

WALMER CASTLE, DEAL, KENT ANALYSIS OF THE GLASS

TECHNOLOGY REPORT

David Dungworth and Brice Girbal



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WALMER CASTLE, DEAL, KENT

ANALYSIS OF WINDOW GLASS

David Dungworth and Brice Girbal

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SUMMARY

This report presents the results of chemical analysis of historic window glass at Walmer Castle. Previous research using laboratory-based techniques has demonstrated the relationship between the chemical composition of glass and its age. This report presents the first attempt to use a portable instrument to analyse historic window glass without damaging it. The benefits and limitations of a portable X-ray fluorescence (pXRF) spectrometer are explored through the analysis of samples of glass which had been analysed previously using laboratory-based techniques. The problems of analysing glass which also has a UV-absorbing film are also assessed through the analysis of 75 panes analysed from both inside and outside surfaces. This shows that the pXRF analysis of glass through a UV-absorbing film is not rewarding. The analysis of 661 of the Walmer Castle window panes is reported and the results are interpreted in relation to previous laboratory-based analyses and the architectural history of Walmer Castle. Four panes of glass are shown to have been made using seaweed ash and so can be dated to c1700–c1835. 235 panes of glass are shown to be made using synthetic soda prior to the introduction of mechanised drawing techniques, ie c1835–c1930. 222 panes of glass are shown to be made after the introduction of mechanised drawing, ie post-c1930. 43 panes of glass are shown to be made from an unusual potassium-calcium silicate glass. This glass includes the pink and purple glass in the dining room. There are few modern analyses of glass of this composition and historic sources provide little information. It is suggested that this glass was imported from Germany or Bohemia.

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DATE OF RESEARCH

2010

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ABBREVIATIONS

float	float glass (ie synthetic soda glass manufactured after c1960)
kelp	kelp glass (ie glass made using the ash of seaweed, between c1700 and c1835)
mech	Mechanised glass (ie synthetic soda glass manufactured after c1930)
potash	Potassium-rich glass made using refined (terrestrial) plant ash
SS	Synthetic Soda glass (ie glass manufactured after c1835)
SSC	Synthetic Soda Cylinder glass (ie synthetic soda glass manufactured before c1930)

INTRODUCTION

This report presents the first attempt to apply non-destructive chemical analysis of *in situ* historic window glass in order to date its manufacture. English Heritage has undertaken significant research into historic window glass. This research has been divided into two phases. In the first phase samples of historic window glass obtained from a wide range of architectural and archaeological contexts have been analysed using laboratory-based techniques (summarised in Dungworth forthcoming). This has established that a series of changes in glass composition have occurred over the past five centuries. The chronological changes in glass composition have been interpreted as the result of the rapid adoption of new technologies and raw materials as these have become available. This report is the first contribution to the second phase of the Historic Window Glass Project, in which the results of the first phase are used to inform non-destructive *in situ* chemical analysis of historic windows.

Almost all glass produced in Britain during the medieval period was made using sand and terrestrial plant ashes (primarily bracken) and has a distinctive potassium-rich composition (Dungworth and Clark 2004). The arrival of French glassmakers in the 16th century saw a change to a high-lime low-alkali (HLLA) glass. HLLA glass was probably made using sand and the ash of hardwoods (such as oak). This HLLA glass remained in use until the end of the 17th century when it was superseded by a glass made using sand and seaweed (kelp) ash (Dungworth *et al* 2009; Parkes 1823; Watson 1782). This kelp glass dominated the window glass industry until the early part of the 19th century when it was abandoned in favour of glass made using synthetic soda (Cooper 1835; Ure 1844; Muspratt 1860).

Nicholas Leblanc invented a process for the manufacture of synthetic soda at the end of the 18th century. Common salt was heated with sulphuric acid to produce sodium sulphate (soda saltcake). The sodium sulphate was then heated with lime and charcoal or coal to produce sodium carbonate. Initially, glass could only be made with sodium carbonate, but glassmakers soon discovered that the sulphate could be used directly if it was combined with charcoal or coal. Glass made for the century or so following the 1830s was a simple soda-lime-silica glass with low levels of impurities (Dungworth 2009a). The plant ashes used before the introduction of Leblanc soda all naturally contained enough calcium (lime) to ensure that the glass manufactured was durable. Leblanc soda contained no calcium and from the 1830s lime was an essential ingredient in window glass recipes (batch).

The early decades of the 20th century saw the introduction of mechanisation in the window glass industry (Cable 2004; McGrath and Frost 1937). Ultimately, mechanisation allowed continuous production of huge quantities of flat glass; however, it was accompanied by problems of devitrification —small crystals would tend to form in the glass. This problem was overcome by replacing a proportion of the calcium in the batch with magnesium (Turner 1926) and virtually all window glass made in Britain since 1930 has contained 2–5wt% magnesia (Šmrček 2005). An examination of the

Table 1. Average chemical composition of historic window glass at different periods

Phase	1	2a	2b	3	4a	4b	5a	5b
Start		c1567	c1600	c1700	c1835	c1870	c1930	c1960
End	c1567	c1600	c1700	c1835	c1870	c1930	c1960	
Na ₂ O	2.5±0.3	1.4±0.7	2.4±1.4	7.9±0.7	12.7±0.9	12.9±2.1	13.9±0.5	13.3±0.4
MgO	7.3±0.7	3.4±0.5	3.0±0.7	5.3±0.3	0.2±0.1	0.2±0.2	2.8±0.2	3.8±0.1
Al ₂ O ₃	1.6±0.5	2.8±1.0	3.0±1.3	2.6±0.6	0.6±0.1	1.2±0.3	0.9±0.6	1.3±0.2
SiO ₂	55.8±2.5	60.4±1.8	60.9±2.0	66.5±1.4	70.8±1.2	71.9±0.4	72.2±0.7	72.2±0.5
SO ₃	0.3±0.1	0.2±0.1	0.4±0.2	0.2±0.1	0.4±0.1	0.4±0.2	0.4±0.2	0.2±0.1
Cl	0.4±0.2	0.3±0.2	0.2±0.1	0.6±0.1	0.1±0.1	<0.1	<0.1	<0.1
P ₂ O ₅	3.2±0.4	2.1±0.2	2.1±0.6	1.1±0.2	<0.2	<0.2	<0.2	<0.2
K ₂ O	11.4±1.5	5.6±1.6	5.1±1.9	4.2±0.2	0.1±0.1	0.5±0.2	0.1±0.1	0.6±0.1
CaO	15.3±1.6	21.5±1.9	21.1±1.7	10.4±1.0	14.0±0.8	12.9±1.6	9.7±0.8	8.3±0.6
MnO	1.26±0.30	0.94±0.37	0.24±0.20	<0.10	<0.10	<0.10	<0.10	<0.10
Fe ₂ O ₃	0.65±0.13	1.01±0.20	1.31±0.29	0.71±0.14	0.22±0.06	0.21±0.06	0.13±0.03	0.12±0.01
As ₂ O ₃	<0.20	<0.20	<0.20	<0.20	0.22±0.16	<0.20	<0.20	<0.20
SrO	0.07±0.01	0.09±0.02	0.07±0.01	0.45±0.10	0.03±0.01	0.02±0.01	0.01±0.01	0.01±0.01

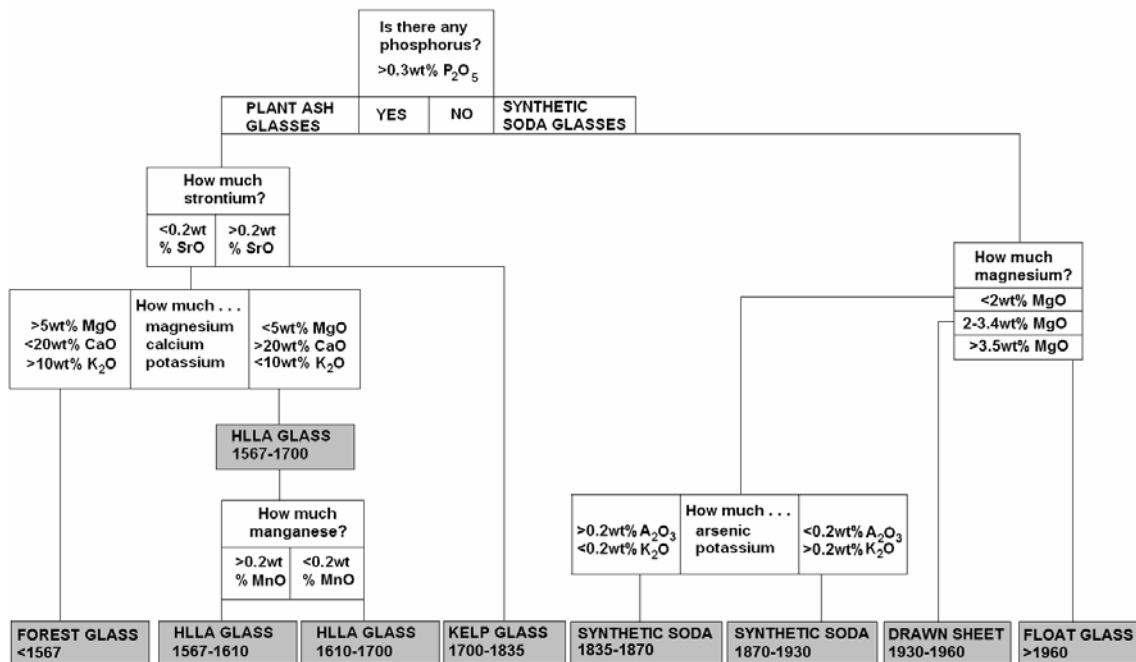


Figure 1. Model for assigning glass to a chronologically significant compositional group

