0.0086

Appendix C: Dún Ailinne, Co. Kildare

Beads										
Sample No.	E79.449	E79.723	E79.907	E79.1002	E79.1603	E79.2101	E79.2209	E79.2910	E79.3301	E79.3326
Description:	*Green bead with white decoration*	*Amber glass bead*	*Blue bead*	*Blue and white bead*	*Blue bead*	*Blue ring bead*	*Purple damaged bead (heat?)*	*Half a blue bead*	*Blue bead*	*Blue bead*
Al_2O_3	8.34	15.88	23.6	40.91	52.26	10.48	9.73	14.19	13.66	27.9
As_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BaO	nd	0.0076	0.014	0.093	nd	0.0111	0.0367	0.0206	0.0131	0.0132
CaO	6.64	3.39	4.07	4.00	3.03	6.32	6.05	5.66	6.99	4.49
Cl	0.687	0.459	0.472	0.368	0.485	0.829	0.626	0.833	0.641	0.537
Co_3O_4	nd	nd	0.0583	0.0201	nd	0.042	nd	0.0424	0.0847	0.0408
CuO	nd	nd	0.0651	0.0147	1.39	0.0586	0.0053	0.0286	0.0243	0.0759
Fe_2O_3	1.53	0.197	5.00	2.428	0.419	0.916	0.477	1.53	0.083	0.584
K_2O	1.88	1.85	0.784	0.525	0.179	0.842	1.089	0.611	0.709	0.43
MnO	1.38	0.041	0.186	0.388	0.0198	1.22	2.24	1.18	0.557	0.603
Na_2O	3	nd	4.39	nd	nd	4.62	nd	8.86	4.71	nd
OsO_4	0.27	nd	0.117	0.2203	0.0358	0.0166	nd	nd	0.0055	nd
PbO	1.41	nd	0.843	0.321	0.305	0.102	nd	0.304	0.296	0.024
Sb_2O_3	0.156	nd	nd	0.0079	nd	nd	nd	nd	nd	nd
SiO_2	72.81	78.08	60.31	50.35	41.68	74.42	79.47	66.31	70.18	70.555
SnO2	0.573	nd	0.0066	0.347	0.0924	0.0148	nd	0.286	1	nd
SO_3	1.05	nd	nd	nd	nd	nd	nd	nd	nd	4.81
SrO	0.071	0.0358	0.0312	0.0298	0.0171	0.0481	0.179	0.0481	0.0444	0.0438
TiO_2	0.107	0.0333	0.0356	0.0425	0.0649	0.0549	0.061	0.0518	0.119	0.16
V_2O_5	nd	nd	nd	nd	nd	0.0065	nd	nd	nd	0.0078
ZnO	nd	nd	0.0086	0.0071	0.0108	0.0074	nd	nd	0.0063	0.0144
ZrO_2	nd	nd	nd	nd	nd	nd	0.0133	nd	nd	nd

Toggles								
Sample No.	E79.50	E79.52	E79.840	E79.1093	E79.1247	E79.1616	E79.1674	E79.2755
Description:	*Opaque red toggle*	*Green translucent toggle*	*Opaque blue toggle*	*Elongated orange toggle*	*Green toggle*	*Clear glass toggle*	*Blue glass toggle*	*Opaque blue toggle*
Al_2O_3	22.73	18.91	12.83	14.6	18.85	39.89	51.49	14.93
As_2O_3	0.0099	nd	nd	nd	nd	nd	nd	nd
BaO	nd	0.0085	0.0114	0.0058	0.014	0.0067	nd	nd
CaO	1.77	4.97	6.32	5.78	5.29	3.72	2.9	5.94
Cl	0.549	0.597	0.516	0.581	0.501	0.439	0.324	0.43
Co_3O_4	nd	nd	0.0437	nd	0.0245	nd	0.0229	0.0277
CuO	1.5	nd	0.0798	nd	0.0068	nd	0.051	0.0315
Fe_2O_3	1.09	0.391	1.36	0.318	4.55	0.33	0.0431	0.419
K_2O	1.1	1.68	0.649	0.465	0.647	0.674	0.383	0.591
MnO	0.0837	0.346	0.249	0.0647	0.122	0.24	0.419	0.625
Na_2O	nd	nd	2.08	2.31	3.34	nd	nd	9.51
OsO_4	0.494	nd	nd	nd	0.0058	nd	nd	0.0285
PbO	5.16	0.0051	0.0058	nd	0.0094	nd	0.014	0.202
Sb_2O_3	0.26	nd	nd	nd	nd	nd	nd	0.0192
SiO_2	64.79	72.96	75.78	74.3	65.13	50.19	43.87	67.127
SnO2	0.0629	nd	nd	nd	nd	nd	nd	nd
SO_3	nd	nd	nd	1.48	nd	4.31	nd	nd
SrO	nd	0.0481	0.0353	0.0341	0.0431	0.0312	0.0248	0.0355
TiO_2	0.366	0.0628	0.0278	0.0416	0.0358	0.0407	0.0347	0.0426
V_2O_5	0.0153	nd	nd	nd	nd	nd	nd	nd
ZnO	nd	0.0064	0.0197	0.0076	nd	0.012	0.017	nd
ZrO_2	nd	nd	nd	nd	nd	nd	nd	nd

Appendix C: Dún Ailinne, Co. Kildare

Bracelet fragments											
Sample No.	E79.377	E79.427	E79.451	E79.625	E79.1020	E79.1034	E79.1333	E79.1927	E79.2274	E79.2303	E79.2869
Description:	*Blue bracelet fragment*	*Blue bracelet fragment*	*Blue bracelet fragment*	*Blue bracelet fragment*	*Bracelet fragment*	*Bracelet fragment*	*Clear bracelet fragment*	*Clear bracelet fragment*	*Bracelet fragment*	*Blue bracelet fragment*	*Blue bracelet fragment*
Al_2O_3	18.27	16.24	14.4	18.03	17.29	2.67	3.56	13.13	14.27	11.48	13.27
As_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BaO	0.0112	0.0099	0.0111	0.0109	0.0066	0.0103	0.0096	0.0125	0.0189	0.0141	0.0102
CaO	3.98	5.62	5.15	4.85	4.73	6.96	5.64	6.33	4.97	6.78	5.65
Cl	0.291	0.459	0.682	0.597	0.7155	0.94	0.795	0.06935	0.736	0.658	0.473
Co_3O_4	0.061	0.035	0.0449	0.0513	nd	nd	nd	nd	nd	0.0822	0.0883
CuO	0.0249	0.0407	0.024	0.0264	nd	nd	nd	nd	nd	0.0531	0.0713
Fe_2O_3	7.03	0.824	0.447	0.637	0.24	0.368	0.266	0.446	0.44	1.27	1.4
K_2O	0.795	1.01	0.814	0.702	0.7405	0.675	0.738	1.005	1.086	0.874	0.72
MnO	0.99	0.57	0.842	0.601	0.1055	1.28	0.541	1.715	0.163	1.64	1.18
Na_2O	2.11	2.39	2.36	nd	5.73	11.82	9.22	11.94	nd	3.76	1.95
OsO_4	0.0072	0.0066	nd	0.0082	nd	nd	nd	nd	nd	0.0238	0.0299
PbO	0.0477	0.0741	0.059	0.07	0.0071	0.0263	nd	nd	0.0064	0.151	0.22
Sb_2O_3	nd	nd	nd	nd	nd	nd	0.153	0.0052	nd	nd	0.021
SiO_2	64.82	72.54	75.03	73.59	70.34	75.06	78.98	64.595	77.72	73.03	74.8
SnO2	0.0145	0.021	0.026	0.0335	nd	nd	nd	nd	nd	0.0185	0.0208
SO_3	1.43	nd	nd	nd	nd	0.201	nd	nd	nd	nd	0.0406
SrO	0.0428	0.0365	0.0394	0.0352	0.0334	0.0497	0.0428	0.055	0.0449	0.057	nd
TiO_2	0.0518	0.0964	0.047	0.0297	0.0441	0.0478	0.0369	0.0625	0.0613	0.0879	0.0512
V_2O_5	nd	0.0065	nd	nd	nd	nd	nd	nd	nd	nd	nd
ZnO	0.009	0.0117	0.01	nd	nd	nd	nd	nd	nd	0.0076	0.0157
ZrO_2	nd	nd	nd	nd	nd	nd	nd	0.0057	nd	nd	nd

Unidentified fragments				
Sample No.	E79.663	E79.1829	E79.2075	E79.2325
Description:	*Blue glass fragment*	*Blue glass sherd*	*Thin blue rod*	*Blue glass sherd*
Al_2O_3	13.39	16.7	28.75	25.86
As_2O_3	nd	nd	nd	nd
BaO	nd	nd	nd	0.0063
CaO	6.87	6.57	4.11	4.85
Cl	0.826	0.722	0.46	0.52
Co_3O_4	0.077	0.0314	0.06	0.0291
CuO	0.0327	0.071	0.0509	0.0236
Fe_2O_3	1.17	0.081	0.956	0.55
K_2O	0.958	0.548	0.377	0.418
MnO	0.87	0.855	0.89	0.359
Na_2O	3.51	3.18	nd	8.82
OsO_4	0.047	nd	0.014	0.0147
PbO	0.309	0.0467	0.168	0.097
Sb_2O_3	nd	nd	0.0066	0.0086
SiO_2	71.35	63.96	64.08	58.31
SnO2	0.189	0.0152	0.0079	0.0342
SO_3	nd	6.37	nd	nd
SrO	0.0557	0.0511	0.0257	0.0289
TiO_2	0.12	0.0425	0.0297	0.0312
V_2O_5	nd	nd	nd	nd
ZnO	nd	nd	0.0102	nd
ZrO_2	nd	nd	nd	nd

Appendix D: Analysis of glass from Glencurran Cave, The Burren, Co. Clare, excavation number 04E0432

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Appendix D: Glencurran Cave, Co. Clare

1. Introduction

This report details the analysis of a number of Viking glass beads which were uncovered during the excavations at Glencurran Cave, Co. Clare. The multi-elemental analysis was carried out using X-ray Fluorescence at I.T. Sligo. The aim of this was to determine trace elements within the glass beads which could potentially answer questions about their origin or production. The samples included a range of Viking glass beads of varying types and colour.

2. Methodology

2.1. Sample collection and selection

Viking glass beads from the Glencurran Cave excavations of various colours were provided by Dr. Marion Dowd for the purpose of this study. A number of samples had to be excluded from the analysis due to their highly fragile nature. These had heavy iridescent surface layers which were beginning to flake away from the glass, were fragmented or were otherwise considered too delicate to be handled for the purpose of this analysis. In total, 38 beads were analysed using XRF analysis. A table detailing the samples which underwent analysis as well as a brief description can be seen in Appendix 1. The numbering system of the samples refers to the context then find No.. All of the samples were uncovered generally within a 3m x 2m section in the same area of the cave; Area IV (Dowd 2009, 97).

2.2. Calibration/Quality Control

The XRF was calibrated monthly using the standard procedure for this instrument. The accuracy of the instrument is also tested regularly using standard glass reference material. Table 1 illustrates the accuracy and precision of the instrument using a standard sample. The sample was run 5 times and an average taken of the results.

	Stated concentration (%w/w)	**Average obtained (%w/w)**	**Relative Standard Deviation%**	**%Error**
SiO_2	72.26	72.62	0.360	0.503
Na_2O	13.78	12.88	1.399	-6.516
CaO	10.05	10.71	0.598	7.000
MgO	3.40	3.64	2.423	-0.0549
SO_3	0.270	0.027	9.658	-90.074
TiO_2	0.033	0.0237	7.413	-28.121
Fe_2O_3	0.021	0.0177	4.058	-15.619

Table 1: Reference sample results obtained

2.3. Sample washing and preparation

No washing or other preparation was carried out on these samples prior to their analysis in the XRF. It is desirable to gently clean the surface of archaeological samples using a 1:1 ratio solution of deionised water and 99% ethanol solution prior to elemental analysis to remove surface contamination on the glass. However, due to the highly delicate nature of these samples, it was considered safer to analysis them as they were.

2.4. Testing of samples

Each sample was run through the XRF in triplicate and the results averaged. Samples were analysed in the condition they were received with no preparation. XRF was chosen for this analysis as it provides a highly sensitive, multi-elemental analysis and is completely non-destructive. XRF is a surface technique, therefore the elemental composition it gives is indicative of the surface layers only and this may not be an accurate representation of the whole sample. It does, however, highlight the amount of leaching and corrosion which the samples have been subjected to.

3. Results

The results of the analysis (given in percentage w/w) along with a brief description of the samples can be seen in Appendix 1. It shows the results from 38 glass beads that were obtained during this study.

4. Discussion

4.1 Condition of samples

The majority of the Viking beads were in a corroded state. Several were considered too fragile for the purpose of the analysis. The majority of the beads also exhibited an iridescent sheen to varying extents. This is most likely due to corrosion caused by exposure to water in the soil. The iridescent patination forms on the glass surface before eventually flaking off.

4.2 Elemental Composition

4.2.1 Major elements

Since glass was first produced in antiquity, it has been consistently made up of a glass former, such as sand or quartz pebbles (SiO_2), a modifier, such as soda (Na_2O) or potash (K_2O), and a stabilizer such as lime ($CaCO_3$). In addition, glass may contain a variety of colouring agents or opacifiers, added either intentionally or unintentionally (Goffer 2007, 124). The main component of the glasses analysed from the majority of the Glencurran beads is silica (SiO_2), as would be expected. It accounts for between 44.77% and 77.58% for most of the samples analysed. The only two exceptions are 23:045 and 23:047 which demonstrated very low silica content; 19.91% and 3.69% respectively. These two beads also show a very high level of alumina which suggests high level of corrosion within their surface layers. They most likely had silica levels comparable to the other beads when they were first produced. Something that is readily apparent in the results from the Glencurran

beads is the low proportion of soda (Na_2O) and potash (K_2O) detected in the analysis for many of the fragments. The composition of ancient glass is typically around 73% silica, 23% soda/potash and around 5% lime (Gratuze and Janssens 2004, 665). The majority of the Glencurran glass contains no sodium and only very low levels of potash (ranging from 0.016% and 2.82%). Only samples 11:049 and 18:180 contain soda; 4.06% and 2.98% respectively. They also both contain potash but only in tiny amounts (0.279% and 0.401%). The low levels detected in these beads are due to their corroded nature. Ground water can interact with buried glass material affecting the stability of the object. Signs that a glass fragment may have been affected by this include a flaky coating and iridescence on the surface of the object (Pollard and Heron 2008, 178). This is due to the soda or potash in the glass leaching out and leaving only porous, hydrated silica behind.

Glass corrosion is a complex process, affected by many different factors and it is not perfectly understood. In some cases, there may be no obvious signs on the glass that it has been subject to any decay. However it is thought that it occurs due to the preferential leaching of alkali ions to be replaced by hydrogen ions (Wayne Smith 2003, 94). The reaction begins at the surface of the object and spreads inwards (Varshneya 1994, 398). Cox and Ford (1993, 5639-43) conducted a detailed elemental study of multiple layers of medieval glass and concluded that corroded surface layers can be depleted of most oxides except silica (Si), aluminium (Al) and iron (Fe), and what is left behind is poorly crystalline hydrated silicates and aluminosilicates with varying amounts of calcium, phosphate and manganiferous minerals. The results obtained from the Glencurran glass highlight the level of corrosion that they have suffered. The low percentage of alkali metals such as sodium and potassium found in many of the samples, coupled with unusually high levels of aluminium oxide (Al_2O_3), would suggest that the surface layers have lost some of their original composition. Typical Roman natron glasses contain between 1.7% and 3.5% alumina depending on the source of sand. Even high alumina glasses which occur mainly in India, Africa and the Far East only contain alumina levels of up to 12% (Henderson 2013, 65). As can be seen from the results, the surface layers of the Glencurran beads contain considerably more than this in most cases. Samples 23:045 and 23:147 are the

most extreme examples, consisting almost entirely of alumina (78.37% and 92.97% respectively).

As mentioned already, the level of soda (Na_2O) or potash (K_2O) in the surface layers of the Glencurran samples is much lower than it would have originally been due to corrosion. However, while all of the beads seem to have traces of potash, only a small proportion show traces of soda (11:049 and 18:180 are the only examples). This would indicate that the beads were either based on potash or mixed alkali based. Soda, potash or a mixture of the two was an essential component when producing glass in ancient times. It acted as a flux, lowering the melting point of silica from 1700ºC to 1000ºC, a temperature which was obtainable in ancient furnaces (Goffer 2007, 115). Potash would have been sourced from wood ash as opposed to soda alkali sources which were generally retrieved from marine plants. Potash glass became increasingly popular during the medieval period when demand for glass was growing and there was an incentive to search for a more readily accessible alkali source (Moran 2010, 17).

While the majority of the Glencurran beads seem to be potash-based glass, with no soda detected during the XRF analysis, it is possible that they originally contained some soda which was leached away. The corroded nature of some of the glass would support the idea that the glass was mainly potash however, as potash has an increased susceptibility to corrosion and decay due to its high alkalinity (Moran 2010, 17). In the case of the two beads which had both potash and soda, it is impossible to determine which, if not both, were added as a flux. A mix of potash and soda could have been added intentionally. It could also have been accidental. For example, potash sources may occasionally contain traces of soda. It is also possible that cullet (broken pieces of glass) may have been used when producing the glass, and this would further complicate the elemental composition of the mixture. The degraded nature of the surface of these glass fragments is unfortunate as it makes it difficult to determine what their original composition could have been. Nevertheless, the analysis reveals information about the nature of the glass, the raw materials used to produce it and how it has survived in its burial context.

4.2.2 Other elements

Manganese (MnO) is another element which is present in many of the glass fragments. Used on its own without the presence of iron, manganese gives a violet tinge to the glass, but when included in glass production in the presence of iron, it masks the green colour caused by the iron, giving the glass a grey/clear colour (Goffer 2007, 121). While this element is sometimes used as a decolourant, in this case it was quite possible that it was added unintentionally as part of the potash that was sourced, as it is known to occur in trace amounts when sourcing potash from burnt wood (Wilson 1855, 261). Trace amounts of arsenic (As) were found in two beads; 11:049 and 23:189. Arsenic provides a milky white opaque appearance when added in quantity to glass (Bray 2001, 177). However as 11:049 is a blue translucent bead and 23:189 is not particularly white compared to other similar beads, the arsenic in these samples was probably added unintentionally as a trace contaminant.

4.2.3 Segmented beads

The largest group of beads in this study was the segmented type, which made up 15 out of the 38 examples analysed. Twelve of these contained traces of silver (Ag_2O). These 12 beads were the only examples which contained silver; no beads of any other shape showed any trace of this element. However, not all segmented beads which were analysed contained silver. Three segmented beads (23:042, 23:147 and 52:22) contained none. Silver when used in the production of glass is known to add a yellow colour (Goffer 2007, 122). In this case, as many of the Glencurran beads which contain silver do not exhibit any yellow hue, it is possible it was not added for this purpose. While they all appear to be a similar creamy-white opaque colour, they contain slightly different hues when examined closely, including white, blue and brown shades. Examples of the different hues can be seen in Plate 1. Examples of opaque yellow segmented beads uncovered from a Viking burial at Kneep on the Isle of Lewis in Scotland (Welander *et al*. 1987, 164) were also found to contain traces of silver when analysed with XRF. However, in this case the vivid yellow colour was

thought to have been caused by salts of tin and lead contained in the glass (Welander *et al*. 1987, 164). It is possible that the degradation of the Glencurran beads has affected the original colour of these silver-containing beads and that they may have all had a yellow hue at some point. It is also possible that silver was added for a reason unrelated to colour or appearance. Perhaps it was simply as a sign of wealth or considered important in the production of these high status items.

With regards the Glencurran assemblage, tin oxide (SnO_2) is present in many of the glass beads, and it was most likely used as an opacifier. The three segmented beads with the slight yellow hues; 18:106, 23:042 and 23:146, also contain three of the highest levels of tin found in the segmented examples with 0.0352%, 0.0166% and 0.0324% respectively. Quantities of tin were used in ancient glass to provide an opaque white colour. Usually another substance, such as lead antimonate, would have to be added to achieve a yellow colour (Henderson 2000, 74). No lead is apparent in the majority of the segmented beads from Glencurran, yet three of the four beads with the highest tin concentration still show slight yellow colouring. Since there is no other apparent difference between these beads and the others, it is possible that the tin is responsible for the yellow hue. The one exception to this is bead number 23:147 which despite containing 0.0376% tin oxide has a blue hue. This is most likely due to the relatively high concentration of cobalt (Co_3O_4) which it contains; 0.0226%. Cobalt is a powerful colorant which was used in ancient glass, capable of imparting a bright blue hue to glass even in very small quantities.

One more notable aspect of the segmented beads is that none of them contain osmium (OsO_4), despite many of the other types of beads containing traces of it. Osmium is one of the rare metals and was not an intentional additive to ancient glass, instead being an accidental inclusion due to its presence in some of the raw materials. It is generally found either in natural alloys such as those containing nickel, platinum and copper or as an uncombined element, in which case it is generally found in igneous rock or soils with meteorite or comet residue (Emsley 2003, 199-200). It's absence from these segmented beads, whilst being present in 13 of

the other 24 analysed beads, and this would indicate the use of different raw materials.

When examining the results from the segmented beads, there does not immediately appear to be a pattern of elemental composition based on the number of segments in the beads, with beads containing 2, 3 and 4 segments all having a range of trace element concentrations. However by looking at the averaged results of the different types, some interesting trends emerge (Figure 1 and Appendix 2). It can be seen by examining this graph that the highest levels of SiO_2, CaO, K_2O and TiO_2 are found in the 4 segments beads, followed by the 3 segment and 2 segment beads respectively. The reverse is true for the concentrations of Fe_2O_3, Al_2O_3 and SO_3, with the highest to lowest concentrations being 2 segment, 3 segment and finally 4 segment beads. This would suggest that the beads have been corroded differently. The 2 segment beads in particular have an unusually high level of $Al2O_3$ and SO_3, at the expense of other elements and this suggests that the surface layers have been leached to a greater extent than the 3 and 4 segment beads. There are a number of reasons why this might be so. The 2 segment beads have a different surface area to volume ratio than the 3 or 4 segments beads and this may be a contributing factor to their faster corrosion. Burial environment can also impact corrosion rates, however since all the beads were found in close proximity to each other, and since original elemental composition is the main factor which determines how a glass object will corrode, these averages results would suggest that the different types of segment beads had different origins.

4.2.4 Oval and globular beads

Many oval and globular blown glass beads were also included in the assemblage. These samples varied quite widely in their elemental composition, containing differing types and concentrations of trace elements. Even beads which have a similar appearance can appear quite different when the elemental composition is analysed. For example, beads 19:300, 23:132 and 23:181 have a similar appearance

with regards colour and corrosion (see Plate 2). However, their elemental composition varies. None of the three contain copper and only one contains any amount of cobalt, despite having blue colouring on part of their surfaces. It is possible that their colour comes from ferrous additives to the glass mixture, as this can cause a blue colouring when subjected to a reduced environment in the furnace (Davidson 2008, 74). However their iron content varies considerably, from 0.424% to 1.06%. This, coupled with differences in other trace elements (such as 23:132 containing traces of cobalt and sulphur which is absent from the other two) would suggest that while a similar technique would have been followed to make them, slightly different types and quantities of raw materials were probably used. Bead number 23:130 is a considerably darker blue colour than other similar blown glass examples. It has a much higher concentration of iron (2.12%) than other similar samples which were analysed such as 19.300 which had an iron concention of 0.424%. As well as this, the bead contained considerable amounts of chromium (Cr_2O_3) and copper (CuO) with 0.0084% and 0.0482% respectively. This would seem to support the idea that the blue colour is caused by iron in at least some of these samples, as the higher proportion of iron in this bead is found alongside a darker shade of blue.

4.2.5 Flat annular beads

A number of flat annular beads were also analysed, ranging in colour from oqaque cream to some with a bluish tinge. Joanne O'Sullivan (forthcoming), states that these examples are similar in nature to blue translucent versions found at different Viking sites including Knowe of Moan, Scotland and Peel on the Isle of Man. She further reasons that the opaque cream colour could have been caused by calcification of the beads and that their original appearance may have been blue, similar to samples such as those mentioned above (O'Sullivan forthcoming). Examples of these beads can be seen in Plate 3. When subjected to elemental analysis, it was found that some of these beads, such as 23:037 and 23:047 contain amounts of cobalt (Co_3O_4) and copper (CuO), which may hint that they originally had a blue hue. The amount of

calcium found in their surface, as with all the beads, is very low however. This is not consistent with calcification, which would be expected to add layers of calcium (CaO) to the surface of the beads. The analysis instead shows up high levels of aluminium in the surface layers; these high percentages most likely caused by the leaching out of other major components. There are also significant levels of iron, which would also have been left behind if leaching had occurred.

4.2.6 Blue translucent beads

11:049, 18:180 and 19:134 are three examples of blue translucent glass beads. Although all three are blue and translucent, the colour varies between them, each having different hues of blue. They are all a rounded shape, but not identically shaped as can be seen in Plate 4. Their elemental composition confirms the different raw materials used to produce them. 11:049, a dark blue bead, shows levels of both cobalt (Co_3O_4) and copper (CuO), both of which could impart a blue colour to the glass. Cobalt in particular, as mentioned already, is a very powerful blue colorant. Neither of the other two contain any cobalt at all. Blue tones ranging from bluish green to a very pale blue could also be achieved by adding cupric oxide (CuO) (Bhardwaj 1979, 42-43). 18:180 in particular has a notable copper concentration with 1.09%. 19:134 has a much lower concentration of copper, and it is possible that the blue hue in this case is the result of ferrous iron (Fe^{2+}), which is iron added in a reducing environment in the glass furnace. This bead also has a greenish tint to the blue colour which is also achievable through the use of iron. The varying compositions of these three beads is quite interesting as it highlights the different methods that were used to create quite similar beads, suggesting that they probably came from different origins.

5. Conclusions

XRF analysis suggests that these beads are degraded potash-based or mixed alkali-based glass which has undergone corrosion during their time exposed to groundwater. This has caused alkalis such as potash and soda in the surface to leach away, leaving a disproportionate amount of heavier elements such as aluminium behind. It is surprising to note the low levels of calcium in the surface of the beads, given the calcium-rich environment that they were found in. Unfortunately it is impossible to know what the originally composition of these beads would have been without utilising more destructive methods in order to expose non-corroded layers deeper in the samples.

The Viking beads from Glencurran show a great variety in their composition. Even examples which can be loosely grouped together (such as the segmented beads which contain silver or the blue translucent examples) vary widely in the types and concentrations of trace elements that they contain. Of course, the degraded state of the beads makes interpretation of the results more difficult, but even so it is apparent that these beads are likely to have several different origins.

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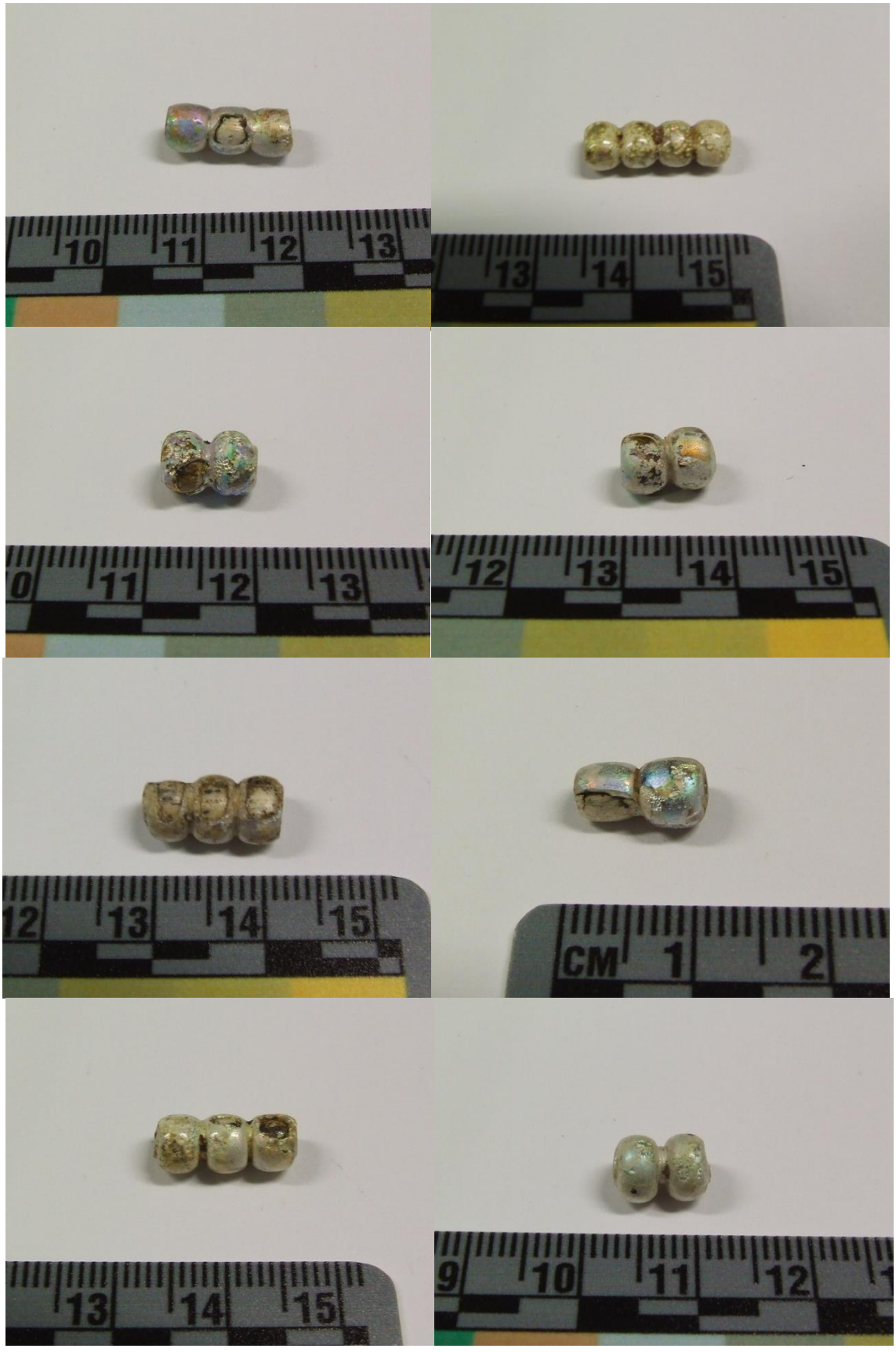

Plate 1: Segmented beads containing silver. Clockwise from top left: 18:100, 18:106, 23:045, 23:131, 23:177, 23:146, 23:126, 23:042

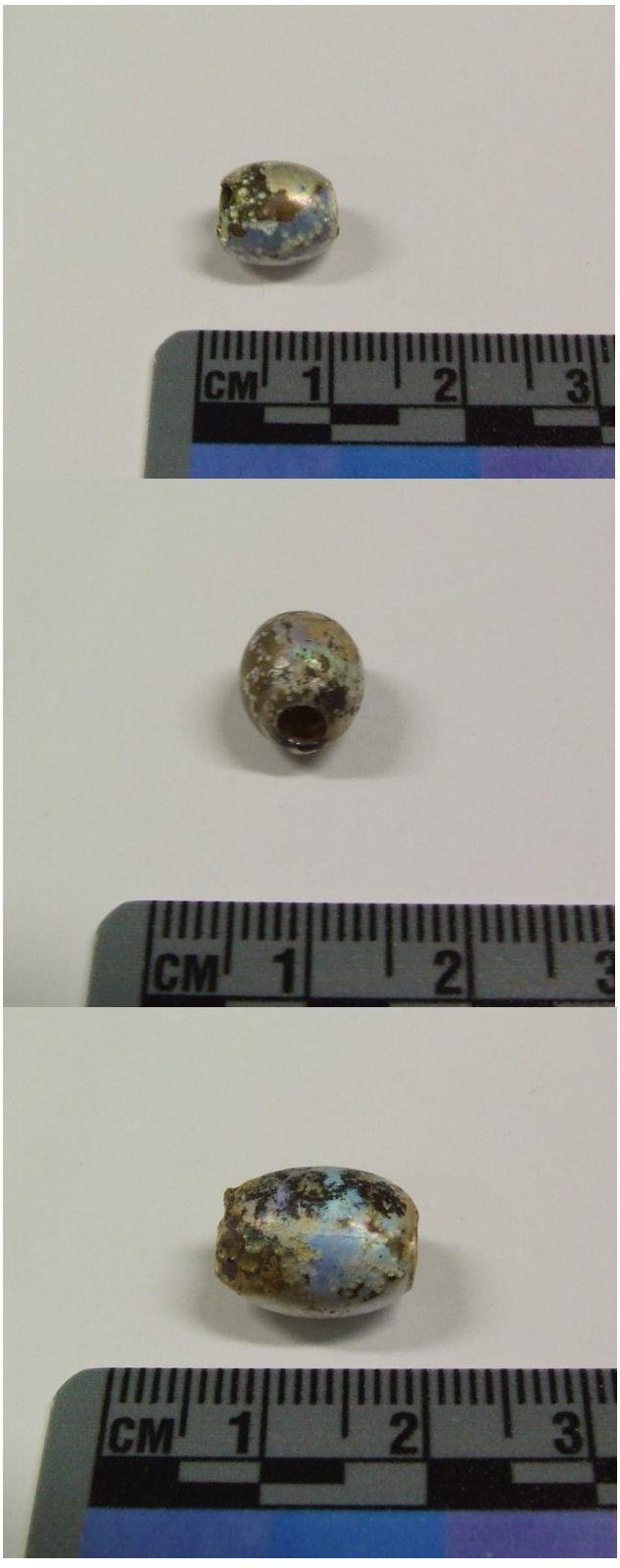

Plate 2: Beads no 19:300, 23:132 and 23:181 (top to bottom)

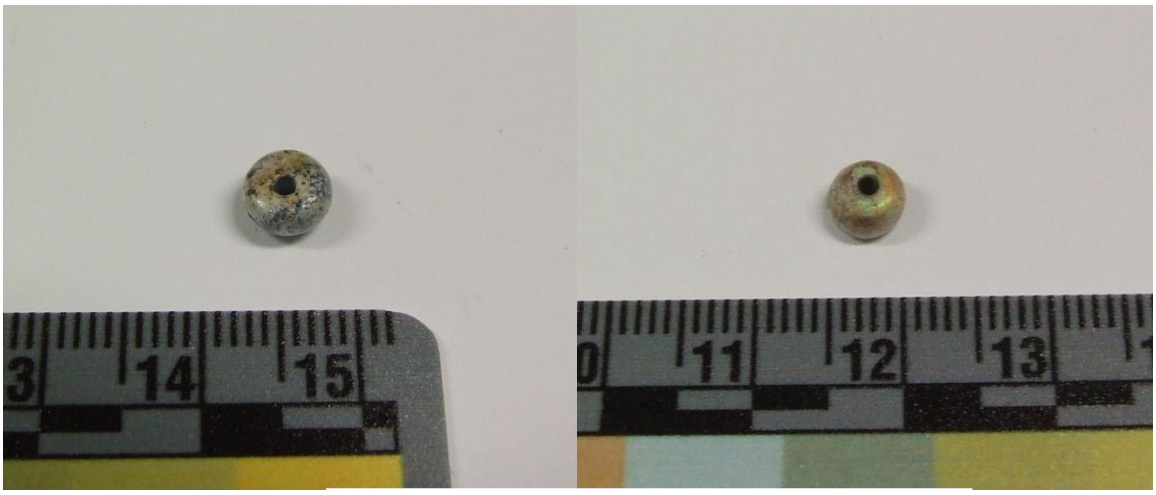

Plate 3: Beads no: 18:096 (left) and 23:047 (right)

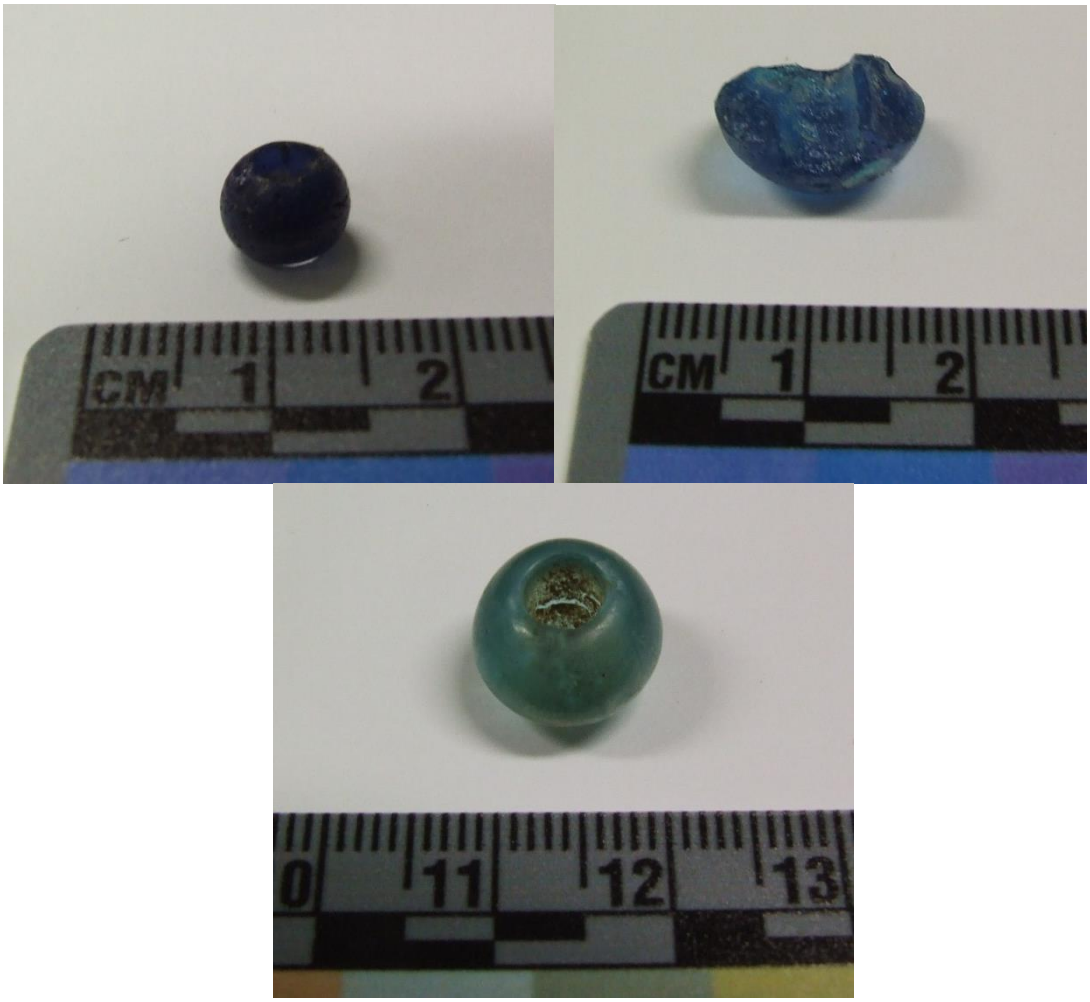

Plate 4: Beads no: 11:049 (top left), 18.180 (top right) and 19:134)

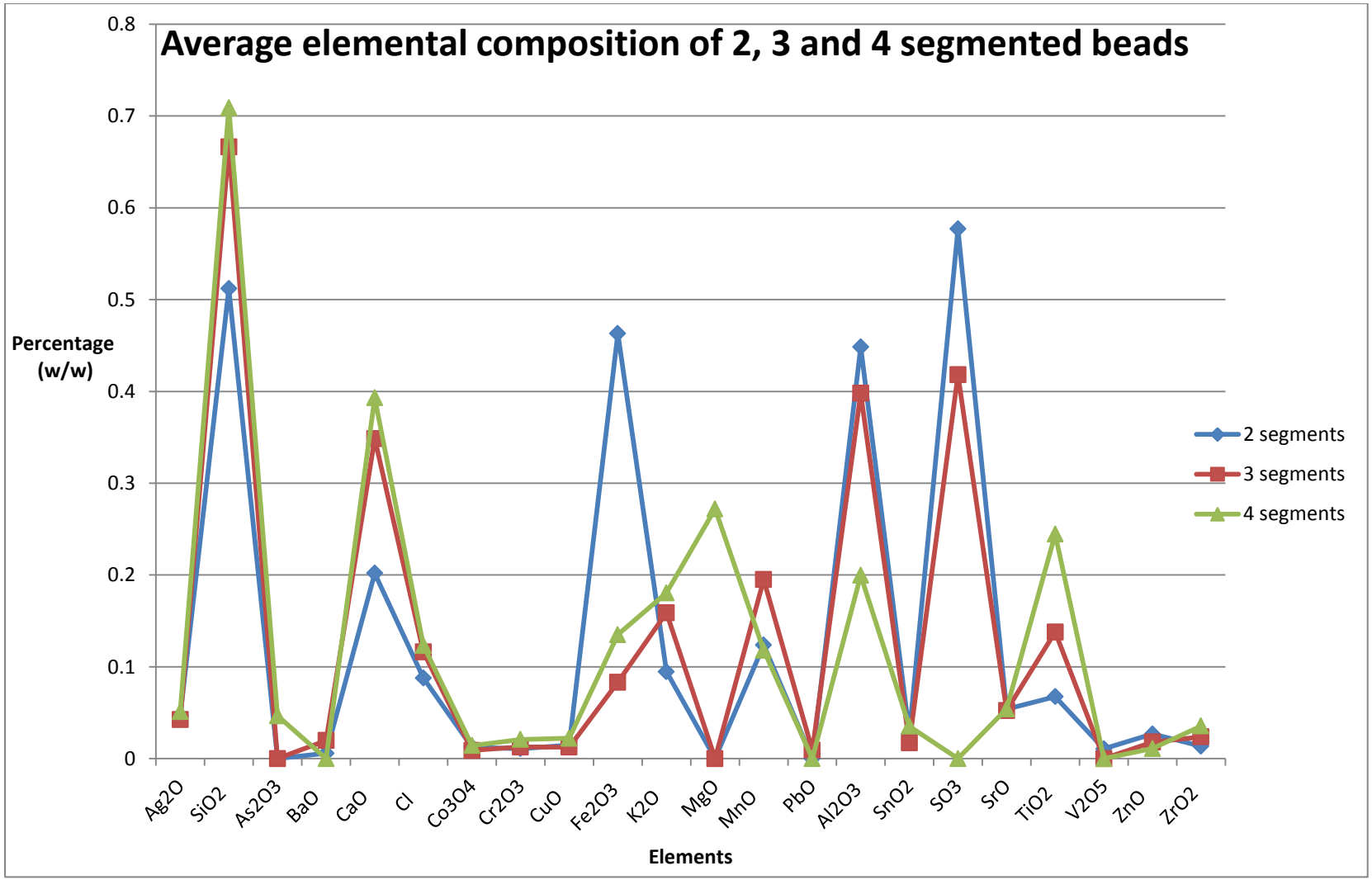

Figure 1: Average Elemental Compositions of 2, 3 and 4 segmented beads (SiO_2 and Al_2O_3 have been reduced by a factor of 100. CaO, Fe_2O_3, K_2O and MgO have been reduced by a factor of 10).

