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 neck 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main phases of activity were identified during excavations; Medieval and Post-Medieval (Grassroots Archaeology Project unpublished).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site could mean that early glass-working or production was taking place on this site (Grassroots Archaeology Project unpublished).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 is 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 machine using a standard sample. The sample was run 5 times and an average taken of the results.

	Standard sample – given composition (%w/w)	Standard sample – Results obtained (%w/w)	%Difference	RSD
SiO_2	72.26	72.62	0.496	0.360
Na_2O	13.78	12.88	-6.988	1.399
CaO	10.05	10.71	6.162	0.598
MgO	3.4	3.64	6.593	2.423
SO_3	0.27	nd	nd	nd
K_2O	nd	0.027	100.000	nd
TiO_2	0.033	0.0237	-39.241	4.058
Fe_2O_3	0.021	0.0177	-18.644	0.360

Table 1: Standard 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. Find 12 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. Out of the five glass finds, four exhibited no obvious signs of pitting, crusting or an iridescent sheen which are common features of many ancient glass artefacts. Find 14 was the exception to this, showing a crusting, corroded layer on its surface. Find 12 also displayed some mild brown discoloration on its surface which could possibly have been caused by encrusted dirt.

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 number 10

Find number 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 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 1700ºC to 1000ºC, 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 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 in Ireland over the course of the medieval period when demand for glass was growing and there was incentive to search for a more readily accessible alkali source. There is also 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 15 which will be discussed in Section 4.2.6.

The greenish colour of this find was due to iron oxide (Fe_2O_3), 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 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. 10. This accounted for 0.582% of find 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 number 11

Find number 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 number 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 number 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 number 11 was coloured by the presence of iron oxides (Fe_2O_3). The concentration of 0.794% found in find number 11 was very similar to the 0.707% in find number 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 find 10 and find 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 therefore 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 number 12

Find number 12 was a cloudy fragment of glass with a greenish tinge and some evidence of discolouration on its surface (Plate 3). While its function is not clear, it appears to have been either partially molten or not properly formed in the past. It could potentially be waste glass from glass production. Such finds are generally fragmentary, discoloured by heat and have a distorted appearance as this one does. However, such material will generally be found in greatest concentration near the gathering holes of the furnace on sites where glass-working has taken place (Taylor and Hill 2008, 249). While this doesn't rule out glass-working, the unstratified location of this find makes it more difficult to attribute it to glass-working on 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 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 numbers 11 and 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 number 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. Differences in the trace elements of this find when compared to finds 10 and 11 would suggest a different production method or raw materials were used for find 12. For example, it contains 0.0263% osmium oxide (OsO_4) while there are no detectable amounts of this in finds 10 and 11. Find 12 also contains 0.19% lead oxide (PbO) which is not detected in find 10 and accounts for only 0.0079% of find 11. In addition, analysis of find 12 did not detect many substances found in 10 and 11 including vanadium oxide (V_2O_5), barium oxide (BaO) and zirconium oxide (ZrO_2).

4.2.4 Find number 13

Find number 13 consists of a piece of vitreous slag material (Plate 4). Slag is known to be resistant to weathering or corrosion, difficult to date and complicated to classify elementally (Bachmann 1982, 1). The dark colour and angular lump-like shape of Find 13, as well as its porous and lightweight nature, make it visually similar to other slags identified as products of iron smelting. Iron begins to produce slag at a minimum temperature of 1050 degrees Celsius (Bachmann 1982, 5, 30).

Find 13 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. Silica and aluminium oxide would be expected in metal-working slag as they are undesirable impurities removed as part of the smelting process. A certain amount of iron would also be expected in slag from iron smelting as ancient smelting was not capable of extracting all of the metal from the ore (Blakelock et al. 2009, 1745). It has been noted in other studies that the elemental composition of slag material is influenced by a number of variables including the type of ore used, ash from the fuel, the furnace lining and furnace conditions such as temperature and duration of the smelt (Paynter 2006, 272). The lack of any significant quantities of tin (Sn), zinc (Zn) or copper (Cu) in find 13 would suggest that this slag was certainly not the result of smelting copper or metals used in copper alloys from their ores.