magnesium content of flat glass produced since the introduction of mechanisation suggests that there are two groups: one with 2.5–3.0wt% MgO and one with 3.5–4.5wt% MgO. Contemporary technical literature does not provide an explanation for this; however, it is likely that the introduction of the float process (Pilkington 1969) saw the re-emergence of devitrification problems which were overcome by increasing the MgO:CaO ratio (from 0.3 to 0.4–0.5, Dungworth and Wilkes 2010).

The chemical analysis of over 800 samples of historic window glass suggests that such glass can be quickly assigned to a chronologically significant compositional group on the basis of a small range of oxides (especially MgO, P₂O₅, SrO, MnO and As₂O₃). A model for this process is given as Figure 1 and typical glass for each period is summarised in Table 1. The chemical analysis of window glass can provide important information about the date of manufacture and its installation. This information can provide a sound basis for informed conservation (Clark 2001) of historic window glass. Knowing the date of individual panes of glass in a building will allow the identification of original and replacement glass. Such identifications are essential to understand and so value and manage the window glass in historic buildings (cf English Heritage 2005). The use of laboratory-based techniques can provide the necessary information; however, this is only possible where a window is broken or is undergoing renovation (cf Dungworth and Loaring 2009; Freestone *et al*/2010). As such this approach is of limited use for providing information about *in situ* glass. The solution proposed in this report is the use of a portable X-Ray Fluorescence (pXRF) spectrometer which will allow non-destructive *in situ* analysis. The remainder of this report describes the pXRF method development, the historic building on which the pXRF was tested (Walmer Castle), the nature of the results and the recommendations for future research.

METHODOLOGY

The pXRF instrument chosen to undertake the *in situ* non-destructive analysis of historic window glass was a Niton XL3t (Cu/Zn Mining Mode) which allowed the simultaneous determination of the concentration of over 20 elements including almost all of those determined using the laboratory-based techniques. The only element which was routinely determined using laboratory-based techniques but which could not be determined with the Niton XL3t was sodium. The Niton X3Lt uses a helium flush to improve the detection of light elements (especially magnesium, aluminium, silicon and phosphorus) but it was still not possible to determine sodium. Initial tests suggested that the detection of light elements was rather poor without the helium purge.

Table 2. Niton XL3t Cu/Zn Mining Mode

Condition	Voltage	Target	Elements detected
Main	40kV	Silver	Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Zr, Nb, Mo, Pd, Ag, Cd, Sn, Sb, Hf, Ta, W, Re, Au, Pb, Bi
High	50kV	Molybdenum	Pd, Ag, Cd, Sn, Sb, Ba
Low	20kV	Iron	K, Ca, Ti, V, Cr
Light	6kV	None	Mg, Al, Si, P, S, Cl

The Niton XL3t Cu/Zn Mining Mode uses four separate conditions to determine the concentration of different elements (Table 2). The data is combined in a fundamental parameters method to determine the concentration of all of the detected elements.

Initially the instrument was tested (against reference materials) using a count time of 60 seconds for each condition. Such a long count time; however, would mean that it would have taken two to three weeks to complete the number of analyses required to characterise the window glass of a historic building. Several steps were taken to reduce the total count time so that analysis could proceed as quickly as possible. The first step was to reduce the count time for the High condition to 0 seconds; this can be justified on the grounds that this condition is used to detect elements (Table 2) which have not been shown to help assign historic window glass to chronologically significant compositional groups. The second stage comprised a gradual reduction in the count time for the Main, Low and Light conditions. As the count times were reduced the effect on accuracy and limit of detection were determined (Figure 2). The identification of acceptable accuracy and limits of detection were framed by the data obtained from the laboratory-based analysis of historic window glass (Figure 1; Table 1). It was found that count times of 5 seconds each for Main and Low conditions and 15 seconds for Light condition provided sufficient accuracy and limits of detection (Table 3).

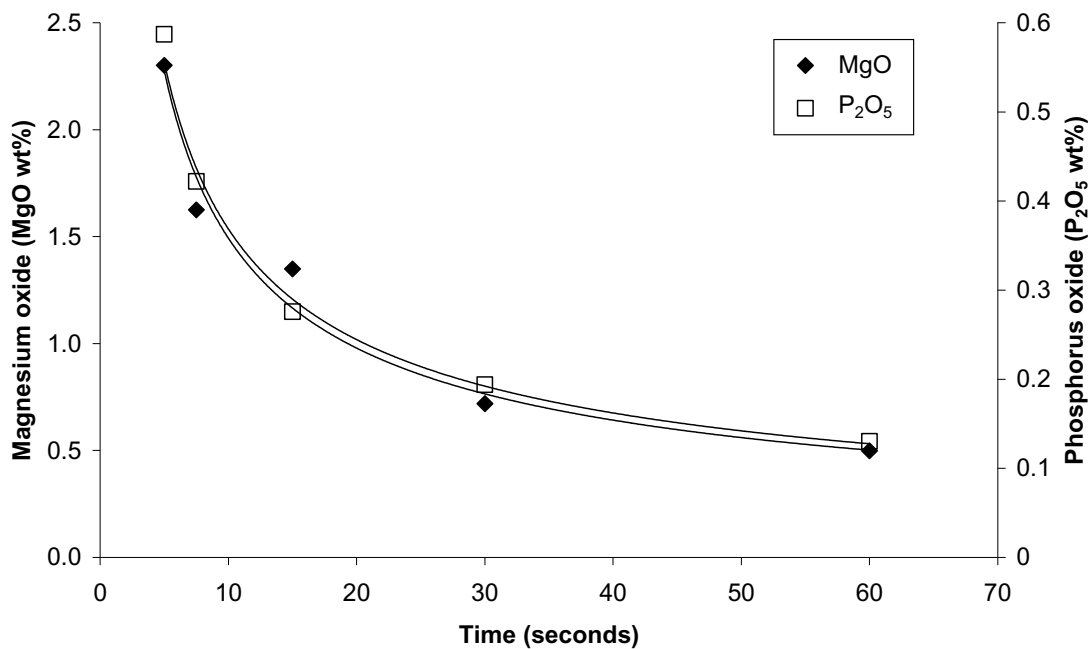


Figure 2. Limits of detection for magnesium and phosphorus oxides for different count times

The Niton XL3t Cu/Zn Mining Mode was used to analyse a wide range of reference materials in order to test the accuracy of the instrument/software (Figure 3 and Table 3). The reference materials analysed included a range of commercial certified reference materials (eg NIST, DGG, etc) as well as non-certified reference materials (eg Newton/ESF/Pilkington, Corning, etc). For most elements there was a very good relationship between the actual and analysed concentrations (Figure 3) although a best fit straight line through the data rarely had a slope of 1 (ie the measured concentrations

tended to be consistently over- or under-estimated). The slope values for the best fit lines were used as calibration factors for the raw analysed data (empirical calibration).