Appendix D: Glencurran Cave, Co. Clare

Appendix 1: Glass results (Results given in percentage w/w) (nd = not detected)

	11:049	18:090	18:091	18:096	18:100	18:103	18:106	18:117	18:119	18:180	19:300	19:094	19:095
	Small blue bead	*White coated bead*	*Small flat annular whitish bead*	*Small flat annular whitish bead*	*Three part segmented irridescent white bead*	*White coated oval bead*	*Four part segmented white/ gold bead*	*Three part segmented whitish/blue bead*	*Small flat annular bead*	*Half a large blue bead*	*Flakey whitish/blue coated bead*	*Flakey whitish bead*	*Small flat annular brown/whitish bead*
Ag_2O	nd	nd	nd	nd	0.053	nd	0.0467	0.0356	nd	nd	nd	nd	nd
Al_2O_3	39.05	18.41	36.44	48.38	29.44	24.64	29.59	18.02	24.45	15.09	25.46	15.97	35.24
As_2O_3	0.1637	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BaO	nd	nd	nd	nd	0.0197	nd	nd	nd	nd	nd	nd	nd	nd
CaO	4.95	2.49	2.88	3.13	5.23	3.69	3.09	2.69	2.56	4.24	2.34	2.64	2.84
Cl	0.741	0.0663	nd	0.171	0.213	nd	0.0973	nd	nd	0.636	0.045	nd	0.0737
Co_3O_4	0.109	0.0085	0.0386	nd	0.0095	0.0153	0.0143	0.0077	0.0102	nd	nd	nd	nd
Cr_2O_3	nd	0.0045	nd	nd	0.011	0.0142	0.0168	0.0123	nd	nd	nd	0.0108	nd
CuO	0.2927	nd	0.0536	nd	nd	nd	nd	nd	0.0929	1.09	nd	nd	nd
Fe_2O_3	0.807	0.883	0.923	0.774	1.03	1.5	1.39	0.791	0.931	0.212	0.424	0.695	0.54
Ga_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.0108
HfO_2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.0162
K_2O	0.401	1.56	1.11	1.84	2.82	2.14	1.95	1.47	1.13	0.279	1.26	1.91	0.942
MgO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MnO	0.4037	0.605	0.425	0.63	0.285	0.472	0.118	0.226	0.0104	nd	0.379	0.107	0.151
Na_2O	4.06	nd	nd	nd	nd	nd	nd	nd	nd	2.98	nd	nd	nd
OsO_4	0.0714	nd	0.0267	nd	nd	nd	nd	nd	0.1093	0.161	nd	nd	0.341
PbO	0.4347	0.128	0.108	0.0315	nd	0.183	nd	0.0091	0.883	1.1	0.0419	0.143	2.33
Sb_2O_3	0.861	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SiO_2	47.32	75.66	57.66	44.7	60.55	67.00	63.46	76.52	69.4	73.22	69.93	77.58	55.07
SnO2	nd	nd	0.0789	0.0271	nd	0.0166	0.0352	0.0102	0.244	nd	0.0163	0.75	0.396
SO_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.94	nd	nd	2.02
SrO	nd	0.0441	0.0321	0.0428	0.1116	0.0494	0.053	0.0475	0.0113	0.0091	0.0263	0.055	nd
TiO_2	0.1383	0.0819	0.0981	0.1021	0.1667	0.222	0.187	0.122	0.1104	0.0368	0.055	0.0948	0.0809
V_2O_5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
ZnO	nd	0.0067	0.089	0.0152	0.0093	0.007	0.011	0.007	0.0086	nd	0.0066	nd	0.0134
ZrO_2	nd	0.0145	0.0176	0.0096	0.0343	0.0233	0.0229	0.0213	0.0106	nd	0.0074	0.0232	nd

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	19:134	19:151	22:195	23:037	23:042	23:044	23:045	23:046	23:047	23:067	23:126	23:130
	Turquoise round bead, transparent	*Flakey whitish/blue coated bead*	*Segmented white coated bead*	*Small flat annular coated bead*	*Two part segmented whitish/gold coated bead*	*Two part segmented whitish/blue coated bead*	*Two part whitish, irridescent coated bead*	*Flat annular whitish coated bead*	*Small flat annular irridescent coated bead*	*Oval whitish irridescent coated*	*Three part degraded segmented coated bead*	*Round flakey blue coated bead*
Ag_2O	nd	nd	0.0303	nd	nd	0.035	0.0197	nd	nd	nd	0.0085	nd
Al_2O_3	43.69	29.59	24.99	28.29	23.02	30.94	78.37	34.81	32.21	41.64	21.35	14.9
As_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BaO	nd	nd	0.0052	nd	nd	nd	nd	nd	nd	nd	nd	nd
CaO	4.82	7.56	2.61	3.77	2.18	2.47	0.808	1.36	2.11	2.61	3.29	3.9
Cl	0.544	0.325	0.0548	nd	0.106	0.04	0.106	nd	nd	0.102	0.041	0.0398
Co_3O_4	nd	nd	nd	0.0329	0.0058	nd	nd	nd	0.0235	nd	0.0095	0.0749
Cr_2O_3	nd	nd	nd	nd	nd	nd	0.0063	0.0081	nd	nd	0.0147	0.0084
CuO	0.0066	nd	nd	0.0321	nd	nd	nd	nd	0.0127	nd	nd	0.0482
Fe_2O_3	0.607	1.69	0.452	1.53	0.458	0.327	0.179	0.627	1.14	0.432	0.876	2.12
Ga_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
HfO_2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
K_2O	0.598	2.67	1.46	1.21	1.29	1.37	0.276	1.017	0.892	1.07	1.36	1.6
MgO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MnO	0.213	1.44	0.463	0.264	0.122	0.0802	0.0418	0.0311	0.0379	0.203	0.146	0.599
Na_2O	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	0.0112	0.1191	nd	0.0134	nd	nd	nd	nd	nd	nd	nd	nd
PbO	0.0387	0.682	0.0066	0.0901	nd	nd	nd	nd	0.0201	0.0218	nd	0.0139
Sb_2O_3	0.1073	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SiO_2	49.01	51.05	69.8	64.37	73.01	64.25	19.91	61.9	63	53.85	72.42	75.29
SnO2	nd	0.0277	0.0075	0.0256	0.0166	nd	nd	nd	0.051	0.0173	0.0087	nd
SO_3	0.264	4.43	nd	nd	nd	nd	nd	nd	0.346	nd	nd	nd
SrO	0.0224	0.0957	0.0369	0.0247	0.024	0.038	0.0136	nd	0.0158	0.0215	0.0349	0.0255
TiO_2	0.0464	0.1753	0.0699	0.154	0.0627	0.0667	0.0452	0.0602	0.0836	0.0616	0.146	0.203
V_2O_5	nd	nd	nd	nd	nd	nd	0.0119	nd	nd	nd	nd	nd
ZnO	0.0084	0.0211	0.0095	0.074	0.007	0.0096	0.0206	0.0121	0.054	0.0195	0.0086	0.0749
ZrO_2	nd	0.0247	0.0138	0.0192	0.0173	0.0156	nd	0.0199	0.0143	0.0073	0.019	0.0119

Appendix D: Glencurran Cave, Co. Clare

	23:131	23:132	23:146	23:147	23:161	23:165	23:177	23:178	23:179	23:181	23:185	23:189	52:22
	Two part segmented bluish irridescent coated bead	*Flakey oval coated bead*	*Three part segmented white and gold coated bead*	*Two part segmented bluish coated bead*	*Flakey oval coated bead*	*Flakey gold coated bead*	*Two part segmented whitish coated bead*	*Three part segmented whitish coated bead*	*Small flat annular whitish coated bead*	*Flakey oval bluish/white coated bead*	*Oval brownish irridescent coated bead*	*Four part segmented whitish irridescent coated bead*	*Two part segmented whitish bead*
Ag_2O	0.066	nd	0.0827	nd	nd	nd	0.0647	0.0326	nd	nd	nd	0.0558	nd
Al_2O_3	18.77	26.82	32.51	92.97	27.48	16.45	24.26	97.63	20.26	14.66	30.77	10.33	45.62
As_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.0466	nd
BaO	0.0062	nd	nd	nd	nd	nd	nd	nd	nd	0.007		nd	0.0052
CaO	3.43	4.7	5.09	1.61	2.9	3.06	2.34	1.13	3.93	2.38	1.27	4.77	1.3
Cl	0.14	0.253	0.04	0.0859	0.0752	0.133	nd	0.171	nd	nd	nd	0.149	0.0485
Co_3O_4	nd	0.0102	nd	0.0226	0.0142	nd	0.0092	nd	0.0157	nd	nd	nd	nd
Cr_2O_3	nd	nd	nd	nd	nd	nd	0.0154	nd	nd	nd	nd	0.0249	nd
CuO	0.0078	nd	0.0126	0.0219	0.151	nd	nd	nd	0.0856	nd	0.0099	0.0222	nd
Fe_2O_3	0.661	0.939	1.41	0.455	0.54	0.665	0.995	0.0554	1.24	1.06	0.459	1.31	0.167
Ga_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
HfO_2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
K_2O	1.35	2.04	2.05	0.302	0.974	1.17	1.45	0.245	1.51	1.27	1.07	1.66	0.588
MgO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	2.72	nd
MnO	0.495	1.05	0.1229	0.016	0.284	0.356	0.0525	nd	0.322	2.01	0.0929	0.118	0.0593
Na_2O	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	nd	0.0167	nd	nd	0.065	0.1079	nd	nd	0.228	0.0115	nd	nd	nd
PbO	nd	0.127	nd	nd	0.421	0.525	nd	nd	1.35	0.056	0.0869	nd	nd
Sb_2O_3	nd	nd	nd	nd	0.161	nd	nd	nd	nd	nd	nd	nd	nd
SiO_2	74.9	62.98	57.06	3.69	66.73	73.41	70.59	nd	70.37	78.32	66.1	78.32	52.13
SnO2	nd	0.0139	0.0324	0.0376	0.0889	0.0936	nd	nd	0.468	0.0235	0.0165	nd	nd
SO_3	nd	0.841	0.264	0.577	nd	3.85	nd	0.572	nd	nd	nd	nd	nd
SrO	0.0412	0.0584	0.0565	0.0194	0.0266	0.0381	0.037	0.0116	0.0236	0.0345	0.0297	0.0553	0.204
TiO_2	0.0873	0.117	0.182	0.0297	0.0573	0.0967	0.158	0.0726	0.149	0.118	0.0517	0.302	0.0229
V_2O_5	nd	nd	nd	0.0136	nd	nd	nd	nd	nd	nd	nd	nd	0.0066
ZnO	0.0087	nd	0.018	0.125	nd	0.0095	0.0084	0.0474	0.0119	0.0179	0.0059	nd	0.0085
ZrO_2	0.0144	0.0133	0.0204	nd	nd	0.0133	0.0137	nd	0.0335	0.0155	0.0107	0.0483	0.007

Appendix 2: Average elemental composition of 2, 3 and 4 segmented beads (Results given in percentage w/w) (nd = not detected)

	2 segments	3 segments	4 segments
Ag_2O	0.0463	0.04248	0.05125
Al_2O_3	44.85	39.79	19.96
As_2O_3	nd	nd	0.0466
BaO	0.0057	0.0197	nd
CaO	2.012	3.486	3.93
Cl	0.0877	0.116	0.1232
Co_3O_4	0.0125	0.0089	0.0143
Cr_2O_3	0.0108	0.0127	0.0209
CuO	0.0149	0.0126	0.0222
Fe_2O_3	0.463	0.932	1.35
K_2O	0.947	1.589	1.805
MgO	nd	nd	2.72
MnO	0.124	0.195	0.118
PbO	nd	0.0091	nd
SiO_2	51.2114	66.64	70.89
SnO2	0.0271	0.0171	0.0352
SO_3	0.577	0.418	nd
SrO	0.0539	0.0524	0.0541
TiO_2	0.0675	0.1389	0.2445
V_2O_5	0.0107	nd	nd
ZnO	0.0269	0.0181	0.011
ZrO_2	0.0136	0.02375	0.0356

Appendix E: Analysis of glass from Lagore, Co. Meath

Excavation no. E14

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Appendix E: Lagore Crannog, Co. Meath

1. Introduction

This report details the analysis of a number of glass artefacts which were uncovered during the excavations at Lagore, Co. Meath. The multi-elemental analysis was carried out using X-ray Fluorescence at I.T. Sligo. The aim of this analysis was to determine trace elements within the glass beads which could potentially answer questions about their origin or production. The report will cover the interpretation of the results obtained from this assemblage.

The site of Lagore consisted of a crannog located near Dunshaughlin in Co. Meath. Excavation of the site was carried out by the Harvard Archaeological Expedition between 1934 and 1936 and highlighted three periods of occupation Both Hencken (1950, 6) and later Warner (1985/1986, 75) concurred on a date of no earlier than the 7th century and possibly as late as the 8th century for the earliest occupation of the site, with the site most likely having been abandoned around the 10th or 11th century AD (Hencken *et al*. 1950, 3, 7). The three periods of occupation were named Period I, Period II and Period III. Period I includes the earliest occupation phase, which as mentioned would have been the 7th or 8th century. Only a few of the glass objects were found in Period I contexts and it was suggested that these pieces were most likely imported as broken pieces for the production of studs for bronze ornaments. Moulds which would have been used for producing such studs were also found. Periods II and III did not give any evidence of date but instead refers to when the site was rebuilt on two occasions after its initial construction. Annal records state that the structure was destroyed twice; firstly in 850AD and then again in 934AD. This may mark the beginning of Periods II and III respectively (Hencken *et al*. 1950, 9). The period that each of the glass pieces was found in is listed in the appendices. The majority of the glass that was analysed, 46 out of the 68 pieces, came from unstratified contexts, 12 pieces came from Period I contexts 10 pieces came from Period II contexts.

The samples in this analysis included a range of glass beads, bracelet fragments and a few miscellaneous pieces. The large assemblage of beads uncovered at Lagore is perhaps the most notable collection of Early Medieval beads which have been found

in Ireland. The finds included many different shapes including tubular and dumbbell shaped in a range of different colours including blue, white, yellow and green. Hencken *et al*. (1950, 139) noted the similarity of some of the tubular examples to beads which were commonly found in Anglo Saxon burials, suggesting that these samples could well have been imported from Britain. Some of the beads from Lagore made up a sample group of 42 objects from various sites which were examined using XRF in a previous study (Warner and Meighan 1994, 53-65). These objects came from numerous sites including Lagore, Garranes, Garryduff and Clogher and varied considerably in colour and in shape. The analysis made it possible to divide the beads into different groups based on their percentages antimony, manganese and arsenic. This allowed the beads to be assigned to chronological groups based on their elemental analysis. It highlighted some trends in glass objects over time such as the increased use of antimony as a decolourant in beads found in Ireland around the 7th or 8th century AD. The researchers were also able to show the types of colourants which were used in the production of these objects such as the use of lead compounds to colour a yellow bead and the use of cuprous oxide in a red example (Warner and Meighan 1994, 53-65).

2. Methodology

2.1. Sample collection and selection

A selection of glass beads and bracelet fragments from the Lagore excavations were obtained from the National Museum of Ireland for the purpose of this study. The samples were chosen from the Lagore glass assemblage with a number of objects being excluded due to their fragmented nature or small size. In total, 68 artefacts from the assemblage were analysed using XRF analysis, as the rest of the artefacts were either too small or too fragmented for analysis. This number included 51 beads, 12 bracelet fragments, 1 toggle and 4 unidentified fragments.

2.2. Calibration/Quality Control

The XRF was calibrated monthly using the standard procedure for this instrument. The accuracy of the instrument is also tested regularly using glass reference material. Table 1 below illustrates the accuracy and precision of the instrument using a reference sample. The sample was run five times and an average taken of the results. The percentage difference and relative standard deviation was then calculated from the results.

	Stated concentration (%w/w)	**Average obtained (%w/w)**	**Relative Standard Deviation%**	**%Error**
SiO_2	72.26	72.62	0.360	0.503
Na_2O	13.78	12.88	1.399	-6.516
CaO	10.05	10.71	0.598	7.000
MgO	3.40	3.64	2.423	-0.0549
SO_3	0.270	0.027	9.658	-90.074
TiO_2	0.033	0.0237	7.413	-28.121
Fe_2O_3	0.021	0.0177	4.058	-15.619

Table 1: Reference sample results obtained

2.3. Sample washing and preparation

A solution consisting of a 1:1 ratio of deionised water and 99% ethanol solution was prepared in a volumetric flask. The surface of each sample was gently cleaned using a clean cotton swab dipped in the deionised water/ethanol solution prior to being analysed in the XRF. The purpose of this technique was to remove surface contamination on the surface of the glass. Different trace elements can be left on the glass from many processes such as salts left behind from washing with ordinary water or chlorine transferred from handling the samples with bare hands. By removing such elements, a clearer result of the elemental composition of the surface

layers of the glass can be obtained. The above washing method was decided in consultation with the National Museum of Ireland after extensive experimentation on modern glass samples. The samples were left to dry completely before undergoing analysis. All samples were handled using gloves to avoid adding any further surface contamination.

2.4. Testing of samples

Each sample was analysed by XRF in triplicate and the results averaged. Samples were analysed in the condition they were received with no preparation other than the washing method which was outlined in Section 2.3. XRF was chosen for this analysis as it provides a highly sensitive, multi-elemental analysis and is completely non-destructive. XRF is a surface technique, therefore the elemental composition it gives is indicative of the surface layers only and this may not be an accurate representation of the whole sample.

3. Results

The results of the analysis (given in percentage w/w) can be seen in three appendices at the end of this report. Appendix 1 shows the results obtained for the 51 beads and bead fragments which were analysed, Appendix 2 shows the results for the 12 bracelet fragments and Appendix 3 shows the results for the single toggle and the 4 miscellaneous fragments.

4. Discussion

4.1 Condition of samples

Some of the artefacts were in a fragmented condition including all of the bracelet pieces and the miscellaneous fragments. Some of the beads were also in a broken state but most of them were complete. The majority of the glass was in very good

condition with no visible signs of corrosion, pitting, crusting or an iridescent sheen which can often develop on ancient glass. One notable exception was find No. 1476, a brown annular bead with a speckled appearance. This find exhibited some signs of pitting and crumbling on its surface. It also did not have a consistent colour on its surface. This may have been due to poor production conditions in the furnace, such as inconsistent or inadequate temperatures.

4.2 Elemental Composition

From ancient times, glass has been consistently made up of a glass former, such as sand or quartz pebbles (SiO_2), a modifier, such as soda (Na_2O) or potash (K_2O), and a stabilizer such as lime ($CaCO_3$). As well as this, glass may contain a variety of colouring agents, opacifiers and other trace elements, added either intentionally or unintentionally (Goffer 2007, 124). From an analytical point of view, the composition of ancient soda-lime glass is typically 73% SiO_2 (silica), 23% Na_2O (soda) and 5% CaO (calcium oxide) (Gratuze and Janssens 2004, 665). Potash or a mixture of potash and soda can be used to produce potash or mixed alkali glasses. Generally, the lowest concentrations of modifier which would have been added would have been at least 15% (Shortland 2012, 101).

4.2.1 Beads

A total of 51 beads were analysed from this assemblage, representing a wide range of colours and shapes. The majority were blue in colour, with 17 plain round blue, 10 decorated blue and 3 segmented examples. There were also 7 yellow opaque, 7 white opaque, 2 green and 5 polychrome examples. The vast majority of the beads were uncovered from unstratified contexts and so it is not possible to accurately date them from where they were found.

4.2.1.1 Blue beads with no decoration

Plain blue beads made up the largest group that underwent analysis with 17 finds, examples of which can be seen in Plate 1. The find Nos. were 1469, 1470, 1477, 1487, 1488, 1492, 1494, 1499, 1500, 1502, 1511, 1526, 1527, 1528, 1557, 1559 and 1595. The majority were small round examples, however find No. 1559 and 1595 were larger melon beads. Twelve of these were found in unstratified contexts, three were found in Period I contexts and two were found in Period 2 contexts. The main component of these beads, silica (SiO_2), accounted for between 52.64% and 79.76%.

Soda, potash or a mixture of the two was an essential component when producing glass in ancient times. It acted as a flux, lowering the melting point of silica from 1700^{o}C to 1000^{o}C, a temperature which was obtainable in ancient furnaces (Goffer 2007, 115). All of these blue beads contained potash (K_2O), with concentrations of between 0.439% and 2.17%. Only six of the 17 blue beads contained detectable amounts of soda (Na_2O) with between 2.43% and 9.09%. As mentioned, the concentrations of modifier, soda or potash, can be up to around 23% for ancient glass and the lowest that would have been added would have been at least 15%. The results from these blue beads show that much of the modifier material that they would have contained has been lost, which again highlights the corroded condition of their surface layers.

Of the 17 blue glass beads, 11 contained no detectable amounts of soda and only trace amounts of potash. Potash would have been sourced from wood ash as opposed to soda which was generally retrieved from marine plants (Henderson 2013, 28). While the corrosion process has removed much of the modifier material from the surface of these 11 objects, the fact that these pieces contained almost no traces of modifier beyond trace amounts of potash would suggest that they were a potash-based glass. While corrosion may affect glass for a number of reasons, such as environmental factors, the most important factor in most cases is the original elemental composition of the glass. This determines the resistance of the glass to agents which can cause corrosion such as water, acidic and basic solutions and other

atmospheric substances (Pollard and Heron 2008, 166). Potash glass is more susceptible to corrosion than soda-based glass due to its high alkalinity and so it often does not survive as well when exposed to the elements (Moran 2010, 17). The fact that several pieces of soda-lime glass have maintained their modifier concentrations to a much greater extent, such as find No. 1511 with a soda concentration of 9.09% and a potash concentration of 0.439% would further support the fact that these 11 pieces were in fact potash-based.

Some of the beads analysed were most likely produced using a soda-lime type glass. Find No. 1511, for example, contained 9.09% soda and 0.439% potash. While this is still well below the minimum 15% concentration which would be expected, it is clear that this bead had maintained its structural integrity better than many of the other samples. The beads which contained smaller amounts of both soda and potash, such as find No. 1470 which contained 3.09% and 0.526% of soda and potash respectively may well have been formed from a mixed alkali glass type. A mix of potash and soda could have been added intentionally or it may have been accidental. For example, potash sources may occasionally contain traces of soda (Shortland 2012, 101). It is also possible that cullet (broken pieces of glass) may have been used when producing the glass, which would have further complicated the elemental composition of the mixture.

The aluminium oxide (Al_2O_3) content was between 6.49% and 42.00%. The low levels of silica and the elevated levels of aluminium highlights the corroded nature of the surface layers of some of these glass beads. Aluminium which existed in the structure of the glass originally may have been held preferentially compared to other elements. There is also the possibility that the surface layers contained aluminium which had entered from the environment. Corrosion can change the visual appearance of glass by causing pitting, crusting or an iridescent layer to form on the object. However, it can also occur without any obvious visible change. These blue glass beads did not appear visually corroded, yet the elemental analysis highlights how significant corrosion of the surface layers has taken place. Glass is particularly susceptible to corrosion while buried in the ground due to interactions with water

and other environmental factors. The corrosion itself is a complex reaction which is not well understood and many different factors affect it. However it is thought that it occurs due to the preferential leaching of alkali ions to be replaced by hydrogen ions (Wayne Smith 2003, 94). This leaching starts in the surface layers of the glass and gradually spreads inwards (Varshneya 1994, 398). As mentioned, the low percentage of silica, coupled with unusually high levels of aluminium oxide (Al_2O_3) in a number of samples, is indicative of corrosion in the surface layers of these blue glass beads, which has clearly altered their original composition. Low levels of silica in the samples were found to be associated with high levels of aluminium oxide (Al_2O_3), and an inversely proportional trend can be observed when the two results are plotted against each other (see Figure 2 at the end of this report). An r^2 value of 0.7175 is observed for this graph. On a scale of 0 to 1, where 0 represents no correlation and 1 shows a very strong correlation, it can be seen that the result here does indeed indicate a significant correlation between the two. If the silica and aluminium oxide concentrations for all 50 of the glass beads analysed are plotted against each other, an r^2 value of 0.8339 is apparent, highlighting an even stronger correlation between the two (see Figure 1). The glass which contained soda (Na_2O) had a lower range of aluminium oxide concentrations, between 2.42% and 27.55% that the potash (K_2O) glasses which contained between 6.07% and 99.40%. This further demonstrates that soda-lime glass is more resistant to corrosion than potash-based.

The blue colour in 16 of these beads was caused by the presence of highly oxidised cobalt (Co_3O_4) with concentrations of between 0.0076% and 0.154% The only blue bead which did not contain cobalt oxide was find 1557. Cobalt is the most powerful transition metal when used as a colourant in glass and typical levels of cobalt oxide in ancient soda-lime-silica glass are often around 0.05% (Henderson 2000, 29). Much of the other blue glass, including the decorated blue beads and bracelet fragments which will be discussed later, were also coloured with cobalt oxide. It seems likely that the same source of cobalt was not used for all the beads, based on other trace elements that they contain. In modern glass, this would not be apparent due to the fact that refined cobalt would be used. However, in archaeological glass, it would

have been cobalt-bearing ores that would have been used and these would add different trace elements based on the source. For example, trianite ($2Co_2O.CuO.6H_2O$) would add trace amounts of copper (Cu) to the glass mix while skutterudite ($(Co.Ni.Fe)As_2$) would add nickel and arsenic (Henderson 2000, 30). The results show that 8 of the blue beads containing cobalt also contained traces of arsenic oxide (As_2O_3) with concentrations of between 0.0148% and 0.104%. Furthermore, 7 of the 8 beads which contained arsenic oxide also contained detectable amounts nickel oxide of between 0.0091% and 0.0376%. This would suggest that these beads were produced using the same type of cobalt ore, which is consistent with the elemental composition of skutterdite. Find No. 1557, the only blue bead which was not coloured with cobalt oxide, appeared considerably lighter in colour than the other blue beads, having an almost greyish tinge. Its colour may have been caused by copper oxides (CuO), which it contained at a concentration of 0.062%. This piece also contained a much higher amount of sulphur oxide (SO_3) than the rest of the blue glass beads with 1.21%. Sulphur additives can react with other elements to form many different colours from yellow to brown and even black (Davidson 2008, 77).

As will be discussed in Section 4.2.1.2, it seems likely that tin oxide (SnO_2) was being utilised for the purpose of white decoration in the decorated blue beads but 15 of the 17 undecorated blue beads also contained traces of this substance. Tin oxides are known to produce opaque whites in glass (Henderson 2000, 74) and seem to be responsible for varying degrees of opacity in these blue beads. For example, find Nos. 1494 and 1477, which contain two of the highest concentrations of tin oxide at 0.0596% and 0.091% respectively, appear noticeably lighter and more opaque than finds such as 1500 which contained significantly less of this substance at 0.0149%. Of the 17 blue beads, 16 contained concentrations of lead oxide (PbO) of between 0.0815% and 0.539%. This may have contributed to a more opaque appearance in the beads as lead oxide imparts a white opaque colour. It may also have lowered the softening temperature (Moorey 1999, 207).

4.2.1.2 Blue beads with decoration

The next group which was analysed consisted of 10 decorated blue glass beads; 1457, 1556, 1558, 1564, 1582, 1583, 1590, 1592, 1596 and 1931. Six were found in unstratified contexts, one was found in a Period I context and 3 were found in Period II contexts. A selection of these can be seen in Plate 2. There was a greater diversity in the shape of these beads compared with the undecorated examples. Five of the ten beads were small round beads, all of which had white decoration, but the other five examples were fragments of larger beads which had more intricate decoration including white, yellow and red glass. The silica (SiO_2) content for these decorated blue beads was between 43.17% and 79.59% while the aluminium oxide (Al_2O_3) concentrations were between 6.07% and 54.67%. Like the undecorated blue beads, there is a strong correlation between the amount of aluminium oxide and the loss of silica in these finds. As can be seen in Figure 3 at the end of this report, an r^2 value of 0.89 is observed when these two components are plotted against each other.

There was a mixture of modifiers found in these 10 beads. All 10 contained traces of potash (K_2O) of between 0.678% and 2.12% but only four contained detectable amounts of soda (Na_2O) with concentrations of between 1.63% and 10.59%. The glass finds that contained soda in their composition retained much more modifier material overall than the finds which did not. The seven finds which contained only potash had the lowest amounts of modifier overall and most likely were produced from potash-based glass given their greater susceptibility to corrosion.

Like the majority of the undecorated blue beads, all of the decorated examples contained cobalt oxide (Co_3O_4) which would have caused the bright blue hues which they exhibit. The concentrations of this substance range from 0.0081% to 0.106%. Significant concentrations of tin oxide (SnO_2) were also found in 7 of the 10 examples, which is unsurprising given that the beads had opaque white decoration and tin oxide was widely used to impart an opaque white colour to glass in antiquity (Henderson 2000, 74). The three examples that did not have detectable amounts of tin oxide, 1556, 1596 and 1931, either had much thinner lines of white decoration or had very little amounts of decoration on their surfaces. There is a chance that a

different substance was used to impart the white colour in these cases, however no substance that would have done so was noticeable in the results. It is most likely that the analysis simply could not detect the elements as the decoration was too sparse in these three examples.

Find No. 1558 had areas of yellow decoration on its surface. This was most likely caused by a concentration of lead oxide (PbO) which was considerably higher than that of the other samples at 1.22%. This, along with the tin oxide it contained could account for the yellow hue decoration overlaid on the blue glass, as tin and lead oxides together are known to produce opaque yellows (Henderson 2000, 74). Find No. 1564 contained small amounts of white, yellow and red decoration; however the results of the elemental analysis did not highlight significant concentrations of any of elements that would have caused either of these colours such as lead and copper oxides. This is most likely because the decoration made up such a small part of the surface of the object. Analysis of red glass and enamel from elsewhere in Ireland and Britain for the Early Medieval would suggest that the most likely cause for the hue in this case would be a mixture of lead and copper oxides in its structure (Bertini *et al*. 2011, 2765, Stapleton *et al.* 1999, 913-915).

4.2.1.3 Blue segmented beads

There were three segmented beads among the glass which was analysed, all of which were blue in colour. They were find Nos. 1549, 1550 and 1551 and they can be seen in Plate 3. Two of the finds were unstratified and find No. 1549 was from a Period I context. The silica (SiO_2) concentrations for these beads were 64.09%, 79.96% and 72.13% respectively while the aluminium oxide (Al_2O_3) concentrations were 29.64%, 7.05% and 20.85% respectively. With regards to modifier substances, the potash (K_2O) concentrations of these pieces was 0.795%, 1.03% and 0.52% respectively while only find No. 1550 contained detectable amounts of soda (NaO_2) at 1.31%. Even just examining these major elements, it seems clear that there are significant differences in the elemental compositions of the beads and they were

most likely manufactured differently. Find No. 1550 appears to be a mixed alkali type and exhibits less corrosion than the other two segmented examples as can be seen by its much lower concentration of aluminium oxide concentration. The other two finds, 1549 and 1551, were most likely formed from potash-based glass.

All three of the segmented beads were coloured with cobalt oxide, which accounted for 0.0259%, 0.0497% and 0.0158% of their composition. They also contained concentrations of copper oxide (CuO) of 0.677%, 0.215% and 0.150% respectively which could have further added to their blue hue. There were significant quantities of tin oxide (SnO2) found in these finds with concentrations of 0.665%, 0.395% and 0.708% respectively which had the effect of causing a more opaque appearance to the blue colour of these beads. All three beads contained concentrations of lead oxide (PbO) of between 0.190% and 0.612%, which, like in the other blue beads, would have lowered the softening temperature of the glass as well as giving them a more opaque appearance. Find 1550 differed in the amount and type of trace elements it contained compared to the other two. Its concentration of iron oxide (Fe_2O_3) at 1.21% was considerably higher than the concentrations found in finds 1549 and 1551 which were 0.38% and 0.448% respectively. It also had no detectable traces of either sulphur oxide (SO_3) or strontium oxide (SrO) which both of the other beads contained in concentrations of 0.33% and 0.42% sulphur oxide, and 0.0185% and 0.0227% strontium oxide respectively. This would suggest that the beads were exposed to different trace materials during their manufacture however they were likely created using similar techniques.

4.2.1.4 Yellow opaque beads

A total of seven opaque yellow beads and bead fragments were analysed as part of this study (Plate 4). Four finds were unstratified and three were from Period II contexts. No yellow beads were found in Period I contexts, suggesting that they were not present during the earliest phase of occupation. One of the glass finds, no 1520, had some green decoration on its surface, but for the purpose of this analysis

its yellow surface was analysed. The silica (SiO_2) concentrations for these beads varied from 40.99% to 57.8% which was considerably lower than the silica concentrations found in the blue beads. Likewise the aluminium oxide (Al_2O_3) concentrations for these beads were considerably higher than the blue beads with levels of between 9.61% and 58.00% detected. These beads also show correlation between the silica and aluminium oxide concentrations as can be seen in Figure 4 at the end of this report. The r^2 value for this correlation was found to be 0.8406, which indicates a strong correlation. The potash (K_2O) levels for the seven beads were between 0.297% and 0.728%. Only two of the seven yellow beads contained detectable amounts of soda (Na_2O) with levels of 3.06% and 4.23%. Overall it would seem that these yellow beads had undergone corrosion of their surface layers to a greater degree that the blue beads which were discussed previously. As the majority of the beads were found in unstratified contexts, it is difficult to compare corrosion levels between the different colours. However, as elemental composition is generally the most important factor to be considered when it comes to how well glass will resist corrosion, and given that the yellow beads show greater signs of corrosion regardless of whether they were from definite contexts or unstratified, it is most likely their different elemental composition which makes them more susceptible to corrosion than the blue glass beads.

The yellow hue of these beads was achieved by using tin oxide (SnO_2) and lead oxide (PbO) as these elements together are known to produce opaque whites and yellows (Henderson 2000, 74). The tin oxide levels were found to be between 0.019% and 0.615% while the lead oxide levels were between 1.66% and 3.86%. Four of the seven beads contained small trace amounts of gallium oxide (Ga_2O_3) with concentrations of between 0.0084% and 0.0206%. Gallium does not occur in nature as a natural metal and minerals containing this substance are relatively rare. It is most often found as a trace element in the aluminium ore bauxite and a zinc ore called sphalerite (Butcher and Brown 2014, 150). Given the very small trace amounts of zinc that were found, it would seem unlikely that it came from sphalerite. The four pieces of glass which contain gallium also have high levels of sulphur oxides (SO_3) of between 10.02 and 17.71%. Given that these high levels of sulphur oxides distinguish

them from the other finds, it is possible that trace amounts of gallium were introduced in the form of gallium sulphides (Ga_2S_3).

4.2.1.5 White opaque beads

A group of seven white opaque beads were among the glass beads analysed from the Lagore assemblage (Plate 5). Four of the white finds were unstratified, two were from Period I contexts and one was from a Period II context. Of the seven, five contained silica (SiO_2) concentrations of between 44.11% and 65.34%, with two beads having no detectable traces of the substance at all. The five which contained silica had aluminium oxide (Al_2O_3) concentrations of between 18.96% and 55.15%, while the two which did not had aluminium oxide concentrations of 97.91% and 99.40% respectively. This analysis was repeated in triplicate with a %RSD of 3.185%. Clearly the two with the large concentrations of aluminium oxide had undergone heavy corrosion of the surface areas where the analysis took place, to the point that the majority of the substance was in fact aluminium oxide. Five of the white beads had detectable potash (K_2O) concentrations of between 0.081% and 1.05%, while only a single bead, 1474, had detectable amounts of soda (Na_2O) of 4.79% and the highest amount of potash at 1.05%. Find no 1474, the only one likely to be of mixed alkali type, was the least corroded white bead with the highest amount of modifier substance and the lowest amount of aluminium oxide at 18.96%. Like all the other groups of beads discussed so far, a correlation was apparent between the amount of silica and the amount of aluminium oxide present in their surface layers, with a very strong r^2 value of 0.9868 observed when the two sets of concentrations were plotted against each other (see Figure 5).

The white colour for the majority of these beads was caused by the presence of tin oxides (SnO_2) in their structure. This compound accounted for between 0.47% and 3.89% for six of the seven samples. The only opaque white bead which did not contain detectable amounts of this substance was find No. 1472. It is difficult to say what could have coloured this bead based on the results obtained. Perhaps it did

contain tin oxide, just not in high enough concentrations to be detected by the XRF or leached away as the surface layers underwent corrosion. It is noteworthy that this bead was the only example to contain traces of cadmium oxide (CdO), however this substance would usually impart a yellow tinge to the glass, not white (Henderson 2013, 113). This find contained small amounts of lead oxide (PbO) at 0.271% which may have contributed to its white opaque colour.

4.2.1.6 Green beads

There were two green beads among those analysed, find Nos. 1560 and 1561 (Plate 6). Find 1560 was unstratified while find 1561 was from Period I. The beads had two different hues, with 1560 having a light green tinge and 1561 having a "khaki" colour with more of a yellow tinge than 1560. The silica (SiO_2) concentrations for these two beads were 73.28% and 73.44% respectively. Find No. 1560 was the only ibe which did not contain detectable amounts of aluminium oxide (Al_2O_3) while find 1561 had concentrations of 10.76%. The two green beads had potash (K_2O) concentrations of 5.79% and 0.752% respectively while their soda (Na_2O) concentrations were 3.11% and 4.44% respectively. This would suggest that both pieces were made from a mixed alkali glass.

The greenish colour of these finds were due to iron oxide (Fe_2O_3), which accounted for 0.314% and 0.542% of their surface composition. Other substances known to act as green colourants, such as oxides of copper, chromium and nickel, were absent with the exception of very low trace amounts of copper oxide (CuO) in find 1561 at 0.051%. Iron impurities, both ferrous (Fe^{2+}) and ferric (Fe^{3+}), occur frequently in sand, which was often used as a silica source. As such, iron contaminants were often added unintentionally to the glass melt during glass production which is why green is one of the most common colours for ancient glass (Henderson 2013, 75). The cause of the different green hue of 1561 is difficult to account for but it was possibly due to oxidation conditions in the furnace environment. It is also possible that the copper oxide played a role. Copper has been found to impart a wide range of colours in

glass (Bhardwaj 1979, 42-43). This includes blue tones ranging from bluish green to a very pale blue that could also be achieved by adding cupric oxide (CuO) to the glass. Adding cuprous oxide (Cu_2O), meanwhile, results in a reddish brown colour (Bhardwaj 1979, 42-43). Finally, the yellowish-green colour of 1561 may have been caused by the elevated concentration of manganese oxide of the glass which was 1.07%. Manganese, when added to other elements such as carbon and sulphur, is known to impart an amber hue. This, when added to a darker green glass, may have produced the more yellowish-green colour of this particular find. Unfortunately it is not possible to detect carbon using XRF analysis, but sulphur oxide (SO_3) was detected in the glass with a concentration of 1.17%.

4.2.1.7 Polychrome/Miscellaneous coloured beads

A total of five beads with multiple colours were analysed, find Nos. 1456, 1476, 1530, 1581 and 1588 (Plate 7). All five were from unstratified contexts. Find No. 1456 was opaque green, red and white. The silica (SiO_2) content of this bead was found to be 60.86% while the aluminium oxide (Al_2O_3) content was 20.68%. The potash (K_2O) and soda (Na_2O) concentrations for this piece were 2.56% and 3.11%, suggesting that the glass was most likely a mixed alkali glass. The opaque white colour in the bead most likely came from tin oxide (SnO_2) which was detected in its surface layer at concentration of 0.98%. The red colour in this bead made it very unusual for a bead uncovered from a medieval context as red glass is very rare in Ireland particularly for this period (Laing 1975, 337). There was a block of red enamel reputedly found at the Hill of Tara, however whether the artefact was truly discovered there is disputed. When this enamel block was analysed it was found to be comprised of a typical soda-lime-silica glass with 27% lead oxide (PbO) and 9% copper oxide (CuO) added to it (Stapleton *et al*. 1999, 913-915). The lead oxide and copper oxide of this bead from Lagore was 1.73% and 0.77% respectively. It must be borne in mind that the surface of this bead has most definitely undergone corrosion and as such the results were not entirely representative of its original composition. Finally the green colour from this bead was most likely caused by concentrations of both iron oxide

(Fe_2O_3) and chromium oxide (Cr_2O_3) with 1.46% and 0.0055% respectively. Both of these elements are known to produce green colours in glass (Bhardwaj 1979, 42-43).

Find No. 1476 was a deep amber colour with a flecked appearance. Its silica and aluminium oxide concentrations were 53.41% and 9.05% respectively while its concentration of potash was 0.629%. There was no detectable amount of soda found in its surface layers and it was most likely a potash-based glass. With regards to its amber hue, the concentrations of both manganese oxide (MnO) and sulphur oxide (SO_3) for this piece were significant with concentrations of 2.97% and 4.41% respectively. When manganese and sulphur are added to glass, along with carbon in the glass furnace which would not be detected using XRF, it can result in various shades of amber (Bray 2001, 65). The iron oxide (Fe_2O_3) concentration was also very high at 11.34% and may have further added to the brownish-orange colour of the glass bead.

Find No. 1530 had shades of blue, green and yellow which swirled together. Its silica concentration was 71.66% while its aluminium oxide concentration was 5.97%. With regards to modifier additives, this piece had 4.32% potash and 9.68% soda. This was considerably higher than many of the other beads which were analysed and much closer to the minimum amount of 15% modifier which would be expected from uncorroded layers of glass. This would suggest that this piece may have been more recent than other glass bead finds from the site. It came from an unstratified context and had a shinier, almost plastic-like appearance compared to the other beads. In addition, this particular bead had much lower amounts and types of trace elements than many of the other beads. This bead contained a number of different colourant materials including 0.0792% cobalt oxide (Co_3O_4), 0.0246% chromium oxide (Cr_2O_3) and 0.475% lead oxide (PbO) which would have imparted the blue, green and yellow hues respectively.

Find 1581 was a fragment of a cylindrical bead with shades of blue, white, yellow and red. Its silica and aluminium oxide concentrations were 67.93%% and 11.47% respectively. Its potash and soda concentrations were 1.13% and 6.73% respectively which would suggest a mixed alkali glass. Like find 1530, this bead contained a wide

range of colourants including 0.0075% cobalt oxide (Co_3O_4), 1.79% lead oxide (PbO), 1.31% tin oxide (SnO_2) and 1.69% sulphur oxide (SO_3). These elements would cause blue, yellow, white and yellow shades respectively in glass. The red colour of the bead may have been caused by its concentration of copper oxide (CuO) at 0.0075%.

Finally, find 1588 was a dull red, white and green colour. Its silica concentration was 60.92% and its aluminium oxide concentration was 18.77%. Its potash and soda concentrations were 0.98% and 12.08% respectively which would suggest a predominantly soda-lime based glass. The white and green parts of this bead were coloured by concentrations of 1.42% iron oxide (Fe_2O_3) and 0.181% tin oxide (SnO_2) respectively. The red colour of the bead, like that found in find 1456, was most likely caused by concentrations of both copper oxide (CuO) and lead oxide (PbO) in its structure, which accounted for 0.172% and 0.24% respectively.

4.2.2 Toggles

A single green toggle which was unstratified, find No. 1563, was analysed (Plate 8). This was only one of several toggles which were uncovered from the site; however reproducible results could not be obtained from any of the others, most likely due to their much smaller size. Toggles are most likely unique to Ireland (Edwards 1996, 94). They occur only very rarely outside of the country, and may have been imported to these places from Ireland. Examples include a toggle recovered from a dun at Kildalloig, in Western Scotland (Ritchie 1991, 153) and ones found at an Iron Age roundhouse on the Isle of Man. They are sometimes referred to as dumbbell beads and are often technically not beads at all, as many examples are not perforated (Gelling 1958, 95-96). These glass objects are particularly problematic as it is unknown what their function was, such as whether they were used for personal adornment. One suggestion has been that they are in fact manufacturing debris; the ends of glass rods which had been used for producing beads, which were clipped off while the glass was still soft. It has been suggested that the narrowest centre of the

bead, which prompted the name dumbbell, was caused by whatever held the rod while the glass was still soft (Johnston 2007, 121).

The elemental analysis for find 1563 highlighted heavy corrosion in its surface layers. The silica (SiO_2) and aluminium oxide (Al_2O_3) concentrations of this bead were 42.27% and 55.11% respectively. The level of modifier in this toggle was one of the lowest in any of the glass analysed from this site with only traces of potash (K_2O) present at 0.204%. There was no significant concentration of colourants in this toggle aside from 0.0737% iron oxide (Fe_2O_3) which could have been added accidentally as a contaminant in the raw materials. This would account for the light green tinge that this bead exhibits.

4.2.3 Bracelets

A total of 12 glass bracelet fragments were examined (Plates 9 and 10). Of these, nine were unstratified, two came from Period I contexts and a single example came from Period II. Ten of the fragments were a more translucent bright blue with white decoration while the other two, find Nos. 1600 and 1601, were a lighter and more opaque greenish-blue. When the results of the glass bracelets were compared to the beads, the silica (SiO_2) levels in the bracelet fragments were much more in line with the levels expected from uncorroded ancient glass which would be around 73%. With the exceptions of find No. 1924, which had a silica concentration of 61.15%, all of the bracelet fragments contained silica levels of between 69.32% and 80.33%. Many also contained low levels of aluminium oxide (Al_2O_3), concentrations which could be reasonably expected in archaeological glass which has not undergone extensive corrosion. This included find Nos. 1578 and 1576 which had 2.67% and 3.51% respectively. The rest of the fragments contained aluminium oxide concentrations of between 6.95% and 22.97%. When looking at the levels of silica and aluminium oxide in these bracelet fragments, it is clear that the correlation between them was considerably weaker than that found in the glass beads, with a correlation coefficient of only 0.6561 (Figure 6). This may be due to the less corroded nature of

these objects. It is unclear what caused the bracelet fragments to survive better than the other glass objects. It is possible that a different glass production method was used for these objects, resulting in an elemental composition more resistant to agents of corrosion. In particularly, it seems that these bracelet fragments were more likely to have higher concentrations of soda (Na_2O). It could also be due to the different relative surface area to volume ratio of the bracelet fragments when compared with that of the beads.