Find 13 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. This would further the suggestion that this slag is not related to the glass artefacts which were analysed in this report. Overall it seems likely that this piece is from iron smelting.

4.2.5 Find number 14

Find number 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. Its appearance and colour is typical of bottle glass dating 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).

The silica (SiO_2) concentration of find 14 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 numbers 11 and 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 (Fe_2O_3) in its structure, which accounted for 1.75%.

4.2.6 Find number 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 neck 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, suggesting less degradation than for the other samples. 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 number 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%. Find 15 did not contain detectable levels of many trace elements which were present in some of the other glass finds including zinc (Zn), zirconium (Zr), magnesium (Mg) and cobalt (Co). Overall, the relatively good condition of this piece and its lack of many trace element impurities would suggest that it was most likely a modern find.

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 two glass rod fragments, Finds 10 and 11, appear to be of a similar composition to each other and are possibly from the same source. Find 12, a distorted glass fragment, differs significantly from finds 10 and 11 as far as trace elements are concerned and it may well have had a different origin. Find 14 appears to be a fragment of low quality bottle glass, possibly dating to the Post-Medieval period. Find 15 appears to be relatively modern as the level of corrosion in its surface is quite low. Many trace elements which would have been difficult to eliminate using ancient glass-making techniques were not detected in this find. It does not appear to be related to finds 10, 11 or 12 based on its elemental composition.

Find 13, the vitreous glass slag, appears to be unrelated to the glass finds which were analysed as it contains elements which were not detected in the glass. Its appearance and elemental composition suggests that it was possibly produced during iron smelting.

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. It could also imply that there simply was not a demand for highly decorative glass objects.

Bibliography

Bachmann, H. (1982) *The identification of slags from archaeological sites., Institute of Archaeology Occasional Publications Vol. 6,* London: Institute of Archaeology.

Blakelock, E., Martinón-Torres, M., Veldhuijzen, H. A. and Young, T. (2009) 'Slag inclusions in iron objects and the quest for provenance: an experiment and a case study', *Journal of Archaeological Science*, 36, 1745-1757.

Goffer, Z. (2007) *Archaeological Chemistry,* New Jersey: John Wiley & Sons.

Grassroots Archaeology Project (2014) 'Grassroots Archaeology. A community project determined to unearth the story of a forgotten monument.', [online], available: http://grassrootsarchaeology.ie/?page_id=2 [accessed

Grassroots Archaeology Project (unpublished) *Seagrange, Baldoyle*.

Gratuze, B. and Janssens, K. (2004) 'Provenance analysis of glass artefacts.' in Janssens, K. and Grieken, R. V., eds., *Comprehensive Analytical Chemistry. Volume XLII: Non-Destructive Microanalysis of Cultural Heritage Materials.*, Amsterdam: Elsevier.

Henderson, J. (2000) *The Science and Archaeology of Materials: An investigation of inorganic materials.,* London: Routledge.

Moran, J. (2010) 'Medieval Stained and Painted Window Glass: The Irish Problem' in Hearne, J. M., ed. *Glassmaking in Ireland: From the Medieval to the Contemporary*, Dublin: Irish Academic Press, 15-32.

Paynter, S. (2006) 'Regional Variations in Bloomery Smelting Slag of the Iron Age and Romano-British Periods', *Archaeometry,* 48(2), 271-292.

Pollard, A. M. and Heron, C. (2008) *Archaeological Chemistry in Archaeology.,* Cambridge: Cambridge University Press.

Roche, N. (2007) 'The manufacture and use of glass in post-medieval Ireland' in Horning, A., Ó'Baoill, R., Donnelly, C. and Logue, P., eds., *The Post-Medieval Archaeology of Ireland 1550-1850*, Dublin: Wordwell Ltd, 405-420.

Taylor, M. and Hill, D. (2008) 'Experiments in the reconstruction of Roman wood-fired glass-working furnaces', *Journal of Glass Studies,* **50**, 249-270.