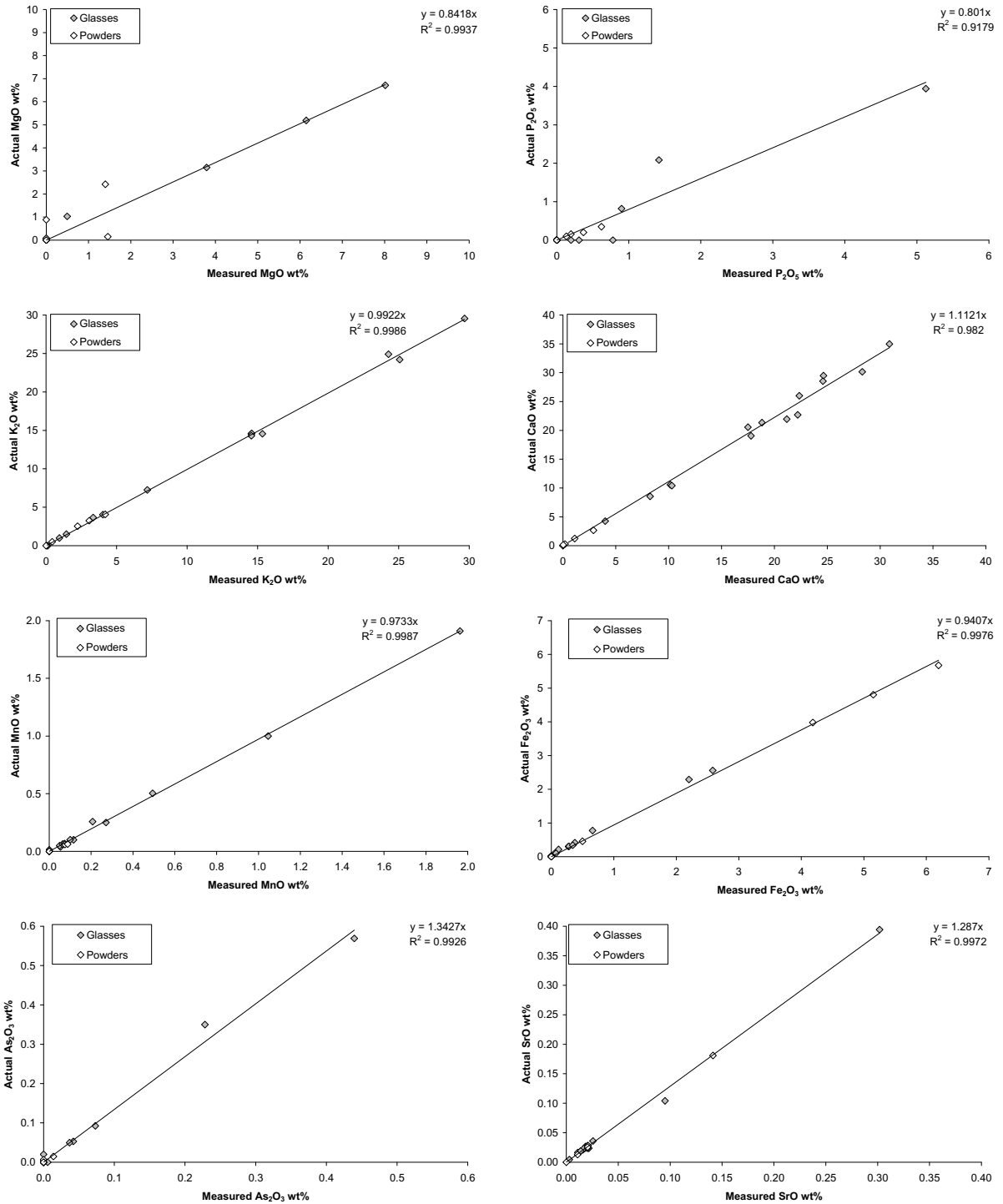


Figure 3. Charts showing the relationship between measured and actual concentrations of selected elements present in the reference materials analysed

The analysis of the reference materials also allowed an estimation of the likely analytical errors and limits of detection (Table 3). For the light elements the accuracy and limits of detection are slightly inferior to the data that can be obtained using laboratory-based techniques and this is most marked for the lightest elements (especially magnesium). For heavier elements the accuracy and limits of detection are equal to or superior to those obtainable with laboratory-based techniques.

Table 3. Error and limit of detection (LoD) for the analysed oxides

Oxide	Error (1 sd)	Precision (1 sd)	LoD
MgO	0.3	0.3	2.0
Al ₂ O ₃	0.7	0.1	0.5
SiO ₂	1.1	0.8	NA
P ₂ O ₅	0.1	0.1	1.0
SO ₃	0.05	0.02	0.2
Cl	0.05	0.02	0.2
K ₂ O	0.3	0.05	0.1
CaO	0.8	0.5	0.05
TiO ₂	0.02	0.01	0.02
MnO	0.02	0.01	0.02
Fe ₂ O ₃	0.05	0.01	0.02
As ₂ O ₃	0.01	0.005	0.02
Rb ₂ O	0.001	0.0005	0.001
SrO	0.005	0.0005	0.002
ZrO ₂	0.005	0.0005	0.002

Further tests were undertaken with the Niton XL3t to determine precision (i.e. repeatability of analytical data). Repeat analyses carried out using reference materials suggested that precision values were generally smaller than accuracy values. Further tests carried out on two windows at Walmer Castle (Tables 4 and 5) confirmed that errors due to accuracy were greater than those due to precision.

Further tests were undertaken to determine what effect if any the thickness of the glass had on the analytical data. All of the calibration analyses undertaken on reference materials used samples which were relatively thick (5–10mm) such that the thickness of the glass would have little or no effect on the results. Safety tests; however, showed that a proportion of the X-rays would pass through glass up to at least 20mm thick. A series of analyses were carried out using the Niton XL3t on microscope cover slides. Each of these is 0.2mm thick and composed of soda-lime-silica glass of identical composition. Figure 4 clearly shows that (using Cu/Zn Mining Mode with the Niton XL3t) glass thickness has an effect on the analytical result. The increase in analysed concentration in thin glass is a consequence of the fundamental parameters method (Jenkins *et al* 1995) used by the Niton XL3t. This uses the Compton scattering peak to estimate the average atomic number of the material being analysed and this average atomic number is then used to improve the accuracy of the estimates of the various elements detected. A very thin sample (with air behind it) will inevitably give rise to extra Compton scattering which will

feed into the fundamental parameters calculations and indicate a lower average atomic number affecting the analysed result (Figure 4).

Table 4. Repeated analyses of a single window pane at Walmer (W21.P11)

	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	As ₂ O ₃	Rb ₂ O	SrO	ZrO ₂
1	<1.5	<0.5	66.5	0.62	0.10	16.7	0.03	0.17	0.077	<0.001	0.0107	0.0036
2	<1.5	<0.5	66.8	0.61	<0.1	15.1	0.03	0.18	0.082	<0.001	0.0106	0.0030
3	<1.5	<0.5	66.5	0.62	0.11	16.6	0.03	0.17	0.081	<0.001	0.0115	0.0030
4	<1.5	<0.5	64.1	0.61	0.14	16.5	0.02	0.17	0.082	<0.001	0.0102	0.0028
5	<1.5	<0.5	66.5	0.63	0.12	16.9	0.03	0.16	0.083	<0.001	0.0109	0.0036
6	<1.5	<0.5	65.7	0.58	0.11	16.7	0.03	0.16	0.076	<0.001	0.0103	0.0031
7	<1.5	<0.5	66.2	0.65	0.11	16.8	0.04	0.18	0.080	<0.001	0.0103	0.0032
8	<1.5	<0.5	67.1	0.62	<0.1	15.3	0.03	0.18	0.081	<0.001	0.0106	0.0020
9	<1.5	0.6	65.7	0.57	0.10	16.5	0.04	0.18	0.076	<0.001	0.0105	0.0029
10	<1.5	<0.5	67.0	0.63	0.11	16.8	0.04	0.17	0.083	<0.001	0.0107	0.0035
11	<1.5	<0.5	66.6	0.61	0.10	15.0	0.03	0.17	0.081	<0.001	0.0097	0.0026
12	<1.5	0.5	66.9	0.62	0.11	16.8	0.03	0.19	0.085	<0.001	0.0102	0.0030
13	<1.5	<0.5	66.1	0.62	0.11	16.4	0.03	0.19	0.080	<0.001	0.0105	0.0028
14	<1.5	<0.5	66.1	0.64	0.12	16.7	0.04	0.20	0.079	<0.001	0.0107	0.0029
15	<1.5	<0.5	66.0	0.59	0.10	16.5	0.03	0.17	0.079	<0.001	0.0104	0.0034
mean			66.2	0.61	0.11	16.3	0.03	0.18	0.081		0.0105	0.0030
sd			0.8	0.02	0.01	0.6	0.00	0.01	0.003		0.0004	0.0004

Table 5. Repeated analysis of a single window pane at Walmer (W22.P11)