In several examples, the bracelet fragments contained higher concentrations of modifier than other glass objects in this assemblage. Only two of the bracelet fragments, find Nos. 1599 and 1600 did not contain detectable levels of soda (Na_2O) while the other ten contained concentrations of between 2.27% and 7.54%. Potash (K_2O) concentrations ranged from 0.546% to 2.18% for all 12 samples. It seems to be the case that the glass artefacts in these contexts were losing the potash in their surface layers, while soda was surviving to a greater extent, at least in these bracelet fragments. As already discussed, corrosion occurs as preferential leaching of alkali ions to be replace by hydrogen ions, and potash based glasses are more susceptible to this than soda-lime based ones (Wayne Smith 2003, 94).

All 12 of the bracelet fragments contained traces of cobalt oxide (Co_3O_4), ranging from 0.0163% to 0.166%. This would account for their colour as cobalt imparts a strong blue hue to glass even with such small amounts. All of the fragments bar one find also contained varying amounts of copper oxide (CuO) additives, between 0.0063% and 0.129%. Copper oxide can also impart a blue colour to glass but as there was no visible difference between the fragment that did not contain copper and those that did, it was probably not added as a colourant in this case. Tin oxide (SnO_2) was also found in all 12 finds at concentrations of between 0.0581% and 0.731%. This likely caused the opaque white decoration which was present on all the blue bracelet fragments. Finally, the two greenish-blue examples, find No. 1600 and 1601, had higher levels of lead oxide (PbO) than the rest at 1.43% and 2.17% and this may have caused the more opaque appearance compared to the other bracelet fragments.

4.2.4 Miscellaneous fragments

There were four pieces of miscellaneous glass fragments analysed (Plates 11, 12, 13 and 14). Find No. 1609 was a clear vessel rim sherd with a slight hint of a green tinge. It was found in a Period I context. The silica (SiO_2) content of this pierce was found to be 69.56% while the aluminium oxide (Al_2O_3) content was 21.56%. The potash (K_2O) and soda (Na_2O) concentrations for this piece were 0.63% and 3.05% respectively, suggesting that the glass was most likely a mixed alkali glass. The slight green colour in this sherd was caused by the presence of 0.311% iron oxide (Fe_2O_3). Manganese oxide (MnO) was sometimes used as a decolourant to counteract the green caused by iron impurities and produce a clear colour. While this substance is present in this piece, it only accounts for 0.125%. Such a low quantity was probably not purposely added in an attempt to decolour the glass and instead was most likely added unintentionally as part of the modifier that was used. The high level of corrosion in this piece, as can be seen from the high aluminium oxide level and the low level of modifier, further supports it dating to the earliest phase of occupation.

Find No. 1611 was a flat sherd of blue glass which was unstratified. The piece exhibits crizzling of its surface, which appears as small fine cracks on its surface. This was most likely caused by an imbalance of alkali in its surface or by the humidity of the environment of the piece of glass changing suddenly (Bray 2001, 215). Its silica and aluminium oxide concentrations were 74.27% and 2.42% respectively while its concentrations of potash and soda were 0.959% and 9.42% respectively. The bright blue hue it exhibited came from its concentration of cobalt oxide (Co_3O_4) which was 0.0746%. This piece was likely a soda-lime silica glass which may have formed part of a window.

Find No. 1613 was a small sherd of clear glass (Plate 13). Despite its very clear appearance, the visible air bubbles in its structure suggest that it is in fact ancient as these would be removed in the manufacturing process by the high heat which is attainable in modern furnaces. This is unsurprising given that the piece was found in a Period I context. Its silica concentration was 78.71% while its aluminium oxide

concentration was 5.12%. With regards to modifier additives, this piece had 1.15% potash and 3.71% soda. The piece, although very small, appeared slightly curved so it is likely to be vessel glass rather than window glass.

Find No. 1553 was a fragment of blue glass which looked similar to an elongated toggle (Plate 14). Its silica and aluminium oxide concentrations were 67.01%% and 15.11% respectively. Its potash and soda concentrations were 0.646% and 8.26% respectively, indicating that this piece was most likely a predominantly soda-lime based glass. Like the blue beads, this piece contained concentrations of cobalt oxide (Co_3O_4) at 0.0406%, which was responsible for the bright blue hue it exhibited. This piece was unstratified but was most likely produced and utilised around the same time as the Early Medieval blue glass beads due to its similarity in appearance and major and trace elements.

Conclusion

The Lagore glass assemblage contained a rich variety of glass types and exhibited the wide range of skills that ancient glassmakers possessed. The collection of beads included many different shapes and colours which would have required a diverse range of materials to create. The results of the analysis show that there is a mixture of potash-based, soda-lime-based and mixed alkali-based glasses which have undergone varying degrees of corrosion during their time exposed to groundwater while buried underground. Much of the modifier material, potash (K_2O) and soda (Na_2O), have leached away from the surface layers while a disproportionate amount of heavier elements such as aluminium oxide (Al_2O_3) are left behind. By examining the levels of silica versus aluminium oxide, a clear correlation between the two can be observed within this assemblage. Unfortunately it is not possible to analyse uncorroded layers of the objects in this case as it would be necessary to use micro-destructive methods to remove corroded layers from the surface. However there is still much information about the production methods and raw materials of these pieces to be gleaned from the analytical results.

Plain blue beads coloured with cobalt oxide (Co_3O_4) made up by far the largest group, which is unsurprising given that small blue translucent glass beads are some of the most common beads found on Irish Early Medieval sites (Stout and Stout 2008, 65). The decorated blue glass beads made up the second largest group of beads, all of which had tin oxide (SnO_2) in the glass which imparted the opaque white hue. All of the decorated and undecorated blue beads were coloured with oxidised cobalt with the exception of find No. 1557 which was coloured with copper oxide (CuO). This is reflected in its appearance which is considerably lighter than much of the other blue beads. The yellow opaque beads that were analysed were found to be coloured with mixtures of lead oxide (PbO) and tin oxide (SnO_2) while the majority of the white opaque examples were coloured using only tin oxides. The two single green bead examples were significantly different from each other both in appearance and elemental composition. While find No. 1560 had only iron oxide (Fe_2O_3) as a colouring agent, find No. 1561 had significant concentrations of copper oxide (CuO), manganese oxide (MnO) and sulphur oxide (SO_3). Finally the miscellaneous and multi-coloured beads had a wide range of colourants including copper oxides, tin oxides, lead oxides, cobalt oxides, chromium oxides and manganese oxides. The single green toggle that was analysed was similar to find No. 1560, the large greenish ring bead, in that it was coloured solely with iron oxides (Fe_2O_3).

The 12 bracelet fragments were all blue in colour, although two of the pieces, find Nos. 1600 and 1601 were a much lighter and more opaque greenish-blue colour than the rest of the pieces. All 12 pieces contained cobalt oxide, much like the majority of the blue glass beads, which imparted a strong blue colour. The two more opaque finds had relatively high levels of lead oxide which may have contributed to their different colour. The four miscellaneous pieces included two clear finds, a vessel rim sherd and a piece of clear glass with large trapped air bubbles which were both ancient despite having very little signs of colouring or corrosion. The two other miscellaneous finds were a blue piece of glass which may well have been an elongated toggle and a blue window sherd.

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Plate 1: Blue glass beads (Left to right; Find Nos. 1492, 1494, 1499, 1500 and 1502)

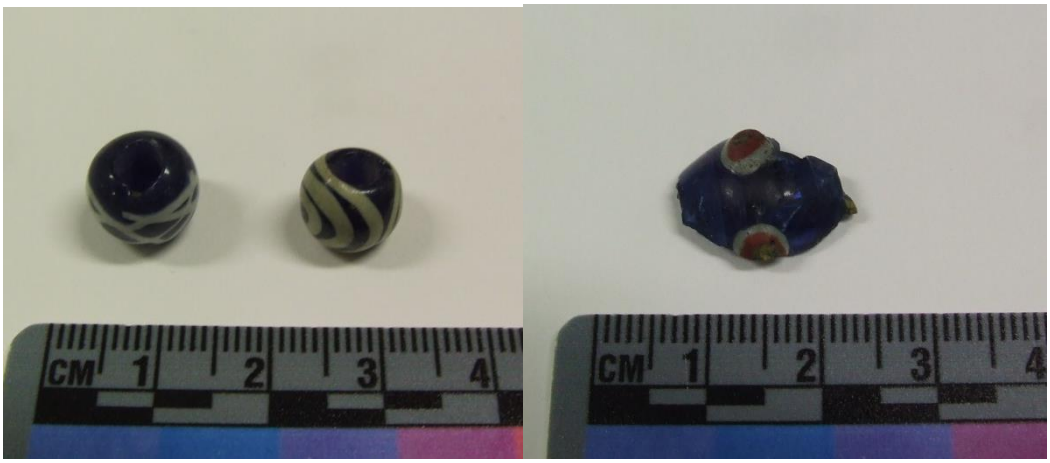

Plate 2: Decorated blue glass beads (Left to right; Find Nos. 1582, 1583 and 1564)

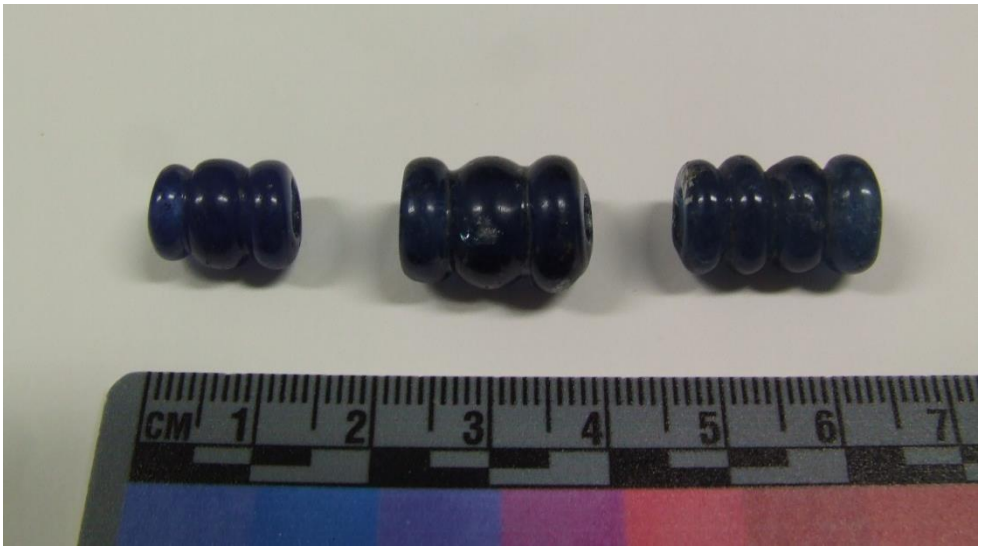

Plate 3: Blue segmented beads (Left to right: Find Nos. 1549, 1550 and 1551)

Plate 4: Yellow opaque beads (Left to right: Find Nos 1518, 1519 and 1520)

Plate 5: White opaque beads (Left to right: Find Nos 1472, 1473 and 1474)

Plate 6: One light green (L: 1560) and one "khaki" green (R:1561)

Plate 7: Polychrome and miscellaneous colours. Clockwise from top: Find Nos. 1456, 1476, 1588, 1530 and 1581

Plate 8: Toggle: Find No. 1563

Plate 9: Blue bracelet fragments; Find Nos. 1576 (top) and 1578 (bottom)

Plate 10: Blue bracelet fragments; Find Nos. 1600 (left) and 1601 (right)

Plate 11: Vessel rim sherd; Find No. 1609

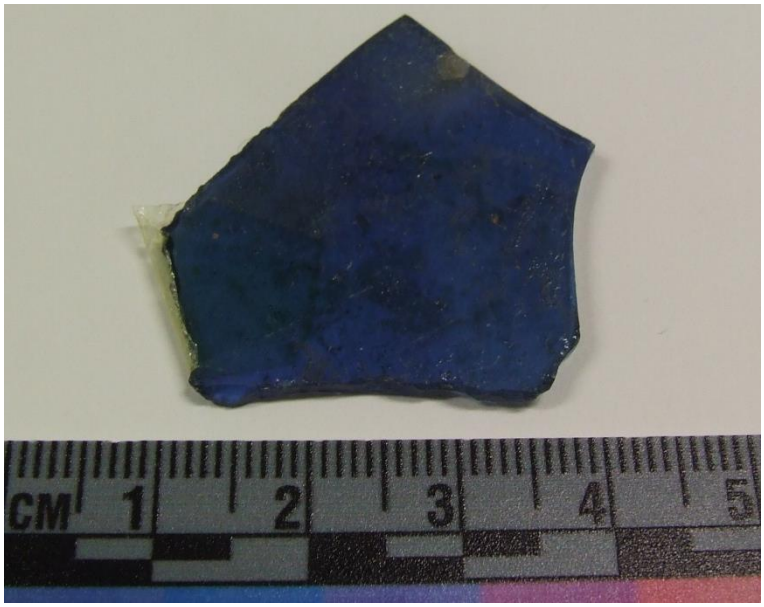

Plate 12: Blue sherd; find No. 1611

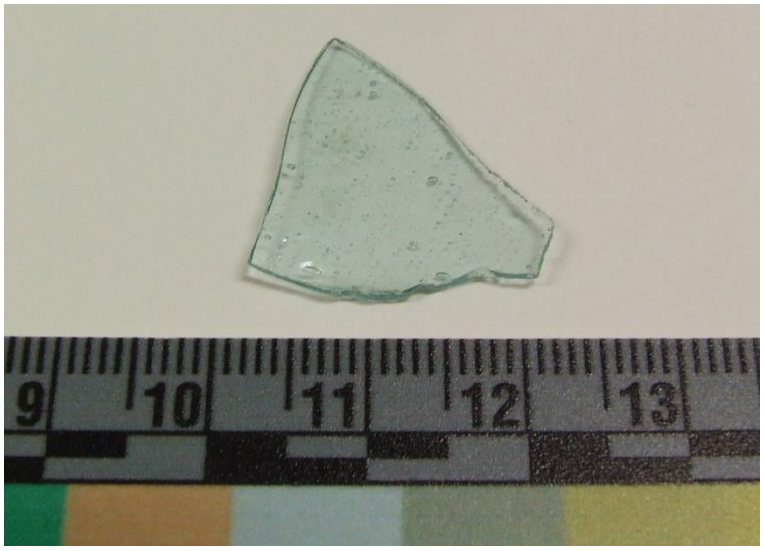

Plate 13: Clear sherd; find No. 1613

Plate 14: Blue glass piece; find No. 1553

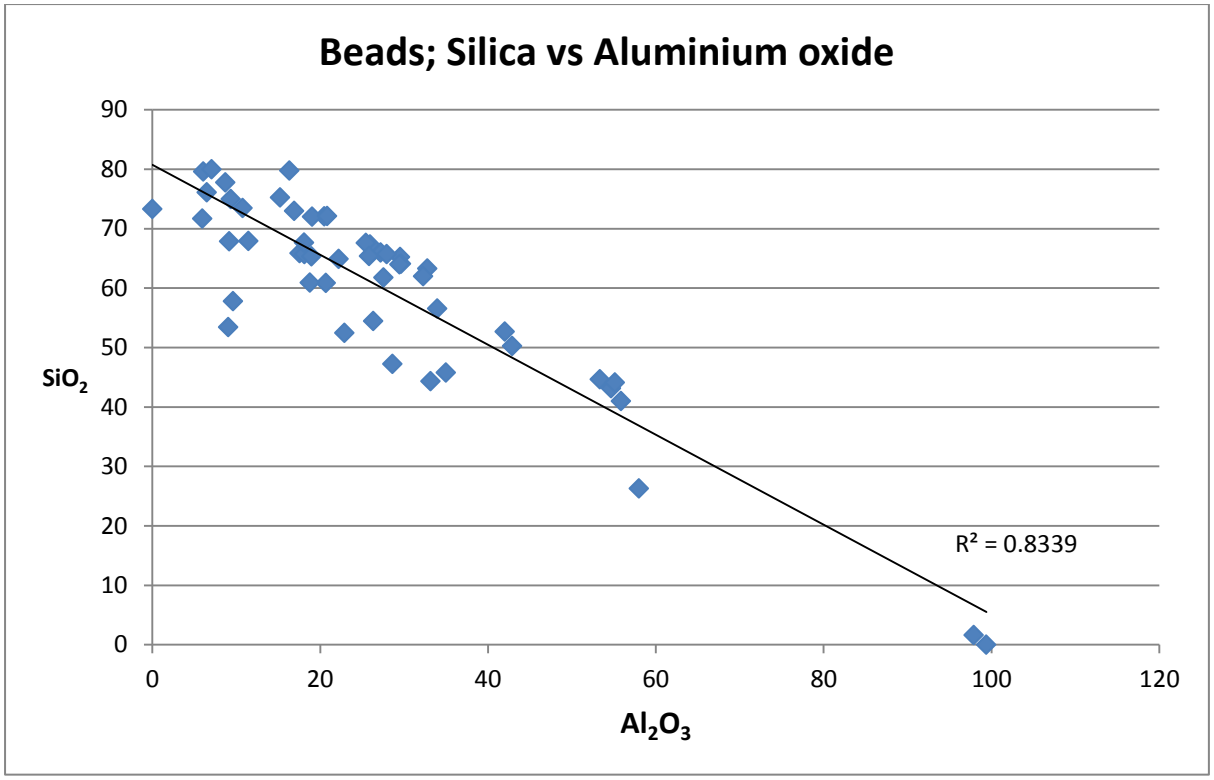

Figure 1: All 50 Lagore beads; silica vs aluminium oxide content

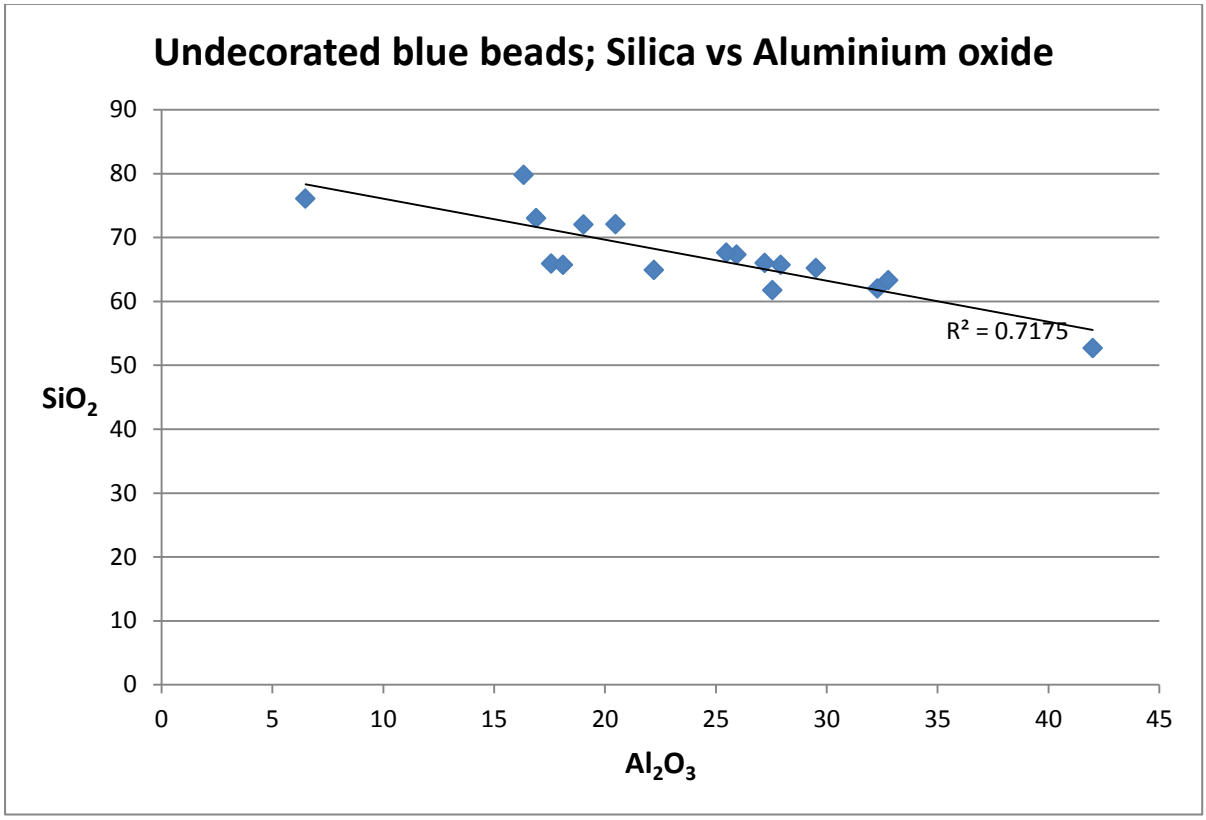

Figure 2: Undecorated blue beads; silica vs aluminium oxide content

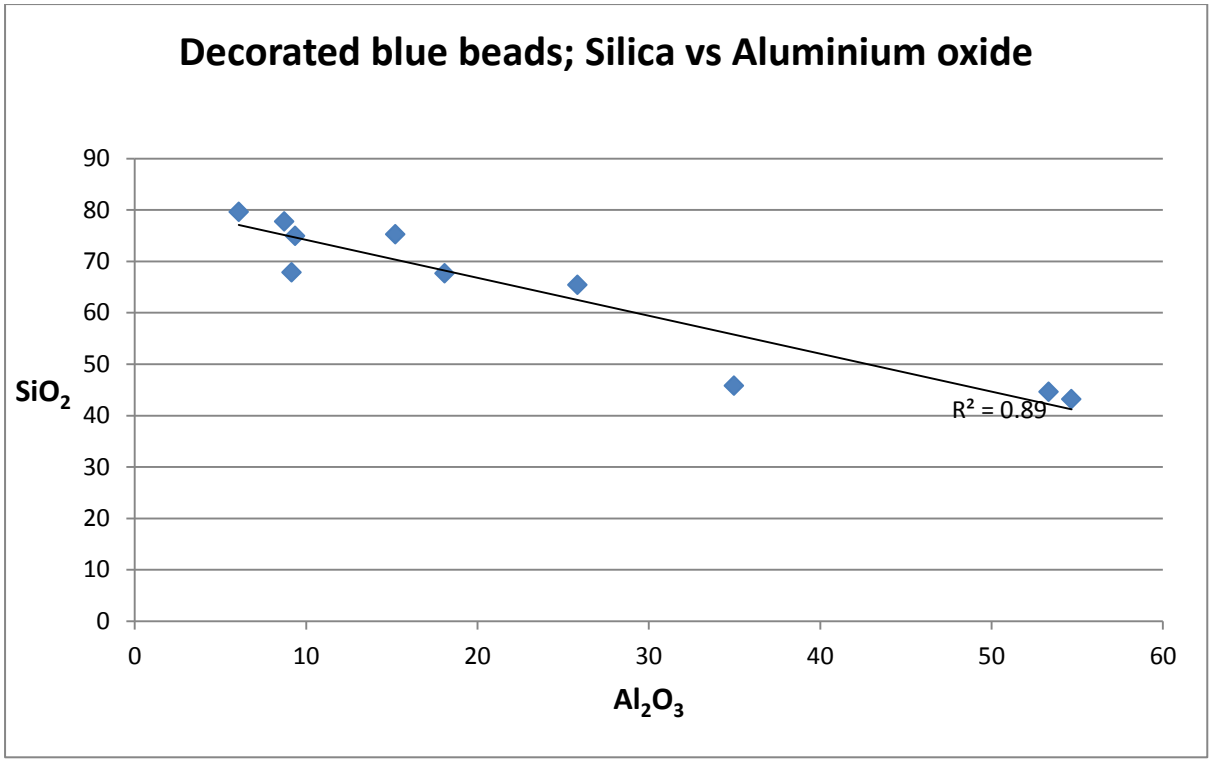

Figure 3: Decorated blue beads; silica vs aluminium oxide content

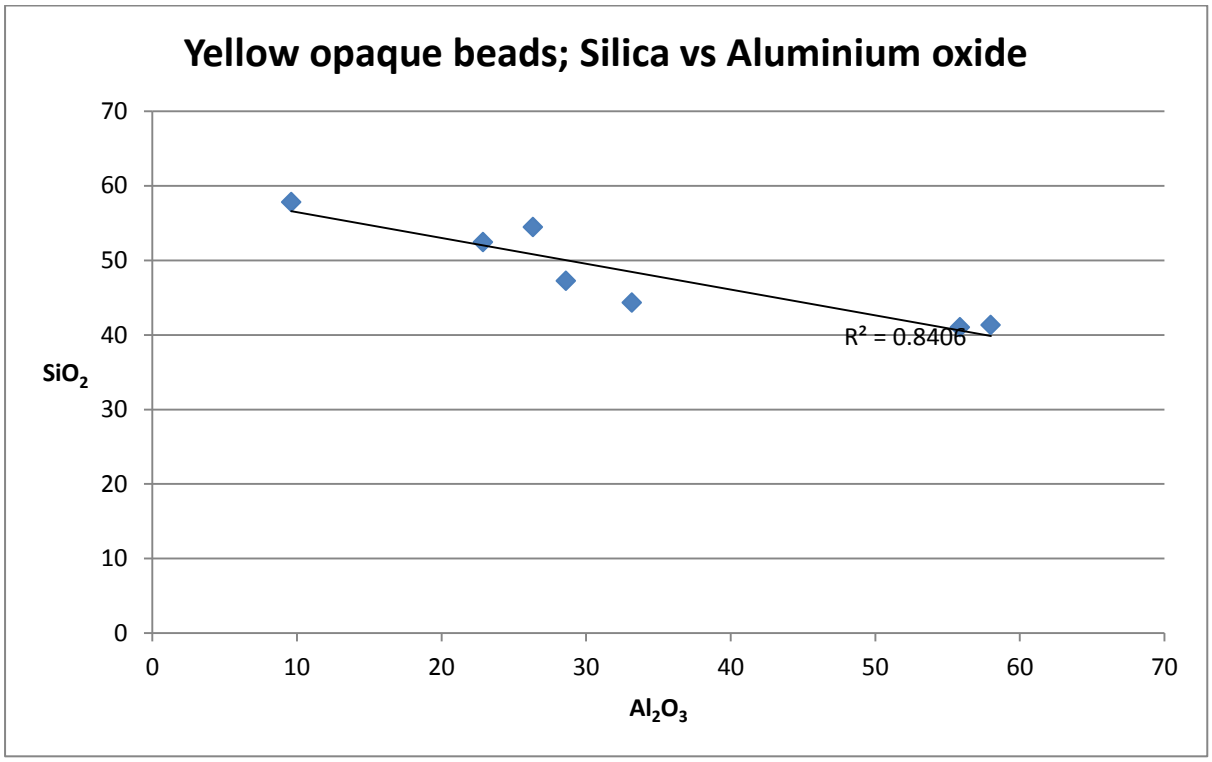

Figure 4: Yellow opaque beads; silica vs aluminium oxide content

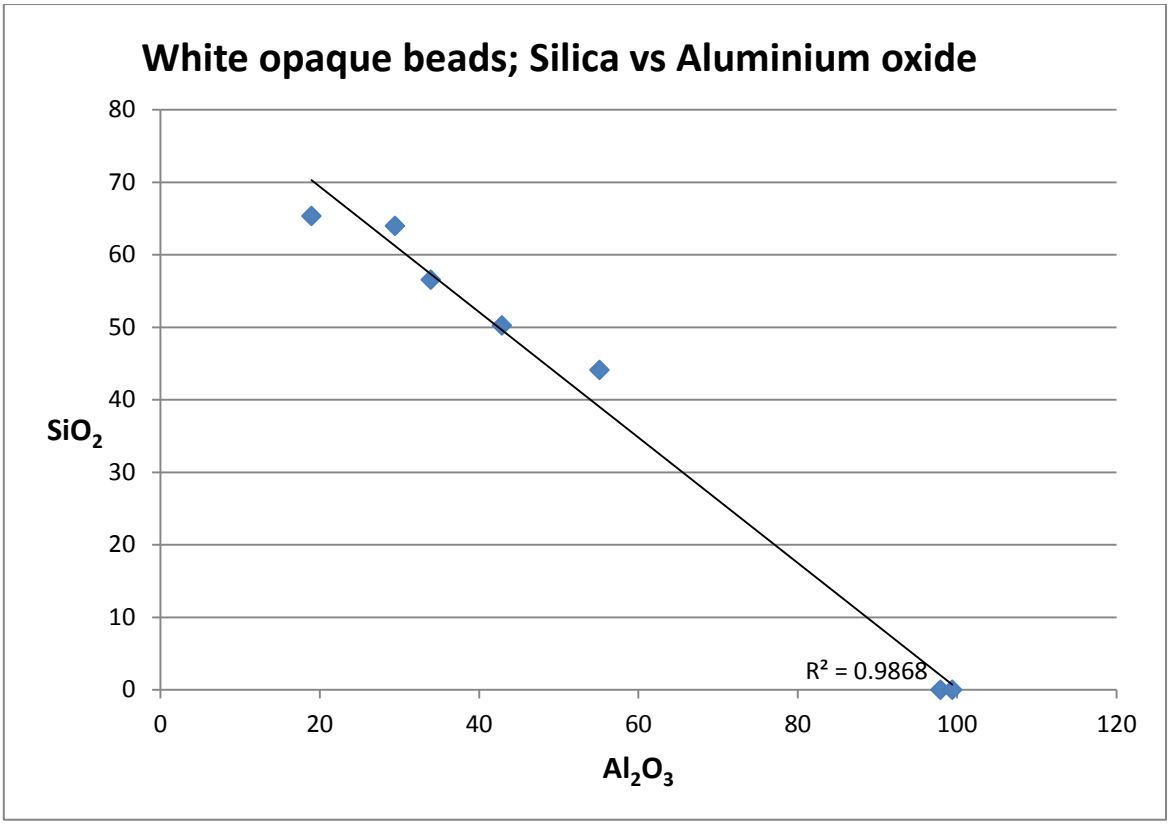

Figure 5: White opaque beads; silica vs aluminium oxide content

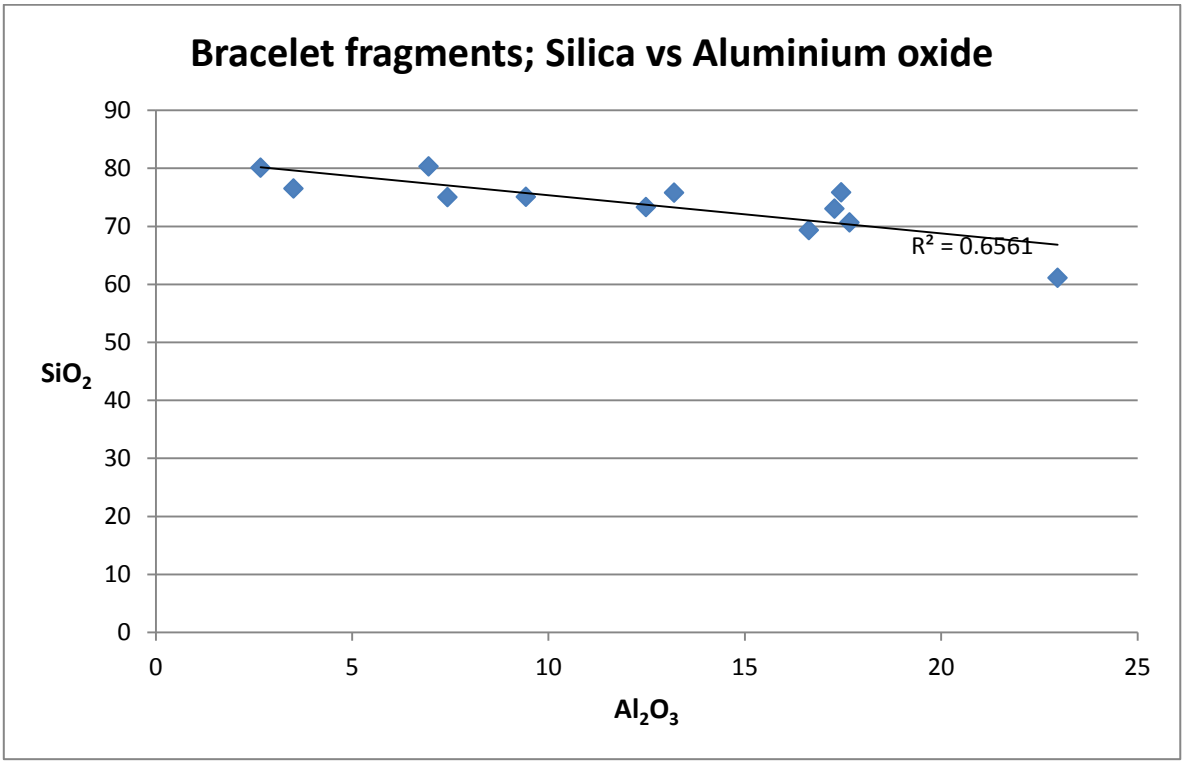

Figure 6: Bracelet fragments; silica vs aluminium oxide content

Appendix 1: Beads (Results given in percentage w/w) (nd = not detected). Context refers to the time periods assigned by Hencken (1950), Period I, II and III.

Excavation No:	E14	E14	E14	E14	E14	E14	E14
Find No.	1456	1457	1469	1470	1472	1473	1474
Description:	*Polychrome bead*	*Blue bead*	*Blue bead*	*Blue bead*	*White bead*	*White bead*	*Bluish white bead*
Context:	*Unstratified*	*Unstratified*	*I*	*Unstratified*	*I*	*II*	*I*
Al_2O_3	20.68	25.84	32.78	27.55	29.45	55.15	18.96
As_2O_3	nd	nd	0.0691	0.104	nd	nd	nd
BaO	0.0065	0.0076	0.0119	0.0108	0.0066	nd	0.006
CaO	5.32	3.90	3.19	3.74	3.12	0.057	4.83
CdO	nd	nd	nd	nd	0.0076	nd	nd
Cl	0.059	1.02	0.442	0.556	0.05	0.128	0.554
Co_3O_4	0.0256	0.0138	0.0783	0.154	nd	nd	nd
Cr_2O_3	0.0055	nd	nd	nd	nd	nd	nd
CuO	0.77	0.268	0.151	0.0768	0.0052	nd	0.0128
Fe_2O_3	1.46	0.562	0.606	0.569	0.227	0.0138	0.466
In_2O_3	nd	0.0063	nd	nd	0.0087	nd	0.0069
K_2O	2.56	0.678	0.525	0.526	0.36	nd	1.05
MnO	0.291	0.156	0.237	0.175	0.13	nd	0.0806
Na_2O	3.11	nd	nd	3.09	nd	nd	4.79
NiO	nd	nd	0.0376	0.0267	nd	nd	nd
OsO_4	0.195	0.043	0.0188	0.046	0.023	nd	0.097
PbO	1.73	0.357	0.171	0.539	0.271	0.0055	1.09
Sb_2O_3	nd	0.398	0.309	0.561	0.174	nd	0.0438
SiO_2	60.86	65.38	63.27	61.74	63.95	44.11	65.34
SnO2	0.98	0.70	nd	nd	nd	0.47	1.89
SO_3	1.07	0.42	0.32	nd	0.25	nd	0.63
SrO	0.0397	0.0243	nd	0.023	0.0204	nd	0.0239
TiO_2	0.203	0.196	0.018	0.0295	0.031	0.0126	0.121
ZnO	0.0647	0.0214	nd	nd	0.0064	0.0218	0.0015

Excavation No:	E14	E14	E14	E14	E14	E14
Find No.	1476	1477	1487	1488	1492	1494
Description:	*Annular bead*	*Blue bead*	*Blue bead*	*Blue bead*	*Blue bead*	*Blue sherd*
Context:	*Unstratified*	*Unstratified*	*Unstratified*	*I*	*Unstratified*	*Unstratified*
Al_2O_3	9.05	29.52	20.48	19.03	27.21	17.57
As_2O_3	nd	nd	nd	nd	0.0452	nd
BaO	0.19	0.011	0.0117	0.0086	0.0122	nd
CaO	13.23	3.33	3.78	4.51	3.68	3.97
Cl	0.071	0.164	0.595	0.683	0.511	0.386
Co_3O_4	0.114	0.0166	0.0185	0.0251	0.0694	0.0579
CuO	0.065	0.0387	0.178	0.233	0.185	0.0372
Fe_2O_3	11.34	0.383	0.498	0.588	0.487	0.604
In_2O_3	nd	nd	0.0095	0.0066	nd	nd
K_2O	0.629	0.998	0.742	0.769	0.49	2.17
MnO	2.97	0.0486	0.2	0.247	0.244	0.255
Na_2O	nd	nd	nd	nd	nd	8.59
NiO	0.0099	nd	nd	nd	0.0091	nd
OsO_4	0.0426	0.0097	0.037	0.055	0.047	0.0197
PbO	0.233	0.113	0.343	0.448	0.335	0.158
Sb_2O_3	nd	nd	0.928	0.822	0.573	nd
SiO_2	53.41	65.20	72.07	72.02	65.97	65.86
SnO2	0.159	0.091	0.0335	0.0378	0.0471	0.0596
SO_3	4.41	nd	nd	0.42	nd	nd
SrO	0.108	0.0225	0.0242	0.0298	0.0293	0.0299
TiO_2	0.586	0.0325	0.0429	0.0446	0.0356	0.0838
ZnO	0.0543	nd	0.0078	0.0092	0.008	0.14

Excavation No:	E14	E14	E14	E14	E14	E14
Find No.	1499	1500	1502	1511	1518	1519
Description:	*Blue bead*	*Blue bead*	*Blue bead*	*Blue bead*	*Yellow glass bead*	*Greenish yellow bead*
Context:	*II*	*II*	*Unstratified*	*I*	*Unstratified*	*Unstratified*
Al_2O_3	32.29	27.92	25.94	18.11	45.86	33.17
As_2O_3	0.0558	0.0152	0.046	nd	nd	nd
BaO	0.012	0.0115	0.0103	0.0075	nd	nd
CaO	2.99	3.54	3.71	5.49	0.471	1.68
Cl	0.398	0.48	0.453	0.28	0.156	0.441
Co_3O_4	0.0961	0.0701	0.106	0.036	nd	0.0141
CuO	0.0982	0.0647	0.073	0.0477	nd	0.0372
Fe_2O_3	0.427	0.475	0.872	0.607	0.0605	0.521
Ga_2O_3	nd	nd	nd	nd	0.0084	0.0206
K_2O	0.572	0.467	0.57	0.439	0.326	0.436
MnO	0.208	0.177	0.256	0.0302	0.0326	0.0559
Na_2O	nd	nd	nd	9.09	nd	nd
NiO	0.0107	nd	0.0198	nd	nd	nd
OsO_4	0.0185	0.0256	0.0231	0.0099	0.213	0.62
PbO	0.189	0.172	0.169	0.0815	1.66	3.71
Sb_2O_3	0.509	0.82	0.312	nd	0.0125	0.265
SiO_2	61.98	65.68	67.31	65.67	40.99	44.29
SnO_2	0.0293	0.0149	0.0202	0.0208	0.145	0.393
SO_3	nd	nd	nd	nd	10.02	14.22
SrO	0.0271	0.0236	0.0252	0.0295	nd	0.0059
TiO_2	0.0626	0.0252	0.0596	nd	0.0215	nd
ZnO	0.0063	0.006	0.0072	nd	nd	0.0065
ZrO_2	0.0081	nd	0.0053	nd	nd	nd

Appendix E: Lagore Crannog, Co. Meath

Excavation No:	E14	E14	E14	E14	E14	E14	E14
Find No.	1520	1523	1524	1526	1527	1528	1529
Description:	*Yellow fragment*	*White bead*	*White bead*	*Blue bead*	*Blue bead*	*Blue bead*	*Yellow bead*
Context:	*Unstratified*	*Unstratified*	*Unstratified*	*Unstratified*	*Unstratified*	*Unstratified*	*II*
Al_2O_3	28.6	97.91	42.89	16.90	22.21	42.00	9.61
As_2O_3	nd	nd	nd	nd	nd	0.0685	nd
BaO	nd	nd	0.0053	0.0133	0.0125	0.011	0.0076
CaO	2.42	0.439	2.66	4.44	3.51	2.76	1.71
Cl	0.736	nd	0.427	0.426	0.172	0.506	1.4
Co_3O_4	0.0218	nd	0.0051	0.0726	0.0131	0.0679	nd
CuO	0.0659	0.0251	nd	0.136	0.173	0.0937	nd
Fe_2O_3	0.496	0.0325	0.2	0.706	0.423	0.388	0.308
Ga_2O_3	0.0139	nd	nd	nd	nd	nd	0.035
In_2O_3	nd	nd	0.0064	0.0062	0.0069	0.0051	nd
K_2O	0.444	0.081	0.351	0.47	0.565	0.553	0.69
MnO	0.182	0.0226	0.131	0.255	0.216	0.169	0.131
Na_2O	nd	nd	nd	2.43	6.62	nd	nd
NiO	nd	nd	nd	nd	nd	0.0163	nd
OsO_4	0.545	nd	0.0142	0.0473	0.041	0.0264	1.39
PbO	3.01	0.0805	0.148	0.277	0.382	0.166	8.37
Sb_2O_3	0.357	0.0736	0.0694	0.638	0.651	0.431	0.0346
SiO_2	47.21	nd	50.23	72.99	64.87	52.64	57.8
SnO_2	0.271	0.787	2.77	0.0572	0.0548	0.0274	0.615
SO_3	15.54	0.46	nd	nd	nd	nd	17.71
SrO	0.0166	nd	0.0162	0.0291	0.0229	0.0228	0.0099
TiO_2	0.0538	0.0286	0.0204	0.0726	0.0427	0.0321	0.0751
ZnO	0.0073	0.0158	0.0104	0.0066	0.0087	0.0096	nd
ZrO_2	nd	nd	nd	0.0073	nd	nd	nd

Appendix E: Lagore Crannog, Co. Meath

Excavation No:	E14	E14	E14	E14	E14	E14
Find No.	1530	1549	1550	1551	1552	1556
Description:	*Polychrome bead*	*Segmented blue bead*	*Segmented blue bead*	*Segmented blue bead*	*White bead*	*Blue bead*
Context:	*Unstratified*	*I*	*Unstratified*	*Unstratified*	*Unstratified*	*Unstratified*
Al_2O_3	5.97	29.64	7.05	20.85	33.97	54.67
As_2O_3	0.0339	nd	nd	nd	nd	nd
BaO	0.133	0.0058	0.0249	0.0105	0.0116	nd
CaO	3.97	3.12	6.37	3.76	2.98	0.443
Cl	0.155	0.401	0.897	0.503	0.464	0.298
Co_3O_4	0.0792	0.0259	0.0497	0.0158	nd	0.0197
Cr_2O_3	0.0246	nd	nd	nd	nd	nd
CuO	0.119	0.0677	0.215	0.15	0.0238	0.0188
Fe_2O_3	0.0902	0.38	1.21	0.448	0.361	0.0803
In_2O_3	nd	0.0069	nd	0.0092	0.0171	0.0069
K_2O	4.32	0.795	1.03	0.52	0.583	0.071
MgO	nd	nd	nd	nd	nd	nd
MnO	0.888	0.183	0.507	0.183	0.383	0.0226
Na_2O	9.68	nd	1.31	nd	nd	nd
NiO	nd	nd	nd	nd	nd	nd
OsO_4	0.105	0.0159	0.086	0.0225	0.069	nd
PbO	0.475	0.19	0.612	0.169	0.519	0.0789
Sb_2O_3	nd	0.665	0.395	0.708	0.0626	0.183
SiO_2	71.66	64.09	79.96	72.13	56.55	43.17
SnO_2	nd	0.0212	0.0783	0.0228	3.89	nd
SO_3	nd	0.33	nd	0.42	nd	0.63
SrO	nd	0.0185	nd	0.0227	0.0214	nd
TiO_2	nd	0.0346	nd	0.0443	0.0654	0.057
ZnO	1.26	0.007	nd	0.0077	0.0052	nd