Varshneya, A. K. (1994) *Fundamentals of Inorganic Glasses,* London: Academic Press Limited.

Wayne Smith, C. (2003) *Archaeological Conservation Using Polymers: Practical Applications for Organic Art,* USA: Texas A&M University Press.


Plate 1: Find number 10


Plate 2: Find number 11

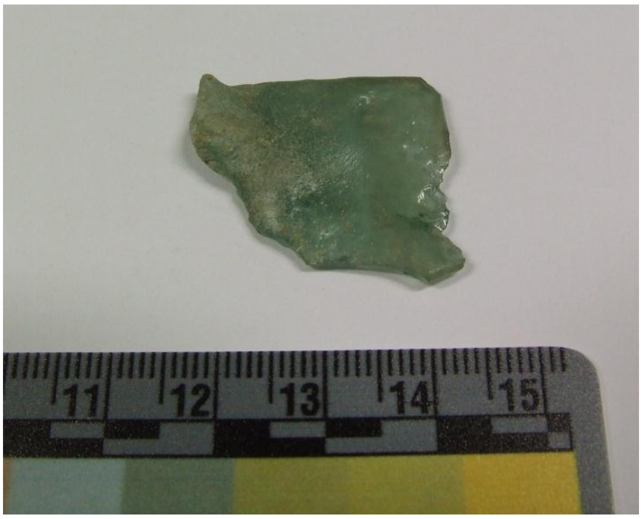
Plate 3: Find number 12


Plate 4: Find number 13

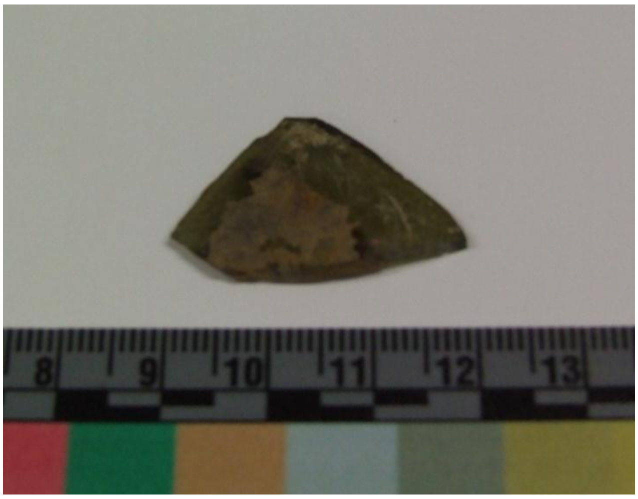
Plate 5: Find number 14

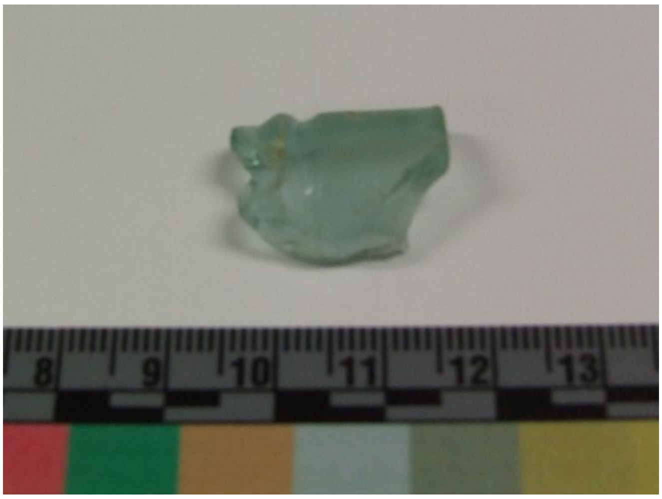
Plate 6: Find number 15

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

Find:	10	11	12	13	14	15
Description:	Thick green glass rod fragment	Thin green glass rod fragment	Distorted glass fragment, tinge of green	Brownish black vitreous slag material	Corroded green glass fragment – possible bottle glass	Glass fragment – possible neck sherd
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