	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	As ₂ O ₃	Rb ₂ O	SrO	ZrO ₂
1	2.2	0.90	64.7	0.21	0.52	8.0	0.043	0.143	<0.02	0.0025	0.0040	0.0074
2	3.1	0.88	65.0	0.21	0.53	8.8	0.056	0.138	<0.02	0.0022	0.0045	0.0075
3	2.0	0.94	65.0	0.23	0.61	8.7	0.050	0.123	<0.02	0.0028	0.0052	0.0069
4	2.3	0.91	65.3	0.26	0.54	8.0	0.042	0.138	<0.02	0.0024	0.0043	0.0077
5	2.6	0.78	64.8	0.26	0.64	8.8	0.049	0.142	<0.02	0.0023	0.0047	0.0080
6	2.1	0.79	64.1	0.23	0.57	8.7	0.050	0.139	<0.02	0.0022	0.0041	0.0074
7	<1.5	0.92	64.9	0.23	0.59	8.9	0.055	0.139	<0.02	0.0026	0.0044	0.0077
8	2.3	0.77	63.8	0.22	0.57	8.8	0.046	0.138	<0.02	0.0024	0.0043	0.0072
9	2.2	0.88	63.9	0.27	0.52	7.8	0.044	0.153	<0.02	0.0022	0.0047	0.0066
10	2.1	0.89	65.4	0.28	0.53	8.0	0.046	0.135	<0.02	0.0028	0.0045	0.0072
11	2.2	0.75	65.4	0.25	0.60	8.8	0.046	0.147	<0.02	0.0024	0.0043	0.0081
12	2.1	0.90	64.2	0.29	0.60	8.7	0.050	0.139	<0.02	0.0024	0.0042	0.0070
13	2.7	0.84	64.8	0.26	0.64	8.8	0.050	0.138	<0.02	0.0026	0.0045	0.0074
14	2.2	0.93	66.5	0.27	0.50	8.0	0.048	0.138	<0.02	0.0024	0.0042	0.0078
15	2.7	0.93	64.8	0.26	0.54	8.0	0.050	0.134	<0.02	0.0023	0.0046	0.0074
mean	2.3	0.87	64.8	0.25	0.57	8.4	0.048	0.139		0.0024	0.0044	0.0074
sd	0.3	0.06	0.7	0.02	0.05	0.4	0.004	0.006		0.0002	0.0003	0.0004

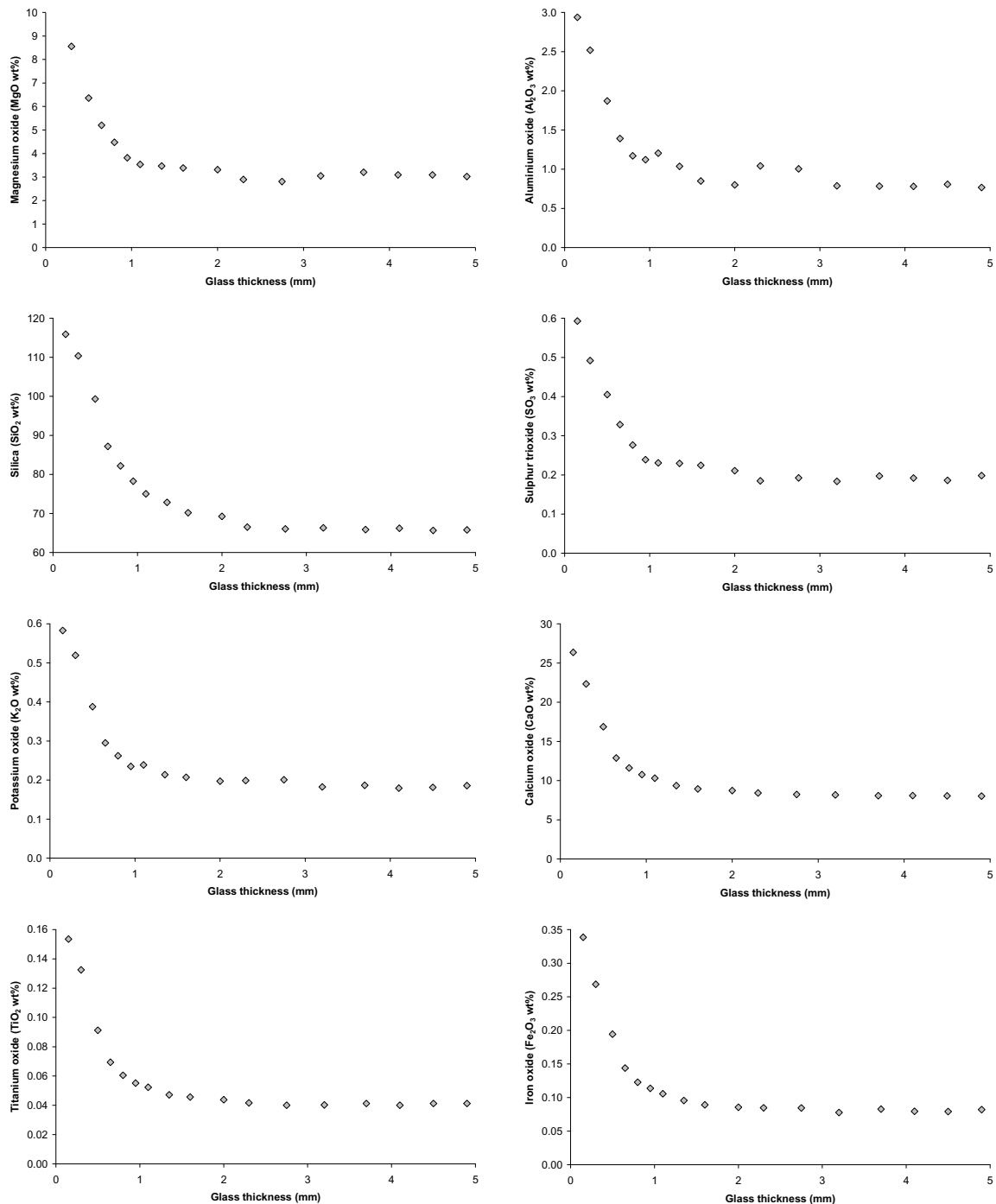


Figure 4. Changes in apparent concentration of various elements with glass thickness

The apparent change in the concentration of different elements is only detectable in glass less than 2mm thick and the increase in apparent concentration is inversely proportional to glass thickness. Glass less than 1mm shows significant apparent changes in composition. The analysis of 104 samples of historic window glass from Shaw House (Dungworth and Loaring 2009) showed that these had an average thickness of 1.4mm (with a minimum thickness of 1.0mm and a maximum of 2.8mm). It is likely, therefore, that the use of the

Niton XL3t in the way described in this report will often yield results which are not entirely accurate. Nevertheless, it is anticipated that the slight increase in the concentration of some elements will still allow the identification of the broad categories of historic window glass discussed above (Table 1).

The testing of the pXRF for the analysis of historic window glass also included a consideration of the effects of ultraviolet (UV) absorbing films. UV-absorbing films are routinely fixed to the interior surface of windows in historic buildings to reduce the damaging effects that UV light has on organic-based materials, such as carpets, upholstery, wood, books, paper, tapestry, and paintings (Saunders 1992). Most UV-absorbing films are polyesters although various manufacturers indicate that these have been specially formulated and/or doped with various metals.

A range of different types of glass (HLLA, kelp, soda, etc) were analysed with a range of UV-absorbing films (supplied by SUN-X) and the results compared with the analysis of the glass without the film. While taking measurements at Walmer Castle it became clear that many of the windows there had UV-absorbing films but in many cases it was possible to analyse the same glass from both the inside and the outside. This allowed a detailed comparison of the effects of the UV-absorbing film on the detection of a range of elements in the glass (Figure 5). The UV-absorbing film clearly attenuates low energy X-rays. In no cases could any magnesium or aluminium be detected even when these elements could be detected by analysing the exterior of the glass. Silicon was detectable at very low concentrations in most samples when analysed through the UV-absorbing film but this data bore no relationship with the actual silicon content of the glass (Figure 5). Phosphorus was detected in most analyses of glass with a UV-absorbing film although the glass itself contained no detectable phosphorus. It is likely that the UV-absorbing film used at Walmer Castle contains a small proportion of phosphorus. Analyses of both potassium and calcium showed a good correlation for most panes of glass although the analyses taken through the UV-absorbing film consistently underestimated the proportion of these elements. In addition, a small number of samples showed anomalous results, such as the same potassium and calcium concentrations both with and without the UV-absorbing film. Heavier elements (those with an atomic number greater than 20) generally showed a strong correlation between the analyses taken with and without the UV-absorbing film. Low atomic number elements generally have low energy characteristic X-rays which are more easily absorbed by the UV-absorbing film.