Appendix E: Lagore Crannog, Co. Meath

Excavation No:	E14	E14	E14	E14	E14	E14
Find No.	1557	1558	1559	1560	1561	1564
Description:	*Blue bead*	*Blue polychrome bead*	*Blue bead fragment*	*Green bead*	*Plain "khaki" bead*	*Blue fragment*
Context:	*Unstratified*	*I*	*Unstratified*	*Unstratified*	*I*	*II*
Al_2O_3	25.47	6.07	6.49	nd	10.76	9.16
As_2O_3	nd	nd	0.0148	nd	nd	nd
BaO	0.0115	0.0207	0.024	0.0495	0.0363	0.0114
CaO	2.39	5.5	7.91	8.79	6.51	6.24
Cl	0.606	0.627	0.47	0.441	0.973	0.917
Co_3O_4	nd	0.0315	0.0507	nd	nd	0.0401
Cr_2O_3	nd	nd	nd	nd	nd	nd
CuO	0.062	0.255	0.163	nd	0.051	0.161
Fe_2O_3	0.73	0.771	0.837	0.314	0.542	0.73
In_2O_3	nd	0.009	nd	nd	nd	nd
K_2O	1.09	1.21	0.823	5.79	0.752	1.92
MgO	nd	nd	nd	4.97	nd	nd
MnO	0.368	0.375	0.0629	0.231	1.07	0.0951
Na_2O	nd	nd	6.56	3.11	4.44	10.59
NiO	nd	nd	0.0092	nd	nd	0.0069
OsO_4	0.0162	0.149	0.038	nd	nd	0.085
PbO	0.148	1.22	0.35	nd	nd	0.776
Sb_2O_3	0.11	0.761	nd	nd	0.0149	nd
SiO_2	67.59	79.59	76.07	73.28	73.44	67.85
SnO_2	0.0092	0.796	0.0091	nd	nd	0.173
SO_3	1.21	2.46	nd	nd	1.17	1.09
SrO	0.0333	0.0365	0.05	0.0179	0.0626	0.0367
TiO_2	0.107	0.0911	0.0738	0.029	0.12	nd
ZnO	0.0095	0.0114	0.0058	0.0128	nd	0.0111

Appendix E: Lagore Crannog, Co. Meath

Excavation No:	E14	E14	E14	E14	E14	E14
Find No.	1581	1582	1583	1584	1588	1589
Description:	*Polychrome fragment*	*Blue bead*	*Blue bead*	*Yellow bead*	*Polychrome bead*	*Yellow and green bead*
Content:	*Unstratified*	*Unstratified*	*II*	*Unstratified*	*Unstratified*	*II*
Al_2O_3	11.47	15.21	93.34	26.33	18.77	28.88
As_2O_3	nd	0.0165	0.0079	nd	nd	nd
BaO	0.0159	0.0138	nd	0.0066	0.0455	0.0063
CaO	5.10	4.68	0.284	3.20	4.02	1.56
Cl	0.515	0.655	0.132	0.612	0.584	0.526
Co_3O_4	0.0075	0.106	0.0081	nd	0.0145	0.0079
Cr_2O_3	nd	nd	0.0114	nd	nd	nd
CuO	nd	0.191	0.0154	0.0065	0.172	0.0541
Fe_2O_3	0.891	0.69	0.0587	0.30	1.42	0.232
In_2O_3	nd	0.0093	0.0081	nd	nd	nd
K_2O	1.13	0.688	0.125	0.563	0.98	0.728
MnO	0.235	0.292	0.0197	0.174	0.402	0.0767
Na_2O	6.73	nd	nd	4.63	12.08	3.06
NiO	nd	nd	nd	nd	nd	nd
OsO_4	0.19	0.054	nd	0.249	0.0369	0.66
PbO	1.79	0.41	0.0399	2.01	0.24	3.86
Sb_2O_3	0.0595	0.697	0.175	0.0884	0.0373	0.411
SiO_2	67.93	75.23	4.64	54.45	60.92	52.42
SnO_2	1.31	0.901	0.403	0.019	0.181	0.267
SO_3	1.69	nd	0.63	4.23	nd	7.16
SrO	0.0272	0.0328	nd	0.0139	0.0268	0.0072
TiO_2	0.0785	0.0963	0.0228	0.0749	0.0505	0.044
ZnO	0.0157	0.0083	0.0228	0.0148	0.0081	nd

Appendix E: Lagore Crannog, Co. Meath

Excavation No:	E14	E14	E14	E14	E14	E14	E14
Find No.	1590	1592	1595	1596	1618	1620	1931
Description:	*Decorated bead*	*Blue bead fragment*	*Green/Blue melon bead*	*Blue bead fragment*	*White bead*	*Yellow bead*	*Blue bead*
Context:	*II*	*Unstratified*	*Unstratified*	*Unstratified*	*Unstratified*	*II*	*Unstratified*
Al_2O_3	34.98	8.72	16.34	18.09	99.40	58.00	9.36
As_2O_3	nd	nd	nd	nd	nd	nd	nd
BaO	0.02	0.014	0.0098	0.0148	nd	nd	0.0125
CaO	5.56	5.84	0.836	5.81	0.039	0.831	6.46
Cl	1.52	0.89	0.381	0.931	0.155	0.281	0.63
Co_3O_4	0.0258	0.0448	0.0076	0.0236	nd	nd	0.0409
Cr_2O_3	nd	nd	nd	nd	0.013	0.0079	nd
CuO	0.397	0.18	0.928	0.0742	nd	0.0117	0.0798
Fe_2O_3	0.875	0.958	0.332	1.06	nd	0.136	1.18
In_2O_3	0.0145	0.0124	nd	nd	nd	nd	nd
K_2O	1.16	0.961	0.691	1.08	nd	0.297	2.12
MnO	0.34	0.334	nd	0.284	nd	0.025	0.123
Na_2O	nd	1.63	nd	3.10	nd	nd	2.56
NiO	nd	nd	nd	nd	nd	0.0057	0.0064
OsO_4	0.096	0.069	nd	0.081	nd	0.278	0.0319
PbO	0.664	0.477	nd	0.467	0.0053	2.15	0.278
Sb_2O_3	1.03	0.872	nd	0.0072	0.0057	0.0131	nd
SiO_2	45.78	77.74	79.76	67.63	nd	41.28	74.94
SnO_2	0.876	1.06	0.176	nd	0.298	0.089	nd
SO_3	0.74	nd	0.419	1.07	nd	5.22	1.78
SrO	0.041	0.0387	0.0112	nd	nd	nd	0.0687
TiO_2	5.84	0.128	0.1	0.169	nd	nd	0.218
ZnO	0.0236	0.0106	0.0057	0.0088	0.026	nd	0.0093

Appendix 2: Glass bracelet fragments (Results given in percentage w/w) (nd = not detected)

Excavation No:	E14	E14	E14	E14	E14	E14
Find No.	1572	1573	1574	1576	1578	1598
Description:	*Blue bracelet fragment*	*Blue bracelet fragment*	*Blue bracelet fragment*	*Blue bracelet fragment*	*Blue bracelet fragment*	*Blue bracelet fragment*
Context:	*I*	*II*	*I*	*Unstratified*	*Unstratified*	*Unstratified*
Al_2O_3	7.43	13.20	6.95	3.51	2.67	9.43
As_2O_3	0.149	nd	0.106	0.138	0.0876	nd
BaO	0.0146	0.0089	0.0241	0.0216	0.0138	0.0336
CaO	6.86	4.91	5.63	7.41	6.33	6.68
Cl	0.419	0.465	0.521	0.504	3.72	1.33
Co_3O_4	0.0782	0.0358	0.122	0.129	0.0679	0.081
CuO	nd	0.11	0.0169	0.129	0.0153	0.0186
Fe_2O_3	0.354	0.551	0.682	0.693	0.518	0.871
In_2O_3	nd	0.0071	nd	0.0053	nd	nd
K_2O	1.08	0.546	1.56	1.35	1.22	1.28
MnO	0.319	0.215	0.59	0.364	0.291	0.881
Na_2O	7.54	3.1	2.27	6.89	3.65	3.31
NiO	0.115	nd	0.0236	0.0458	0.0091	nd
OsO_4	0.026	0.0256	0.106	0.133	0.128	0.0411
PbO	0.107	0.198	0.53	0.787	0.69	0.202
Sb_2O_3	0.0907	0.638	0.11	0.347	0.179	0.127
SiO_2	75.02	75.81	80.33	76.51	80.12	75.11
SnO_2	0.261	0.0731	0.239	0.87	0.157	0.314
SO_3	nd	nd	nd	nd	nd	nd
SrO	0.0411	0.0264	0.0414	0.0502	0.041	0.0536
TiO_2	0.0699	nd	0.131	0.0952	0.0798	0.198
ZnO	nd	0.0055	0.008	nd	0.0061	0.0085

Excavation No:	E14	E14	E14	E14	E14	E14
Find No.	1599	1600	1601	1603	1604	1924
Description:	*Blue bracelet fragment*	*Blue bracelet fragment*	*Blue bracelet fragment*	*Blue bracelet fragment*	*Blue bracelet fragment*	*Bracelet fragment*
Context:	*Unstratified*	*Unstratified*	*Unstratified*	*Unstratified*	*Unstratified*	*Unstratified*
Al_2O_3	17.46	17.29	16.64	17.67	12.49	22.97
As_2O_3	nd	0.104	0.0148	0.0779	0.153	0.0111
BaO	0.0056	0.0162	0.0069	0.0068	0.0106	0.0053
CaO	3.28	3.54	4.13	3.81	5.14	4.12
Cl	0.289	0.46	0.584	0.412	0.696	0.796
Co_3O_4	0.0345	0.0601	0.0163	0.0677	0.166	0.108
CuO	0.102	0.0089	0.0063	0.0633	0.032	0.0886
Fe_2O_3	0.495	0.411	0.408	0.317	0.529	0.499
In_2O_3	0.008	nd	nd	nd	nd	0.0054
K_2O	1.03	2.18	0.95	0.782	1.69	1.02
MnO	0.184	0.205	0.241	0.211	0.253	0.17
Na_2O	nd	nd	3.82	4.73	3.56	5.44
NiO	nd	0.0595	0.0065	0.0196	0.0301	nd
OsO_4	0.0379	0.258	0.338	0.079	0.139	nd
PbO	0.212	1.43	2.17	0.458	0.706	1.34
Sb_2O_3	0.603	0.115	nd	0.126	0.147	0.331
SiO_2	75.87	73.07	69.32	70.65	73.34	61.15
SnO_2	0.0581	0.666	0.249	0.45	0.731	0.259
SO_3	0.27	nd	0.93	nd	nd	1.41
SrO	0.0215	0.0289	0.0226	0.0193	0.0305	0.0151
TiO_2	0.0335	0.0771	0.0749	0.0385	0.134	0.0838
ZnO	0.0054	nd	0.0051	nd	nd	0.0113

Appendix 3: Glass toggle and miscellaneous fragments (Results given in percentage w/w) (nd = not detected)

Excavation No:	E14	E14	E14	E14	E14
Find No.	1563	1609	1611	1613	1553
Description:	*Green toggle*	*Vessel rim sherd*	*Blue glass fragment*	*Blue-grey body sherd*	*Blue glass rod*
Context:	*Unstratified*	*I*	*Unstratified*	I	*Unstratified*
Al_2O_3	55.11	21.56	2.42	5.12	15.11
BaO	0.0109	0.01	0.0114	0.0055	0.0148
CaO	1.88	4.44	8.04	9.41	6.21
Cl	0.191	0.178	0.83	0.62	0.647
Co_3O_4	nd	nd	0.0746	0.0122	0.0406
CuO	nd	0.0101	0.315	0.0193	0.0816
Fe_2O_3	0.0737	0.311	1.11	0.73	0.881
K_2O	0.204	0.63	0.959	1.15	0.646
MnO	0.0634	0.125	0.456	0.235	0.845
Na_2O	nd	3.05	9.42	3.71	8.26
OsO_4	nd	nd	0.094	0.0099	nd
PbO	nd	0.0162	0.533	0.0424	0.071
Sb_2O_3	nd	0.018	1.26	0.0247	0.006
SiO_2	42.27	69.56	74.27	78.71	67.01
SnO_2	nd	nd	0.048	nd	0.0443
SrO	0.0137	0.0257	0.0555	0.0675	0.0519
TiO_2	0.015	0.0405	0.0763	0.11	0.0477
ZnO	0.0171	nd	0.0088	0.0059	0.0081
ZrO_2	nd	nd	0.0095	0.0109	nd

Appendix F: Analysis of glass from Kilteasheen, Knockvicar, Co. Roscommon, excavation number 05E0531

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1. Introduction

This report details the analysis of a number of glass fragments and glaze covered stones which were uncovered during excavations at Kilteasheen, Knockvicar, Co. Roscommon. The multi-elemental analysis was carried out using X-ray Fluorescence (XRF) at I.T. Sligo. The aim of this analysis was to determine trace elements within the glass objects which could potentially answer questions about their origin or production. A total of 27 glass pieces and eight stones with glaze on their surface were analysed. The site which was excavated at Kilteasheen is known as the "Bishop's Seat", a Late Medieval ecclesiastical site. The site was known to date to 1253 from records in the annals and excavations revealed a complex site with evidence of activity from the Neolithic, Bronze Age and Early and Late Medieval. The high status of this site is evident from the numerous times it is mentioned in annals from the 13th century, its strategic location alongside the Boyle River and its association with the O'Conor kings in Connacht. The excavations were run for five seasons as part of the Kilteasheen Archaeological Project which was led by Mr. Christopher Read from the Institute of Technology, Sligo and Dr. Thomas Finan from St. Louis University (Read 2010, 41, 45, 66).

2. Methodology

2.1. Sample collection and selection

The glass fragments from excavations at Kilteasheen were provided by Chris Read from the Institute of Technology, Sligo for the purpose of this study. The samples were chosen from the Kilteasheen glass assemblage, with a number of objects being excluded. For example, a number of other glazed stone pieces from the site had to be excluded from the analysis as they were either too large to fit in the XRF or their surfaces were too flaky. In total, 35 pieces of glass and glazed stones were analysed using XRF analysis. This included eight pieces of glazed stone, five beads or fragments of beads, 2 pieces of black glassy material and 20 sherds of glass of various colours, 11 of which were found during field-walking. A table detailing the

glass pieces which were analysed as well as a brief description can be seen in Appendix 1 at the end of this report and the glazed stones which were analysed can be seen listed in Appendix 2.

2.2. Calibration/Quality Control

The XRF was calibrated monthly using the standard procedure for this instrument. The accuracy of the instrument is also tested regularly using standard glass reference material. Table 1 below illustrates the accuracy and precision of the instrument using a standard sample. The sample was run 5 times and an average taken of the results.

	Stated concentration (%w/w)	**Average obtained (%w/w)**	**Relative Standard Deviation%**	**%Error**
SiO_2	72.26	72.62	0.360	0.503
Na_2O	13.78	12.88	1.399	-6.516
CaO	10.05	10.71	0.598	7.000
MgO	3.40	3.64	2.423	-0.0549
SO_3	0.270	0.027	9.658	-90.074
TiO_2	0.033	0.0237	7.413	-28.121
Fe_2O_3	0.021	0.0177	4.058	-15.619

Table 1: Reference sample results obtained

(nd = not detected, nc = not calculated)

2.3. Sample washing and preparation

A solution consisting of a 1:1 ratio of deionised water and 99% ethanol solution was prepared in a volumetric flask. The surface of each sample was gently cleaned using a clean cotton swab dipped in the deionised water/ethanol solution prior to being analysed in the XRF. The purpose of this technique was to remove surface

contamination on the surface of the glass. Different trace elements can be left on the glass from many processes such as salts left behind from washing with ordinary water or chlorine transferred from handling the samples with bare hands. By removing such elements, a clearer result of the elemental composition of the surface layers of the glass can be obtained. The above washing method was decided in consultation with the National Museum of Ireland after extensive experimentation on modern glass samples. The samples were left to dry completely before undergoing analysis. All samples were handled using gloves to avoid adding any further surface contamination.

2.4. Testing of samples

Each sample was analysed by XRF in triplicate and the results averaged. Samples were analysed in the condition they were received with no preparation method utilised aside from the washing technique outlined above. XRF was chosen for this analysis as it provides a highly sensitive, multi-elemental analysis and is completely non-destructive. XRF is a surface technique, therefore the elemental composition it gives is indicative of the surface layers only and this may not be an accurate representation of the whole sample.

3. Results

The results of the analysis (given in percentage w/w) can be seen in Appendices 1 and 2 at the end of this report. The first shows the results from the 28 glass samples, while the second shows the results from the eight pieces of glazed stone that were obtained during this study.

Discussion

4.1 Condition of samples

The majority of the glass analysed from this site, with the exception of a blue glass bead found in F532 in Cutting J, consisted of small fragments. However the condition of the surface of these glass pieces was very good for the most part. The only piece that exhibited visible signs of corrosion of the surface layers was the find from C15 in Trench C which had a heavily corroded gold-coloured layer on its surface. This layer was beginning to flake away from the main body of glass.

4.2 Elemental Composition

From ancient times, glass has been consistently made up of a glass former, such as sand or quartz pebbles (SiO_2), a modifier, such as soda (Na_2O) or potash (K_2O), and a stabilizer such as lime ($CaCO_3$). As well as this, glass may contain a variety of colouring agents, opacifiers and other trace elements, added either intentionally or unintentionally (Goffer 2007, 124). From an analytical point of view, the composition of ancient soda-lime glass is typically 73% SiO_2 (silica), 23% Na_2O (soda) and 5% CaO (calcium oxide) (Gratuze and Janssens 2004, 605). Potash (K_2O) may have been added to the mixture instead of soda, or sometimes a mixture of the two was used as a modifier substance. Generally, the lowest concentrations which would have been added would have been at least 15% (Shortland 2012, 101).

4.2.1 Thin bead fragments; Cutting B, context F98, find nos. 1772. 1773 and 1774

These three small thin bead fragments, find Nos. 1772, 1773 and 1774, were uncovered from Cutting B (Plate 1). They were associated with burial no 11, a juvenile burial and found near the mid spine, abdomen and cervical vertebrae respectively. The three samples can be seen in Plate 1. Given the close proximity of these beads to the burial remains, it seems likely that they were interred as part of the grave and may have significance to the burial.

The main components of these three glass pieces were silica (SiO_2) and aluminium oxide (Al_2O_3). Silica accounted for 61.75%, 59.52% and 61.5% of finds 1772, 1773 and 1774 respectively while the aluminium oxide concentration for the three pieces was 22.58%, 26.01% and 21.7% respectively. The high level of aluminium oxide in these three pieces would indicate that they had undergone heavy leaching or corrosion of elements in their surface layers. Corrosion in glass is a complex mechanism which is not well understood as it is affected by many different factors. However it is thought to occur due to the preferential leaching of alkali ions in the surface to be replaced by hydrogen ions (Wayne Smith 2003, 94). The reaction begins at the surface of the object and spreads inwards (Varshneya 1994, 398). Cox and Ford (1993, 5639-43) conducted a detailed elemental study of multiple layers of medieval glass and concluded that corroded surface layers can be depleted of most oxides except silica (Si), aluminium (Al) and iron (Fe), and what is left behind is poorly crystalline hydrated silicates and aluminosilicates with varying amounts of calcium (Ca), phosphate (P) and manganiferous (Mn) minerals. When glass is buried, ground water and other environmental factors can interact with the material affecting the stability of the object. Signs that a glass fragment may have undergone corrosion can sometimes be apparent from the visual appearance of the glass. It may develop an iridescent sheen on its surface or the outer layers may begin to crust and flake away. This is essentially a "leached" layer where the ratios of the elements are significantly altered from the bulk glass (Henderson 2013, 614). However in some cases, such as can be seen with these three thin bead fragments, there was no visual evidence of corrosion on the glass. Despite their appearance however, it is clear from the elemental analysis that these pieces have been significantly affected by corrosion.

These pieces of glass also had very low quantities of modifier. Modifier, either soda (Na_2O) or potash (K_2O), can be up to *c.* 23% for ancient glass. Generally, the lowest concentrations which would have been added would have been at least 15%. However, these fragments had concentrations of between 4.20% and 4.72% potash and had no detectable quantities of soda. Soda, potash or a mixture of the two was an essential component when producing glass in ancient times. It acted as a flux, lowering the melting point of silica from 1700°C to 1000°C, a temperature which was

obtainable in ancient furnaces (Goffer 2007, 115). While it is difficult to tell for certain what type of modifier was used in this piece based on the trace amounts remaining in it, it is likely that it was a potash-based glass. As the burials in Cutting B were typically medieval (Read 2010, 58), it is not surprising to see that glass associated with them was typical of glass found from this time period in Ireland. Potash glass became increasingly popular during the medieval period when demand for glass was growing and there was incentive to search for a more readily accessible alkali source (Moran 2010, 17). Potash would have been sourced from wood ash as opposed to soda which was generally retrieved from marine plants. While corrosion may affect glass for a number of reasons, such as environmental factors, the most important factor in most cases is the original elemental composition of the glass. This determines the resistance of the glass to agents which can cause corrosion such as water, acidic and basic solutions and other atmospheric substances (Pollard and Heron 2008, 166). With regards to medieval window glass for example, it has been noted that potash-based examples were more susceptible to weathering than soda-based examples due to the high alkalinity of the glass (Moran 2010, 17).

The blue colour of these bead fragments was caused by concentrations of between 0.0489% and 0.0655% cobalt oxide (Co_3O_4). Cobalt is a powerful colorant which was used in ancient glass, which would impart a bright blue hue to the glass even in very small quantities. Blue tones ranging from bluish green to a very pale blue could also be achieved by adding cupric oxide (CuO) (Bhardwaj 1979, 42-43), however there was no copper detected in any of these three pieces. As previously discussed the major elemental compositions of the pieces were very similar and in addition to this, the concentrations of the trace elements were closely matched. In addition, many of the concentrations of trace elements were very closely matched in the three pieces. For example they all contained similar amounts of arsenic oxide (As_2O_3), iron oxide (Fe_2O_3), lead oxide (PbO) and sulphur oxide (SO_3), as can be seen in Appendix 1. This would suggest that the three pieces all came from the same source.

4.2.2 Lightweight glassy material; Cutting F, pieces from F13, find Nos. 318 and 319

These two samples of lightweight glassy material were both found in Cutting F, from context F13. Find No. 319 can be seen in Plate 2. Cutting F contained burials, the earliest of which dated to the 7th century AD. The large numbers of prehistoric lithic finds from medieval layers at this site suggest that these finds, or soils that contained them, were moved here from elsewhere. This could have been to cover burials and Cutting F in particular had dump layers associated with the burials (Read 2010, 52). It is possible that the two pieces of glassy material may also have been introduced from elsewhere, particularly given their small size. This also makes it difficult to speculate on what their original function would have been. Since the dump layers are associated with the burials, they may have been introduced to the site at any time when burial was taking place on the site from the 7th to the 13th century. While the latest burials in Cutting F have not been dated, the layout of them suggests that they could represent some of the earliest burials on the site (Read 2007). Both pieces of glass were noticeable for their light weight and both had a blackish colour underneath a caked layer of dirt on their surface. The caked dirt was removed from the small area of each piece that was analysed. The silica (SiO_2) contents for these two pieces were 61.54% and 66.22% respectively while the aluminium oxide (Al_2O_3) contents were 15.44% and 18.16% respectively. With regards to the modifier used, these samples contained no detectable amounts of soda (Na_2O) and only trace amounts of potash (K_2O) with 3.61% and 4.94% respectively. Like the thin glass bead fragments which were discussed in the previous section, these were most likely composed of potash-based glass which has corroded after being buried for so long.

A black colour in glass can be caused by a variety of factors, such as an abundance of coal in the glass furnace, which adds carbon to the mixture (Varshneya 1994, 217). As XRF cannot detect elements lighter than sodium, carbon would not be detected in the elemental results. Black glass was purposely produced in the Post-Medieval in Britain using a specific mixture of elements in the glass melt. Examples of black glass were known to have been produced by combining iron, manganese and sulphur in

the glass melt and coupling this with a smoky atmosphere in the furnace (Davidson 2008, 77). These two finds had high levels of iron oxide (Fe_2O_3) at 14.8% and 8.66% respectively and levels of manganese oxide (MnO) in concentrations of 0.211% and 0.0316% respectively, although neither had any sulphur oxide (SO_3) detected during their analysis. It is probable that the dark colour was caused by a reaction of these substances with carbon in the furnace during the production of the glass.

4.2.3 Olive glass fragments; Cutting I, find No. 08256 and six pieces from F387

A number of olive green glass sherds were uncovered from Cutting I including find No. 08256 and six pieces from F387. Cutting I was located outside the wall of the hall-house and F387 was a stone collapse associated with the demolition of the hall-house which was spread over the entirety of the cutting (Read 2008). Find No. 08256 can be seen in Plate 2 and the largest three pieces from F387 can be seen in Plate 4. All of the pieces looked similar and were visually in good condition, exhibiting no signs of corrosion. The silica content (SiO_2) for six of these seven pieces ranged between 64.27% and 69.00% although find No. 5 from F387 exhibited an unusually low amount at 40.08%. The aluminium oxide concentration was between 9.38% and 21.07% for six of the pieces with find No. 5 again proving the exception with 53.01%. All the pieces contained a mixture of both soda (Na_2O) and potash (K_2O), with the exception of find No. five which contained only potash with a concentration of 0.384%. The soda concentrations for the other six pieces ranged from 2.48% to 6.77%. The potash concentrations for the seven ranged from 0.384% to 1.18%. The small amounts of both soda and potash detected in these finds suggests they may well have been formed from a mixed alkali glass type. A mix of potash and soda could have been added intentionally or it may have been accidental. For example, potash sources may occasionally contain traces of soda (Shortland 2012, 101). It is also possible that cullet (broken pieces of glass) may have been used when producing the glass, and this would further complicate the elemental composition of the mixture.

All of these olive green sherds show significant concentrations of iron oxide of between 0.639% and 2.32%. There are a few different causes of an olive or yellow-green hue in glass. The first was caused by the presence of trace amounts of sulphur oxides (SO_3) within the glass which, in conjunction with iron oxides will cause an olive colour (Freestone 2009, 81). None of these samples contained any detectable amount of sulphur however. Another factor is the oxidation state of the iron oxides. The presence of iron in the glass, whether intentional or as an accidental contaminant, causes a green colour. When the iron content is high in iron (II) the colour is green, but when the iron is present in mainly iron (III) form, the glass will exhibit a more yellow-green colour (Fenzi *et al.* 2010, 331). This would suggest that there may have been an oxidising environment in the glass furnace at time of production which would have allowed the iron to oxidise into iron (III). This would imply that the glass-makers either intentionally wanted to produce olive green glass, that there was little control over the flow of air into the furnace or that this factor was not considered particularly important in this case.

Overall, these pieces of olive glass from Cutting I had very similar compositions with regards to what major and trace elements they contained, albeit having been affected to different extents by corrosion. They have the typical appearance, colour and elemental composition of bottle glass, most likely produced in the Post-Medieval period based on their composition and the amount of corrosion that their surface layers have undergone. Find No. five appeared to have similar elements present as the other six pieces although the quantity of these elements had been severely altered by corrosion. This would suggest that it originally had a similar composition to the other pieces, however its surface layers had undergone corrosion to a much greater degree than the other pieces. Piece 5 was one of the smaller pieces and it was also a considerably thinner than any of the other six pieces. This may have made it more susceptible to corrosion than the glass pieces. Visually, all the olive-coloured pieces from this context were very similar to each other and there was no outwardly sign of corrosion on any of them. Find No. five does appear to be thinner than the other fragments however, so perhaps this may have contributed to it being affected by corrosion to a much greater extent than the other pieces.

4.2.4 Blue glass fragment; Cutting J, piece from F451, find No. 1779

This small blue glass fragment was found in Cutting J, which was in the interior of the hall-house. The find may have been part of a bead originally and can be seen in Plate 5. It had a silica (SiO_2) concentration of 65.48% and its aluminium oxide (Al_2O_3) concentration was 20.55%. This elevated level of aluminium oxide would suggest that the piece had undergone considerable corrosion. With that in mind, the level of soda (Na_2O) which was detected in this piece, 6.65%, was quite significant. It suggests that this glass piece was produced using soda-based glass, as this type of glass is more resistant to weathering than potash-based examples.

The blue colour in this fragment was caused by the presence of highly oxidised cobalt (Co_3O_4) (Gratuze and Janssens 2004, 665). The small concentration of just 0.0315% was responsible for the bright blue hue that this piece exhibits. Cobalt is the most effective transition metal when used as a colourant in glass and typical levels of cobalt oxide in ancient soda-lime-silica glass are often around 0.05% (Henderson 2000, 29). The other blue bead, from context F532, which was analysed and which will be discussed in Section 4.2.5 was also coloured with cobalt. However, it seems likely that the source of cobalt for the two pieces was different, based on other trace elements that they contain. In modern glass, this would not be apparent due to the fact that refined cobalt would be used. However, in archaeological glass, it would have been cobalt-bearing ores that would have been used and these would add different trace elements based on the source. For example, trianite ($2Co_2O.CuO.6H_2O$) would add trace amounts of copper (Cu) to the glass mix while skutterudite ($As_2(Co.Ni.Fe)$) would add nickel and arsenic (Henderson 2000, 30). As can be seen from the results, while this glass fragment from F451 contained no detectable traces of nickel or arsenic, it did contain 0.117% copper oxide (CuO). The blue bead from F532, conversely, contained a lower amount of copper oxide at 0.0893% and also contained traces of nickel oxide (NiO) and arsenic oxide (As_2O_3) with 0.0256 and 0.0608% respectively. It seems likely therefore that one piece had cobalt obtained from skutterudite while the other had cobalt from trianite.

4.2.5 Blue bead; Cutting J, find from F532, find No. 1779

This blue bead was found in F532, which was also located in Cutting J inside the hall house (Plate 5). The silica (SiO_2) and aluminium oxide (Al_2O_3) were 52.96% and 41.8% respectively, which would suggest a high level of corrosion in the surface layers of the glass. This is further highlighted by the amounts of modifier it contains, with no detectable amounts of soda (Na_2O) and only 0.377% potash (K_2O). Like the blue glass fragment from F532 which was discussed in the previous section, the blue colour of this piece was caused by the presence of cobalt oxides (Co_3O_4) in its structure with 0.0462% present.

4.2.6 Corroded sherd, Find from Trench C, context C15

This piece of glass, as seen in Plate 6, is the only sherd analysed from this assemblage which exhibits signs of heavy corrosion in the form of a crusting gold layer on its surface. The silica (SiO_2) concentration of this was in line with what would be expected of ancient glass at 71.56%. Its aluminium oxide (Al_2O_3) concentration, while higher than expected at 9.38%, was not particularly high compared to the other glass fragments which were visually in better condition. This highlights how the visual appearance of glass is not always a good indication of the level of corrosion it has suffered.

This piece contains a significant amount of iron oxide (Fe_2O_3) at 5.09% which would suggest that its colour prior to developing the thick layer of corrosion was most likely a deep bottle green. The iron oxide content of this glass is typical of the type of glass used to produce bottle glass during to the Post-Medieval and later. Bottle glass was cheaply manufactured and widely used during the Post-Medieval. The glass used for making bottles was almost always of a lower quality that that of other vessels and usually had a very dark green colour, caused by varying iron impurities (Roche 2007, 411).

4.2.7 Field-walking 1: Dark green body sherd

The first of the pieces discovered during field-walking was a thick dark green body sherd, most likely from a bottle. This can be seen in Plate 7 along with the second and third pieces from field-walking. Many of the fragments of glass that were found during field-walking appear modern, however this piece looked as though it could be older as it was thicker and darker green than the other pieces. Its silica (SiO_2) concentration was 62.38% and its aluminium oxide (Al_2O_3) was 9.52%. Its concentrations of soda (Na_2O) and potash (K_2O) were 1.37% and 0.533%. The bottle green colour it exhibited was caused by its concentration of iron oxide (Fe_2O_3) at 2.23%. Its composition would suggest typical low-quality bottle glass, quite possibly Post-Medieval given that the surface layers have undergone a great deal of corrosion.

4.2.8 Field-walking 2: Clear bottle neck sherd

This piece consisted of the neck sherd of a clear glass bottle (see Plate 7). Its silica (SiO_2) and aluminium oxide (Al_2O_3) concentrations were 71.87% and 5.41% respectively, while the modifier consisted of 7.67% soda (Na_2O) and 1.15% potash (K_2O). These concentrations would suggest a soda-lime-silica glass which has had time to corrode. Iron oxide in glass, even in very small amounts, will add a green colour to the glass so in clear glass it is likely that the glassmakers made every effort to eliminate iron contaminants to as high a degree as possible (Almirall 2001, 67). The clear sherds from this site had the lowest concentrations of iron oxide (Fe_2O_3) which is not surprising. This particular piece had 0.424%. However it is very difficult to remove iron impurities from the raw materials of glass so there will usually be at least some amount of iron remaining. In archaeological glass, clear glass is very likely to contain some type of decolourant as there just was not the same ability to remove iron impurities from the sand as exists today (Goffer 2007, 120). This particular glass piece contains traces of arsenic oxide (As_2O_3) and manganese oxide (MnO) at concentrations of 0.0916% and 0.109%, both of which could have acted as

decolourants. This piece also contains the highest quantity of lead oxide (PbO) of any of the glass fragments at 0.641% which causes a higher density in the glass as well as lowering the softening temperature (Moorey 1999, 207). Overall, the level of corrosion in this piece, coupled with its concentrations of decolourants and trace elements may suggest a Post-Medieval or early modern date as opposed to a more recent one.

4.2.9 Field-walking 3: Clear sherd

This clear sherd contained concentrations of 70.26% (SiO_2), 5.46% aluminium oxide (Al_2O_3), 10.34% soda (Na_2O) and no detectable amounts of potash (K_2O). It had only 0.171% iron oxide (Fe_2O_3) and contained no concentrations of any elements which would have acted as decolourants. It also had very few trace elements within its structure, which would suggest a modern date. It had likely been exposed to the elements for some amount of time given that there is some evidence of corrosion based on the aluminium oxide and soda concentrations being slightly elevated and somewhat too low respectively. This highlights the fact that this particular sherd was modern, as a much wider and higher percentage of trace elements would be expected in the composition of glass produced in ancient furnaces where it was much harder to exclude impurities. Although a small fragment, its shape would suggest that it came from a sheet of window glass.

4.2.7.10 Field-walking 4: Green base sherd

This piece of glass came from the base of a bottle and was similar in appearance to the first piece of glass recovered from field-walking (Plate 8). Its silica (SiO_2), aluminium oxide (Al_2O_3), soda (Na_2O) and potash (K_2O) concentrations were 65.15%, 5.43%, 3.12% and 1.48% respectively. Like the first green sherd from field-walking, the bottle green colour of this sherd was caused by the presence of iron oxide (Fe2O3) at 1.64%. This piece contains low levels of soda and potash in the

surface layers and a wide variety and quantities of trace elements which would suggest that it consisted of low-quality bottle glass, most likely dating to the Post-Medieval period, as with the other green piece from field-walking.

4.2.7.11 Field-walking 5: Thin green sherd

This piece of glass had a similar green hue to that of the field-walking pieces numbers 1 and 4, however it was thinner than those two pieces (Plate 8). The silica (SiO_2), aluminium oxide (Al_2O_3), soda (Na_2O) and potash (K_2O) concentrations of this piece were 63.25%, 17.27%, 2.34% and 0.39% respectively. Its iron oxide (Fe_2O_3) concentration, which was the cause of its green colour, was 1.16%. Like those pieces, it most likely came from low quality glass bottle. Its elemental composition suggested that it had corroded to a greater extent than the other two pieces, given the higher level of aluminium oxide and lower levels of potash and soda. There are several potentially reasons for this, the most probable being that it had a considerably different elemental composition than the others which was more susceptible to corrosion. However it could also have simply been due to it being considerably thinner than the other two pieces.

4.2.7.12 Field-walking 6: Green sherd

This sherd had a light shade of green (Plate 8). It contained concentrations of 64.11% silica (SiO_2), 10.49% aluminium oxide (Al_2O_3), 4.83% soda (Na_2O) and 2.14% potash (K_2O). It had 1.32% iron oxide (Fe_2O_3) which as mentioned already will cause a green colour in glass. Unlike the other green pieces, it also contained concentrations of chromium oxide (Cr_2O_3) which would have also contributed to its green hue and is likely the reason that the piece looks a noticeably different shade of green. Given its composition and high levels of iron oxide, it most likely came from a low quality glass bottle.

4.2.7.13 Field-walking 7: Clear sherd with slight green tinge

This sherd had percentages of silica raw materials closest in line with what would be expected from a modern soda-silica glass which did not have time to degrade to the same extent as some of the other samples (Plate 9). It had a composition of 73.79% silica and 11.11% soda, which was in line with the results obtained from analysing the standard sample, which had results of 72.26% silica and 13.78% soda. Its aluminium oxide (Al_2O_3) was also very low compared to some of the other finds at only 0.936%. Its slight green tinge was caused by levels of iron oxide in its structure at 1.32%. This sherd was also noticeable for containing very few trace contaminants which, like field-walking find No. 3, would make it unlikely that this piece had any archaeological significance. Its flat shape overall and slight curve along its edge which may have been where it was fitted into a pane would suggest that this piece was originally part of a sheet of window glass. It is possible that this piece came from the same source as field-walking find No. 3.

4.2.7.14 Field-walking 8: Clear sherd

This clear sherd had a composition which is typical of modern soda-lime-silica glass at 69.8% silica (SiO_2) and 13.7% soda (Na_2O). It did not contain any detectable amount of potash (K_2O). Its aluminium oxide (Al_2O_3) level, while slightly high at 5.79%, was much lower than many of the other pieces uncovered at the site. It contained a very low concentration of iron oxide (Fe_2O_3) at 0.0411% and only very small amounts of trace elements which can be seen in Appendix 1. This piece was undoubtedly a modern sample given the uncorroded nature of its surface layers and the lack of trace elements in its structure which would have been impossible to exclude in an ancient furnace. Unfortunately, its small size makes it difficult to determine what its original function may have been.

4.2.7.15 Field-walking 9: Clear sherd with slight green tinge

This sherd had percentages of silica (SiO_2) and aluminium oxide (Al_2O_3) of 70.5% and 11.65% respectively (Plate 9). It contained 8.81% soda (Na_2O) and no detectable amounts of potash. Its slight green tinge was caused by levels of iron oxide in its structure at 0.186%. This concentration of iron oxide was higher than that found in any of the other clear sherds which resulted in a noticeable green tinge in this piece. It also appears to have undergone corrosion to a greater degree as can be seen in the relatively high aluminium content and relatively depleted concentration of modifiers. When compared with other clear sherds such as field-walking find No. 8, it appears that this sherd is both older and of lower quality. For example, the soda concentration of field-walking find no 8 was 13.7% while this piece only contains 8.81% in comparison. This piece also had a higher level of aluminium oxide than the 5.79% detected in field-walking find No. 8, suggesting that it had undergone corrosion in its surface layers to a greater degree. It is difficult to determine what its original function might have been, given its small size. However, since it is flat, it is possible that it was a sherd of window glass.

4.2.7.16 Field-walking 10: Clear sherd with slight purplish tinge

This clear sherd contained concentrations of 84.9% silica (SiO_2), 10.57% aluminium oxide (Al_2O_3), 0.483% potash (K_2O) and no detectable amounts of soda (Na_2O) (Plate 9). It had only 0.0394% iron oxide (Fe_2O_3). The slight purplish tinge to the glass may have been caused by the small concentration of manganese oxide (MnO) which at 0.0488%, was the highest concentration of manganese in any of the clear samples. In many cases, manganese can be added unintentionally to the glass mix as impurities found in raw materials that were sourced (Wilson 1855, 261). It was sometimes added intentionally as a decolourant in glass production as it masks the green colour caused by iron, however, when used on its own without significant levels of iron, it gives a purple colour (Goffer 2007, 121). The use of a decolourant and the levels of corrosion in this piece would suggest that it was not modern. Most likely it was Post-

Medieval in date, like the second piece of glass found during field-walking. It appeared to be a rim sherd of some kind, although the angle of this small remaining piece would suggest that the original piece was not cylindrical.

4.2.7.17 Field-walking 11: Small cloudy colourless piece

This small piece (Plate 9) had concentrations of 68.20% silica (SiO_2), 26.77% aluminium oxide (Al_2O_3), 0.221% potash (K_2O) and no detectable concentration of soda (Na_2O). Its iron oxide (Fe_2O_3) was 0.257% and it also contained traces of arsenic oxide (As_2O_3) and manganese oxide (MnO) at concentrations of 0.114% and 0.024% respectively. It seems likely that this piece, similar to the field-walking find No. 2, was possibly Post-Medieval in date, given that it not only had traces of decolourant elements in it but also showed corrosion in its surface layers. This piece was too small to come to any conclusions as to what its original function may have been.

4.2.8 Glazed stones

A total of eight stones with glaze were analysed as part of this study. Three of these samples were found in Cutting I, which was located outside the wall of the hall house. Two more were found in Cutting K. The final three were located in Cutting C, Cutting D and Cutting G. A list of the stones analysed can be seen in Appendix 2 and the eight stones can be seen in Plates 10, 11, 12 and 13. While the function of these pieces is not clear, it appears that they were formed when molten glass dropped on to stones. It could potentially be waste glass from glass production or pottery glazing. However, such material will generally be found in greatest concentration near the furnaces on sites where glass-working has taken place (Taylor and Hill 2008, 249). This makes it unlikely that they were made as part of glass-working on this site.

The silica (SiO_2) concentrations for these stones were between 51.6% and 83.77% while the aluminium (Al_2O_3) concentrations were found to be between 8.65% and

42.76%. Again, this concentration is elevated in many of the glazed stone finds and this was probably an effect of corrosion on the surface layers of the object. Only five of the eight finds had detectable amounts of soda (Na_2O) with concentrations of between 2.08% and 8.54%.The level of potash (K_2O) for these all eight of the finds was between 2.00% and 6.51%. The results would suggest that five of the eight may have been a mixed alkali type. However as the majority of the modifier which the surface layers would have contained when the glass was first produced has been leached away, it is impossible to say for sure. All eight of these glazed stones contain iron oxides (Fe_2O_3), with concentrations of between 0.97% and 3.17%. This was again likely an unintentionally contaminant added in with the raw materials used. The only evidence that the glassmakers attempted to manipulate the colour of this glass material was the fact that seven of the eight glazed stones also contained trace concentrations of copper oxide (Co_3O_4) of between 0.010% and 0.041% which could potentially have acted as a colourant. However these traces were in such small concentrations that it is possible that this was added in unintentionally as part of the raw materials of the glass. There was no detectable amounts of lead oxide (PbO) in any of the glazed stones, a compound which was commonly found in pottery glazes (Henderson 2000, 126). However, evidence from 11th and 12th century sites in the UK showed that glaze was sometimes "splashed" onto the pot which would account for the spilling of glaze onto the stones at this site. Since the elemental composition and material characteristics are much the same for pottery glazes as they are for glasses, it is difficult to say with any certainty where the glaze on these stones came from.

Conclusion

The XRF analysis suggests a mixture of soda-lime, potash-based and mixed alkali-based glasses from a number of different time periods which have been subjected to varying degrees of corrosion due to being exposed to groundwater over time. This has caused alkalis such as potash and soda in the surface to leach away, leaving a disproportionate amount of heavier elements such as aluminium behind. It can be seen that the visual condition of the objects is not a good indication of the level of

corrosion that has undergone. Unfortunately it is impossible to know what the original composition of these objects would have been without utilising more destructive methods in order to expose non-corroded layers deeper in the finds.

The three bead fragments uncovered from the burial in Cutting B, find Nos. 1772, 1773 and 1774 were heavily corroded pieces of glass, most likely potash-based, with their blue colour having come from their concentrations of cobalt oxide. Their composition is typical of glass found from the medieval period in Ireland. The lightweight black glassy material, also from Cutting F, from context F13 also appeared to be potash-based glass. However these pieces do not seem to have been purposely deposited for a specific reason, unlike the thin blue fragments which were included as grave goods in the burial context.

The seven olive glass fragments from Cutting I were composed of a mixed-alkali glass and coloured by the presence of iron oxides. The small blue glass fragment found in F451 in Cutting J was a piece of soda-based glass, coloured by highly oxidised cobalt. The other piece of blue glass from this assemblage, found in F532 in Cutting J, appeared to be potash-based instead of soda-based, and the trace elements it contained suggested that a different source of cobalt was used for this piece. The sole piece of glass, from context C15 in Trench C, appeared to be a piece of Post-Medieval bottle glass. The high iron content of this piece would suggest that it was originally a very dark green colour. Of the 11 pieces of glass uncovered during field-walking, eight of them have compositions which suggest that they could possibly be Post-Medieval. Three of the pieces are undoubtedly modern, given their lack of corrosion and lack of trace elements in their structure.

The glazed stones could potentially be waste glass from glass production or from the production and application of glazes to pottery, and were most likely formed when molten glass or glaze fell on them.

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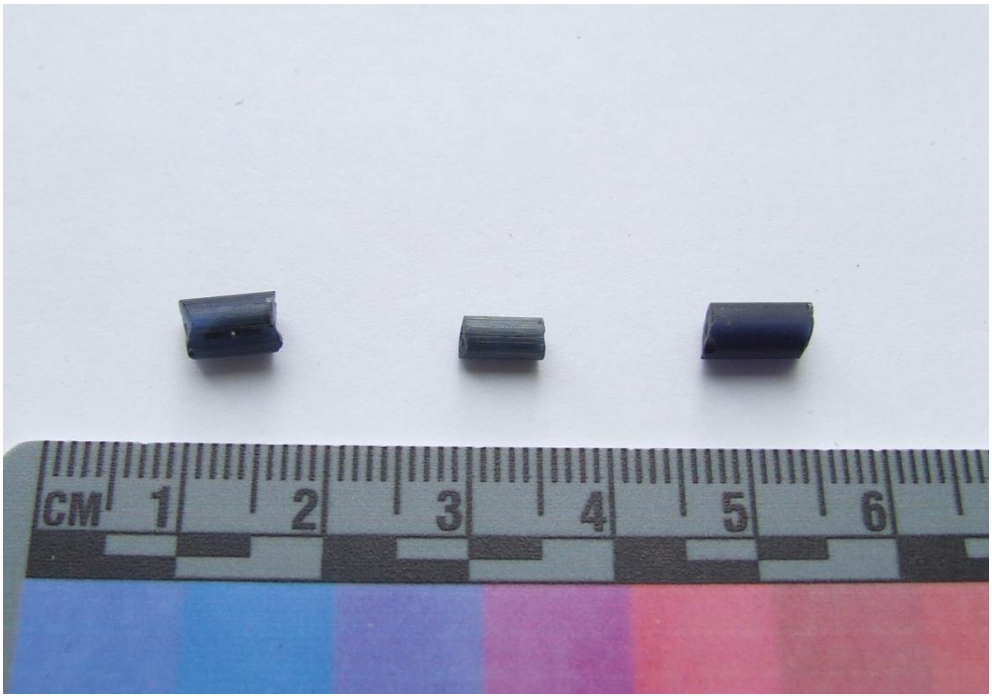

Plate 1: Thin blue glass bead fragments from Cutting B

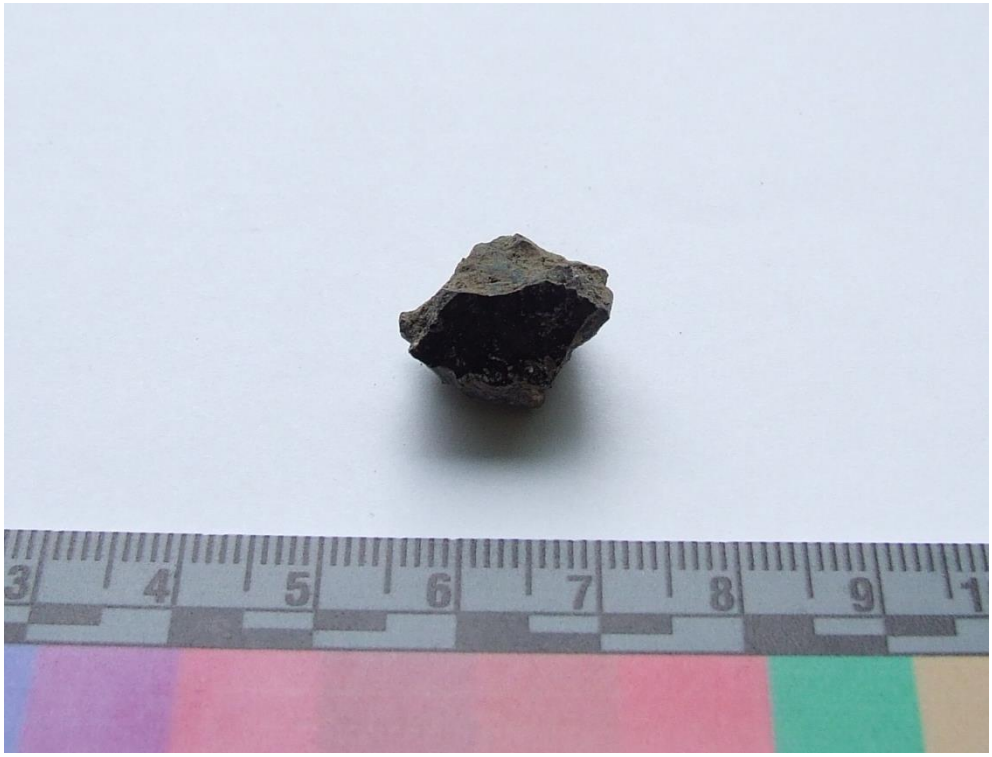

Plate 2: Lightweight black glassy material from F13 in Cutting B

Plate 3: Find No. 08256, olive green glass sherd

Plate 4: The largest three pieces of olive glass uncovered from F387

Plate 5 Blue bead from F532 (left) and bead fragment from (F451)

Plate 6: Corroded sherd from Trench C, context C15

Plate 7: Field-walking finds numbers 1, 2 and 3 (left to right)

Plate 8: Field-walking finds numbers 4, 5 and 6 (left to right)

Plate 9: Field-walking finds no 7, 8, 9, 10 and 11 (left to right)

Plate 10: Glazed stones from Cutting C, Cutting D and Cutting G (left to right)

Plate 11: Glazed stone from Cutting I, context F1

Plate 12: Glazed stones from Cutting I, from topsoil (left) and F387 (right)

Plate 13: Glazed stones from Cutting K, from C1(left) and F568 (right)

Appendix F: Kilteasheen, Knockvicar, Co. Roscommon

Appendix 1: Glass results (Results given in percentage w/w) (nd = not detected)

Cutting:	Cutting B	Cutting B	Cutting B:	Cutting F	Cutting F	Cutting I	Cutting I	Cutting I	Cutting I
Feature:	F98/Br11	F98/Br11	F98/Br11	F13	F13		F387 (1)	F387 (2)	F387 (3)
Find No:	1772	1773	1774	318	319	08256	08087	08087	08087
Description	Thin bead fragment	Thin bead fragment	Thin bead fragment	Light glassy material	Light glassy material	Thick olive green sherd	Olive glass sherd	Olive glass sherd	Olive glass sherd
Al_2O_3	22.58	26.01	21.7	15.44	18.16	12.34	9.76	9.38	9.76
As_2O_3	0.0348	0.0295	0.0446	nd	nd	0.0569	0.0412	0.0425	0.0661
BaO	0.116	0.0639	0.129	0.0345	0.0211	0.0451	0.024	0.0331	0.0606
Bi2O3	0.0949	0.169	0.0984	nd	nd	nd	nd	nd	nd
CaO	8.64	7.88	9.67	2.84	1.79	13.21	10.71	11.05	13.47
Cl	0.211	0.262	0.248	nd	nd	nd	nd	0.265	0.146
Co_3O_4	0.0489	0.0544	0.0655	0.203	0.067	0.0231	nd	nd	0.0272
Cr2O3	nd	nd	nd	0.0125	nd	nd	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe_2O_3	0.41	0.338	0.49	14.8	8.66	2.26	1.59	1.72	2.32
K_2O	4.72	4.2	4.28	3.61	4.94	1.18	0.988	1.03	1.13
MgO	nd	nd	nd	nd	nd	nd	nd	nd	nd
MnO	0.239	0.238	0.275	0.211	0.0316	1.5	1.1	1.18	1.57
Na_2O	nd	nd	nd	nd	nd	2.48	6.5	6.77	5.01
NiO	0.0149	0.0063	0.02	nd	nd	nd	nd	nd	nd
OsO_4	0.112	0.102	0.109	nd	nd	0.0445	0.0275	0.0286	0.0412
PbO	0.867	0.677	0.716	nd	nd	0.0084	0.0052	0.0055	0.0088
Sb_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd
SiO_2	61.75	59.52	61.5	61.54	66.22	66.53	69	68.25	66.04
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd
SO_3	0.0075	0.47	0.48	nd	nd	nd	nd	nd	nd
SrO	nd	nd	nd	0.016	nd	0.0215	0.0154	0.0165	0.0234
TiO_2	nd	nd	nd	0.351	0.0901	0.259	0.206	0.196	0.282
V_2O_5	nd	nd	nd	0.0256	nd	0.0113	nd	nd	nd
ZnO	nd	nd	nd	0.0108	nd	nd	nd	nd	nd
ZrO_2	nd	nd	nd	0.0223	0.0089	nd	0.0106	0.0116	nd

Appendix F: Kilteasheen, Knockvicar, Co. Roscommon

Cutting:	Cutting I	Cutting I	Cutting I	Cutting J	Cutting J	Trench C
Feature:	F387 (4)	F387 (5)	F387 (6)	F451	F532	C15
Find No:	08087	08087	08087	1778	1779	
Description	Olive glass sherd	Olive glass sherd	Olive glass sherd	Blue glass fragment	Blue glass bead	Corroded sherd
Al_2O_3	10.92	53.01	21.07	20.55	41.8	9.38
As_2O_3	0.0431	0.023	0.0229	nd	0.0608	nd
BaO	0.0435	0.0117	0.0289	0.0067	0.0076	0.308
Bi2O3	nd	nd	nd	nd	nd	nd
CaO	11.42	5.21	8.52	3.98	2.77	9.4
Cl	0.052	0.083	nd	0.574	0.425	0.307
Co_3O_4	0.0169	0.0128	nd	0.0316	0.0462	0.058
Cr2O3	nd	nd	nd	nd	nd	nd
CuO	nd	nd	nd	0.117	0.0893	0.0062
Fe_2O_3	1.77	0.639	1.14	0.76	0.616	5.09
K_2O	1.01	0.384	0.665	0.596	0.377	1.47
MgO	nd	nd	nd	nd	nd	nd
MnO	1.19	0.444	0.774	0.365	0.186	0.188
Na_2O	5.83	nd	3.3	6.65	nd	nd
NiO	nd	nd	nd	nd	0.0256	nd
OsO_4	0.033	0.0081	0.0222	0.0284	nd	0.0062
PbO	0.0062	nd	nd	0.23	0.161	0.0138
Sb_2O_3	nd	nd	nd	0.466	0.357	nd
SiO_2	67.39	40.08	64.27	65.48	52.96	71.56
SnO2	nd	nd	nd	0.0161	0.0253	nd
SO_3	nd	nd	nd	nd	nd	0.0782
SrO	0.0172	0.0068	0.0114	nd	nd	0.453
TiO_2	0.223	0.058	0.154	0.223	0.058	nd
V_2O_5	nd	nd	nd	nd	nd	nd
ZnO	nd	nd	nd	nd	nd	nd
ZrO_2	nd	0.0055	0.0085	nd	0.0055	

Appendix F: Kilteasheen, Knockvicar, Co. Roscommon

Context:	Field-walk (1)	Field-walk (2)	Field-walk (3)	Field-walk (4)	Field-walk (5)	Field-walk (6)	Field-walk (7)	Field-walk (8)	Field-walk (9)	Field-walk (10)	Field-walk (11)
Description:	Thick dark green body sherd	Clear bottle neck sherd	Clear sherd	Green base sherd	Thin green sherd	Green sherd	Clear sherd, slight green tinge	Clear sherd	Clear sherd, slight green tinge	Clear sherd, slight purplish tinge	Small white piece
Al_2O_3	9.52	5.41	6.46	5.43	17.27	10.49	0.936	5.79	11.56	10.57	26.77
As_2O_3	nd	0.0916	nd	0.0113	0.0509	nd	nd	0.0318	0.149	0.595	0.114
BaO	0.033	0.069	nd	nd	0.0255	0.0276	nd	nd	0.0061	0.642	0.0574
Bi2O3	nd	nd	nd	109	nd	nd	nd	nd	nd	nd	nd
CaO	20.98	11.95	11.37	17.78	14.68	16.54	14.05	6.18	8.34	2.21	4.07
Cl	0.696	0.33	nd	nd	0.376	nd	nd	nd	0.069	0.231	0.188
Co_3O_4	0.0263	nd	nd	0.0221	0.0141	0.017	nd	nd	nd	nd	nd
Cr2O3	nd	nd	nd	nd	nd	0.0228	nd	nd	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe_2O_3	2.23	0.424	0.171	1.64	1.16	1.32	0.123	0.0411	0.186	0.0394	0.257
K_2O	0.533	1.15	nd	1.48	0.39	2.14	0.075	nd	0.271	0.483	0.221
MgO	1.74	nd	nd	4.67	nd	nd	nd	nd	nd	nd	nd
MnO	0.0858	0.109	nd	0.28	0.246	0.192	nd	nd	0.03	0.0488	0.024
Na_2O	1.37	7.67	10.34	3.12	2.34	4.83	11.11	13.7	8.81	nd	nd
NiO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	nd	0.112	nd	0.0204	0.0166	nd	nd	0.0106	0.0373	0.153	0.0338
PbO	0.0079	0.641	0.0055	0.0453	0.01	nd	nd	nd	nd	nd	nd
Sb_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SiO_2	62.38	71.87	70.26	65.15	63.25	64.11	73.79	62.20	70.5	84.9	68.2
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SrO	0.0414	0.0157	0.0071	0.0166	0.0288	0.025	0.0072	nd	nd	0.0255	0.0058
TiO_2	0.285	0.0651	0.0419	0.184	0.123	0.215	0.0214	0.0164	0.0256	0.08	0.0351
V_2O_5	0.0151	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.0069
ZnO	nd	nd	nd	nd	nd	0.0059	nd	nd	nd	nd	nd
ZrO_2	nd	nd	0.0052	nd	nd	nd	nd	nd	nd	nd	nd

Appendix 2: Glazed stones results (Results given in percentage w/w) (nd = not detected)

Cutting:	Cutting C	Cutting D	Cutting G:	Cutting I	Cutting I	Cutting I	Cutting K	Cutting K
Context:	F15	F134/122	F63	F1	Topsoil	F387	C1	F568
Find No:	41	197	405	08001	8051	08061	42	200
Description:	Stone with glaze	Stone with glaze	Stone with glaze	Stone with glaze	Stone with glaze	Stone with glaze	Stone with glaze	Stone with glaze
Al_2O_3	42.76	8.65	16.69	9.48	9.97	16.85	12.07	9.34
As_2O_3	nd	nd	nd	nd	nd	nd	nd	nd
BaO	0.0063	0.0223	0.0132	0.0234	0.0447	0.0148	0.0651	0.0355
CaO	1.59	1.01	0.765	1.19	1.25	2.33	2	3.03
Cl	0.252	nd	0.199	nd	1.22	0.113	0.263	0.209
Co_3O_4	0.0126	0.0298	0.0157	0.0213	0.0148	0.034	0.0204	0.0111
CuO	0.0074	0.041	0.0205	0.0213	0.0268	nd	0.015	0.0251
Fe_2O_3	1.49	2.51	1.5	1.8	1.07	3.17	1.77	0.971
K_2O	2.00	5.84	4.33	6.51	1.86	3.12	4.83	3.41
MnO	0.0666	0.0659	0.0307	0.0228	0.0729	0.073	0.098	0.0425
Na_2O	nd	7.75	6.07	8.54	nd	nd	2.08	2.39
OsO_4	nd	nd	nd	nd	nd	nd	nd	nd
PbO	nd	nd	nd	nd	nd	nd	nd	nd
Sb_2O_3	nd	nd	nd	nd	nd	nd	nd	nd
SiO_2	51.6	73.53	70.00	72.11	83.77	73.75	76.34	80.38
SnO2	nd	nd	nd	nd	nd	nd	nd	nd
SO_3	nd	nd	nd	nd	nd	nd	nd	nd
SrO	nd	0.0141	0.0065	0.0117	0.0087	0.0158	0.0117	0.0088
TiO_2	0.162	0.412	0.289	0.203	0.272	0.392	0.273	0.114
V_2O_5	0.013	0.0129	nd	nd	nd	nd	nd	nd
ZnO	0.0084	0.0612	0.0383	0.0344	nd	0.0951	nd	nd
ZrO_2	0.007	nd	nd	0.0124	nd	0.0196	nd	0.0171

Appendix G: Analysis of glass from Blackfriary, Trim, excavation number E4127

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1. Introduction

This report details the analysis of a number of glass fragments which were uncovered during excavations at Blackfriary, Trim, Co. Meath. The multi-elemental analysis was carried out using X-ray Fluorescence (XRF) at I.T. Sligo. The aim of this analysis was to determine trace elements within the glass objects which could potentially answer questions about their origin or production. A total of 6 glass pieces were analysed. Black Friary, situated in the Blackfriary townland in Trim, Co. Meath is the site of a Dominican Friary which was founded in the 13th century. The excavations from 2010, the first year of excavations, consisted of two cuttings adjacent and within what was thought to be the church. Remains of walls relating to the belfry tower of the church were uncovered in these cuttings. The layers were heavily interspersed with waste material from dumping which dated to both the modern period and the Post-Medieval. Excavations in the following three years focused on exposing other elements of the church and cloister, and included the excavation of human remains within the nave, cloister garth and ambulatory (O'Carroll 2014).

2. Methodology

2.1. Sample collection and selection

The glass fragments from excavations at Blackfriary were provided by Bairbre Mullee of The Irish Archaeology Field School for the purpose of this study. The samples were chosen from the Blackfriary glass assemblage, with a number of objects being excluded due to their heavily fragmented nature or small size. In total, six pieces of glass were analysed using XRF analysis which included a sherd of blue glass, a green heavily corroded sherd, a piece of black glass, a rounded piece with four-leaf decoration, a reddish brown fragmented piece and a pale green translucent sherd. A table detailing the samples which underwent analysis as well as a brief description can be seen in Appendix 1 at the end of this report.

2.2. Calibration/Quality Control

The XRF was calibrated monthly using the standard procedure for this instrument. The accuracy of the instrument is also tested regularly using standard glass reference material. Table 1 below illustrates the accuracy and precision of the instrument using a standard sample. The sample was run 5 times and an average taken of the results.

	Stated concentration (%w/w)	**Average obtained (%w/w)**	**Relative Standard Deviation%**	**%Error**
SiO_2	72.26	72.62	0.360	0.503
Na_2O	13.78	12.88	1.399	-6.516
CaO	10.05	10.71	0.598	7.000
MgO	3.40	3.64	2.423	-0.0549
SO_3	0.270	0.027	9.658	-90.074
TiO_2	0.033	0.0237	7.413	-28.121
Fe_2O_3	0.021	0.0177	4.058	-15.619

Table 1: Reference sample results obtained

(nd = not detected, nc = not calculated)

2.3. Sample washing and preparation

A solution consisting of a 1:1 ratio of deionised water and 99% ethanol solution was prepared in a volumetric flask. The surface of each sample was gently cleaned using a clean cotton swab dipped in the deionised water/ethanol solution prior to being analysed in the XRF. The purpose of this technique was to remove surface contamination on the surface of the glass. Different trace elements can be left on the glass from many processes such as salts left behind from washing with ordinary water or chlorine transferred from handling the samples with bare hands. By removing such elements, a clearer result of the elemental composition of the surface layers of the glass can be obtained. The above washing method was decided in

consultation with the National Museum of Ireland after extensive experimentation on modern glass samples. The samples were left to dry completely before undergoing analysis. All samples were handled using gloves to avoid adding any further surface contamination.

2.4. Testing of samples

Each sample was analysed by XRF in triplicate and the results averaged. Samples were analysed in the condition they were received with no preparation method utilised aside from the washing technique outlined above. XRF was chosen for this analysis as it provides a highly sensitive, multi-elemental analysis and is completely non-destructive. XRF is a surface technique, therefore the elemental composition it gives is indicative of the surface layers only and this may not be an accurate representation of the whole sample.

3. Results

The results of the analysis (given in percentage w/w) can be seen in Appendix 1 at the end of this report. These show the results from the six samples that were obtained during this study.

4. Discussion

4.1 Condition of samples

The glass pieces from this site were all in a fragmented state and several of them also exhibited visible signs of corrosion. The find from context F335 was a green piece which showed heavy signs of corrosion and its surface appeared black. It also appeared very fragile, with several small flakes having chipped away. The find from context F401, a small black piece showed no obvious sign of corrosion. The blue glass sherd, found in context F101, exhibited an iridescent sheen on its surface,

indicative of corrosion which had occurred in its surface layers. The finds from context F708 consisted of two fragmented pieces, the larger of which had four-leaf decoration and signs of pitting on the back of the piece. Finally, the find from context F709 was a pale translucent green sherd which showed no obvious signs of pitting, crusting or an iridescent sheen.

4.2 Elemental Composition

From ancient times, glass has been consistently made up of a glass former, such as sand or quartz pebbles (SiO_2), a modifier, such as soda (Na_2O) or potash (K_2O), and a stabilizer such as lime ($CaCO_3$). As well as this, glass may contain a variety of colouring agents, opacifiers and other trace elements, added either intentionally or unintentionally (Goffer 2007, 124). From an analytical point of view, the composition of ancient soda-lime glass is typically 73% SiO_2 (silica), 23% Na_2O (soda) and 5% CaO (calcium oxide) (Gratuze and Janssens 2004, 605).

4.2.1 Fragment of corroded green glass from context F335

This fragment was a heavily corroded green sherd which can be seen in Plate 1. The piece was found associated with burial no. 5 in context F335 and has a possibly medieval date. The piece was somewhat similar in appearance to the 2 fragments from context no F708, however this particular piece had no sign of decoration on its surface. Burial 5 was a full adult inhumation which was orientated east to west. Other finds associated with this burial included a piece of metal, a stone, a piece of lead and 5 shroud pins. As this context was situated within the nave of the church, this piece was most likely a sherd of stained window-glass. The lead could also have come from a stained-glass window and may be indicative of the destruction of a window at an earlier stage (O'Carroll 2014, Appendix 6).

The main component of this piece was silica (SiO_2) which accounted for 69.02% of its elemental composition. Its aluminium oxide (Al_2O_3) concentration was 5.78%. Low

levels of modifier were immediately apparent from the results obtained from this fragment. The levels of modifier, either soda (Na_2O) or potash (K_2O), can be up to around 23% for ancient glass. Generally, the lowest concentrations which would have been added would have been at least 15%. However this fragment only had 0.571% potash and had no detectable amounts of soda at all. The low level of modifier highlights the corroded nature of the surface layers of this glass piece.

Soda, potash or a mixture of the two was an essential component when producing glass in ancient times. It acted as a flux, lowering the melting point of silica from 1700ºC to 1000ºC, a temperature which was obtainable in ancient furnaces (Goffer 2007, 115). While it is difficult to tell for certain what type of modifier was used in this piece based on the trace amounts remaining in it, it is likely that it was a potash-based glass. This is not surprising given that the piece was discovered in a medieval context. Potash glass became increasingly popular during the medieval period when demand for glass was growing and there was incentive to search for a more readily accessible alkali source (Moran 2010, 17). Potash would have been sourced from wood ash as opposed to soda which was generally retrieved from marine plants. While corrosion may affect glass for a number of reasons, such as environmental factors, the most important factor in most cases is the original elemental composition of the glass. This determines the resistance of the glass to agents which can cause corrosion such as water, acidic and basic solutions and other atmospheric substances (Pollard and Heron 2008, 166). With regards to medieval window glass for example, it has been noted that potash-based examples were more susceptible to weathering due to the high alkalinity of the glass (Moran 2010, 17). The small amounts of modifier found in this sample, along with a lack of soda detected would suggest that it was possibly potash-based. This suggestion is strengthened when it is considered that soda has survived to a greater extent in other glass pieces from this site such as the find from F401, which will be discussed later in this report.

Another factor which would suggest that this was a potash-based glass was the presence of phosphorus oxide (P_2O_5) and chlorine (Cl) in its structure, having concentrations of 4.595% and 0.405% respectively. Medieval glass made using potash

sourced from burnt tree ash, or 'forest glass' as it is called, often has significant levels of phosphorus and chlorine (Goffer 2007, 155-156). It also often has concentrations of magnesium oxide (MgO), although there was none detected in this particular piece. The presence of such levels of phosphorus oxide in a glass can also increase the separation of the phases in the glass, reducing its chemical resistance (Goffer 2007, 172). This would further account for the susceptibility of this piece to corrosion as was evident from the dark layers which had developed on its surface.

The green colour of the find was most likely due to iron oxide contaminants in the glass melt, as the levels of iron oxide were found to be quite high at 2.185%. The results also showed 0.03026% copper oxide (CuO) and 0.01135% nickel oxide (NiO), both of which can act as green colourants in glass and which could have further added to the green hue of this piece. The find from context F335 also had a significant concentration of manganese oxide (MnO) at 4.835%. This substance was sometimes added intentionally as a decolourant in glass production as it masks the green colour caused by iron. When used on its own without significant levels of iron, it gives a purple colour (Goffer 2007, 121). If it was added for this purpose, it was not successful, as the glass still had a greenish hue.

Chlorine (Cl) was found in all six of the glass finds which were analysed. This accounted for 0.405% of the piece from context F335. Chlorine can be transferred onto the surface of glass from handling objects with bare hands or from rinsing the finds with tap water (Henderson 2000, 94). However, as these beads were submitted to a washing technique, it would be expected that much of this sort of contamination would be removed. Gloves were used when handling the finds at all times during their analysis, so any contamination was not added immediately prior to analysis and would have been present on the surface of the glass for some time. As was previously mentioned, it is very likely that the chlorine in this find could have been added in as part of the potash source, particularly as other elements which are found in burnt ash were also present, such as phosphorus oxide.

4.2.2 Piece of black glass from F401

The second piece of glass was a small black sherd of glass with no visible signs of corrosion which was found in context F401 (Plate 2). Context F401 consisted of a natural accumulation of topsoil (O'Carroll 2014, Appendix 4). The silica (SiO_2) and aluminium oxide (Al_2O_3) concentrations of this find were 70.71% and 6.135% respectively. It also had the highest levels of modifier of any of the pieces analysed with 9.19% soda (Na_2O) and 1.05% potash (K_2O). While this was still well below the minimum 15% concentration which would be expected, it is clear that this piece had maintained its structural integrity better than many of the other samples. The levels of potash and soda indicate that the piece was either a soda-lime glass or a mixed alkali glass. A mix of potash and soda could have been added intentionally or it may have been accidental. For example, potash sources may occasionally contain traces of soda (Shortland 2012, 101). It is also possible that cullet (broken pieces of glass) may have been used when producing the glass, and this would further complicate the elemental composition of the mixture. This piece was the only one of the six analysed to have any detectable level of soda and exhibited the least amount of corrosion of modifier from its surface layers. This is unsurprising due to the better resistance of soda-lime glasses to corrosion compared to potash examples which has been mentioned already in section 4.2.1.

The dark black colour that this glass piece exhibits can be caused by a variety of factors, such as an abundance of coal in the glass furnace, which adds carbon to the mixture (Varshneya 1994, 217). As XRF cannot detect elements lighter than sodium, carbon would not be detected in the elemental results. This particular dark piece of glass may have been produced in a similar way to 17th century black glass from Britain. Examples there were known to have been produced by combining iron, manganese and sulphur in the glass melt and coupling this with a smoky atmosphere in the furnace (Davidson 2008, 77). This find had iron oxide (Fe_2O_3), manganese oxide (MnO) and sulphur (SO_3) in concentrations of 0.9265%, 0.023% and 0.71% respectively, so it is possible that such a reaction with carbon may have taken

place during its production. In addition, there were also traces of chromium oxide (Cr_2O_3) in this piece, 0.0182%, a powerful green colourant which would have served to darken the colour of the glass even further. It seems likely from the relatively uncorroded nature of this piece that it was Post-Medieval or early modern in date.

4.2.3 Fragment of blue glass from context F101

This glass find from context no. F101 was a fragment of blue translucent glass (Plate 3). Context no F101 was a modern accumulation of soil which contained a wide range of finds including modern pottery, plaster, a perforated kiln brick, a nail and this piece of medieval glass (O'Carroll 2014, Appendix 4).

The elemental analysis showed that this piece had a silica (SiO_2) concentration of 66.44%. It also had by far the highest concentration of aluminium oxide (Al_2O_3) of any of the pieces analysed at 26.64%. This was much greater than any of the other glass pieces analysed which had aluminium oxide levels of up to 7.69%. This would indicate that the piece from F101 had undergone heavy corrosion of its surface layers. Ground water can interact with buried glass material affecting the stability of the object. Signs that a glass fragment may have been affected by this include a flaky coating and iridescence on the surface of the object (Pollard and Heron 2008, 119, 178). This piece also had an iridescent sheen on its surface which would further indicate that corrosion had taken place (this is clearly visible in Plate 3). This iridescent coating is essentially a "leached" layer where the ratios of the elements are significantly altered from the bulk glass (Henderson 2013, 614). Glass corrosion is a complex process which is not well understood, affected by many different factors. However it is thought that it occurs due to the preferential leaching of alkali ions to be replaced by hydrogen ions (Wayne Smith 2003, 94). The reaction begins at the surface of the object and spreads inwards (Varshneya 1994, 398). Cox and Ford (1993, 5639-43) conducted a detailed elemental study of multiple layers of medieval glass and concluded that corroded surface layers can be depleted of most oxides except silica (Si), aluminium (Al) and iron (Fe), and what is left behind is poorly crystalline

hydrated silicates and aluminosilicates with varying amounts of calcium (Ca), phosphate (P) and manganiferous (Mn) minerals. The low percentage of silica, coupled with high levels of aluminium oxide (Al_2O_3) in this find, would suggest that its surface layers had lost some of their original composition. Aluminium may have existed in the structure of glass originally in smaller amounts and was held preferentially compared to other elements. There is also the possibility that the surface layers had aluminium which had entered from the environment.

The amount of modifier detected in this piece is very similar to that in the find from F335 in that there was no detectable amount of soda and only trace amounts of potash (K_2O) at 0.124%. However many of the trace elements associated with the addition of potash from burnt wood such as magnesium oxide (MgO) and phosphorus oxide (P_2O_5) were not detected in this piece. Therefore, it is difficult to say with certainty if this piece was been produced using mostly potash or whether it originally had a mixture of potash and soda. The results from this find show significant levels of cobalt oxide (Co_3O_4) in its composition at 0.0531%. Cobalt is a very powerful blue colorant, with even trace amounts causing a bright blue hue in glass. Blue tones ranging from bluish green to a very pale blue could also be achieved by adding cupric oxide (CuO) (Bhardwaj 1979, 42-43), however there was no copper detected in this find and so the colour probably came from the cobalt it contained. This piece also had no detectable amounts of many of the trace elements found in the other pieces such as barium oxide (BaO), strontium oxide (SrO), sulphur oxide (SO_3) and lead oxide (PbO). This, coupled with its much higher levels of corrosion, as indicated by the elevated levels of aluminium oxide, would suggest that this piece was produced with significantly different raw materials or that the production method used was different than the other pieces. This could suggest that this piece was imported from a different area than the others or that it dates to a different time than some of the other pieces that were analysed. It is unfortunate that this piece was found in a modern layer as its context was disturbed, however its composition is typical of medieval potash-based glass.

4.2.4 Rounded glass piece with four-leaf decoration from context F708

The first of two finds from context F708 was a glass piece with four-leaf decoration which can be seen in Plate 4. The decoration is a brownish colour and appears to have been painted onto the glass. The piece itself is flat and is similar in appearance to other stained-glass window fragments from this site. Context F708 consisted of a modern trampled clay-rich layer located beneath the rubble of F709 (O'Carroll 2014). The silica (SiO_2) content of this piece was 71.11% and it had no detectable amounts of aluminium oxide. With regard to modifier levels, this piece did not have detectable amounts of soda (NaO_2) and the concentration of potash (K_2O) was only 0.135%. It had significant levels of phosphorus oxide (P_2O_5), chlorine (Cl) and manganese oxide (MnO) with 3.25%, 0.105% and 6.57% respectively but had no detectable traces of magnesium oxide (MgO). The manganese concentration could have added to the brownish colour. This piece has a significant quantity of iron oxide (Fe_2O_3) which may also account for its brownish colour. Overall the composition of the piece seems to fit with that of a piece of decorative medieval potash-based glass.

4.2.5 Small fragmented reddish-brown piece from context F708

The second piece of glass from context F708 was a small reddish-brown fragmented piece (Plate 5). The silica (SiO_2) content of this piece was 58.74% and its aluminium oxide (Al_2O_3) was 3.80%. Like the larger decorated piece from this context, it had no detectable amounts of soda (Na_2O) however its potash (K_2O) content was much higher at 12.8%. Such a high level of potash is quite unusual, particularly considering that potash does not appear to have survived well in any of the other pieces which were analysed. As has been discussed already, potash from burnt wood ash can add in many different types of trace elements into the composition of a finished glass product, however these can vary widely depending on the type of wood used, and even differ significantly for different parts of the same tree (Goffer 2007, 172). It is possible that the potash for this particular piece came from a different

source because the trace elements vary considerably. The finds from F335, F709 and the decorated piece from F708 had significant levels of phosphorus oxide (P_2O_5), chlorine (Cl) and manganese oxide (MnO) but had no detectable traces of magnesium oxide (MgO). The decorated piece from F708, for example had 3.25%, 0.105% and 6.57% of phosphorus oxide, chlorine and manganese respectively The second piece from F708 by comparison, had much lower amounts of manganese oxide and phosphorus oxide at 0.969% and 1.86% respectively, a higher concentration of chlorine at 1.13% and a significant concentration of magnesium oxide at 3.56%.

Unlike the larger decorated piece, the smaller glass fragment had a relatively low concentration of iron oxide at 0.515%. It did, however, have a significant proportion of copper oxide (CuO) at 1.29%. Depending on the oxidation conditions of the furnace, this could certainly have imparted the reddish-brown colour that it exhibits (Pollard and Heron 2008, 163). Given the small size and fragmented nature of this piece, it is difficult to determine what its original function may have been but it is likely that it is a fragment of medieval stained-glass.

4.2.6 Pale green translucent sherd from F709

The final glass piece from this assemblage was a translucent pale green glass fragment (Plate 6). The context it was discovered in, F709, consisted of a deposit of rubble collapse of the north range and cloister, dating to the early modern period (O'Carroll 2014, Appendix 4). It is difficult to tell what the original function of this glass piece was given its small size. Visually, it exhibited no sign of corrosion or discoloration. Its silica (SiO_2) and aluminium oxide (Al_2O_3) concentrations were 53.07% and 7.69% respectively. Overall, the elemental composition showed that this find had suffered a great deal of corrosion in its surface layers, despite its appearance. This can most clearly be seen in the concentrations of modifier which were found to consist of 0.162% potash (K_2O) and no detectable levels of soda (Na_2O), suggesting considerable degradation of the surface layers. Like most of the

other samples discussed, with the exception of F401, this would suggest a potash-based glass. As already discussed, corrosion occurs as preferential leaching of alkali ions to be replace by hydrogen ions, and potash-based glasses are more susceptible to this than soda-lime-based ones (Wayne Smith 2003, 94). The green tinge in the glass was most likely caused by the significant level of iron oxide (Fe_2O_3) at 5.84%. It also had small amounts of other green colourants including copper oxide (CuO) and nickel oxide (NiO) at 0.051% and 0.0323% respectively, which could have further enhanced its green appearance.

Conclusion

The XRF analysis suggests that the majority of the glass in this study was potash-based glass which had been subjected to varying degrees of corrosion due to being exposed to groundwater over time. This has caused the modifiers in their surfaces to leach away leaving a disproportionate amount of heavier metals behind, such as aluminium. It can be seen that the visual condition of the objects is not always a good indication of the level of corrosion which has occurred. Unfortunately it is impossible to know what the original composition of these objects would have been without utilising more destructive methods in order to expose non-corroded layers deeper in the finds. However despite these problems it is still possible to glean a lot of information about the glass and its production from the elemental analysis.

The find from F335, and the two pieces from F708 all appear to be potash-based glass. They also exhibited significant levels of iron oxide in their compositions which may have caused their colours. The colour in these pieces may have been added to by other colourants that were detected in trace amounts in their composition, such as copper oxide (CuO), nickel oxide (NiO) and manganese oxide (MnO). The results from the two finds from F708 also highlighted the differences in the elemental composition of the two pieces. Despite being found in close proximity to one another and despite having a somewhat similar appearance in the sense that they are both

flat pieces with evidence of corrosion, the elemental composition of these two pieces differed significantly and it would seem unlikely they came from the same source.

Find F401, the black glass sherd was the only soda-lime glass from the six samples analysed and was also the least corroded elementally. While corrosion can be caused by many factors, including environmental factors, the original structure of the glass is the most important factor. The relatively good condition of this find is unsurprising given that it is a soda-lime example, which is chemically more resistance to corrosion than potash-based glasses. Find F101, in contrast, had an iridescent sheen on its surface and exhibited heavy signs of corrosion elementally. Its high concentration of aluminium oxide highlighted the amount of leaching of elements which had occurred in its surface. The more extensive corrosion of this piece compared to the other potash-based examples may have occurred for a variety of reasons, including its original composition. It may also have been due to its surface area to volume ratio as it was a particularly narrow, long piece or possibly as a result of dating to an earlier time than the other material and as such being exposed to the elements for longer. Finally, F709 was a pale translucent green glass which also exhibited signs of corrosion despite its good visual appearance. Like most of the other pieces, it appeared to be potash-based and was most likely coloured by iron impurities in its structure.

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Plate 1: F335 – Green heavily corroded sherd

Plate 2: F401- Black glass fragment

Plate 3: F101- Blue glass sherd

Plate 4: F708 - Rounded piece with decoration

Plate 5: F708- Reddish brown fragmented piece

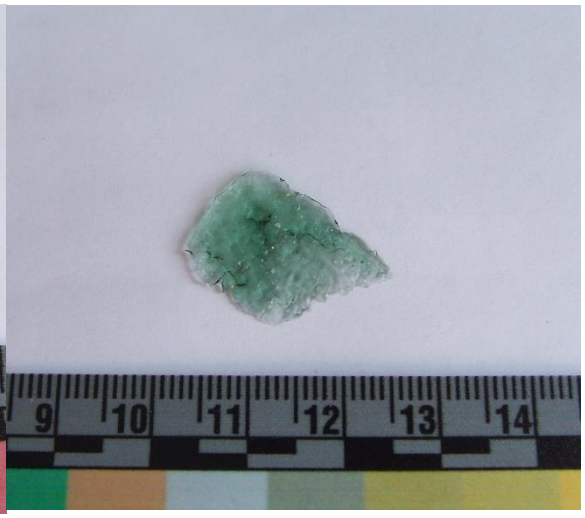

Plate 6: F709 - Pale green translucent sherd

Appendix G: Blackfriary, Trim, Co. Meath

Appendix 1: Glass results (Results given in percentage w/w) (nd = not detected)

Context:	F335	F401	F101	F708	F708	F709
Description:	Green heavily corroded sherd	Light black glass	Sherd of blue glass	Rounded four-leaf decoration	Reddish brown fragmented piece	Pale Green Translucent
Al_2O_3	5.78	6.135	26.64	nd	3.80	7.69
As_2O_3	nd	nd	0.168	nd	nd	nd
BaO	0.0631	0.0082	nd	0.0899	0.0311	0.0329
CaO	8.99	10.70	4.89	11.76	14.83	10.507
Cl	0.405	1.075	0.686	0.105	1.13	0.335
Co_3O_4	0.0268	0.0076	0.0531	nd	nd	0.0579
Cr_2O_3	nd	0.0182	nd	nd	nd	nd
CuO	0.0302	nd	nd	0.254	1.29	0.051
Fe_2O_3	2.185	0.9265	0.437	4.24	0.515	5.84
K_2O	0.571	1.05	0.124	0.135	12.8	0.162
MgO	nd	nd	nd	nd	3.56	nd
MnO	4.835	0.023	0.304	6.57	0.969	7.58
Na_2O	nd	9.19	nd	nd	nd	nd
NiO	0.0113	nd	nd	0.0077	nd	0.0323
OsO_4	0.057	nd	0.46	0.0613	0.0127	0.258
P_2O_5	4.595	nd	nd	3.25	1.86	3.38
PbO	0.189	nd	0.048	0.218	0.0524	0.963
SiO_2	69.02	70.71	66.44	71.11	58.74	53.07
SnO_2	0.0057	nd	nd	nd	0.0425	0.0292
SO_3	2.695	0.721	nd	1.60	nd	9.01
SrO	0.0554	0.0185	nd	0.0445	0.075	0.0538
TiO_2	0.328	0.113	0.135	0.367	0.172	0.679
V_2O_5	0.0173	nd	nd	0.0337	0.0106	0.041
ZnO	0.122	0.0073	0.0056	0.139	0.0871	0.102
ZrO_2	0.0213	0.0172	nd	0.037	0.0138	0.107

Appendix H: Analysis of glass from Bective Abbey, Co. Meath, excavation number E4028

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Appendix H: Bective Abbey, Co. Meath

1. Introduction

This report details the preliminary analysis of a number of glass fragments uncovered during the excavations at Bective Abbey, Co. Meath. The multi-elemental analysis was carried out using X-ray Fluorescence at IT Sligo. The aim of this analysis was to determine trace elements within the surface layers of the glass fragments which could potentially answer questions about their origin or production. A range of glass types are included in the study; from medieval window glass to modern glass bottle.

2. Methodology

2.1. Sample collection and selection

Glass fragments from the Bective Abbey excavations of various types and colours were provided by Matthew and Geraldine Stout for the purpose of this study. A number of samples had to be excluded from the analysis due to their highly corroded nature. These samples had heavy iridescent surface layers which were beginning to flake away from the glass. In total, 101 fragments were analysed. Descriptions of the samples analysed can be seen in the tables of results in the appendices at the end of this report.

2.2. Calibration/Quality Control

The XRF was calibrated monthly using the standard procedure for this instrument. The accuracy of the instrument is also tested regularly using standard glass reference material. Table 1 below illustrates the accuracy and precision of the instrument using a standard sample. The sample was run 5 times and an average taken of the results.

	Stated concentration (%w/w)	**Average obtained (%w/w)**	**Relative Standard Deviation%**	**%Error**
SiO_2	72.26	72.62	0.360	0.503
Na_2O	13.78	12.88	1.399	-6.516
CaO	10.05	10.71	0.598	7.000
MgO	3.40	3.64	2.423	-0.0549
SO_3	0.270	0.027	9.658	-90.074
TiO_2	0.033	0.0237	7.413	-28.121
Fe_2O_3	0.021	0.0177	4.058	-15.619

Table 1: Reference sample results obtained

2.3. Sample washing and preparation

A solution containing a 1:1 ratio of deionised water and 99% ethanol solution was prepared in a volumetric flask. The surface of each sample was gently cleaned using a clean cotton swab dipped in the deionised water/ethanol solution prior to being analysed in the XRF. The purpose of this technique was to remove surface contamination on the surface of the glass. Different trace elements can be left on the glass from many processes such as salts left behind from washing with ordinary water or chlorine transferred from handling the samples with bare hands. By removing such elements, a clearer result of the elemental composition of the surface layers of the glass can be obtained. Of the 101 samples which were analysed, a total of 36 also underwent analysis prior to any washing to highlight any surface contamination which may have been present. The above washing method was decided in consultation with the National Museum of Ireland after extensive experimentation on modern glass samples. The samples were left to dry completely before undergoing analysis.

2.4. Testing of samples

Each sample was run through the XRF in triplicate and the results averaged. Samples were analysed in the condition they were received with only the basic washing procedure described above. No other preparation method was utilised. XRF was chosen for this analysis as it is a multi-elemental analysis and is completely non-destructive. XRF is a surface technique, therefore the elemental composition it gives is indicative of the surface layers only and this may not be an accurate representation of the whole sample. It does, however, highlight the amount of leaching and corrosion which the samples have been subjected to.

3. Results

The results of the analysis (given in percentage w/w) can be seen in the appendices at the end of this document. Appendix 1 shows the results obtained from the 36 samples prior to cleaning the surface of the glass as well as the percentage difference of the elemental composition of the 36 glass samples before and after washing. This was determined with the below formula:

$$\% \text{ difference} = (E1 - E2) \div (0.5 \times (E1 + E2)) \times 100$$

where E1 is the composition of the glass before treatment and E2 is the composition after treatment

Appendix 2 shows the results of the 101 samples obtained after the cleaning procedure has been carried out.

Discussion

4.1 Condition of samples

A large quantity of the glass fragments exhibit visible signs of corrosion. This varies from an iridescent sheen on the surface of the fragments, to heavy crusting or pitting of the surface layers. Some samples show no obvious signs of corrosion, although based on their appearance some of these appear to be modern glass. This is on the

basis of the clear glass having no tinge of colour, which would have been highly difficult to achieve in production of glass prior to modern times. The elemental analysis shows these are indeed modern.