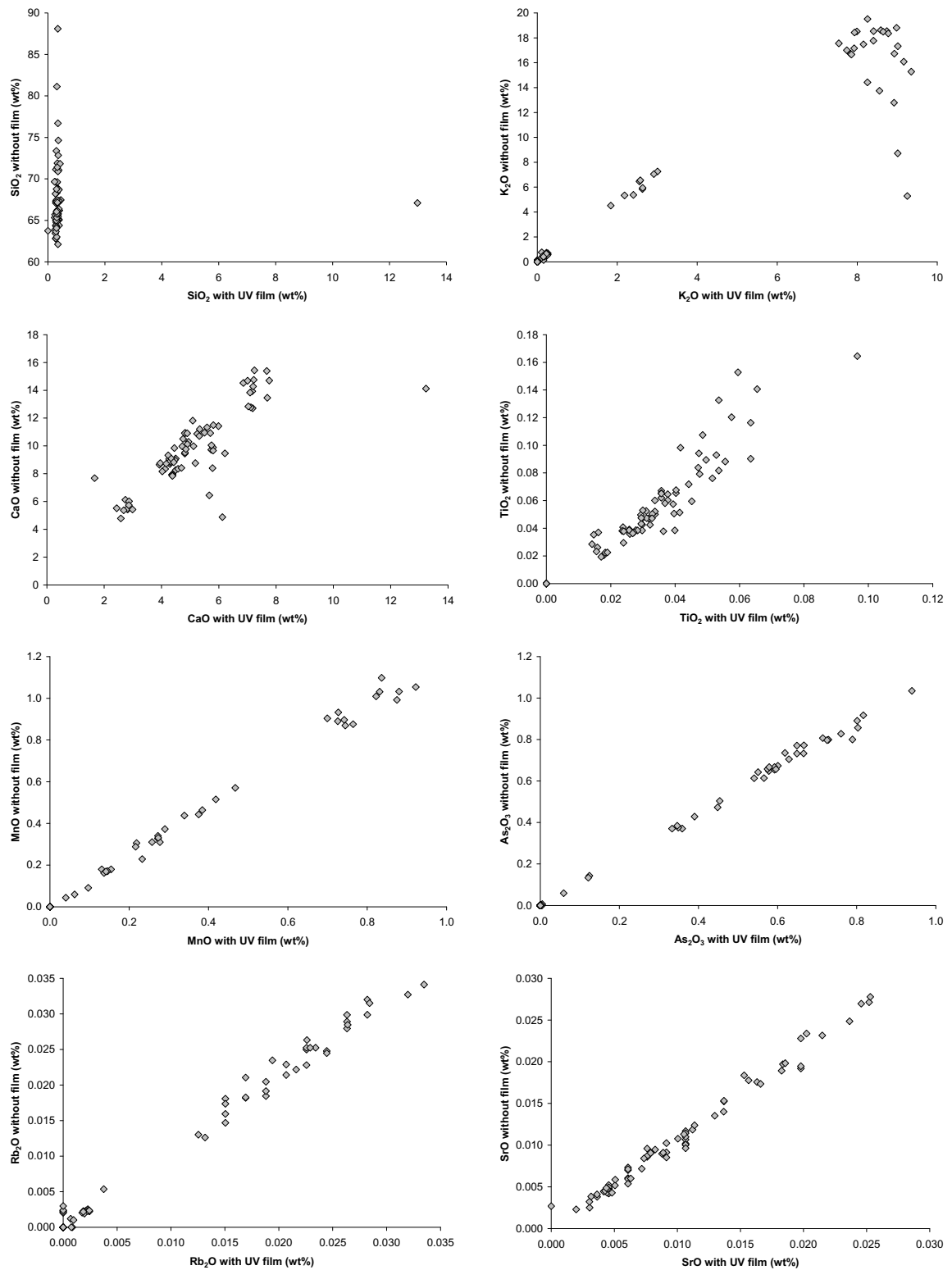


Figure 5. Effects of UV-absorbing films

Analyses of glasses with significant surface corrosion were effectuated. Three samples of corroded HLLA window glass recovered from excavations at Basing House (Dungworth 2009b) were first analysed with the surface corrosion products *in situ*. The corrosion products were then removed using silicon carbide abrasive paper and the glass re-analysed (Table 6).

Table 6. pXRF analyses of three samples of Basing House glass before and after removal of corrosion products from one surface

	BH03		BH06		BH08	
	corroded	clean	corroded	clean	corroded	clean
MgO	<2.0	7.5	<2.0	3.9	2.8	4.1
Al ₂ O ₃	1.2	2.5	9.2	5.7	5.4	4.6
SiO ₂	27.9	75.3	84.5	75.4	76.1	75.7
P ₂ O ₅	<1.0	3.6	2.2	1.9	1.5	1.7
SO ₃	1.0	<0.2	3.6	0.2	<0.2	<0.2
K ₂ O	0.2	8.6	4.4	7.3	7.0	7.7
CaO	40.6	15.2	15.5	20.9	19.3	20.5
TiO ₂	0.11	0.22	0.41	0.36	0.36	0.19
MnO	0.76	0.99	1.05	1.13	0.09	0.10
Fe ₂ O ₃	0.68	0.63	0.67	0.55	1.45	1.40
SrO	0.024	0.032	0.043	0.044	0.084	0.086

This revealed that light elements were most affected by corrosion. Magnesium was not detected or was present at much lower concentrations in corroded glass compared with results when the corrosion was removed. The aluminium, silica, phosphorus, sulphur, potassium and calcium contents were also either over or under represented due to corrosion. In the most extreme case, one sample recorded 40wt% calcium oxide when the actual composition was around 15wt%. The most affected samples were those where corrosion was most visually extreme; in the samples tested the older sample (forest glass, BH03) showed greater corrosion. The changes in chemical composition at the surface of glass are varied and can be produced by several different mechanisms. In most cases, alkalis are removed from the glass and, being soluble, are washed away leaving a surface that is rich in silica. The corroded surface may also contain some thin films of adhering dirt. In order to minimise the effects of corrosion and surface dirt on the analyses of the Walmer Castle window glass were wiped clean with a soft cloth.

The Niton XL3t has been developed using the Cu/Zn Mining Mode with a total count time of 25 seconds to allow the non-destructive chemical analysis of historic window glass *in situ*. It has been shown that the results can be significantly affected by the presence of UV-absorbing films. It is also likely that weathered or corroded glass will return results which do not accurately reflect the nature of the underlying glass. Very thin glass (any glass <2mm thick, but especially glass 1–2mm thick) will also yield apparent compositions which may be misleading.

WALMER CASTLE

Walmer Castle was originally built in 1539 as one of a chain of coastal artillery forts during the reign of Henry VIII (Morley 1976). Walmer formed one of three forts (the other two being Deal and Sandown) which guarded the anchorage of the Downs (Colvin 1982, 369). As originally built these forts would have comprised a central tower three-stories high surrounded by four two-storey high bastions (Colvin 1982, 461). The small permanent garrison would have been quartered in the central tower. It is unclear whether any of the openings in the wall of the original castle would have been glazed with glass. As most openings were probably gun ports it is likely that they would have had wooden shutters rather than glass windows. The upkeep of Walmer Castles and its garrison declined somewhat in the early 17th century. The castle was besieged and damaged during the short-lived Royalist uprising which followed the execution of Charles I in 1648. The Downs forts continued to operate during the Dutch Wars of the 1650s and 1660s but by the end of the century they represented obsolete military technology and were again neglected. Visiting in 1697, Ceilia Feinnes referred to them as, "3 little forts or Castles . . . but I should think they would be of little effect and give the enemy no great trouble" (Morris 1949, 128).