4.2. Effects of surface cleaning

The results of the analysis show that rinsing the glass samples in the ethanol/deionised water solution can affect the elemental composition of the surface layers. The effects of the water washing can be seen by comparing the percentage difference between the unwashed glass and the second analysis undertaken after the samples were cleaned. The trace elements are the most affected by this washing. This is not surprising due to the small amounts which the sample contains, which leaves a greater scope for error. In the cleaned samples, the percentage increase can be as high as 89.08% as in the case of the barium oxide (BaO) content of sample Q03:08. A similarly high percentage decrease of 85.40% can be observed in the arsenic oxide (As_2O) content of sample 301:1(1). Differences in the trace elements are apparent in all of the samples which were tested in this way. Silica (SiO_2) and soda (Na_2O) are among the least affected by the surface corrosion with the majority of the samples having less than a 5% difference for both elements and many considerably less. Most of the trace elements appear to decrease in concentration after the washing is carried out. In contrast, the proportion of higher concentration elements tends to rise as the proportion of trace elements falls. This is probably due to trace elements masking some of the main constituents of the glass. These are removed by the washing technique. The high levels of surface contamination should not be surprising, given that the samples had been buried underground and exposed to elemental contamination from the soil and groundwater. Washing of the samples with ordinary tap water could have added different traces of salts, and handling the glass with bare hands could add even further small amounts of trace elements. It can be expected that a deionised water-and-ethanol solution may aid washing away trace contaminants on the surface of the sample and it certainly seems to be doing so in this case.

4.3 Elemental Composition

Since earliest times, glass has been consistently made up of a glass former, such as sand or quartz pebbles (SiO_2), a modifier, such as soda (Na_2O) or potash (K_2O), and a stabilizer such as lime ($CaCO_3$). In addition, glass may contain a variety of colouring agents or opacifiers, either intentionally or unintentionally (Goffer 2007, 124). The main component of the glasses analysed from Bective is silica (SiO_2) as would be expected, and this accounts for between 55.75% to 80.95% for the samples analysed. Immediately noticeable in the results from the Bective Abbey glass, however, is the low proportion of soda (Na_2O) and potash (K_2O) detected in the analysis for many of the fragments. Ground water can interact with buried glass material affecting the stability of the object. Signs that a glass fragment may have been affected by this include a flaky coating and iridescence on the surface of the object (Pollard and Heron 2008, 178). This is due to the sodium or potassium in the glass leaching out and leaving only porous, hydrated silica behind.

The corrosion of glass is a complex matter, affected by many different factors and it is not perfectly understood. In some cases, there may be no obvious signs on the glass that it has been subject to any decay. However it is thought that it occurs due to the preferential leaching of alkali ions to be replaced by hydrogen ions (Wayne Smith 2003, 94). The reaction begins at the surface of the object and spreads inwards (Varshneya 1994, 398). Cox and Ford (1993, 5639-43) conducted a detailed elemental study of multiple layers of medieval glass and concluded that corroded surface layers can be depleted of most oxides except silica (Si), aluminium (Al) and iron (Fe), and what is left is poorly crystalline hydrated silicates and aluminosilicates with varying amounts of calcium, phosphate and manganiferous minerals. The results obtained from the Bective glass would suggest that many of the samples have suffered corrosion to some extent, even those with no obvious sign of corrosion on the surface. The low percentage of alkali metals found in many of the samples, coupled with unusually high levels of calcium oxide (CaO) and aluminium oxide (Al_2O_3), would suggest that the surface layers have lost some of their original composition and possibly contain heavy metals which have entered from the

environment. Even some glass fragments which appear modern, for example Q05.3, show signs of corrosion with lower than expected levels of alkali material and high levels of aluminium and calcium.

Soda, potash or a mixture of the two act as a flux when added to a glass mixture, lowering the melting point of the silica from 1700ºC to 1000ºC (Goffer 2007, 115). They are an essential component when producing glass, particularly in ancient times as they lower the melting point of the silica to a temperature which was obtainable in furnaces at the time. Potash would have been sourced from wood ash as opposed to soda alkali sources which were generally retrieved from marine plants. Potash glass became increasingly popular during the medieval period when demand for glass was growing and there was incentive to search for a more readily accessible alkali source. The use of a wood ash often adds small amounts of lime ($CaCO_3$), magnesia (MgO) and phosphorus pentoxide (P_2O_5) (Goffer 2007, 169-172). It can be seen from the results that a number of the glass fragments contain traces of both magnesia and phosphorus pentoxide. Manganese oxide (MnO) is another element which is present in many of the glass fragments. While this element is sometimes used as a decolourant, in this case it was most likely added unintentionally as part of the potash that was sourced.

A large proportion of the Bective glass seems to be potash-based glass, with no soda detected during the XRF analysis. It is possible that they originally contained some soda which was leached away, but the corroded nature of some of the glass would support the idea that the glass was mainly potash, due to the increased susceptibility of this type of glass to corrosion and decay. The degraded nature of the surface of these glass fragments is unfortunate as it would be necessary to analyse polished cross-sections of the glass in order to get a truer sense of their original composition. Nevertheless, the analysis reveals information about the nature of the glass, the raw materials used to produce it and how it has survived in its burial context. There are a number of fragments which appear to be a mixed alkali type (containing both soda and potash) such as 001:030 (1) and E01:73, however due to the low levels of both, it is difficult to determine what their original composition could have been. A mix of

potash and soda could have been added intentionally. It could also have been accidental. For example, potash sources may occasionally contain traces of soda. It is also possible that cullet (broken pieces of glass) may have been used when producing the glass, and this would further complicate the elemental composition of the mixture.

Most of the glass which was analysed was uncovered in Phase 08 contexts. The next largest concentrations of glass were found in Phase 10 contexts and Garden Phase 04 contexts respectively. Smaller amounts were found in Phases 02, 06, 07 and 09. In some cases, there is a distinction apparent between glasses found in the different types of contexts. For example, samples 101.2a and SS01.16 are both green coloured glass which were found in Phase 08 and Phase 10 respectively. It can be seen that 101.2a (see Figure 1 below) shows a much higher amount of corrosion than sample SS01.16 (see Figure 2 below), However, this does not hold true for all of the samples uncovered and it would appear there is a great deal of overlap with glass found in different contexts on the site. For example, sample nos. 301.1(1) and 301.1(2), both sherds of clear glass found in a Phase 08 context, have an elemental composition more consistent with either modern glass or glass which had not suffered any significant corrosion than any other glass sample analysed from this site. 301.1(1) has 74.22% Si_2O, 14.55% Na_2O and 10.5% CaO; proportions that would be expected from glass which had not been subject to corrosion or siginificant lost of elemental composition. There are a number of sherds found in the Garden Phase 04 contexts which exhibit signs of corrosion such as samples K02.3 and M01.3a.

Figure 1: Sample no. 101:2(a)

Figure 2: Sample no. SS01:16

A number of fragments have trace amounts of arsenic (As); 301.1, 001:002(7), 001:030(3), 001:030(5), H01:5, L02.1a-b, M01.3c, Q01:27, Q03:08, Q05:3-16, SN01:6-8, SS01:04. With the exception of several green sherds, which are most likely from the same bottle (Q05:3-16), this element is only found in clear sherds on this site. In more recent times, arsenic oxides were added to glass for the purpose of removing bubbles from the melts (Shelby 2005, 43). Arsenic was also used as an opacifier in historical glass, giving glass a milky white appearance (Bray 2001, 177). However as the clear glass fragments are translucent, it is unlikely that the arsenic was added for this purpose. Therefore in this case, it would seem that the arsenic was added for the former reason, and the glass is likely to be modern.

The majority of the glass found appears to be bottle glass, a name referring to a cheap and widely manufactured glass used mainly in the production of bottles (Rynne 2006, 184). Glass used for making bottles was almost always of a lower quality than that of other vessels and they usually appear a very dark green colour, caused by varying iron impurities (Roche 2007, 411). Although there is not much documentary evidence for the production of bottles in Ireland compared to elsewhere by the end of the 17th century, there are records of it being carried out from the 18th century in Dublin and in Waterford City (Thorpe 1969, 272). As stated already, the most common colourant for green is iron and a variety of different green hues can be obtained depending on its state of oxidation within the glass, as well as conditions and temperature within the kiln during the production of the glass. With the lack of other elements associated with green colouring such as chromium and copper, it suggests that the green colour was a side-effect of using iron-rich sands and not an intentional addition. Some of the glass fragments have an extremely dark or even black colour. This can be caused by a variety of factors, such as an abundance of coal in the glass furnace, which adds carbon to the mixture (Varshneya 1994, 217). The black glass at Bective may have been produced in a similar way to 17th century black glass from Britain. Examples there were known to have been produced by combining iron, manganese and sulphur in the glass melt and coupling this with a smoky atmosphere in the furnace (Davidson 2008, 77). Q01.001 from the Bective results is an opaque black sherd which contains iron, manganese and

sulphur, as well as cobalt which would have served to darken the colour of the glass even further. This composition, along with the post-dissolution context it was found in, would suggest a production method similar to the one outlined above.

Fragments 301.25 and A01:010, both found in the Phase 08 post-dissolution contexts, appear to be a type of window glass. The results obtained from their analysis shows they are a potash based glass, although some of the alkali material appears to have been leached away, with only 3.13% and 3.18% K_2O respectively. While window glass made from soda-lime glass has been noted elsewhere, including England and Scotland, early Irish church or monastery coloured window fragments uncovered to date have generally been manufactured using potash. As mentioned already, potash glass is much more susceptible to decay due to its highly alkaline nature, which is why window glass found in medieval Irish contexts often shows varying degrees of corrosion (Moran 2010, 17). Due to the context they were found in, it is probable that these fragments are medieval glass that were broken in the post-dissolution period.

H01.5 is an amber coloured sherd, and appears to be a modern soda-lime glass. Its orange-brown hue is most likely caused by relatively high levels of manganese oxide (2.56%), much higher than the amount found in clear sherds. 13 sherds of clear glass (101.2b, 301.1, 001:002 (7), 001:030 (3), L02.1a, L02.1b, M01.3c, P0:14-16, P01:235, Q01:002, SS01:5) have elemental compositions which suggest that they are modern soda-silica glass. The low amount of trace elements shows that the producers of this glass were capable of eliminating contamination from the raw materials that were used. This is something which, to a large extent, was not possible for ancient glassmakers. In addition, the percentages of silica (SiO_2) and soda (Na_2O) are in line with what would be expected from a modern soda-silica glass and this has not had time to degrade to any significant extent. For example, 001:002(7) had a composition of 77.74% silica and 12.41% soda, which is in line with the results obtained from analysing the standard sample, which had results of 72.26% silica and 13.78% soda when analysed.

Only one artefact was shown to not contain glass at all. This was sample 207.18, which was found to contain almost no silica, which is the main component of glass.

The major element for this substance is aluminium. Further analysis would be beneficial in determining what sort of substance it is.

Conclusions

The majority of the glass from this site appears to be degraded potash-based or mixed alkali-based glass which has been subjected to ground-water corrosion. Previous work on the decay of glass in burial contexts would support the idea that alkali in the surface of the glass fragments has been leached away, leaving a disproportionate amount of the heavier elements behind. It is also possible that some heavy metals may have entered the structure of the glass from their environment.

Despite these limitations, the elemental composition of the glass does give suggestions as to the raw materials utilised and the types of colourants which were used. Further work would be beneficial in this regard, involving polishing and analysis of cross-sections of the glass in order to obtain a truer elemental analysis of the original glass composition.

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Appendix H: Bective Abbey, Co. Meath

Appendix 1: Bective Abbey results – unwashed vs. % difference from washed results												
	001:002 (1)	**001:002 (1)**	**001:002 (2)**	**001:002 (2)**	**001:002 (3)**	**001:002 (3)**	**001:002 (4)**	**001:002 (4)**	**001:002 (5)**	**001:002 (5)**	**001:002 (6)**	**001:002 (6)**
	Thick rounded glass sherd	*% difference from washed*	*Thick green glass sherd*	*% difference from washed*	*Thick green glass sherd*	*% difference from washed*	*Black, light, glassy material*	*% difference from washed*	*Black, light, glassy material*	*% difference from washed*	*Small thin green sherd*	*% difference from washed*
Al_2O_3	7.8	2.54	5.9	10.63	7.75	3.84	24.66	-0.30	24.38	-22.04	7.28	-4.13
As_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BaO	0.0251	-3.59	0.198	-3.26	0.0246	60.43	nd	nd	nd	nd	0.0162	-2.02
CaO	25.86	-0.67	26.63	-1.53	26.07	13.20	16.54	-18.41	21.38	-3.81	26.14	-0.28
Cl	0.316	nd	0.157	nd	0.331	0.61	1.54	10.00	1.02	-34.05	0.341	-10.18
Co_3O_4	0.0237	-17.04	0.028	-5.19	0.034	44.89	0.1145	82.42	0.037	7.98	0.0365	nd
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe_2O_3	2.77	-0.48	3.16	3.95	2.94	43.18	1.41	-23.78	3.53	3.32	2.65	4.19
K_2O	1.89	5.63	2.96	0.91	1.78	15.58	0.412	-10.43	0.544	20.71	1.71	-0.77
MgO	0.66	nd	3.06	-3.57	nd	nd	nd	nd	nd	nd	1.03	-13.45
MnO	0.15	-0.88	0.309	0.65	0.162	35.38	0.602	-59.16	1.31	52.92	0.153	27.86
Na_2O	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.85	nd
NiO	nd	nd	nd	nd	nd	nd	0.0192	-14.29	0.0094	-35.32	nd	nd
OsO_4	nd	nd	nd	nd	nd	nd	nd	nd	0.0125	nd	nd	nd
P_2O_5	2.3	3.92	1.22	5.78	2.79	90.05	nd	nd	nd	nd	1.39	14.88
PbO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Rb_2O	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SiO_2	57.51	-0.99	55.75	-0.55	57.4	-5.73	27.99	-4.00	30.51	67.48	58.33	0.15
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SO_3	nd	nd	nd	nd	nd	nd	22.2	17.63	17	nd	nd	nd
SrO	0.213	-0.93	0.152	-9.16	0.224	nd	0.0283	-34.34	0.0283	nd	0.211	nd
TiO_2	0.401	-0.66	0.362	5.03	0.449	48.84	0.209	-12.06	0.171	-37.67	0.366	12.50
V_2O_5	0.0115	nd	0.0164	nd	nd	nd	0.0207	nd	nd	nd	nd	nd
ZnO	nd	nd	nd	nd	0.0097	nd	0.1832	87.96	0.0273	10.23	nd	nd
ZrO_2	0.0198	-7.76	0.0293	-7.76	0.0228	43.70	nd	nd	nd	nd	0.0231	13.42
Results of unwashed samples given in percentage w/w. nd = not detected												

Appendix 1: Bective Abbey results – unwashed vs. % difference from washed – cont.												
	001:002 (7)	**001:002 (7)**	**001:17**	**001:17**	**001:030 (1)**	**001:030 (1)**	**001:030 (2)**	**001:030 (2)**	**001:030 (3)**	**001:030 (3)**	**001:030 (4)**	**001:030 (4)**
	Large clear glass sherd	*% difference from washed*	*Heavily corroded glass sherd*	*% difference from washed*	*Corroded green sherd*	*% difference from washed*	*Green sherd*	*% difference from washed*	*Clear glass sherd*	*% difference from washed*	*Brown glass sherd*	*% difference from washed*
Al_2O_3	0.93	-11.99	9.87	21.30	7.29	2.82	10.45	24.55	9.84	12.41	9.68	-13.62
As_2O_3	0.0175	-8.70	nd	nd	nd	nd	nd	nd	0.0167	14.12	nd	nd
BaO	0.0315	0.21	0.0184	41.54	0.0147	29.33	0.013	-8.88	0.0224	-12.50	0.0064	1.05
CaO	8.95	3.23	12.03	-30.74	22.09	0.49	7.91	-12.01	7.16	-0.56	7.35	9.00
Cl	0.05	nd	nd	nd	0.286	30.51	nd	nd	0.0353	-27.81	nd	nd
Co_3O_4	nd	nd	0.096	95.12	0.015	-10.71	0.0088	-29.03	nd	nd	nd	nd
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe_2O_3	0.0356	-1.48	8.06	85.43	1.84	-1.08	1.15	-16.06	0.0462	19.48	0.125	19.27
K_2O	0.0437	-3.67	1.001	-16.61	1.85	1.09	0.44	-9.96	0.0256	-49.67	0.637	12.08
MgO	nd	nd	nd	nd	1.17	0.57	nd	nd	nd	nd	nd	nd
MnO	nd	nd	0.334	68.69	0.111	56.78	1.42	-15.48	nd	nd	nd	nd
Na_2O	12.32	-0.48	nd	nd	nd	nd	13.1	-3.20	14.31	16.75	12.73	-2.15
NiO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	0.007	nd	0.0098	nd	nd	nd	nd	nd	nd	nd	nd	nd
P_2O_5	nd	nd	6.32	78.53	1.6	5.26	0.0078	nd	nd	nd	nd	nd
PbO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Rb_2O	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SiO_2	77.61	-0.11	61.59	-4.84	63.27	-0.35	65.37	0.01	68.43	-4.35	69.35	1.55
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SO_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SrO	0.0059	4.73	0.202	22.18	0.159	12.77	0.0128	-12.33	0.0051	nd	0.0059	nd
TiO_2	0.0188	-24.19	0.407	92.28	0.266	3.10	0.047	-24.27	0.0225	21.18	0.036	13.92
V_2O_5	nd	nd	0.0213	96.62	0.0093	nd	0.0074	-5.93	nd	nd	nd	nd
ZnO	nd	nd	0.021	57.50	nd	nd	0.0064	-21.31	nd	nd	nd	nd
ZrO_2	0.0062	10.71	0.0188	46.88	.0179	-2.25	0.0065	-10.96	nd	nd	0.0091	8.76
Results of unwashed samples given in percentage w/w. nd = not detected												

Appendix 1: Bective Abbey results – unwashed vs. % difference from washed – cont.												
	001:030 (5)	**001:030 (5)**	**110:003**	**110:003**	**301:1 (1)**	**301:1 (1)**	**301:1 (2)**	**301:1 (2)**	**A01:10**	**A01:10**	**B01:043**	**B01:043**
	Light green/brown sherd	*% difference from washed*	*Corroded glass sherd*	*% difference from washed*	*Clear sherd*	*% difference from washed*	*Clear sherd*	*% difference from washed*	*Window glass sherd*	*% difference from washed*	*Green body sherd*	*% difference from washed*
Al_2O_3	8.22	-20.19	11.99	-30.81	0.69	7.25	7.6	-3.06	10.13	20.45	8.88	-21.83
As_2O_3	0.0263	20.83	nd	nd	0.0223	-85.40	nd	nd	nd	nd	nd	nd
BaO	0.0212	12.77	0.237	16.75	0.0444	0.30	nd	nd	0.0133	-9.11	0.0575	26.56
CaO	8.74	10.82	12.75	9.19	10.37	-0.83	8.42	9.73	11.44	-27.13	20.08	11.18
Cl	nd	nd	nd	nd	0.08	0.00	0.0637	nd	0.059	nd	0.214	3.55
Co_3O_4	0.0111	nd	0.0144	31.71	nd	nd	nd	nd	0.0128	nd	0.0262	19.45
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe_2O_3	1.15	17.11	1.59	50.76	0.054	9.61	0.0681	8.04	1.18	41.60	2.39	30.13
K_2O	0.64	25.16	1.36	22.16	0.0463	-21.21	0.085	11.35	2.36	-18.81	2.19	10.42
MgO	nd	nd	0.0881	nd	nd	nd	nd	nd	nd	nd	1.68	-2.70
MnO	1.95	14.93	nd	nd	0.006	-1.10	nd	nd	0.153	-1.71	0.139	26.67
Na_2O	13.06	-3.45	nd	nd	14.92	1.68	10.71	-0.50	nd	nd	nd	nd
NiO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	0.073	25.00	nd	nd	0.0068	-26.09	nd	nd	nd	nd	nd	nd
P_2O_5	nd	nd	nd	nd	nd	nd	nd	nd	1.21	98.36	0.5	nd
PbO	0.19	17.77	0.0074	nd	nd	nd	nd	nd	nd	nd	nd	nd
Rb_2O	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SiO_2	65.83	1.70	71.55	199.39	73.73	-0.44	72.79	-0.75	73.13	2.85	63.48	-1.09
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SO_3	nd	nd	nd	nd	nd	nd	0.236	nd	nd	nd	nd	nd
SrO	0.015	17.19	0.105	nd	0.0079	0.00	nd	nd	0.0342	-3.02	0.0829	26.56
TiO_2	0.0564	2.05	0.228	52.00	0.0216	-9.75	0.0201	-43.70	0.28	57.89	0.241	25.30
V_2O_5	nd	nd	0.0152	nd	nd	nd	nd	nd	nd	nd	nd	nd
ZnO	0.0172	12.66	0.0164	26.80	nd	nd	nd	nd	0.0228	-2.56	0.0143	26.55
ZrO_2	nd	nd	0.012	13.21	0.0078	-2.50	nd	nd	0.0096	5.88	0.029	22.19
Results of unwashed samples given in percentage w/w. nd = not detected												

Appendix H: Bective Abbey, Co. Meath

Appendix 1: Bective Abbey results – unwashed vs. % difference from washed – cont.												
	B01:044	**B01:044**	**B01:045**	**B01:045**	**B02:111**	**B02:111**	**B09:29**	**B09:29**	**B021:101**	**B021:101**	**E01:073**	**E01:073**
	Green body sherd	*% difference from washed*	*Green body sherd*	*% difference from washed*	*Corroded glass sherd*	*% difference from washed*	*Clear glass sherd*	*% difference from washed*	*Green body sherd*	*% difference from washed*	*Glass piece*	*% difference from washed*
Al_2O_3	7.26	-2.94	9.15	12.64	5.98	-51.46	14.92	11.68	12.17	-1.40	12.61	41.84
As_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BaO	0.0387	7.00	0.0476	-14.49	0.0257	-17.89	nd	nd	0.228	2.40	nd	nd
CaO	19.64	2.65	18.41	-5.31	8.41	-2.40	9.58	7.24	12.49	-1.16	4.79	-17.74
Cl	0.206	4.04	0.208	0.00	nd	nd	0.0169	nd	nd	nd	0.216	-2.11
Co_3O_4	0.0213	-4.20	0.042	-8.30	nd	nd	nd	nd	nd	nd	nd	nd
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe_2O_3	1.81	7.52	4.07	3.21	1.8	-14.29	0.261	2.35	2.29	-7.29	0.387	-15.81
K_2O	2.07	0.98	1.93	-4.30	2.28	-12.08	0.45	-15.84	2.4	-1.10	2.07	-16.19
MgO	3.63	-0.73	nd	nd	nd	nd	nd	nd	nd	nd	2.81	-21.44
MnO	0.114	11.04	0.174	-1.14	0.0756	nd	nd	nd	0.138	-11.16	0.0166	-14.43
Na_2O	nd	nd	nd	nd	nd	nd	11.32	0.18	nd	nd	3.35	-5.28
NiO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
P_2O_5	0.414	10.50	5.37	22.51	3.79	12.24	nd	nd	2.27	2.71	nd	nd
PbO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Rb_2O	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SiO_2	64.49	-0.75	60.14	-1.61	77.21	8.94	63.31	-2.29	67.63	0.88	73.49	-1.64
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SO_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SrO	0.068	7.03	0.18	-1.46	0.0589	-15.74	0.0054	-5.81	0.0912	-7.32	0.192	-5.57
TiO_2	0.183	4.17	0.29	11.25	0.241	-17.75	0.114	-1.16	0.256	-5.88	0.0476	-71.15
V_2O_5	0.0119	14.06	0.0106	50.00	nd	nd	nd	nd	nd	nd	nd	nd
ZnO	nd	nd	0.0143	-4.03	0.0181	-12.84	nd	nd	0.0064	-14.29	nd	nd
ZrO_2	0.0248	5.08	0.0222	-4.86	0.0127	-20.79	0.0051	-9.47	0.0173	-7.16	0.0091	-14.95
Results of unwashed samples given in percentage w/w. nd = not detected												

Appendix 1: Bective Abbey results – unwashed vs. % difference from washed – cont.												
	E02:052	E02:052	E02:056	E02:056	E02:126	E02:126	E02:127	E02:127	H07:04	H07:04	P01:014	P01:014
	Base bottle sherd, green	*% difference from washed*	*Body sherd*	*% difference from washed*	*Bottle body sherd, green*	*% difference from washed*	*Bottle base sherd, green*	*% difference from washed*	*Olive green sherd*	*% difference from washed*	*Clear glass sherd*	*% difference from washed*
Al_2O_3	8.87	-6.93	7.65	26.87	8.66	-16.68	11.43	3.25	9.54	-0.69	nd	nd
As_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BaO	0.0252	18.13	0.0103	-27.63	0.0651	57.12	0.0169	-7.65	0.0526	2.60	nd	nd
CaO	16.24	9.83	20.35	-13.78	20.31	14.25	19.88	-5.93	12.19	2.41	13.16	-0.10
Cl	nd	nd	0.15	nd	0.18	29.81	0.67	-4.74	nd	nd	nd	nd
Co_3O_4	0.0398	21.10	0.0094	-74.78	0.0274	8.44	0.0281	-26.12	nd	nd	nd	nd
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe_2O_3	2.63	18.65	1.06	-24.29	2.49	26.83	2.58	-7.64	3.62	-0.91	0.51	35.88
K_2O	2.92	7.35	1.08	-10.99	2.72	14.61	0.772	-7.73	3.31	1.22	0.195	0.69
MgO	nd	nd	0.97	6.59	nd	nd	1.51	-1.74	nd	nd	5.6	-1.52
MnO	0.3	20.00	0.0455	-48.59	0.159	38.26	0.0957	-6.08	0.168	2.86	0.0166	6.41
Na_2O	1.17	10.03	nd	nd	nd	nd	1.73	5.70	nd	nd	6.83	-2.10
NiO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
P_2O_5	nd	nd	1.14	-1.72	1.8	16.88	nd	nd	2.73	2.25	nd	nd
PbO	nd	nd	0.0151	-24.63	0.0082	nd	nd	nd	0.0093	-18.66	nd	nd
Rb_2O	0.0079	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SiO_2	67.3	-2.40	67.29	3.26	63.09	-3.26	60.88	2.01	67.74	-0.20	73.14	0.61
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SO_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SrO	0.0797	19.73	0.0895	-27.73	0.123	61.14	0.0609	-9.06	0.109	-0.61	0.274	181.51
TiO_2	0.308	14.64	0.117	-21.12	0.3	48.03	0.298	-7.84	0.451	-2.73	0.0465	9.93
V_2O_5	0.0128	nd	nd	nd	nd	nd	0.0103	-8.31	0.0125	-37.40	nd	nd
ZnO	nd	nd	nd	nd	0.038	44.30	nd	nd	0.0196	-36.77	nd	nd
ZrO_2	0.0529	21.24	0.0083	-48.45	0.0257	62.32	0.0192	-11.38	0.0306	-25.61	0.0055	-29.79

Appendix 1: Bective Abbey results – unwashed vs. % difference from washed – cont.												
	P01:015	**P01:015**	**P01:016**	**P01:016**	**P01:26**	**P01:26**	**P01:27**	**P01:27**	**Q001:001**	**Q001:001**	**Q001:002**	**Q001:002**
	Clear glass sherd	*% difference from washed*	*Clear glass sherd*	*% difference from washed*	*Olive green sherd*	*% difference from washed*	*Olive green sherd*	*% difference from washed*	*Opaque black bottle base sherd*	*% difference from washed*	*Clear glass sherd*	*% difference from washed*
Al_2O_3	0.72	nd	nd	nd	8.22	-32.51	13.76	-16.17	10.99	-0.60	1.71	-0.39
As_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BaO	nd	nd	nd	nd	0.0186	-33.89	0.314	-29.81	0.0294	15.14	nd	nd
CaO	11.37	-1.62	14.26	27.85	7.76	-0.17	17.32	18.58	23.07	-0.06	12.29	-6.30
Cl	0.0645	16.22	nd	nd	nd	nd	0.336	35.48	0.389	64.18	0.11	10.00
Co_3O_4	nd	nd	nd	nd	0.0129	-14.57	0.0197	nd	0.0599	55.58	nd	nd
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe_2O_3	0.0659	-63.78	0.361	23.21	1.17	-13.76	1.58	50.38	3.57	3.28	0.0419	3.12
K_2O	0.052	-9.62	0.202	14.34	0.359	-3.75	1.88	29.36	1.31	0.00	0.125	-4.58
MgO	nd	nd	3.96	-1.33	nd	nd	3.16	nd	1.87	0.36	nd	nd
MnO	nd	nd	0.0096	34.58	1.44	-18.80	0.256	51.18	0.184	91.80	nd	nd
Na_2O	15.74	-2.48	5.18	5.43	15.17	-2.57	nd	nd	nd	nd	15.14	13.89
NiO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
P_2O_5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PbO	nd	nd	nd	nd	0.0076	-14.29	nd	nd	nd	nd	nd	nd
Rb_2O	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SiO_2	71.98	0.32	75.85	0.15	65.77	8.13	60.93	-5.29	57.65	0.13	70.47	-1.47
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SO_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SrO	nd	nd	0.0107	43.95	0.0118	-1.67	0.113	29.59	0.0397	nd	0.0063	-5.97
TiO_2	0.0162	nd	0.049	-46.15	0.0384	-34.99	0.283	nd	0.526	51.73	0.0184	12.65
V_2O_5	nd	nd	nd	nd	nd	nd	nd	nd	0.0187	49.60	nd	nd
ZnO	nd	nd	nd	nd	0.0056	-14.29	nd	nd	0.0062	nd	0.0745	-4.45
ZrO_2	nd	nd	0.0057	nd	0.0068	-7.27	0.0131	16.62	0.0249	25.97	nd	nd
Results of unwashed samples given in percentage w/w. nd = not detected												

Appendix H: Bective Abbey, Co. Meath

Appendix 2: Bective Abbey results – washed													
	001:002 (1)	**001:002 (2)**	**001:002 (3)**	**001:002 (4)**	**001:002 (5)**	**001:002 (6)**	**001:002 (7)**	**001:017**	**001:30 (1)**	**001:030 (2)**	**001:030 (3)**	**001:030 (4)**	**001:030 (5)**
	Thick rounded glass sherd	*Thick green glass sherd*	*Thick green glass sherd*	*Black, light, glassy material*	*Black, light, glassy material*	*Small thin green sherd*	*Large clear glass sherd*	*Heavily corroded glass sherd*	*Corroded green sherd*	*Green sherd*	*Clear glass sherd*	*Brown glass sherd*	*Light green/ brown sherd*
	Phase 8 precinct	Phase 8 precinct	Phase 8 precinct	Phase 8 precinct	Phase 8 precinct	Phase 8 precinct	Phase 8 precinct	Phase 8 precinct	Phase 8 precinct	Phase 8 precinct	Phase 8 precinct	Phase 8 precinct	Phase 8 precinct
Al_2O_3	7.51	5.05	7.32	24.77	34.72	7.75	1.12	7.27	6.99	7.36	8.21	11.97	11.34
As_2O_3	nd	nd	nd	nd	nd	nd	0.02	nd	nd	nd	0.0136	nd	0.0195
BaO	0.0265	0.208	0.0107	nd	nd	0.0167	0.0314	0.0103	0.0097	0.0149	0.0272	0.0063	0.0176
CaO	26.12	27.25	21.51	22.14	22.65	26.25	8.53	20.04	21.93	9.53	7.22	6.44	7.46
Cl	.3.11	nd	0.328	1.33	1.81	0.399	nd	nd	0.1857	nd	0.0557	nd	nd
Co_3O_4	0.031	0.0303	0.0182	0.0369	0.0329	nd	nd	0.0258	0.0177	0.0142	nd	nd	nd
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe_2O_3	2.79	2.98	1.61	2.07	3.36	2.49	0.0364	2.49	1.87	1.48	0.0349	0.0947	0.898
K_2O	1.739	2.92	1.42	0.484	0.404	1.73	0.0462	1.3	1.82	0.513	0.0635	0.534	0.447
MgO	nd	3.23	3.85	nd	nd	1.27	nd	nd	1.16	nd	nd	nd	nd
MnO	0.152	0.306	0.0985	1.91	0.63	0.103	0.0136	0.13	0.0507	1.81	nd	nd	1.57
Na_2O	nd	nd	nd	nd	nd	nd	12.41	nd	0.478	13.75	11.23	13.15	13.76
NiO	nd	nd	nd	0.024	0.0171	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	nd	nd	nd	0.0178	nd	nd	nd	nd	nd	nd	nd	nd	0.0511
P_2O_5	2.17	1.12	0.807	nd	3.22	1.12	nd	2.15	1.48	nd	nd	nd	nd
PbO	nd	0.0211	nd	nd	nd	nd	nd	nd	nd	0.0098	nd	nd	0.147
SiO_2	58.37	56.21	62.63	29.74	12.07	58.2	77.74	66.29	63.6	65.36	73.1	67.76	64.18
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.008
SO_3	nd	nd	nd	17.21	nd	nd	nd	nd	nd	nd	nd	nd	nd
SrO	0.216	0.175	nd	0.0505	nd	nd	0.0055	0.147	0.132	0.0155	nd	nd	0.0117
TiO_2	0.405	0.336	0.228	0.252	0.326	0.305	0.0278	0.114	0.254	0.0696	0.0166	0.0294	0.0547
V_2O_5	nd	nd	0.0151	nd	0.119	nd	nd	0.0056	nd	0.0081	nd	nd	nd
ZnO	0.016	0.11	nd	0.0546	0.0235	0.011	nd	0.0095	nd	0.009	nd	nd	0.0143
ZrO_2	0.0223	0.033	0.0124	nd	nd	0.019	0.0053	0.0098	0.015	0.0077	nd	0.008	nd
Results given in percentage w/w. nd = not detected													

Appendix 2: Bective Abbey results – washed - cont													
	001.37	**101.2A**	**101.2B**	**102.16**	**102.2**	**103.18**	**110.3**	**203.3**	**207.18**	**207.21**	**207.23**	**301.1(1)**	**301.1 (2)**
	Thick dark green sherd	*Corroded glass sherd*	*Corroded glass sherd*	*Corroded glass sherd*	*Clear glass sherd*	*Corroded green sherd*	*Corroded glass sherd*	*Light, black, glassy material*	*Unknown material*	*Clear glass sherd*	*Thin clear glass*	*Clear sherd*	*Clear sherd*
	Phase 8 precinct	Phase 8 precinct	Phase 8 precinct	Phase 07 pre stoney layer	Phase 07 pre stoney layer	Phase 07 pre stoney layer	Phase 07 pre stoney layer	Garden phase 4	Garden phase 04	Garden phase 04	Garden phase 04	Phase 8 precinct	Phase 8 precinct
Al_2O_3	5.87	9.07	4.74	16.32	6.63	9.26	20	59.27	98.98	14.953	11.68	0.62	7.96
As_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.218	nd
BaO	0.0986	0.069	0.0415	0.0561	nd	0.18	0.186	0.0217	nd	nd	0.0126	0.0442	nd
CaO	26.9	19.62	15.12	16.48	13.92	10.38	11.14	5.49	0.13	6.673	16.7	10.5	7.3
Cl	0.148	0.134	nd	0.093	nd	nd	nd	0.316	nd	nd	nd	0.08	nd
Co_3O_4	0.0139	0.0363	nd	0.0148	0.0172	0.0314	0.0092	0.0137	0.007	nd	nd	nd	nd
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	0.0231	nd	nd	nd	nd	nd
Fe_2O_3	1.84	4.47	0.453	1.16	1.42	1.99	0.787	1.21	0.144	0.0668	0.605	0.0469	0.0605
K_2O	2.1	2.35	0.386	1.57	3.9	1.22	0.99	0.306	0.0454	0.0477	2.59	0.065	0.072
MgO	2.59	nd	nd	1.85	2.42	nd	nd	nd	nd	nd	nd	nd	nd
MnO	0.837	0.162	0.357	0.15	0.15	1.39	0.0449	0.173	nd	nd	0.142	0.0061	0.0124
Na_2O	nd	nd	8.2	nd	1.66	nd	nd	nd	nd	15.46	nd	14.55	10.79
NiO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	nd	nd	0.0154	nd	0.07	0.0452	nd	nd	0.0347	nd	nd	0.0104	nd
P_2O_5	0.705	5.91	nd	nd	0.358	4.63	nd	nd	nd	nd	nd	nd	nd
PbO	nd	nd	0.0293	nd	0.584	0.173	nd	nd	0.166	nd	nd	nd	nd
SiO_2	58.04	57.58	70.52	62.35	66.33	70.11	0.073	25.69	0.57	62.58	68.02	74.22	73.61
SnO2	nd	nd	nd	nd	nd	0.0275	nd	nd	nd	nd	nd	nd	nd
SrO	0.113	0.215	0.0141	0.203	0.34	0.0713	nd	0.109	nd	nd	0.0591	0.0079	nd
TiO_2	0.444	0.304	0.06	0.208	0.155	0.432	0.111	0.412	0.0292	0.02	0.139	0.0251	0.0435
V_2O_5	nd	nd	nd	nd	nd	nd	nd	0.0264	nd	0.0057	nd	nd	nd
ZnO	0.0126	0.0165	0.0073	0.0246	nd	nd	0.0112	0.035	0.0304	nd	0.0193	nd	nd
ZrO_2	0.0185	0.0241	0.0078	0.0132	0.0199	0.0266	0.0099	nd	nd	nd	0.036	0.0081	nd
Results given in percentage w/w. nd = not detected													

Appendix 2: Bective Abbey results – washed – cont.													
	301.25	**A01:010**	**B01:43**	**B01:44**	**B01:45**	**B02:111**	**B09:29**	**B021:101**	**B021:102**	**E01:73**	**E02:52**	**E02:56**	**E02:126**
	Clear sherd, mild corrosion	*Window glass sherd*	*Green body sherd*	*Green body sherd*	*Green body sherd*	*Corroded glass sherd*	*Clear glass sherd*	*Green body sherd*	*Green rim sherd*	*Glass piece*	*Base bottle sherd, green*	*Body sherd*	*Bottle body sherd, green*
	Phase 8 precinct	Phase 08 precinct	Phase 09 Pit	Phase 09 Pit	Phase 09 Pit	Phase 08 precinct	Phase 03/04 post barn, tower	Phase 02 barn	Phase 02 barn	Phase 09 pit	Phase 08 precinct	Phase 08 precinct	Phase 08 precinct
Al_2O_3	7.23	7.55	12.6	7.59	7.61	15.49	12.58	12.43	9.99	7.03	9.86	5.22	11.26
As_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BaO	0.0168	0.0153	0.0394	0.0349	0.0597	0.0341	nd	0.22	0.0173	nd	0.0194	0.0162	0.0296
CaO	20.82	17.83	17.05	18.88	19.96	8.72	8.61	12.71	20.24	6.34	14.06	25.23	16.51
Cl	nd	nd	0.203	0.194	0.208	nd	nd	0.116	0.343	0.223	nd	nd	0.118
Co_3O_4	0.0053	nd	0.0198	0.0227	0.0477	0.0286	nd	0.0326	0.0272	nd	0.0294	0.0512	0.0242
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe_2O_3	0.599	0.66	1.56	1.62	3.88	2.25	0.252	2.56	2.09	0.496	2.01	1.57	1.7
K_2O	3.13	3.18	1.88	2.04	2.06	2.75	0.577	2.44	1	2.67	2.62	1.28	2.2
MgO	0.86	nd	1.75	3.67	nd	0.0703	nd	nd	2.04	3.96	nd	0.88	0.347
MnO	0.158	0.157	0.0951	0.097	0.177	nd	nd	0.164	0.0596	0.0208	0.225	0.11	0.093
Na_2O	nd	nd	nd	nd	nd	nd	11.29	nd	0.676	3.63	1.01	nd	nd
NiO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
P_2O_5	nd	0.31	nd	0.355	3.89	3.17	nd	2.18	nd	nd	nd	1.17	1.41
PbO	nd	nd	nd	nd	nd	0.0055	nd	nd	nd	nd	nd	0.0225	nd
SiO_2	66.95	70.09	64.53	65.22	61.62	67.71	65.54	66.75	63.78	75.33	69.78	64.1	66.28
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SO_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SrO	0.0665	0.0358	0.0568	0.0613	0.184	0.0754	0.0059	0.102	0.0362	0.209	0.06	0.141	0.053
TiO_2	0.136	0.126	0.168	0.172	0.246	0.319	0.116	0.28	0.1901	0.2237	0.249	0.164	0.154
V_2O_5	nd	nd	nd	0.0097	0.0053	nd	nd	nd	nd	nd	nd	nd	nd
ZnO	0.0207	0.0237	0.0098	nd	0.0152	0.0221	nd	0.008	nd	nd	nd	0.0142	0.0205
ZrO_2	0.0097	0.0088	0.0211	0.023	0.0239	0.0177	0.0059	0.0193	0.0159	0.0115	0.039	0.02	0.0109

Results given in percentage w/w. nd = not detected													
Appendix 2: Bective Abbey results – washed – cont.													
	E02:127	**H01:5**	**H02:17**	**H07:04**	**K02:3**	**K02:6a**	**K02:6b**	**K03:2a**	**K03:2b**	**K03:5**	**L02:1a**	**L02:1b**	**M01:3a**
	Bottle base sherd, green	*Orange/ brown sherd*	*Ceramic like piece*	*Olive green sherd*	*Corroded green sherd*	*Olive green glass*	*Olive green glass*	*Olive green glass*	*Olive green glass*	*Olive green sherd*	*Clear glass sherd*	*Clear glass sherd*	*Green corroded sherd*
	Phase 08 precinct	Phase 10 Inside Boundary	Phase 08 Precinct	Phase 06 post east/west wall	Garden Phase 04	Garden Phase 04	Garden Phase 04	Garden Phase 04	Garden Phase 04	Garden Phase 04	Phase 08 precinct	Phase 08 precinct	Garden Phase 04
Al_2O_3	10.89	5.79	14.07	9.64	5.46	7.56	11.3	8.21	9.51	5.11	8	16.5	10.69
As_2O_3	nd	0.0239	nd	nd	nd	nd	nd	nd	nd	nd	0.0236	0.0147	nd
BaO	0.019	0.026	nd	0.0506	0.142	0.303	0.256	0.223	0.202	0.327	0.166	0.079	0.0345
CaO	21.76	11.11	5.79	11.76	20.34	25.31	20.45	22.39	20.74	26.53	8.09	5.57	11.38
Cl	0.72	nd	nd	nd	0.0491	0.163	nd	nd	0.169	0.256	0.0505	0.0553	nd
Co_3O_4	0.043	1.39	0.0254	nd	0.0267	0.0206	0.0178	nd	nd	0.0196	nd	nd	nd
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe_2O_3	2.9	nd	2.1	3.67	2.71	2.22	2.17	1.7	1.63	2.34	0.0421	0.0428	3.47
K_2O	0.869	0.68	2.39	3.25	1.88	2.2	1.76	1.95	1.94	2.29	0.0906	0.0445	1.7
MgO	1.55	nd	nd	nd	nd	4.19	2.21	4.94	4.58	3.44	nd	nd	nd
MnO	0.105	2.56	0.0291	0.161	0.262	0.351	0.311	0.269	0.248	0.315	nd	0.0058	0.0813
Na_2O	1.59	12.46	1.14	nd	nd	nd	nd	nd	nd	nd	10.85	12.66	nd
P_2O_5	nd	nd	nd	2.64	0.65	nd	0.439	nd	nd	nd	nd	nd	nd
PbO	nd	0.204	nd	0.0125	nd	nd	nd	nd	nd	nd	nd	nd	0.0061
SiO_2	59.08	65.27	74.22	67.94	65.45	57.33	60.64	59.83	60.62	58.93	72.17	64.86	70.3
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SO_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.35
SrO	0.07	0.0202	0.0122	0.11	0.132	0.153	0.133	0.131	0.105	0.155	0.0111	0.007	0.0732
TiO_2	0.336	0.238	0.197	0.47	1.56	0.265	0.28	0.233	0.223	0.228	0.0447	0.0602	0.671
V_2O_5	0.0117	nd	0.0085	0.0237	nd	0.0158	nd	0.0152	0.0129	nd	nd	nd	nd
ZnO	nd	0.0165	nd	0.0367	0.028	nd	nd	nd	nd	nd	nd	nd	0.0123
ZrO_2	0.0229	nd	0.0077	0.0464	0.0205	0.0272	0.0244	0.084	0.0188	0.0223	0.0162	0.0094	0.0207
Results given in percentage w/w. nd = not detected													

Appendix 2: Bective Abbey results – washed – cont.													
	M01:3b	**M01:3c**	**N02:2a**	**N02:2b**	**N02:2c**	**N02:2d**	**P01:014**	**P01:015**	**P01:016**	**P01:26**	**P01:27**	**P01:235**	**P01:236**
	Green corroded sherd	*Clear sherd*	*Olive green sherd*	*Olive green sherd*	*Olive green sherd*	*Olive green sherd*	*Clear glass sherd*	*Clear glass sherd*	*Clear glass sherd*	*Olive green sherd*	*Olive green sherd*	*Olive green sherd*	*Green glass sherd*
	Garden Phase 04	Garden Phase 04	Not listed	Not listed	Not listed	Not listed	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct
Al_2O_3	10.16	2.34	6.98	7.1	16.39	6.94	1.12	nd	5.29	14.16	17.74	1.69	9.63
As_2O_3	nd	0.121	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BaO	0.0489	0.0158	0.57	0.541	0.175	0.31	nd	nd	nd	0.0329	0.514	0.0793	0.0169
CaO	13.59	18.14	23.59	23.08	10.91	24.95	13.18	11.65	9.6	7.78	13.25	8.82	8.85
Cl	nd	nd	0.29	0.268	nd	0.2	nd	0.051	0.054	nd	0.204	nd	0.057
Co_3O_4	nd	nd	0.0195	nd	nd	nd	nd	nd	nd	0.0162	nd	nd	nd
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe_2O_3	3.39	0.348	2.05	1.79	1.08	2.15	0.308	0.24	0.259	1.45	0.786	0.0567	1.57
K_2O	1.27	0.652	2.18	2.15	1.5	2.15	0.193	0.0603	0.164	0.38	1.24	nd	0.539
MgO	nd	nd	4.02	4.1	2.63	4.37	5.73	nd	4.04	nd	nd	nd	nd
MnO	0.146	0.0103	0.264	0.232	0.208	0.281	0.0151	nd	0.0059	1.94	0.126	nd	2.14
Na_2O	nd	7.04	nd	nd	nd	nd	7.05	16.34	4.78	15.77	nd	15.28	18.09
NiO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	nd	0.0188	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
P_2O_5	2.49	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PbO	0.0089	nd	nd	nd	nd	nd	nd	nd	nd	0.0095	nd	nd	0.011
SiO_2	67.49	70.66	59.55	60.32	61.67	58.22	72.47	71.64	75.68	58.35	66.03	73.99	58.95
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SO_3	0.503	0.52	nd	nd	nd	nd	0.279	nd	nd	nd	nd	nd	nd
SrO	0.109	0.0139	0.236	0.2	0.0788	0.141	0.009	0.0154	0.0058	0.0121	0.0743	0.02	0.0152
TiO_2	0.713	0.0808	0.214	0.21	0.315	0.251	0.0402	nd	0.112	0.0694	nd	0.0444	0.0868
V_2O_5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.006	0.0072
ZnO	0.0195	nd	nd	nd	nd	nd	nd	nd	nd	0.007	nd	nd	0.0086
ZrO_2	0.0289	0.0102	0.0256	0.0173	0.0125	0.0194	0.009	nd	nd	0.0076	0.0103	nd	0.0064
Results given in percentage w/w. nd = not detected													

Appendix 2: Bective Abbey results – washed – cont.													
	P01:237	**P03:1**	**Q01:001**	**Q01:002**	**Q01:27**	**Q01:46**	**Q01:55**	**Q03:08**	**Q03:09**	**Q05:3**	**Q05:4**	**Q05:5**	**Q05:6**
	Green glass sherd	*Corroded bottle rim sherd*	*Black bottle base sherd*	*Clear glass sherd*	*Clear glass sherd*	*Small olive green sherd*	*Green glass sherd*	*Thick base glass sherd*	*Thick base sherd*	*Thin green sherd*	*Thin green sherd*	*Thin green sherd*	*Thin green sherd*
	Phase 10 precinct	Phase 08 precinct	Phase 08 precinct	Phase 08 precinct	Phase 08 precinct	Phase 08 precinct	Phase 08 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct
Al_2O_3	2.61	16.66	11.09	1.72	8.59	12.25	13.54	13.07	10.22	8.14	7.94	8.07	8.26
As_2O_3	nd	nd	nd	nd	0.1645	nd	nd	0.0073	nd	0.119	0.0118	0.0123	0.0057
BaO	0.0227	0.0742	0.0236	nd	0.0171	0.0133	0.0165	0.0088	0.0589	0.0423	0.0562	0.0638	0.0163
CaO	13.57	9.48	23.09	13.53	6.37	10.39	10.92	14.07	10.68	19.52	19.98	19.55	18.62
Cl	0.0572	nd	0.1609	0.095	0.05	nd	nd	0.359	nd	0.438	0.511	0.462	0.473
Co_3O_4	nd	nd	0.0278	nd	nd	0.108	0.0182	0.0145	0.0393	0.0196	0.0177	0.0307	0.0129
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe_2O_3	2.4	2.77	3.4	0.04	0.111	4.73	1.25	1.6	3.23	1.77	1.88	1.78	1.63
K_2O	0.705	1.27	1.31	0.134	0.1023	0.904	1.88	1.18	2.49	2.63	2.67	2.64	2.48
MgO	nd	nd	1.86	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MnO	2.97	0.107	0.0519	nd	0.0055	0.135	0.265	0.0257	0.116	0.1087	0.146	0.186	0.0667
Na_2O	11.73	nd	0.52	12.37	2.92	nd	nd	nd	nd	1.6	1.44	1.53	3.45
NiO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	0.0056	nd	nd	nd	nd	0.0059	nd	nd	0.0094	nd	nd	nd	0.0063
P_2O_5	nd	3.88	nd	nd	nd	nd	nd	nd	3.84	nd	nd	nd	0.327
PbO	0.0161	0.0068	nd	nd	nd	4.35	nd	nd	0.0159	0.0122	0.0128	nd	0.0331
SiO_2	65.72	65.27	57.54	72.05	80.95	66.78	71.87	68.65	68.73	65.37	64.98	65.31	63.87
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SO_3	nd	nd	0.0329	nd	0.452	nd	nd	0.718	nd	nd	nd	nd	0.44
SrO	0.0253	0.0762	nd	0.0069	nd	nd	0.0399	0.0135	0.14	0.0644	0.0709	0.0668	nd
TiO_2	0.0974	0.35	0.257	0.0153	0.0588	0.288	0.151	0.172	0.363	0.211	0.227	0.216	nd
ZnO	0.0134	0.0156	nd	0.0797	0.0156	nd	0.0797	nd	0.0096	nd	nd	0.0242	nd
ZrO_2	0.0084	0.0194	0.0172	nd	0.0194	0.0172	nd	nd	0.0078	0.0259	0.0094	0.0223	0.0134
Results given in percentage w/w. nd = not detected													

Appendix 2: Bective Abbey results – washed – cont.													
	Q05:7	**Q05:8**	**Q05:9**	**Q05:10**	**Q05:11**	**Q05:12**	**Q05:13**	**Q05:14**	**Q05:15**	**Q05:16**	**Q07:03**	**Q07:04**	**R01:39**
	Thin green sherd	*Thin green sherd*	*Thin green sherd*	*Thin green sherd*	*Thin green sherd*	*Thin green sherd*	*Thin green sherd*	*Thin green sherd*	*Thin green sherd*	*Thin green sherd*	*Sherd modern glass*	*Sherd modern glass*	*Sherd of thick opaque glass*
	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 07 pre stoney layer	Phase 07 pre stoney layer	Garden phase 04
Al_2O_3	8.27	8.48	3.56	8.38	8.34	8.46	8.35	8.42	8.38	8.41	8.46	9.92	5.14
As_2O_3	0.0082	0.0061	nd	0.0057	0.00602	0.0085	0.0073	.0079	.0069	.0072	nd	0.0071	nd
BaO	0.0177	0.0148	0.0097	0.0149	0.0142	0.0156	0.018	.0178	.0179	.0165	0.0276	0.026	0.0747
CaO	18.81	18.38	6.63	18.29	18.42	18.34	19.02	18.64	18.98	18.75	18.24	15.22	18.56
Cl	0.511	0.513	0.881	0.521	0.495	0.477	0.532	.489	.515	.492	0.428	0.44	nd
Co_3O_4	nd	0.0135	nd	nd	0.0136	0.0147	0.125	.0129	.0128	.0132	0.0119	0.0152	nd
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.0076
Fe_2O_3	1.66	1.58	0.317	1.59	1.59	1.6	1.69	1.64	1.67	1.62	1.5	1.19	1.68
K_2O	2.48	2.51	0.877	2.46	2.49	2.46	2.55	2.48	2.5	2.48	2.5	2.18	3.31
MgO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MnO	0.0672	0.0649	0.618	0.0616	0.0622	0.062	0.0706	.0690	.0657	.0687	0.0581	0.076	0.186
Na_2O	3.21	3.31	4.72	3.31	2.64	3.24	2.04	2.75	2.70	2.68	1.55	1.81	nd
NiO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
P_2O_5	0.326	0.17	nd	nd	0.174	0.0103	0.23	.211	.198	.052	0.1296	0.26	1.81
PbO	0.0328	0.0093	nd	0.0108	0.0098	nd	0.0109	.0106	.0109	.0102	nd	nd	0.0371
SiO_2	64.31	64.64	82.09	65.07	65.45	65.03	65.115	65.29	65.32	65.19	66.67	68.34	68.85
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SrO	0.0584	0.0556	0.0492	0.0556	0.055	0.0557	0.0593	.0590	.0578	.0581	0.0539	0.043	0.0602
TiO_2	0.202	0.212	0.0468	0.203	0.194	0.203	nd	nd	nd	nd	0.211	0.163	0.234
V_2O_5	0.0105	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.0105	nd	nd
ZnO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.0168
ZrO_2	0.0157	0.0128	nd	nd	nd	0.0056	nd	nd	nd	nd	0.0112	0.0099	0.0207
Results given in percentage w/w. nd = not detected													

Appendix 1: Bective Abbey results – washed – cont.										
	SN01:6	**SN01:7**	**SN01:8**	**SN02:84**	**SS01:04**	**SS01:05**	**SS01:16**	**SS01:17**	**SS01:49**	**SS05:16**
	Clear glass sherd	*Clear glass sherd*	*Clear glass sherd*	*Small clear sherd*	*Clear glass sherd*	*Clear glass sherd*	*Thick green sherd*	*Brown sherd*	*Olive green glass sherd*	*Opaque black sherd*
	Phase 08 precinct	Phase 08 precinct	Phase 08 precinct	Phase 08 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 10 precinct	Phase 02 barn
Al_2O_3	2.08	2.64	2.26	10.73	3.09	1.38	7.72	7.4	3.03	8.55
As_2O_3	0.0326	0.0403	0.0316	nd	0.0454	nd	nd	nd	nd	nd
BaO	0.0129	0.0124	0.0123	nd	0.0145	nd	0.028	0.0206	0.032	0.053
CaO	15.39	17.11	15.42	7.16	18.51	12.41	25.76	9.57	21.55	6
Cl	nd	nd	nd	0.092	nd	nd	0.839	0.053	0.191	nd
Co_3O_4	nd	nd	nd	nd	nd	nd	0.027	nd	nd	0.1057
Cr_2O_3	nd	nd	nd	nd	nd	nd	0.0058	nd	nd	nd
CuO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe_2O_3	0.207	0.306	0.096	0.049	0.326	0.0836	3.21	1.51	1.72	2.14
K_2O	0.096	0.39	nd	0.096	0.128	0.0747	0.608	0.639	1.68	0.9483
MgO	nd	nd	nd	nd	nd	nd	3.03	nd	nd	nd
MnO	0.0252	0.0351	0.0263	nd	0.0416	nd	0.0465	1.97	0.076	2.59
Na_2O	8.34	7.79	7.49	12.29	6.44	13	nd	8	nd	nd
NiO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
OsO_4	nd	0.0077	0.0082	nd	0.0121	nd	nd	0.0127	nd	nd
P_2O_5	nd	nd	nd	nd	nd	nd	nd	nd	nd	3.16
PbO	0.0352	0.0453	0.0381	nd	0.0524	nd	nd	0.0306	nd	nd
SiO_2	73.31	71.71	74.08	69.55	70.82	73.02	58.18	70.62	70.66	75.88
SnO2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SO_3	0.34	nd	0.32	nd	0.43	nd	nd	nd	nd	nd
SrO	0.0094	0.0118	0.0095	nd	0.0137	nd	0.113	0.0094	0.133	0.0451
TiO_2	0.0368	0.0702	0.0369	0.0141	0.0604	0.0171	0.37	0.125	0.218	0.3613
V_2O_5	nd	nd	nd	nd	nd	nd	0.0154	nd	0.0096	0.0174
ZnO	0.0148	0.0183	0.0149	nd	0.0219	nd	nd	0.0092	nd	0.039
ZrO_2	nd	nd	nd	nd	nd	nd	0.0287	0.0104	0.0152	0.0317
Results given in percentage w/w. nd = not detected										

Appendix I: Analysis of glass from Moygara Castle, Co. Sligo, excavation number 13E161

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Appendix I: Moygara Castle, Co. Sligo

1. Introduction

This report details the analysis of a number of glass fragments and glaze-covered stones which were uncovered during excavations at Moygara Castle, Co. Sligo. The multi-elemental analysis was carried out using X-ray Fluorescence (XRF) at IT Sligo. The aim of this analysis was to determine trace elements within the glass objects which could potentially answer questions about their origin or production. A total of twelve glass pieces and two stones with glaze on their surface were analysed. Moygara Castle was one of the main residences of the O'Garas, who were a prominent Sligo family. There are records of the site being attacked in 1538 and again in 1581 by the O'Donnell family and Scottish mercenaries respectively (O'Rorke 1889, 364-365). The current structure consists of a curtain wall with a tower at each corner, a gate-tower in the middle of the west side and the lower courses of a rectangular structure along the inside of the north wall. With the exception of the rectangular structure in the north wall which is most likely the remains of a medieval tower house, the rest of the structure most likely dates to the late 16th or early 17th centuries (Egan *et al*. 2005, 479).

2. Methodology

2.1. Sample collection and selection

The glass fragments from excavations at Moygara were provided by Chris Read from IT Sligo for the purpose of this study. The samples were chosen from the Moygara glass assemblage, with a number of objects being excluded. For example, two other glazed stone pieces from the site had to be excluded from the analysis as they were either too large to fit in the XRF or their surfaces were too flaky. In total, 14 pieces of glass and glazed stones were analysed using XRF analysis.

2.2. Calibration/Quality Control

The XRF was calibrated monthly using the standard procedure for this instrument. The accuracy of the instrument is also tested regularly using standard glass reference material. Table 1 below illustrates the accuracy and precision of the instrument using a standard sample. The reference material was run 5 times and an average taken of the results.

	Stated concentration (%w/w)	**Average obtained (%w/w)**	**Relative Standard Deviation%**	**%Error**
SiO_2	72.26	72.62	0.360	0.503
Na_2O	13.78	12.88	1.399	-6.516
CaO	10.05	10.71	0.598	7.000
MgO	3.40	3.64	2.423	-0.0549
SO_3	0.270	0.027	9.658	-90.074
TiO_2	0.033	0.0237	7.413	-28.121
Fe_2O_3	0.021	0.0177	4.058	-15.619

Table 1: Reference sample results obtained

(nd = not detected, nc = not calculated)

2.3. Sample washing and preparation

A solution consisting of a 1:1 ratio of deionised water and 99% ethanol solution was prepared in a volumetric flask. The surface of each sample was gently cleaned using a clean cotton swab dipped in the deionised water/ethanol solution prior to being analysed in the XRF. The purpose of this technique was to remove surface contamination on the surface of the glass. Different trace elements can be left on the glass from many processes such as salts left behind from washing with ordinary water or chlorine transferred from handling the samples with bare hands. By removing such elements, a clearer result of the elemental composition of the surface

layers of the glass can be obtained. The above washing method was decided in consultation with the National Museum of Ireland after extensive experimentation on modern glass samples. The samples were left to dry completely before undergoing analysis. All samples were handled using gloves to avoid adding any further surface contamination.

2.4. Testing of samples

Each sample was analysed by XRF in triplicate and the results averaged. Samples were analysed in the condition they were received with no preparation method utilised aside from the washing technique outlined above. XRF was chosen for this analysis as it provides a highly sensitive, multi-elemental analysis and is completely non-destructive. XRF is a surface technique, therefore the elemental composition it gives is indicative of the surface layers only and this may not be an accurate representation of the whole sample.

3. Results

The results of the analysis (given in percentage w/w) can be seen in Appendices 1 and 2 at the end of this report. The first shows the results from the 12 glass samples, while the second shows the results from the two pieces of glazed stone that were obtained during this study.

Discussion

4.1 Condition of samples

All of the glass sherds analysed from this site were in a fragmented condition. None of the fragments exhibited any visible signs of corrosion such as crusting, flaking or pitting of their surfaces.

4.2 Elemental Composition

From ancient times, glass has been consistently made up of a glass former, such as sand or quartz pebbles (SiO_2), a modifier, such as soda (Na_2O) or potash (K_2O), and a stabilizer such as lime ($CaCO_3$). As well as this, glass may contain a variety of colouring agents, opacifiers and other trace elements, added either intentionally or unintentionally (Goffer 2007, 124). From an analytical point of view, the composition of ancient soda-lime glass is typically 73% SiO_2 (silica), 23% Na_2O (soda) and 5% CaO (calcium oxide) (Gratuze and Janssens 2004, 605). Potash (K_2O) may have been added to the mixture instead of soda, or sometimes a mixture of the two was used as a modifier substance. Generally, the lowest concentrations which would have been added would have been at least 15% (Shortland 2012, 101).

4.2.1 Light green bottle glass from Cutting 2, context F14

This light green glass sherd, which can be seen in Plate 1, appears to be part of a glass bottle. The main component of this glass piece was silica (SiO_2) which accounted for 66.08% of its composition. The slightly low percentage of silica coincides with a slightly elevated level of aluminium oxide (Al_2O_3) at 6.44%. Aluminium may have existed in the structure of glass originally in smaller amounts and was held preferentially compared to other elements when the surface layers were leached of part of their composition. There is also the possibility that the surface layers contained aluminium which had entered from the environment. In addition, the levels of modifier appeared to have been reduced with only 4.68% soda (Na_2O) and only trace amounts of potash (K_2O) at 0.531%. These low levels highlight the corroded nature of the surface layers of the glass, despite its visual appearance being good.

Ground water can interact with buried glass material affecting the stability of the object. Signs that a glass fragment may have been affected by this include a flaky

coating and iridescence on the surface of the object, however even glass which appears visually in good condition can be heavily affected (Pollard and Heron 2008, 119, 178). There is no sign of pitting, crusting or iridescent sheen on this green sherd yet the elemental analysis shows that corrosion has occurred nonetheless. Glass corrosion is a complex process which is not well understood, being affected by many different factors. However it is thought that it occurs due to the preferential leaching of alkali ions to be replaced by hydrogen ions (Wayne Smith 2003, 94). The reaction begins at the surface of the object and spreads inwards (Varshneya 1994, 398). Cox and Ford (1993, 5639-43) conducted a detailed elemental study of multiple layers of medieval glass and concluded that corroded surface layers can be depleted of most oxides except silica (Si), aluminium (Al) and iron (Fe), and what is left behind is poorly crystalline hydrated silicates and aluminosilicates with varying amounts of calcium (Ca), phosphate (P) and manganiferous (Mn) minerals. The fact that this glass piece has an elevated concentration of aluminium oxide is a good indicator that some amount of corrosion has taken place.

As mentioned already, this piece contained depleted amounts of modifier. Soda, potash or a mixture of the two was an essential component when producing glass in ancient times as it lowered the melting point of silica from 1700^{o}C to 1000^{o}C, a temperature which was obtainable in ancient furnaces (Goffer 2007, 115). As mentioned, the level of soda and potash can be up to around 23% for ancient glass. Generally, the lowest concentrations which would have been added would have been at least 15%. Potash was obtained by burning wood ash while soda was generally sourced from marine plants. Potash glass was produced with increasing frequency during the medieval period when demand for glass was growing and a more readily accessible alkali source was sought. This follows a similar trend in Britain, where analysis shows that potash was being produced in quantity from the 13th or 14th century (Moran 2010, 17). There are many reasons why corrosion may affect glass, such as environmental factors but the most important factor in most cases is the original elemental composition of the glass. This determines the resistance of the glass to agents which can cause corrosion such as water, acidic and basic solutions and other atmospheric substances (Pollard and Heron 2008, 166). In

the case of medieval window glass for example, it has been noted that potash-based examples were more susceptible to weathering due to the high alkalinity of the glass (Moran 2010, 17). The small amounts of both soda and potash in this find would suggest that it was probably produced from a mixed alkali glass.

The greenish colour of this find was due to the iron oxide (Fe_2O_3) it contained, which accounted for 0.735% of its surface composition. Other substances known to act as green colourants, such as oxides of copper, chromium and nickel, were absent. Iron impurities, both ferrous (Fe^{2+}) and ferric (Fe^{3+}) occur frequently in sand which was often used as a silica source. As such, iron contaminants were often added unintentionally to the glass melt during glass production which is why green is one of the most common colours for ancient glass. This would suggest that the green colour of this piece could well have been unintentional. Manganese oxide (MnO) was sometimes used as a decolourant to counteract the green caused by iron impurities and produce a clear colour. While this substance is present in this sherd, it only accounts for 0.264%. Such a low quantity was probably not purposely added in an attempt to decolour the glass and instead was most likely added unintentionally as part of the potash that was sourced. The amount of trace elements in this find, as well as the corrosion of its surface layers would suggest that this piece of glass came from a Post-Medieval glass bottle. Its shape is also consistent with having come from the main body of a glass bottle. Air bubbles are also apparent on visual examination of the piece which would further support a Post-Medieval date for this piece rather than modern, given that such imperfections would be easily eliminating if modern furnaces and glass-making techniques were utilised.

Chlorine (Cl) was found in all except one of the glass finds. It accounted for 0.096% of this greenish sherd. Chlorine can be transferred onto the surface of glass from handling objects with bare hands or from rinsing the finds with tap water. However, as these beads were submitted to a washing technique, it would be expected that much of this sort of contamination would have been removed. Extensive experimentation with modern glass samples highlighted that washing with an ethanol and deionised water solution effectively reduced the amount of trace

elements on the surface of the objects, particularly when the fragments had previously been left exposed outside. Gloves were used when handling the finds at all times during their analysis, so any contamination was not added immediately prior to analysis and would have been present on the surface of the glass for some time. It is possible for glass to contain some chlorine as part of its original structure, added in unintentionally as part of the source of soda or potash (Henderson 2000, 94).

4.2.2 Ten green glass sherds from Cutting 4, context F25 (numbered 1-5 and 7-11 in Appendix 1)

These ten green sherds, as seen in Plate 2, 3 and 5, are dark green body sherds, most likely from a bottle. The silica (SiO_2) concentrations for these pieces were between 59.64% and 70.85%. The concentrations of potash (K_2O) were between 0.0058% and 2.28% while the soda (Na_2O) concentrations were between 1.16% and 6.01% for four of the ten examples with the other six having no detectable amounts of soda. The aluminium oxide (Al_2O_3) concentrations ranged between 2.14% and 21.82%, once again indicating high levels of corrosion in some of the pieces. The bottle green colour exhibited by these sherds was caused by their concentrations of iron oxide (Fe_2O_3) which were between 0.0566% and 2.16%. Other green colourants, such as chromium oxide (CrO) and nickel oxide (NiO) were not detected in any of the pieces suggesting that the levels of iron oxide were high enough to cause the green hue. The composition of all these pieces, with elevated levels of aluminium oxide and reduced amounts of modifier substances would suggest typical low-quality bottle glass, quite possibly Post-Medieval as opposed to modern given that the surface layers have undergone a great deal of corrosion. However the variable amounts of modifier and trace elements would suggest that they did not all come from the same object. For example, only find No. 2 and find No. 11 contained traces of sulphur oxide (SO_3) at 0.38% and 0.0629% respectively, three of the ten pieces contained lead oxide (PbO) of between 0.0057% and 0.0104% and four of the ten pieces contained strontium oxide (SrO) of between 0.0092% and 0.0879%.

4.2.3 Clear sherd from Cutting 4, context F25 (numbered 6 in Appendix 1)

This clear sherd, seen in Plate 4, contained 71.14% (SiO_2), 13.6% soda (Na_2O) and 0.0718% of potash (K_2O). It contained 6.1% aluminium oxide (Al_2O_3) which would suggest some corrosion of the surface layers. It had 0.0321% iron oxide (Fe_2O_3) and contained no concentrations of any elements which would have acted as decolourants. It also had very few trace elements within its structure, containing no detectable levels of zinc oxide (ZnO), zirconium oxide (ZrO_2), copper oxide (CuO) or barium oxide (BaO) which were found in many of the other glass pieces. This suggests that this particular sherd was modern, as a much wider and higher percentage of trace elements would be expected in the composition of glass produced in ancient furnaces where it was much harder to exclude impurities. It had likely been exposed to the elements for some amount of time given that there is some evidence of corrosion based on the aluminium oxide being slightly higher than would be expected. Although a small fragment, its flat shape would suggest that it came from a sheet of window glass.

4.2.4 Glazed stones from Cutting 3, context F4 (numbered 1 and 2 in Appendix 2)

Two stones with glaze were analysed as part of this study from a total of four which were uncovered during the excavations (Plate 6). The others were too large to be analysed by the XRF. All four of the stones were found in Cutting 3, context F4. The results obtained from the two glazed stones can be seen in Appendix 2. While the function of these pieces is not clear, it appears that they were formed when molten glass was dropped on to stones. It could potentially be waste glass from glass production or pottery glazing.

The silica (SiO_2) concentrations for these stones were 75.81% and 79.96% for the first and second stone respectively while the aluminium (Al_2O_3) concentrations were found to be 5.79% and 9.81% respectively. This concentration of aluminium is

slightly elevated and is probably an effect of corrosion on the surface layers of the object. The glaze on both stones had relatively high amounts of silica compared to the glass pieces on the site and is likely indicative of a different production method being used. Only the second stone had detectable amounts of soda (Na_2O) with a concentration of 2.47%.The level of potash (K_2O) for these finds was 10.72% and 3.77% respectively. This result suggests that different types of modifier were used to produce the glaze on each of these stones. Both of these glazed stones contained iron oxides (Fe_2O_3), with concentrations of 2.37% and 1.82% respectively. This may well have been added in unintentionally as part of the raw materials that were used. The two glazes differ in the trace elements that they contained, further supporting the suggestion that they were not produced in the same way. One of the stones also contained low amounts of copper oxide (CuO) at 0.0285%. The only evidence that the glassmakers attempted to manipulate the colour of the glassy material on the second stone was the fact that it contained trace concentrations of copper oxide of 0.012% which could potentially have acted as a colourant. However this amount of copper oxide was in such a low concentration that it is more likely that this was added in unintentionally as part of the raw materials of the glass. The glaze on both stones appeared to have a slight green tinge, however this was most likely caused by the significant level of iron oxides found in both finds.

Conclusion

The majority of the glass found on this site consisted of pieces of Post-Medieval bottle glass. The light green sherd from Cutting 2 as well as the ten green glass sherds from Cutting 4, context F25 all consisted of either potash-based or mixed-alkali Post-Medieval bottle glass which obtained their colour from iron contaminants in their structures. All of the green glass pieces exhibited corrosion of the surface layers with elevated levels of aluminium oxide and reduced amounts of modifier substances. The exception was a clear glass sherd, numbered 6 in Appendix 1 which was a modern soda-lime-silica glass which appeared to have come from a pane of window glass. The layers of glaze on the two stones which were analysed appeared

to have very different production methods. One was obtained its colour solely from its concentrations of iron oxide (Fe_2O_3) while the second had copper oxide (CuO) in addition to iron oxide. Furthermore, the first example seems to have been a potash-based glass while the second was more likely a mixed-alkali example.

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Plate 1: Light green bottle glass from Cutting 2, context F14

Plate 2: Two green sherds from Cutting 4, context F25 (numbered 1 and 2 in Appendix 1)

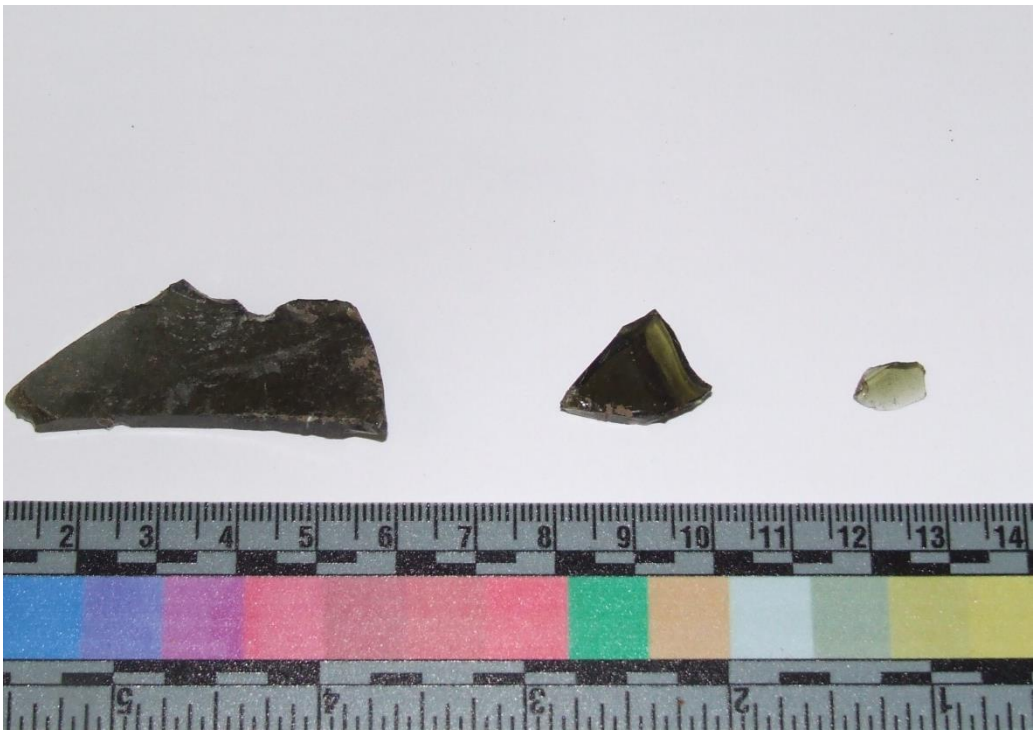

Plate 3: Three green sherds from Cutting 4, context F25 (numbered 3-5 in Appendix 1)

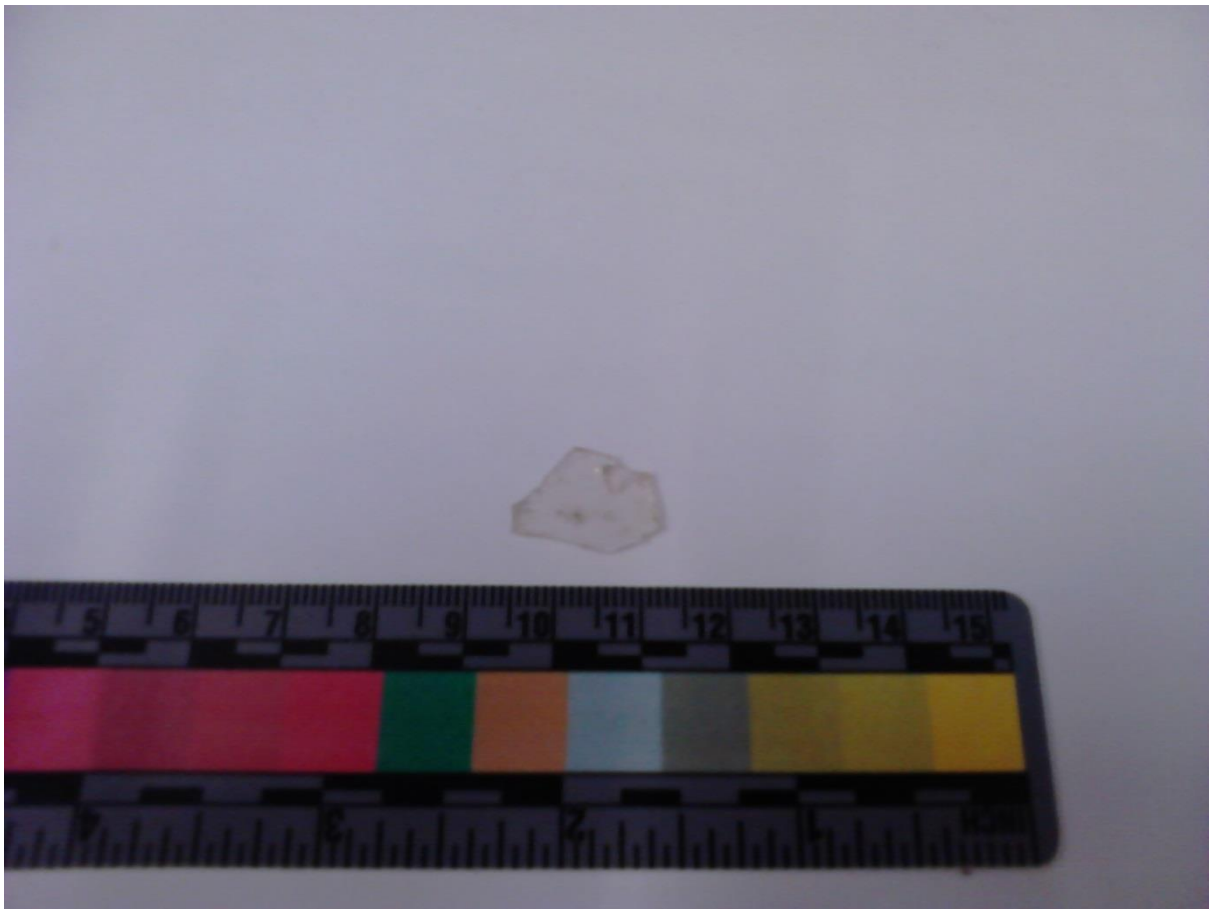

Plate 4: Clear glass sherd from Cutting 4, context F25 (numbered 6 in Appendix 1)

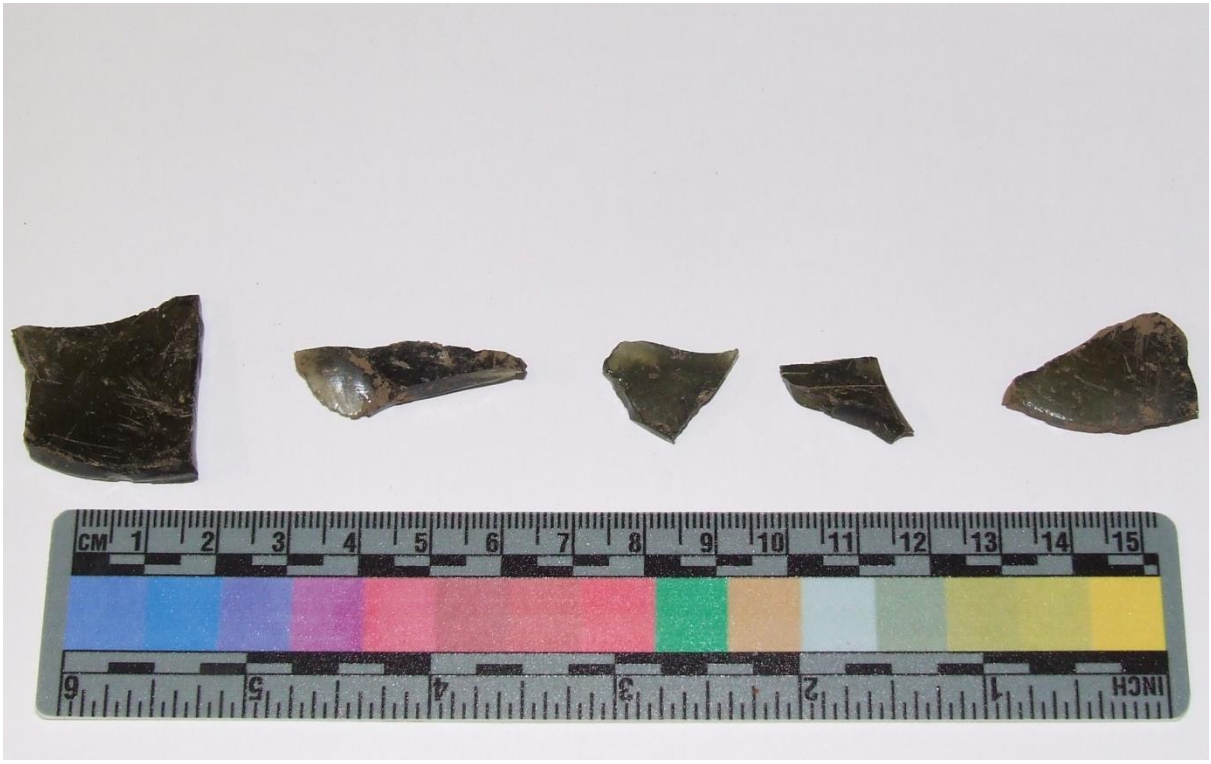

Plate 5: Five green sherd from Cutting 4, context F25 (numbered 7-11 in Appendix 1)

Plate 6: Two glazed stones from Cutting 2, context F4 (numbered 1 and 2 in Appendix 2)

Appendix 1: Glass results (Results given in percentage w/w) (nd = not detected)

Cutting:	C2	C4	C4	C4	C4	C4	C4	C4	C4	C4	C4	C4
Context:	F14	F25	F25	F25	F25	F25	F25	F25	F25	F25	F25	F25
Description:	Green glass	Green glass (1)	Green glass (2)	Green glass (3)	Green glass (4)	Green glass (5)	1 sherd clear glass (6)	Green glass (7)	Green glass (8)	Green glass (9)	Green glass (10)	Green glass (11)
Al_2O_3	6.44	2.30	16.19	5.13	5.61	21.82	6.10	4.60	21.14	9.92	6.95	14.98
BaO	0.0447	0.0554	0.102	0.0934	0.0711	0.0153	nd	0.117	0.0056	0.0628	0.0801	0.0457
CaO	20.21	19.53	7.38	24.31	19.51	14.36	8.86	23.16	10.41	20.22	19.05	16.36
Cl	0.096	0.313	0.07	0.282	0.282	nd	0.068	0.284	0.193	0.218	0.239	0.157
Co_3O_4	nd	0.0139	nd	0.0267	nd	nd	nd	0.0211	0.0149	0.0146	0.0128	0.0121
CuO	nd	nd	nd	0.0065	nd	nd	nd	0.0058	nd	nd	nd	nd
Fe_2O_3	0.735	1.26	0.0566	2.16	1.43	0.778	0.0321	1.99	1.60	1.54	1.46	0.972
K_2O	1.27	1.95	0.058	2.28	1.96	1.29	0.0718	2.07	1.79	1.94	1.89	1.58
MgO	nd	2.5	nd	1.75	2.00	1.62	nd	2.34	2.42	1.4	1.89	0.0672
MnO	0.264	0.0888	0.0076	0.159	0.107	0.0574	0.0875	0.144	0.0841	0.107	0.108	nd
Na_2O	4.68	nd	6.01	1.16	1.27	nd	13.6	2.14	nd	nd	nd	nd
OsO_4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PbO	nd	0.0057	nd	0.0104	0.0064	nd	nd	0.0102	nd	0.0066	0.0067	nd
Sb_2O_3	nd	nd	nd	nd	nd	nd	0.0186	nd	nd	nd	nd	nd
SiO_2	66.08	70.85	69.62	60.83	67.46	59.64	71.14	61.23	61.95	63.73	68.06	65.61
SnO2	nd	nd	nd	0.0051	nd	nd	nd	0.0059	nd	nd	nd	nd
SO_3	nd	nd	0.38	nd	nd	nd	nd	nd	nd	nd	nd	0.0629
SrO	0.0074	0.0817	0.0092	nd	0.0879	0.0474	nd	nd	0.166	0.0963	nd	0.11
TiO_2	0.148	0.141	0.072	nd	0.15	0.088	0.0157	nd	0.203	0.166	0.123	nd
V_2O_5	nd	0.0063	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.0124
ZnO	nd	nd	nd	nd	0.0213	0.0176	nd	nd	0.0058	0.0232	0.0202	0.0119
ZrO_2	0.0151	nd	0.0118	nd	0.0155	0.0076	nd	nd	0.0129	nd	170	nd

Appendix 2: Glazed stones results (Results given in percentage w/w) (nd = not detected)

Cutting:	C3	C3
Context:	F4	F4
Description:	Large stone with glaze (1)	Small stone with glaze (2)
Al_2O_3	5.79	9.81
As_2O_3	nd	nd
BaO	0.0126	0.0121
CaO	4.09	1.3
Cl	nd	nd
Co_3O_4	0.0296	nd
CuO	0.0285	0.012
Fe_2O_3	2.37	1.82
K_2O	10.72	3.77
MnO	0.333	0.0748
Na_2O	nd	2.47
OsO_4	nd	nd
PbO	nd	nd
Sb_2O_3	nd	nd
SiO_2	75.81	79.96
SnO2	nd	nd
SO_3	nd	nd
SrO	0.0167	0.0066
TiO_2	0.302	0.243
V_2O_5	0.0095	0.0125
ZnO	nd	nd
ZrO_2	nd	nd

Appendix J: Analysis of glass from Seagrange, Baldoyle, Excavation No. 13E238

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1. Introduction

This report details the analysis of a number of glass fragments which were uncovered during excavations at Seagrange, Baldoyle, Co. Dublin. The multi-elemental analysis was carried out using X-ray Fluorescence at I.T. Sligo. The aim of this analysis was to determine trace elements within the glass objects which could potentially answer questions about their origin or production.

The finds in this analysis included one piece of thin glass rod which was folded in over itself, one piece of thick glass rod, one corroded fragment which was possibly bottle glass, one fragment of glass which had the appearance of having been partially molten in the past, one glass piece with only a slight green tinge which may have formed part of the rim of a bottle and a piece of vitreous slag. The site in question is located in a suburban estate in Baldoyle, North Dublin. It exhibits several features which are believed to be consistent with those of a medieval moated site. This, alongside the recovery of Leinster Cooking ware sherds from topsoil of a garden, prompted the Grassroots Archaeological Project to conduct targeted excavations in some of the green areas and gardens of the area (Grassroots Archaeology Project 2014). Two main phases of activity were identified during excavations; Medieval and Post-Medieval (Grassroots Archaeology Project unpublished).

2. Methodology

2.1. Sample collection and selection

The glass fragments from excavations at Seagrange, Baldoyle, Co. Dublin were provided by Paul Duffy of Grassroots Archaeological Project for the purpose of this study. In total, 6 pieces of glass were analysed using XRF analysis. A table detailing the finds which underwent analysis as well as a brief description can be seen in Appendix 1 at the end of this report. The glass fragments were uncovered from ploughsoil and were provisionally ascribed to the Early Modern period. The

discovery of a potential medieval glass furnace on the site could mean that early glass-working or production was taking place on this site (Grassroots Archaeology Project unpublished).

2.2. Calibration/Quality Control

The XRF was calibrated monthly using the standard procedure for this instrument. The accuracy of the instrument is also tested regularly using standard glass reference material. Table 1 below illustrates the accuracy and precision of the instrument using a standard sample. The sample was run 5 times and an average taken of the results.

	Stated concentration (%w/w)	**Average obtained (%w/w)**	**Relative Standard Deviation%**	**%Error**
SiO_2	72.26	72.62	0.360	0.503
Na_2O	13.78	12.88	1.399	-6.516
CaO	10.05	10.71	0.598	7.000
MgO	3.40	3.64	2.423	-0.0549
SO_3	0.270	0.027	9.658	-90.074
TiO_2	0.033	0.0237	7.413	-28.121
Fe_2O_3	0.021	0.0177	4.058	-15.619

Table 1: Reference sample results obtained

2.3. Sample washing and preparation

A solution containing a 1:1 ratio of deionised water and 99% ethanol solution was prepared in a volumetric flask. The surface of each find was gently cleaned using a clean cotton swab dipped in the deionised water/ethanol solution prior to being analysed in the XRF. The purpose of this technique was to remove surface contamination on the surface of the glass. Different trace elements can be left on the glass from many processes such as salts left behind from washing with ordinary

water or chlorine transferred from handling the finds with bare hands. By removing such elements, a clearer result of the elemental composition of the surface layers of the glass can be obtained. The above washing method was decided in consultation with the National Museum of Ireland after extensive experimentation on modern glass samples. The finds were left to dry completely before undergoing analysis. All finds were handled using gloves to avoid adding any further surface contamination.