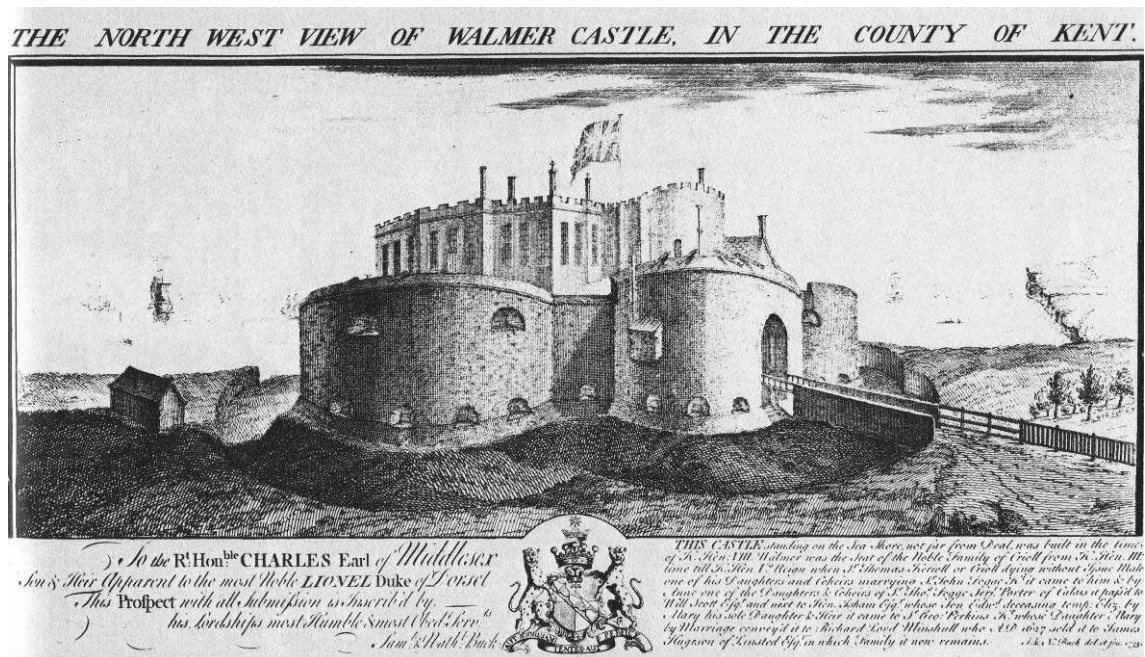


Figure 6. Drawing of Walmer Castle published by Samuel and Nathaniel Buck in 1735

Walmer Castle gained a new lease of life when, in 1708, the new Warden of the Cinque Ports was assigned Walmer as his official residence. The Cinque Ports was a confederation of the towns of Hasting, Romney, Rye, Dover and Sandwich which, since the 12th century, had provided a small naval fighting force to protect the southeast coast and shipping for the channel crossing, in return for various legal and taxation privileges (Murray 1935). The activities of the Cinque Ports often amounted to little more than

piracy and by the 13th century the Crown began to appoint a Lord Warden in an attempt to restrain the Cinque Ports. With the establishment of the Royal Navy the importance and power of the Cinque Ports declined and the post of Lord Warden was merged with the Constable of Dover Castle. Before 1708 the Lord Warden of the Cinque Ports had his headquarters and residence in Dover Castle; however, with the appointment of the Duke of Dorset, Walmer Castle became the official residence. The appointment of subsequent Lords Warden was often undertaken in recognition of service to the Crown and State. Lords Warden have included William Pitt, Lord Wellington, Marquess Curzon of Kedleston, Sir Winston Churchill and HM Queen Elizabeth the Queen Mother.



Figure 7. The Gunners' Quarters added to the south-west bastion in the early 18th century

Much of Walmer Castle comprises the Henrician fort built in the 16th century although the additions and alterations of various Lords Warden can be identified (Newman 1983, 489). The earliest alterations belong to the early 18th century when the Duke of Dorset was Lord Warden (Figure 6). It is likely that the first floor of the central tower was at this time converted to provide accommodation. Rooms were added to the south-west bastion which are labelled on contemporary documents as Gunners' Quarters (Figure 7). Above the north-east bastion, the Duke of Dorset added a series of brick-built rooms with castellated wall summits (Curzon 1927, 14; Newman 1983, 489; Figure 8). Some of

the windows in these rooms contain pink/purple glass (Figure 9) which has traditionally been ascribed to the Earl of Liverpool (1806–1828), 'I was further told that the tinted glass in several of the sash windows of the Castle was introduced because one of his two Countesses had weak eyes, but I should not like to vouch for this legend.' (Curzon 1927, 160).



Figure 8. Brick-built rooms (F14 and F15) added to the north-east bastion in the early 18th century

William Pitt (1792–1806) seems to have been responsible for the conversion of the Gunners' Quarters into accommodation for the Lord Warden and his guests. He is also probably responsible for the extension of these rooms to cover the entire south-west bastion (Figure 7). The Earl of Granville (1865–1891) commissioned considerable alterations to the north-west bastion. It was heightened to provide the Earl with extra accommodation (Figure 10) and 'the outline is now one of picturesque variety' (Newman 1983, 489). The mullioned windows in the south-west bastion are also thought to have been installed at this date.

Plans of Walmer Castle showing the locations of all of the analysed windows are provided in Appendix 1.



Figure 9. Window 41 showing pink/purple glass attributed to Earl Liverpool (1806–1828)



Figure 10. The north-east bastion which was heightened in the 1870s

RESULTS BY GLASS TYPE

Over a period of three days it was possible to analyse 661 panes of glass from 83 windows (see Appendix 4). 222 of the analysed panes were provided with UV-absorbing films but in 75 cases it was possible to analyse these panes twice; once from the inside (with the film) and once from the outside (without the film). A small number of windows were omitted from the analytical survey, eg pattern-rolled glass used for the public toilets on the ground floor.

The results of the analysis of glass without the UV-absorbing film have been divided into four major glass types (Figure 11; Table 7). These major groups are kelp glass, a potash glass and two synthetic soda glasses. The kelp glass appears to have a mixed alkali composition with the relatively high levels of strontium that is typical of glasses made using kelp, or seaweed ash (cf Table 1). The potash glass was an unexpected result — this glass has a high concentration of potassium and (on the basis of the analysed totals) appears to contain little or no sodium. This type of glass has no parallels among any of the glass analysed during the first phase of this project (Dungworth forthcoming). The synthetic soda glasses contain low levels of impurities (such as aluminium, titanium, iron) typical of glasses made after the introduction of Leblanc soda to the glass industry (cf Table 1). Although sodium cannot be detected using the Niton XL3t its presence is implied by the low concentrations of potassium in these glasses. The concentrations of other elements in these glasses conform to previous analyses of synthetic soda glass. The synthetic soda glasses have been divided into two groups based on the detection of magnesium. Samples with no magnesium detected are interpreted as being cylinder glass, made before the introduction of drawn sheet c1930 (SS – cylinder). Samples with magnesium are interpreted as having been made after the introduction of the drawn sheet process (SS – mech).

Table 7. Average composition of the four major window glass types from Walmer Castle

	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	MnO	Fe ₂ O ₃	As ₂ O ₃	Rb ₂ O	SrO	ZrO ₂
Kelp	4.5	2.6	66.8	1.0	4.1	12.0	0.05	0.72	<0.02	<0.001	0.417	0.002
Potash	<1.5	<0.5	69.0	<1.0	14.1	9.0	0.40	0.11	0.54	0.023	0.008	0.011
SS – cylinder	<1.5	0.9	68.4	<1.0	0.3	14.8	0.03	0.17	0.15	<0.001	0.012	0.005
SS – mech	2.5	0.8	66.6	<1.0	0.4	8.3	<0.01	0.11	<0.02	0.001	0.009	0.009

The window glass from Walmer Castle is dominated by synthetic soda glass: 90% of the analysed panes were made after the introduction of Leblanc soda in 1835 (Figure 12). About half of these synthetic soda glasses would have been made prior to 1930 and half afterwards. Less than 1% of the analysed panes are made of kelp glass (c1700 to c1835). The remaining 9% are the potash glasses.

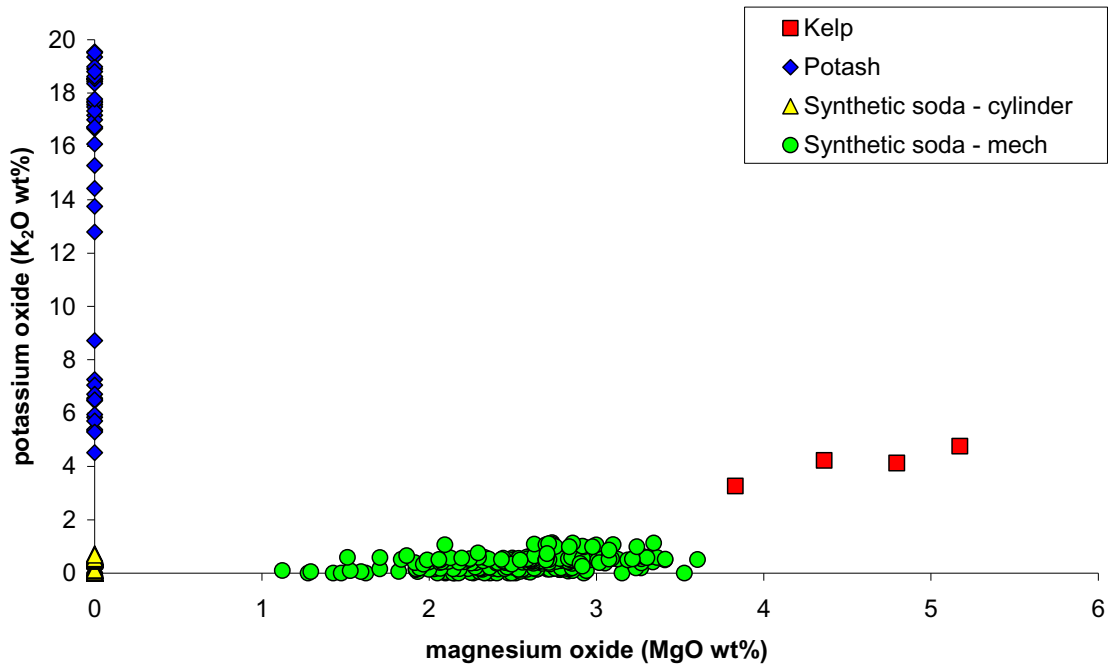


Figure 11. Magnesium and potassium concentrations of window glass from Walmer Castle (includes only samples that were analysed without UV-absorbing films)

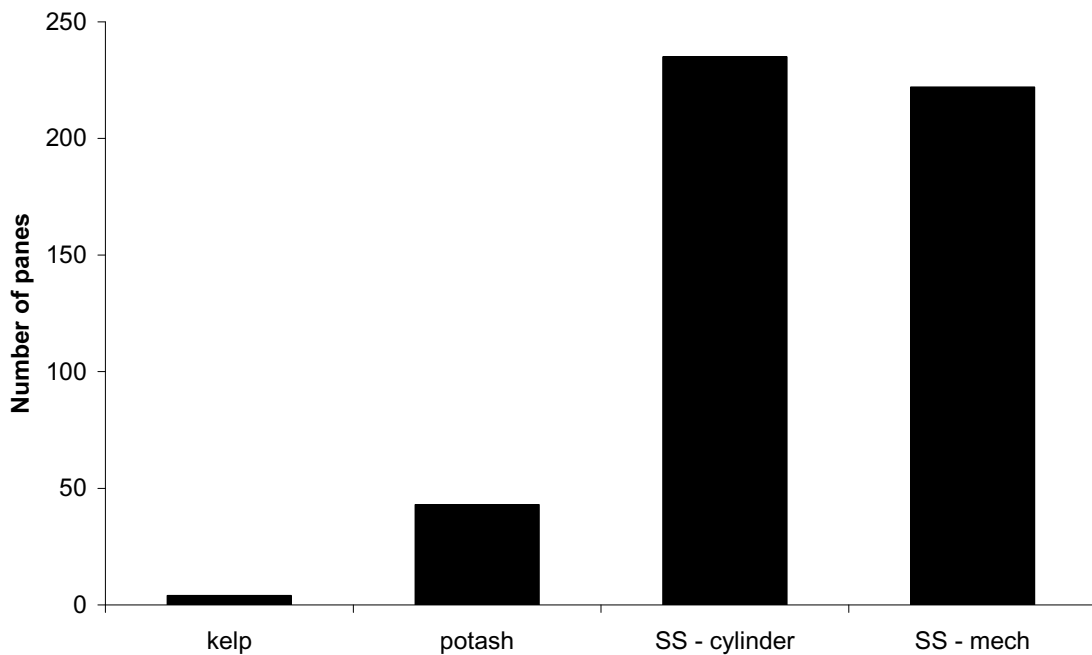


Figure 12. Histogram showing the proportion of different major window glass types from Walmer Castle (includes only samples that were analysed without UV-absorbing film)

Kelp Glass

Window glass made using seaweed or kelp ash as the flux dominated the English window glass industry from the beginning of the 18th century until the 1830s and the introduction of Leblanc soda. The fact that only four panes of such glass remain at Walmer Castle suggests that there has been extensive replacement of its window glass after c1835.

Potash Glass

The potash glass from Walmer Castle is characterised by a high potassium content and low levels of impurities. Its composition does not closely parallel any medieval or post-medieval plant ash glass encountered during the analysis of historic window glass from England and Wales (Dungworth forthcoming). The closest parallel for a high-purity potassium-calcium-silicate glass is Bohemian crystal. This was developed in the late 17th century and is best known for its use in the manufacture of tablewares; however, it was used in the early 19th century for the manufacture of flat glass (Srnec 2005).

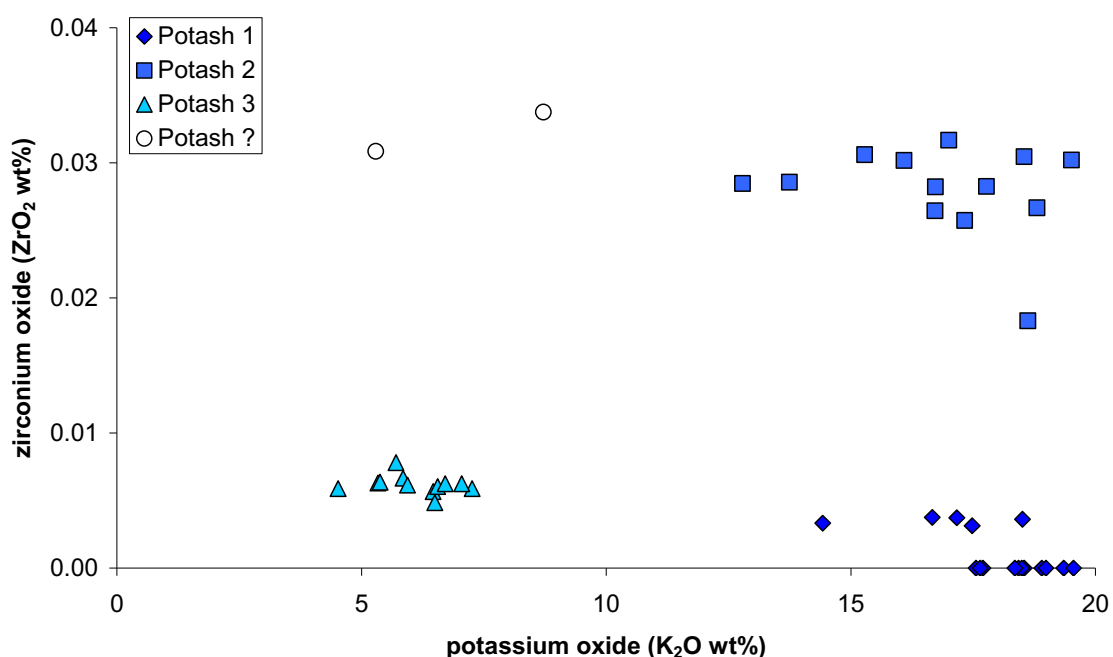


Figure 13. Potassium and zirconium content of the potash glass from Walmer Castle

The potash glass can be divided into three compositional groups (Figure 13; Table 8) which suggests that not all of this glass was made at the same time or place. While some of the potash glass is colourless (Potash 3) most is pink or purple in colour due to the presence of manganese (Table 8).

Table 8. Average composition of the different types of potash glass from Walmer Castle

	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	MnO	Fe ₂ O ₃	As ₂ O ₃	Rb ₂ O	SrO	ZrO ₂
1	<1.5	<0.5	67.3	18.0	10.6	0.34	0.07	0.78	0.024	0.006	0.001
2	<1.5	<0.5	68.9	16.8	10.1	0.83	0.12	0.73	0.023	0.011	0.028
3	<1.5	0.9	71.4	6.1	5.6	<0.01	0.15	<0.02	0.022	0.006	0.006
?	<1.5	<0.5	84.6	7.0	5.7	1.03	0.19	0.75	0.032	0.011	0.032

Synthetic Soda Glass (cylinder)

The synthetic soda glass has been divided into two groups based on the magnesium content. The first group in which no magnesium was detected would have been made after the introduction of Leblanc soda c1835 but before the introduction of mechanised sheet drawing c1930. All of this glass would have been made using a cylinder process. It is likely that most of it was mouth-blown although some could have been produced using the Lubbers process (Cable 2004).