2.4. Testing of finds

Each find was analysed by XRF in triplicate and the results averaged. Finds were analysed in the condition they were received with no preparation method utilised aside from the washing technique outlined above. XRF was chosen for this analysis as it provides a highly sensitive, multi-elemental analysis and is completely non-destructive. XRF is a surface technique, therefore the elemental composition it gives is indicative of the surface layers only and this may not be an accurate representation of the whole sample.

3. Results

The results of the analysis (given in percentage w/w) can be seen in the Appendix 1 at the end of this report. It shows the results from the six finds that were obtained during this study.

Discussion

4.1 Condition of finds

The finds from Seagrange were visually in good condition for the most part. Out of the six finds, five exhibited no obvious signs of pitting, crusting or an iridescent sheen which are common features of many ancient glass artefacts. Find 1.14 was the exception to this, showing a crusting, corroded layer on its surface. Finds 1.10 and

1.11 both showed signs of having been partially melted which has led to the tentative suggestion that these artefacts could have been the result of glass artefact production on this site. Find 1.12 displayed some mild brown discoloration on its surface.

4.2 Elemental Composition

From ancient times, glass has been consistently made up of a glass former, such as sand or quartz pebbles (SiO_2), a modifier, such as soda (Na_2O) or potash (K_2O), and a stabilizer such as lime ($CaCO_3$). As well as this, glass may contain a variety of colouring agents, opacifiers and other trace elements, added either intentionally or unintentionally (Goffer 2007, 124). From an analytical point of view, the composition of ancient soda-lime glass is typically 73% SiO_2 (silica), 23% Na_2O (soda) and 5% CaO (calcium oxide) (Gratuze and Janssens 2004, 665).

4.2.1 Find No. 1.10

Find No. 1.10 was a fragment of thick green glass rod (Plate 1). The main component of this artefact was silica (SiO_2) which accounted for 61.93% of its composition. This is a low concentration of silica for an ancient glass and, along with other results from the elemental analysis, suggests that this glass piece had suffered corrosion of the surface layers to some extent. Ground water can interact with buried glass material affecting the stability of the object. Signs that a glass fragment may have been affected by this include a flaky coating and iridescence on the surface of the object, however even glass which appears visually in good condition can be heavily affected (Pollard and Heron 2008, 119, 178). There is no sign of pitting, crusting or iridescent sheen on find 1.10 yet the elemental analysis shows that corrosion has occurred nonetheless. Glass corrosion is a complex process which is not well understood, being affected by many different factors. However it is thought that it occurs due to the preferential leaching of alkali ions to be replaced by hydrogen ions

(Wayne Smith 2003, 94). The reaction begins at the surface of the object and spreads inwards (Varshneya 1994, 398). Cox and Ford (1993, 5639-43) conducted a detailed elemental study of multiple layers of medieval glass and concluded that corroded surface layers can be depleted of most oxides except silica (Si), aluminium (Al) and iron (Fe), and what is left behind is poorly crystalline hydrated silicates and aluminosilicates with varying amounts of calcium (Ca), phosphate (P) and manganiferous (Mn) minerals.

The low percentage of silica, coupled with unusually high levels of aluminium oxide (Al_2O_3) in this find, 22.93%, would suggest that the surface layers had lost some of their original composition. Aluminium may have existed in the structure of glass originally in smaller amounts and was held preferentially compared to other elements. There is also the possibility that the surface layers contained aluminium which had entered from the environment.

The results from this find showed that it contained very low amounts of modifier. Soda, potash or a mixture of the two was an essential component when producing glass in ancient times. It acted as a flux, lowering the melting point of silica from 1700^{o}C to 1000^{o}C, a temperature which was obtainable in ancient furnaces (Goffer 2007, 115). As mentioned, the level of soda and potash can be up to around 23% for ancient glass. Generally, the lowest concentrations which would have been added would have been at least 15%. However find No. 1.10 contained no detectable levels of soda and only trace amounts of potash, 0.531%. These low levels further highlight the corroded nature of the surface layers of the glass, despite its appearance.

Potash would have been sourced from wood ash whereas soda was generally retrieved from marine plants. Potash glass became increasingly popular during the medieval period when demand for glass was growing and there was incentive to search for a more readily accessible alkali source. This follows a similar trend in Britain, where analysis shows that potash was being produced in quantity from the 13th or 14th century (Moran 2010, 17). While corrosion may affect glass for a number of reasons, such as environmental factors, the most important factor in most cases is the original elemental composition of the glass. This determines the resistance of the

glass to agents which can cause corrosion such as water, acidic and basic solutions and other atmospheric substances (Pollard and Heron 2008, 166). For medieval window glass for example, it has been noted that potash-based examples were more susceptible to weathering due to the high alkalinity of the glass (Moran 2010, 17). The small amounts of modifier found in this find, along with a lack of soda detected would suggest that it was probably potash-based. This suggestion is strengthened when it is considered that soda had survived to a greater extent in other finds recovered from this site; most notably find 1.15 which will be discussed in Section 4.2.6.

The greenish colour of this find was due to iron oxide, which accounted for 0.707% of its surface composition. Other substances known to act as green colourants, such as oxides of copper, chromium and nickel, were absent. Iron impurities, both ferrous (Fe^{2+}) and ferric (Fe^{3+}) occur frequently in sand which was often used as a silica source. As such, iron contaminants were often added unintentionally to the glass melt during glass production which is why green is one of the most common colours for ancient glass. This would suggest that the green colour of this piece could well have been unintentional. Manganese oxide (MnO) was sometimes used as a decolourant to counteract the green caused by iron impurities and produce a clear colour. While this substance is present in find No. 1.10, it only accounts for 0.0442%. Such a low quantity was probably not purposely added in an attempt to decolour the glass and instead was most likely added unintentionally as part of the potash that was sourced.

Chlorine (Cl) was found in four of the six glass finds including find No.. 1.10. This accounted for 0.582% of find 1.10. Chlorine can be transferred onto the surface of glass from handling objects with bare hands or from rinsing the finds with tap water. However, as these beads were submitted to a washing technique, it would be expected that much of this sort of contamination would be removed. Gloves were used when handling the finds at all times during their analysis, so any contamination was not added immediately prior to analysis and would have been present on the surface of the glass for some time. It is possible for glass to contain

some chlorine as part of its original structure, added in unintentionally as part of the source of soda or potash, however the concentrations in some of the finds were large enough that the possibility of contamination should be considered (Henderson 2000, 94).

4.2.2 Find No. 1.11

Find No. 1.11 was a fragment of a thin green glass rod (Plate 2). Its concentration of silica (SiO_2) was found to be 62.77%. Its elevated concentration of aluminium (Al_2O_3) at 13.86%, while not as high as the 22.93% found in find No. 1.10, is indicative of leaching or corrosion occurring in the surface layers, while the concentrations of soda (Na_2O) and potash (K_2O), which were 2.52% and 0.639% respectively, are also suggestive of corrosion.

The small amounts of both soda and potash found suggest this find may well have been formed from a mixed alkali glass type. A mix of potash and soda could have been added intentionally or it may have been accidental. For example, potash sources may occasionally contain traces of soda. It is also possible that cullet (broken pieces of glass) may have been used when producing the glass, and this would further complicate the elemental composition of the mixture. However, other trace elements found in the structure of both this find and find No. 1.12 would suggest that a significant amount of potash from wood ash was used. This will be discussed in more detail in Section 4.2.3.

Find No. 1.11 was coloured by the presence of iron oxides (Fe_2O_3). The concentration of 0.794% found in find number 1.11 was very similar to the 0.707% in find No. 1.10. As mentioned already in Section 4.2.2, iron impurities were often added in with sand which was used as a source of silica for the glass. The silica levels in both 1.10 and 1.11 were also very close to each other at 61.93% and 62.77% respectively. Both finds were missing trace elements which were often included unintentionally as part of raw materials in glass such as copper (Cu), osmium (Os), nickel (Ni), chromium (Cr) and arsenic (As). They also contained amounts of other elements such as iron oxide

(Fe_2O_3), titanium oxide (TiO_2) and barium oxide (BaO) which were comparable to each other. It seems plausible from these results that these two finds may both have been produced using the same source of raw materials.

4.2.3 Find No. 1.12

Find No. 1.12 was a cloudy fragment of glass with a greenish tinge and some evidence of discolouration on its surface (Plate 3). While it's function is not clear, it appears to have been either partially molten or not properly formed in the past. This has led to the suggestion of glass-working at this site. Its silica (SiO_2) concentration was 68.77% while its aluminium (Al_2O_3) concentration was found to be 15.78%. Again, this concentration is elevated and is probably an effect of corrosion on the surface layers of the object.

The concentrations of soda (Na_2O) and potash (K_2O) in this find were 3.24% and 1.87% respectively. Like find 1.11, this object may have been a mixed alkali type. However as the majority of the modifier which the surface layers would have contained when the glass piece was first produced has been leached away, it is impossible to say for sure. As mentioned already in Section 4.2.2 however, there is some indication in the other trace elements that a wood ash-based source of potash was used in their production. The use of wood ash often adds magnesia (MgO) to the glass mix in small quantities. Find Nos. 1.11 and 1.12 were the only two glass objects to contain concentrations of this substance with 2.31% and 2.13% respectively.

Like the other finds discussed so far, find No. 1.12 obtains its greenish hue from the iron oxides (Fe_2O_3) that it contains, with a concentration of 0.65%. This was again likely an unintentionally contaminant added in with the raw materials used. There is no evidence that the glassmakers attempted to manipulate the colour of this glass object.

4.2.4 Find No. 1.13

Find No. 1.13 consists of a piece of vitreous slag material (Plate 4). It contained significant concentrations of silica (SiO_2), aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3) at 40.71%, 32.07% and 17.43% respectively. It also contained a host of trace elements which were not present in any of the glass artefacts including chromium oxide (Cr_2O_3), copper oxide (CuO) and nickel oxide (NiO) at concentrations of 0.0144%, 0.0429% and 0.0171% respectively. All of these elements can be incorporated into glass structure, and indeed are quite powerful colouring agents, and yet were not found in any of the glass finds.

4.2.5 Find No. 1.14

Find No. 1.14 was a small green glass fragment (Plate 5). It was the only piece in this assemblage to show significant visual evidence of corrosion in the form of a flaky iridescent layer. It's appearance and colour is typical of Post-Medieval bottle glass. Its silica (SiO_2) concentration was in line with the results from the other glass fragments at 65.39%. Its aluminium oxide (Al_2O_3) concentration, while higher than expected at 17.83%, was not particularly high compared to the other glass fragments which were visually in better condition. This highlights how the visual appearance of glass is not always a good indication of the level of corrosion it has suffered. Its soda (Na_2O) and potash (K_2O) concentrations were 2.07% and 1.84% respectively. Unlike find Nos. 1.11 and 1.12 however, it contained no detectable amount of magnesia (MgO), which would suggest a different source for the potash which it contained. Again, the colour was derived from iron oxides (Fe2O3) in its structure.

4.2.6 Find No. 1.15

The final glass piece from this assemblage was a clear glass fragment with a very slight green tinge (Plate 6). It appears to have been part of the rim of a bottle.

Visually, it exhibited no sign of corrosion or discoloration. Its silica (SiO_2) and aluminium oxide (Al_2O_3) concentrations were 68.89% and 10.77% respectively. Overall, the elemental composition showed that this find was the least corroded out of the glass fragments in this report. This can most clearly be seen in the concentrations of soda (Na_2O) and potash (K_2O) which were found to be 10.47% and 0.251% respectively. This concentration suggests a soda-lime silica glass. As already discussed, corrosion occurs as preferential leaching of alkali ions to be replace by hydrogen ions, and potash based glasses are more susceptible to this than soda-lime based ones (Wayne Smith 2003, 94). Like every other glass fragment, find No. 1.15 shows no evidence that the glassmakers were concerned with the colouration of the finished product. The very light tinge in the glass corresponds with the lowest level of iron oxide (Fe_2O_3) in any of the glass finds at 0.247%.

Conclusion

The XRF analysis suggests a mixture of soda-lime and mixed alkali-based glasses which have been subjected to varying degrees of corrosion due to being exposed to groundwater over time. This has caused alkalis such as potash and soda in the surface to leach away, leaving a disproportionate amount of heavier elements such as aluminium behind. It can be seen that the visual condition of the objects is not a good indication of the level of corrosion that has undergone. Unfortunately it is impossible to know what the original composition of these objects would have been without utilising more destructive methods in order to expose non-corroded layers deeper in the finds.

The only colourant that was found in these glass objects is iron oxide (Fe_2O_3) which would not have been added intentionally, but would have been present in the raw materials in the glass. There is no evidence that the producers of this glass were particularly concerned with the colour as they did not add other colouring agents nor attempt to add significant quantities of decolourants which would have counteracted the green colour caused by the iron contaminants. This would suggest

that the glassmakers were either not particularly knowledgeable with regards the intricacies of glass production or else that the objects were intended as cheaply manufactured objects.

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Plate 1: Find No. 1.10

Plate 2: Find No. 1.11

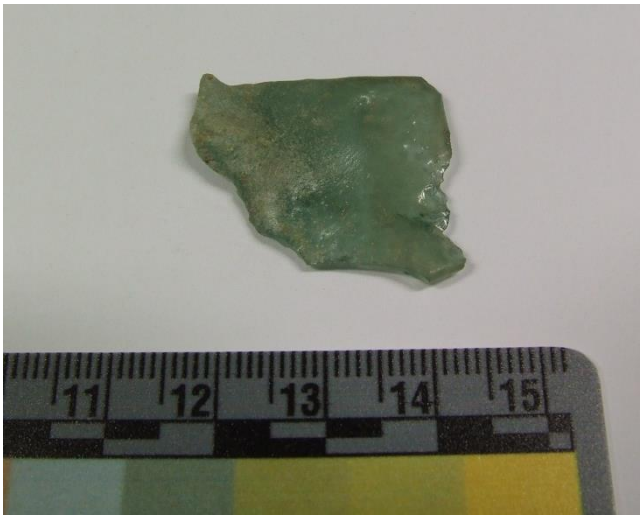

Plate 3: Find No. 1.12

Plate 4: Find No. 1.13

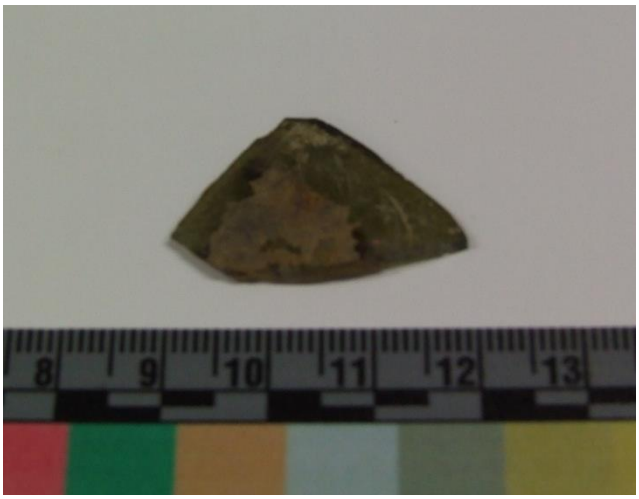

Plate 5: Find No. 1.14

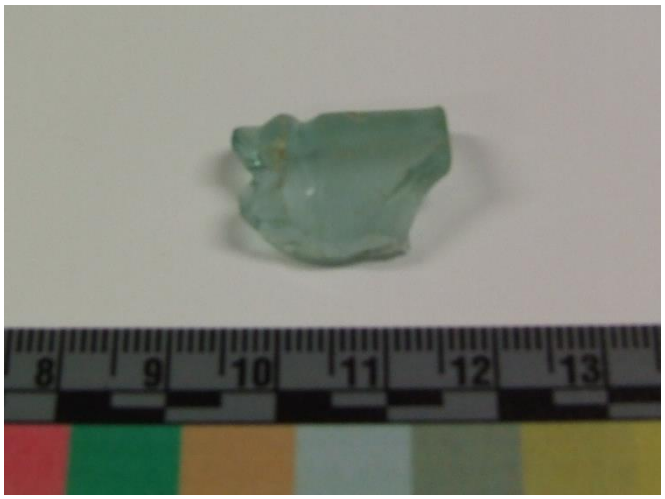

Plate 6: Find No. 1.15

Appendix 1: Glass results (Results given in percentage w/w) (nd = not detected)

	1.10	1.11	1.12	1.13	1.14	1.15
	Thick green glass rod fragment	Thin green glass rod fragment	Cloudy glass fragment, hint of green	Brownish black slag material	Corroded green glass fragment	Cloudy glass fragment
Al_2O_3	22.93	13.86	15.78	32.07	17.83	10.77
As_2O_3	nd	nd	nd	nd	nd	0.0285
BaO	0.0099	0.0089	nd	0.0842	0.0227	0.0582
CaO	13.09	16.05	6.76	4.80	10.27	9.15
Cl	0.582	0.727	0.0309	nd	0.397	nd
Co_3O_4	0.0064	nd	0.0064	0.179	0.0117	nd
Cr_2O_3	nd	nd	nd	0.0144	nd	nd
CuO	nd	nd	nd	0.0429	nd	nd
Fe_2O_3	0.707	0.794	0.65	17.43	1.75	0.247
K_2O	0.531	0.639	1.87	3.61	1.84	0.251
MgO	nd	2.31	2.13	nd	nd	nd
MnO	0.0442	0.0691	0.0327	0.0489	0.121	0.0288
Na_2O	nd	2.52	3.24	nd	2.07	10.47
NiO	nd	nd	nd	0.0171	nd	nd
OsO_4	nd	nd	0.0263	nd	nd	0.0089
PbO	nd	0.0079	0.19	nd	nd	0.035
Rb_2O	nd	nd	nd	0.0141	nd	nd
SiO_2	61.93	62.77	68.77	40.71	65.39	68.89
SrO	0.0581	0.106	0.142	0.0508	0.059	0.0107
TiO_2	0.091	0.104	0.0766	0.798	0.20	0.0387
V_2O_5	0.0054	0.0067	nd	0.058	nd	nd
Y_2O_3	nd	nd	nd	0.0092	nd	nd
ZnO	0.0068	0.0057	0.0083	nd	0.0215	nd
ZrO_2	0.0057	0.0128	nd	0.0357	0.0083	nd

Analysis of glass from Rothe House, excavation number 05E598

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Appendix K: Rothe House, Kilkenny

1. Introduction

This report details the analysis of a number of glass fragments which were uncovered during excavations at Rothe House, Co. Kilkenny. The multi-elemental analysis was carried out using X-ray Fluorescence at I.T. Sligo. The aim of this analysis was to determine trace elements within the glass objects which could potentially answer questions about their origin or production. The samples in this analysis included 12 fragments of a German Stangenglas beer glass, 2 'porridge bowl' sherds, a fragment of clear vessel glass with white decoration and a corroded green glass sherd. The excavations took place within the gardens of Rothe House, an Early Modern townhouse located on Parliament Street, Kilkenny which is maintained by the Kilkenny Archaeological Society. The site is the best-preserved example of an urban mansion of the Irish Renaissance period. The archaeological excavation was undertaken as part of a plan to recreate the original gardens to the rear of the house (Ó Drisceoil 2007). All glassware found on the site was noted to be of Post-Medieval date (Roche unpublished, 1).

2. Methodology

2.1. Sample collection and selection

The glass fragments from excavations at Rothe House were provided by Cóilín Ó Drisceoil of Kilkenny Archaeology for the purpose of this study. In total, 16 pieces of glass were analysed using XRF analysis, with one 'porridge bowl' sherd being analysed twice; once on the interior side and once on the decorated, outer side. A table detailing the samples which underwent analysis as well as a brief description can be seen in Appendix 1 and 2 at the end of this report. As mentioned already, all glassware from the site was deemed Post-Medieval in date and, aside from one fragment which was most likely from a bottle, all fragments which were analysed appeared to have come from fine glassware.

2.2. Calibration/Quality Control

The XRF was calibrated monthly using the standard procedure for this instrument. The accuracy of the instrument is also tested regularly using standard glass reference material. Table 1 below illustrates the accuracy and precision of the instrument using a standard sample. The sample was run 5 times and an average taken of the results.

	Stated concentration (%w/w)	**Average obtained (%w/w)**	**Relative Standard Deviation%**	**%Error**
SiO_2	72.26	72.62	0.360	0.503
Na_2O	13.78	12.88	1.399	-6.516
CaO	10.05	10.71	0.598	7.000
MgO	3.40	3.64	2.423	-0.0549
SO_3	0.270	0.027	9.658	-90.074
TiO_2	0.033	0.0237	7.413	-28.121
Fe_2O_3	0.021	0.0177	4.058	-15.619

Table 1: Reference sample results obtained

(nd = not detected, nc = not calculated)

2.3. Sample washing and preparation

A solution containing a 1:1 ratio of deionised water and 99% ethanol solution was prepared in a volumetric flask. The surface of each sample was gently cleaned using a clean cotton swab dipped in the deionised water/ethanol solution prior to being analysed in the XRF. The purpose of this technique was to remove surface contamination on the surface of the glass. Different trace elements can be left on the glass from many processes such as salts left behind from washing with ordinary water or chlorine transferred from handling the samples with bare hands. By removing such elements, a clearer result of the elemental composition of the surface layers of the glass can be obtained. The above washing method was decided in

consultation with the National Museum of Ireland after extensive experimentation on modern glass samples. The samples were left to dry completely before undergoing analysis. All samples were handled using gloves to avoid adding any further surface contamination.

2.4. Testing of samples

Each sample was analysed by XRF in triplicate and the results averaged. Samples were analysed in the condition they were received with no preparation method utilised aside from the washing technique outlined above. XRF was chosen for this analysis as it provides a highly sensitive, multi-elemental analysis and is completely non-destructive. XRF is a surface technique, therefore the elemental composition it gives is indicative of the surface layers only and this may not be an accurate representation of the whole sample.

3. Results

The results of the analysis (given in percentage w/w) can be seen in the Appendix 1 and Appendix 2, at the end of this report. These show the results from the 16 samples that were obtained during this study.

Discussion

4.1 Condition of samples

The glass pieces from Rothe House were in a fragmented state and several of the fragments showed some visible signs of corrosion. The 12 fragments of the Stangenglas vessel, find Nos. C121:1-3 and C121:9-17 showed no signs of pitting or crusting although on close observation an iridescent sheen was evident on their surface. They also had dirt encrusted on their surface. The 'porridge bowl' sherds, find Nos. 54:1 and 28:54, and the vessel glass fragment, 93:12 also had encrusted dirt

and an iridescent sheen on their surfaces. A fragment of possible bottle glass, find No. 1:354, exhibited a crusting corroded layer. The more prevalent corrosion on this piece may be due to the lower quality of this piece compared to the other fragments, which seemed to be fragments of fine glassware.

4.2 Elemental Composition

From ancient times, glass has been consistently made up of a glass former, such as sand or quartz pebbles (SiO_2), a modifier, such as soda (Na_2O) or potash (K_2O), and a stabilizer such as lime ($CaCO_3$). As well as this, glass may contain a variety of colouring agents, opacifiers and other trace elements, added either intentionally or unintentionally (Goffer 2007, 124). From an analytical point of view, the composition of ancient soda-lime glass is typically 73% SiO_2 (silica), 23% Na_2O (soda) and 5% CaO (calcium oxide) (Gratuze and Janssens 2004, 665).

4.2.1 Stangenglas sherds

A total of 12 fragments, believed to form part of a German Stangenglas, a tall beer glass, were analysed. Three of the fragments, find Nos. 121:1-3, formed part of the base of the glass (Plates 1 and 2). The rest of the fragments, find Nos. 121:9-17 were most likely body sherds from the glass (Roche unpublished, 5). An example of one of these possible body sherds can be seen in Plate 3. All of the samples looked very similar visually, being thin, clear, good quality glass albeit with some iridescence on their surface. The elemental analysis showed a very similar composition for all of the fragments and they all most likely came from the same source.

The main component of these fragments was silica (SiO_2) which accounted for between 67.07% and 80.38% of their composition. These are typical concentrations of silica for an ancient glass. The concentration of aluminium oxide (Al_2O_3) for eight of the twelve fragments was between 1.6% and 5.68% which is within the expected range for ancient glass. However, the levels of this substance in the remaining four

finds appeared elevated with find No. C121:10 having a particularly high aluminium oxide concentration of 22.23%. The high amounts of aluminium oxide in some samples, as well as the varying concentrations in the fragments which are otherwise very similar to each other, suggest that these glass pieces had suffered corrosion of the surface layers to some extent. Aluminium may have existed in the structure of glass originally in smaller amounts and was held preferentially compared to other elements. There is also the possibility that the surface layers contained aluminium which had entered from the environment.

Glass corrosion is a complex process which is not well understood, being affected by many different factors. However it is thought that it occurs due to the preferential leaching of alkali ions to be replaced by hydrogen ions (Wayne Smith 2003, 94). The reaction begins at the surface of the object and spreads inwards (Varshneya 1994, 398). Ground water can interact with buried glass material affecting the stability of the object. Signs that a glass fragment may have been affected by this include a flaky coating and iridescence on the surface of the object, however even glass which appears visually in good condition can be heavily affected (Pollard and Heron 2008, 119, 178). Cox and Ford (1993, 5639-43) conducted a detailed elemental study of multiple layers of medieval glass and concluded that corroded surface layers can be depleted of most oxides except silica (SiO_2), aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3), and what is left behind is poorly crystalline hydrated silicates and aluminosilicates with varying amounts of calcium (Ca), phosphate (P) and manganiferous (Mn) minerals. The most important factor which determines the resistance of the glass to agents which can cause corrosion such as water, acidic and basic solutions and other atmospheric substances is the original elemental composition of the piece (Pollard and Heron 2008, 166). The good survivability of these Stangenglas sherds is another indication of their extremely good quality.

The results from this find showed that it contained somewhat reduced amounts of modifier. Soda (Na_2O), potash (K_2O) or a mixture of the two was an essential component when producing glass in ancient times. It acted as a flux, lowering the melting point of silica from 1700^{o}C to 1000^{o}C, a temperature which was obtainable in

ancient furnaces (Goffer 2007, 115). Potash would have been sourced from wood ash whereas soda was generally retrieved from marine plants. As mentioned, the level of soda and potash can be up to around 23% for ancient glass. Generally, the lowest concentrations which would have been added would have been at least 15%. The Stangenglas fragments were found to contain concentrations of between 2.85% and 7.72% of soda and between 2.32% and 6.17% of potash. The levels of modifier substances, which are considerably lower than would be expected, further hint at the corroded nature of the surface layers of the glass, despite its appearance. The significant quantities of both potash and soda would also suggest that the glass was produced as a mixed alkali type glass. A mix of potash and soda could have been added intentionally or it may have been accidental. For example, potash sources may occasionally contain traces of soda. It is also possible that cullet (broken pieces of glass) may have been used when producing the glass, and this would further complicate the elemental composition of the mixture.

The amount of trace elements contained in the elemental composition of these fragments was quite low. Many elements that would have caused a tint in the glass were not detected at all, such as cobalt (Co), nickel (Ni) and chromium (Cr). Iron oxide (Fe_2O_3) was detected in very small concentrations of between 0.160% and 0.333%. This would indicate that fairly pure sands were used in the production of this piece and was undoubtedly the work of a very skilled glass-maker as the glass is completely clear with no colouration.

The level of corrosion seems to vary quite significantly between the different pieces. As the pieces are all most likely from the same glass object, the difference in corrosion levels could be due to their different surface area. On examining the results of the pieces, which are listed in Appendix 2, it is apparent that the concentrations of aluminium oxide range widely, with concentrations of between 1.06% and 16.26%. The concentrations of many of the trace elements within the glass pieces vary too, such as osmium oxide (OsO_4) which varies from not detected up to 0.0133%, however this is to be expected as the concentrations in question are very small. However, the range of the aluminium oxide is particularly large considering it

makes up a substantial percentage of the pieces, averaging at 8.08%. As discussed already, elevated levels of aluminium oxide in the glass pieces is indicative of corrosion, and the wide range of results in this case highlights how corrosion has occurred to different extents in the different pieces.

4.2.2 'Porridge bowl' sherds

Two sherds of a possible 'porridge bowl', find Nos. 54:1 and 28:54, were analysed (Plate 4). Find No. 54:1 was analysed twice, once on the brown glass of its interior side and once on the white decoration of the exterior side. The smaller piece was tested on the brown glass only. A total of eight fragments from this artefact were uncovered and when reconstructed were found to form a portion of a small bowl with rounded shoulders and a flat, Y-shaped handle. The fragments consisted of a brown glass with white decoration on the exterior side of the pieces (Roche unpublished, 2).

The concentrations of silica (SiO_2) in the brown glass of both find 54:1 and 28:54 were found to be 79.93% and 67.39% respectively, while the aluminium oxide (Al_2O_3) was 4.56% and 17.2%. This would seem to indicate that the smaller find, 28:54, had suffered corrosion to a greater degree. While corrosion may affect glass for a number of reasons, such as environmental factors and the original elemental composition of the glass, in this case where both fragments were from the same item and deposited in the same environment, it is probably due to differing surface areas causing differential leaching of surface elements (Pollard and Heron 2008, 166).

Potash (K_2O) concentrations were 1.79% and 2.17% for the two samples with no detectable levels of soda (Na_2O). The lower level of potash was found in the smaller sherd and corresponds with the higher level of aluminium oxide and lower concentration of silica found in this sample, further highlighting its corroded nature. As already discussed, corrosion occurs as preferential leaching of alkali ions to be replace by hydrogen ions, and potash based glasses are more susceptible to this than soda-lime based ones (Wayne Smith 2003, 94). Potash glass became increasingly

popular in Ireland, Britain and elsewhere from the medieval period onwards when demand for glass was growing and there was incentive to search for a more readily accessible alkali source. It has been noted that potash-based examples were more susceptible to weathering due to the high alkalinity of the glass (Moran 2010, 17). The small amounts of modifier found in these fragments, along with a lack of soda detected would suggest that it was probably potash-based.

There are a number of different possible causes for the brown hue in these pieces. It is possible that the concentrations of iron oxide (Fe_2O_3) in the fragments, 0.75% and 0.834%, may have added to the hue. The concentrations of manganese oxide (MnO) also seem elevated with 3.25% and 3.49%. Manganese, when added to other elements such as carbon and sulphur, is known to impart an amber or brown hue. No sulphur was detected within these particular finds, however it is possible that the brown colour was caused by the addition of a reducing agent, such as carbon, to the glass furnace. Furthermore, when carbon is added to a glass mix containing iron and sulphur, it can result in varying shades of amber and brown (Bray 2001, 65). Unfortunately, carbon is too light an element to be detected by the XRF, so further investigation would be required in order to determine the level of carbon present.

The results from the analysis of the white decoration on the exterior side of find 54:1 showed a high concentration of lead oxide (PbO) at 12.21%. This is known to produce opaque white glass and is undoubtedly what was used to produce the white trail decoration (Henderson 2000, 74). It also contained a high concentration of sulphur trioxide (SO_3), 19.63%, which was not present in the brown glass. Sulphur additives can react with other elements to form many different colours from yellow to brown and even black (Davidson 2008, 77), however it does not seem to have been added for the purpose of colouring in this case as sulphur is not known to produce a white hue. It is possible that is may have been added in as part of the source of lead oxide. For example, galena, the main ore of lead, is composed of lead sulfide (Goffer 2007, 120). The level of silica in the white decoration was considerably less than in the brown glass at 50.66%. Its calcium oxide (CaO) level was also somewhat lower than what was found in the brown glass at 4.84%. This would suggest that it was not

a structural type of glass but instead was valued for its decorative effect. The production of a decorative glass material that was unsuited to making glass objects in its right highlights the detailed knowledge of glassworking that these glass-makers possessed.

It is suggested by Roche (unpublished, 2) that the object which these fragments came from could be a type of bowl used for eating porridge or gruel known as a porringer. Porringers of brown glass with white decoration were produced in late 17th century Germany. The report also mentions a comparable vessel in the form of a Roman patera dating from the 2nd or 3rd century AD (Roche unpublished, 2, 3). The likelihood of a Roman date for these fragments based on the elemental composition seems slim. Firstly, the level of corrosion based on the quantity of aluminium oxide seems quite low if the object is ancient. There is also the fact that the items appear to have been produced using a potash flux. This would be quite unusual for a high quality Roman object, which would have been more likely produced using a high quality soda flux (Freestone 2009,83). If this bowl was indeed a replica of a Roman patera, it was likely produced much later.

4.2.3 Fragment of clear vessel glass

This clear glass vessel fragment, find No. 93:12, was noted to be possibly part of the upper bowl and rim of a wide mouthed drinking glass (Plate 5). It has opaque white trails on its surface and a very slight greenish tint (Roche unpublished, 4). The silica (SiO_2) and aluminium oxide (Al_2O_3) concentrations in this piece were 70.32% and 13.81% respectively, with the Al_2O_3 levels indicating some level of surface corrosion in this piece also. The levels of modifier were also quite low with soda (Na_2O) and potash (K_2O) levels of 1.16% and 3.1% respectively, indicating corrosion in the surface layers.

The greenish colour of this find was due to iron oxide (Fe_2O_3), which accounted for 0.845% of its surface composition. Other substances known to act as green colourants, such as oxides of copper, chromium and nickel, were absent. Iron

impurities, both ferrous (Fe^{2+}) and ferric (Fe^{3+}) occur frequently in sand which was often used as a silica source. As such, iron contaminants were often added unintentionally to the glass melt during glass production which is why green is one of the most common colours for ancient glass. Manganese oxide (MnO) was also detected in this piece at a concentration of 1.021%. In many cases, manganese can be added unintentionally to the glass mix as impurities found in raw materials that were sourced (Wilson 1855, 261). It was sometimes added intentionally as a decolourant in glass production as it masks the green colour caused by iron. When used on its own without significant levels of iron, it gives a purple colour (Goffer 2007, 121). At 1.021%, the concentration was significant enough in this find that it may have been added as a decolourant. This could well have been an attempt to counteract the green colour caused by the iron oxide, an attempt that was not entirely successful.

Roche (Roche unpublished, 4) notes that this fragment is in the style of Venetian glass but it is not of high enough quality for Venetian ware as it displays a greenish tint, which is supported by the elemental composition. The results indicate that this fragment was most likely produced using a potash flux. This is in contrast to the true Venetian wares which were produced using a high quality source of silica and a soda-rich ash and as such were highly clear and transparent. Tinges of green or brown in lower quality Venetian style glassware were often caused by using a mixed alkali rather than a pure soda flux (Willmott 2004, 289).

4.2.4 Corroded green glass sherd

Find No. 1:354 was the only bottle fragment from this assemblage which was analysed (Plate 6). The majority of the glass finds discovered during the Rothe House excavations were fragments of 17th to 19th century wine bottles (Roche unpublished, 1). The bottle fragments exhibited more visible corrosion than the higher quality glass fragments that have already been discussed and this single piece was taken as an example. The glass used for making bottles was almost always of a

lower quality that that of other vessels and usually had a very dark green colour, caused by varying iron impurities (Roche 2007, 411). The colour of find 1:354 was typical of bottle glass, which was cheaply manufactured and widely used during the Post-Medieval.

The silica (SiO_2) concentration of this fragment was in line with the results from the other glass fragments at 65.46%. Its aluminium oxide (Al_2O_3) concentration, while somewhat higher than would be expected at 8.06%, was not particularly high compared to the other higher quality glass fragments which were visually in better condition. This highlights how the visual appearance of glass is not always a good indication of the level of corrosion it has suffered. Its modifier concentrations were the lowest out of all the fragments analysed though, containing only 1.06% potash (K_2O) and no detectable amounts of soda (Na_2O). This find also contained magnesia (MgO) levels of 4.3%. This indicates that a wood ash-based source of potash was used in its production, as the use of wood ash often adds magnesia to the glass mix in small quantities. Like the vessel glass sherd, the colour in this fragment was derived from iron oxides (Fe_2O_3) in its structure, which accounted for 0.819% of its composition.

Conclusion

XRF analysis suggests that these glass samples have undergone varying degrees of corrosion during their time exposed to groundwater. This has caused alkalis such as potash and soda in the surface to leach away, leaving a disproportionate amount of heavier elements such as aluminium behind. Some of the samples were in good visual condition yet the results obtained from the elemental analysis of these fragments, does highlight the corrosion which they were subjected to over the years. Even in cases where corrosion is not physically evident to any great extent, it may still have occurred. The results would suggest that overall the Stangenglas fragments survived the best out of the different groups of glass which make up this assemblage. This may have been due to the high quality of the glass used to produce

this object, as it can be seen from the clear glass that pure sources of modifier and silica must have been used.

The Stangenglas fragments were a high quality, mixed alkali type glass with few trace contaminants and, as mentioned, exhibited the lowest amount of corrosion of any of the fragments analysed from this assemblage. The porridge bowl sherds were most likely potash-based and had decoration which was produced using lead oxide as a colourant and opacifier. The level of corrosion and type of modifier used would seem to suggest a Post-Medieval rather than Roman date for this find. Find 93:12 was a clear glass vessel fragment with a slight green tinge caused by iron contaminants in its composition. An attempt may have been made to counteract the green colouring in the piece by adding manganese oxide to the glass mix however it was not entirely successful. Find 1:354 appears to be a fragment of typical low quality bottle glass, probably dating to the Post-Medieval period.

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Plate 1: C121:1 – Stangenglas fragment

Plate 2: C121:2 and C121:3 - Stangenglas fragments

Plate 3: C121:17 - Stangenglas fragment

Plate 4: 54:1 and 28:54 – 'Porridge bowl sherds'

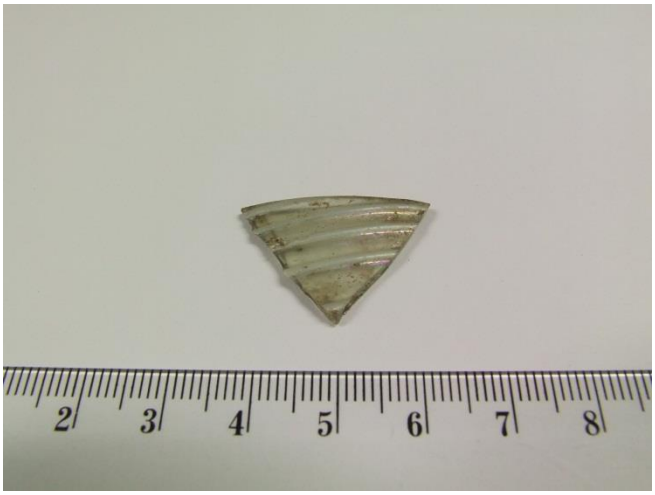

Plate 5: 93:12 – Clear vessel sherd

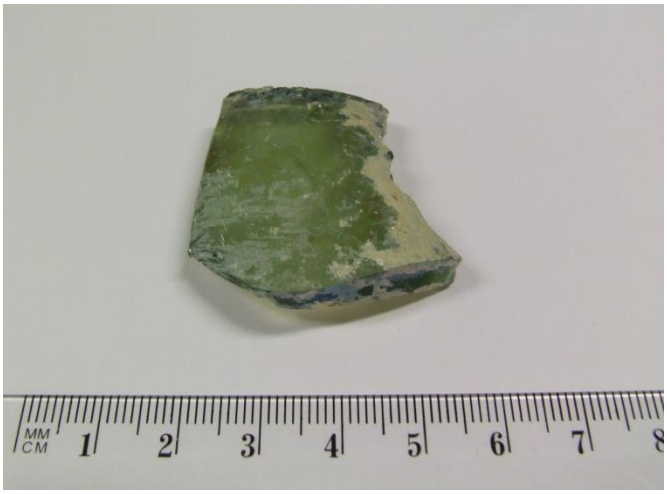

Plate 6: 1:354 – Bottle sherd

Appendix K: Rothe House, Kilkenny

Appendix 1: Glass results; Bottle sherd, 'Porridge bowl' sherds and clear vessel sherd (Results given in percentage w/w) (nd = not detected)

Find	**1.354**	**28:54**	**54.1**	**54.1**	**93.12**
Description	Corroded green glass sherd	Porridge bowl sherd (small sherd)	Porridge bowl sherd (Outside, white decoration)	Porridge bowl sherd (inside)	Clear vessel fragment, white decoration
Al_2O_3	8.06	17.2	nd	4.56	13.81
As_2O_3	0.0099	nd	1.56	nd	nd
BaO	0.0266	0.0756	0.406	0.0632	0.0276
CaO	19.96	5.54	4.84	5.95	7.78
Cl	nd	1.33	1.77	0.881	0.565
Co_3O_4	0.0133	nd	nd	nd	nd
CuO	nd	nd	nd	0.0059	nd
Fe_2O_3	0.819	0.834	0.772	0.75	0.845
K_2O	1.06	1.79	2.14	2.17	3.1
MgO	4.3	nd	nd	nd	nd
MnO	0.019	3.49	1.72	3.25	1.021
Na_2O	nd	nd	nd	nd	1.16
OsO_4	0.0086	0.043	1.47	0.0417	0.076
P_2O_5	nd	1.08	2.38	1.76	nd
PbO	0.0094	0.392	12.21	0.416	0.398
Sb_2O_3	nd	nd	0.0093	nd	nd
SiO_2	65.46	67.39	50.66	79.93	70.32
SnO2	nd	nd	nd	nd	0.633
SO_3	nd	0.58	19.63	nd	nd
SrO	0.071	0.0986	0.215	0.0957	0.0503
TiO_2	0.151	0.116	nd	0.107	0.151
ZnO	nd	0.026	0.0321	0.0244	nd
ZrO_2	0.0115	nd	nd	nd	0.0181

Appendix 2: Glass results; Stangenglas sherds (Results given in percentage w/w) (nd = not detected)

Find	C121.1	C121.2	C121.3	C121.9	C121.10	C121.11	C121.12	C121.13	C121.14	C121.15	C121.16	C121.17	Average
Al_2O_3	4.86	1.06	4.10	4.62	22.23	4.6	11.67	4.62	12.04	5.68	16.26	4.64	8.08
BaO	0.0252	nd	0.0068	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.0027
CaO	5.45	3.69	3.40	3.29	2.73	4.40	3.88	6.23	4.00	3.96	1.84	4.05	3.91
Cl	0.301	0.42	0.421	0.428	0.448	0.47	0.38	0.496	0.409	0.414	0.223	0.3357	0.395
CuO	nd	nd	nd	0.0067	0.0085	0.0096	0.0092	0.0106	0.0077	nd	nd	0.0085	0.0051
Fe_2O_3	0.308	0.222	0.223	0.247	0.288	0.333	0.314	0.327	0.307	0.336	0.16	0.1985	0.274
K_2O	6.17	4.28	4.42	4.42	3.71	5.25	4.4	4.93	4.30	4.56	2.32	5.12	4.49
MnO	1.13	0.62	0.645	0.686	0.841	0.916	0.85	0.95	0.83	0.901	0.374	0.81	0.7961
Na_2O	5.02	7.72	6.93	7.63	3.05	4.93	2.36	6.74	3.18	6.45	2.85	5.77	5.22
OsO_4	nd	0.0071	nd	0.0059	0.0133	0.009	0.0111	nd	0.012	0.0107	nd	0.0065	0.0063
P_2O_5	0.383	0.91	0.171	nd	nd	nd	nd	3.71	nd	0.187	nd	nd	0.447
PbO	0.0622	0.0311	0.0318	0.0335	0.0367	0.0471	0.0425	0.0487	0.0394	0.0461	0.019	0.0399	0.0398
Sb_2O_3	0.0425	0.012	0.0141	0.0099	0.0117	0.015	0.0103	0.0149	0.0089	0.0133	0.008	0.0135	0.0145
SiO_2	75.99	80.38	79.54	78.54	67.07	78.86	75.95	71.74	74.7	77.29	75.89	78.73	76.22
SrO	0.0378	0.0185	0.0197	0.0198	0.0198	0.0288	0.0248	0.0286	0.0227	0.0277	0.012	0.0242	0.0237
TiO_2	0.082	0.0571	0.052	0.058	0.0807	0.0797	0.0743	0.086	0.0726	0.0837	0.0323	0.0688	0.0689
ZnO	0.0117	0.0067	0.0065	0.007	0.0092	0.0111	0.0107	0.0131	0.0102	0.0099	0.0066	0.009	0.0093