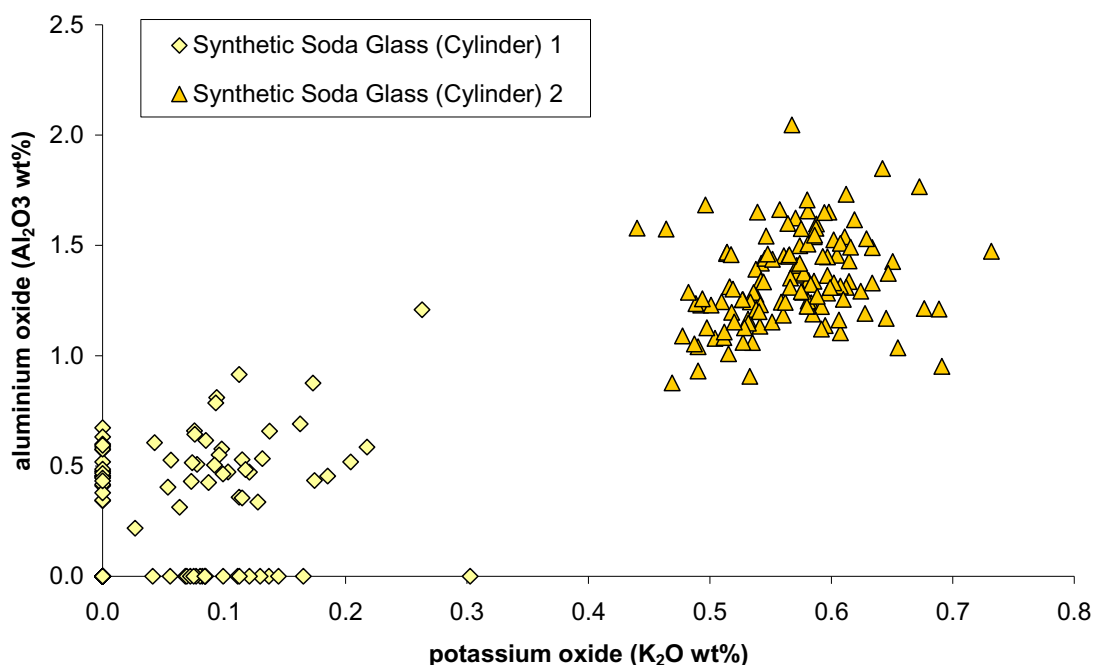


Figure 14. Potassium and aluminium content of Synthetic Soda Glass (Cylinder)

The synthetic soda glass (cylinder) can be divided into two compositional groups: the first with low aluminium and potassium and the second with higher concentrations of both elements (Figure 14; Table 9). There are few other differences between these groups, although the first tends to contain more arsenic. Arsenic appears to have been used as a refining agent for several decades after the introduction of Leblanc soda and then (c1870) largely replaced by potassium nitrate (saltpetre). It is likely that synthetic soda glass (cylinder) 1 was manufactured and installed before synthetic soda glass (cylinder) 2.

Table 9. Comparison of two types of synthetic soda glass (cylinder)

	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	MnO	Fe ₂ O ₃	As ₂ O ₃	Rb ₂ O	SrO	ZrO ₂
1	<0.5	67.8	0.06	15.6	0.07	0.17	0.26	<0.001	0.015	0.005
2	1.3	68.8	0.57	14.2	<0.02	0.18	0.05	<0.001	0.010	0.006

Both sub-types of synthetic soda (cylinder) glass display significant degrees of chemical variation which is probably due to the supply of glass to Walmer Castle from a number of different suppliers over a period of a century or so (c1835 to c1930). An initial attempt to refine these sub-types was abandoned after the identification of more than 10 possible sub-types and numerous ungrouped panes. One significant sub-group within synthetic soda glass (cylinder) 1 worth mentioning is that which is found only in the windows added during the Earl of Granville's 1870s additions to the gatehouse. This sub-group is distinguished by relatively high concentrations of arsenic.

Synthetic Soda Glass — mechanised

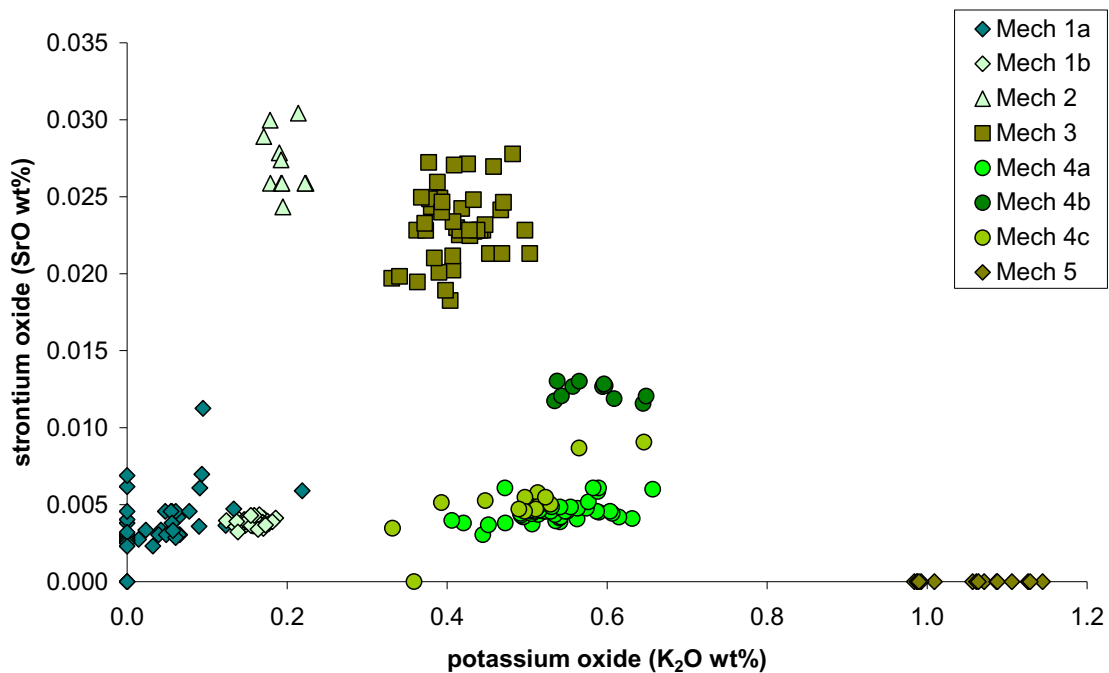


Figure 15. Potassium and strontium content of the mechanised glass

The introduction of drawing techniques saw the continued use of synthetic soda rather than plant-based alkalis; however, mechanisation imposed new requirements on the glass during forming which were met by replacing a proportion of the calcium in the glass with magnesium. Mechanised glass has been identified primarily through the detection of

magnesium. The concentrations of minor and trace elements allow the mechanised glass to be divided into numerous sub-types (Figure 15; Table 10).

While previous work (Dungworth and Wilkes 2010) has suggested a clear difference between drawn sheet glass (c1930–c1960) and float glass (c1960 onwards) the *in situ* pXRF analysis of the Walmer Castle window glass reveals a great deal of apparent overlap between these two groups. Although the calcium concentration in some mechanised glass from Walmer Castle is low enough for it to be considered float glass, the magnesium concentrations are often not high enough. It is possible that glass thickness, surface corrosion and surface dirt have distorted the chemical analysis and led to an underestimation of the magnesium concentration. A comparison of the MgO:CaO ratios may allow these limitations to be overcome. Drawn sheet typically has MgO:CaO values of 0.30–0.33 and float glass has values 0.44–0.52; the Walmer Castle mechanised glass has values ranging from 0.13 to 0.57 and allows the tentative identification of sub-types 2 and 5 as probable float glass (made after c1960). The remaining sub-types are all likely to be drawn sheet (made c1930–c1960).

Table 10. Comparison of average composition of different types of mechanised glass

	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	MnO	Fe ₂ O ₃	As ₂ O ₃	Rb ₂ O	SrO	ZrO ₂
1a	2.2	<0.5	67.4	<0.1	9.0	<0.02	0.09	<0.02	<0.001	0.004	0.008
1b	2.6	<0.5	64.8	0.2	8.3	<0.02	0.09	0.06	<0.001	0.004	0.004
2	2.6	0.9	67.1	0.2	6.8	<0.02	0.14	<0.02	<0.001	0.027	0.011
3	2.6	1.1	66.3	0.4	8.4	<0.02	0.10	<0.02	<0.001	0.023	0.006
4a	2.7	0.9	66.1	0.5	8.7	<0.02	0.12	<0.02	0.001	0.005	0.008
4b	2.8	1.0	67.7	0.6	8.3	<0.02	0.12	<0.02	0.002	0.012	0.008
4c	2.7	0.9	67.1	0.5	8.0	<0.02	0.08	<0.02	<0.001	0.005	0.023
5	2.8	1.1	68.4	1.1	5.9	<0.02	0.13	<0.02	0.008	<0.001	0.013

RESULTS BY WINDOW

This section considers the analytical results window by window. The window numbers are those given in the plans and list in the appendices. In each window the panes were identified individually. The first pane was in the top left hand corner and subsequent pane numbers assigned by 'reading' from left to right and then beginning on a new row (Figure 16). The numbers were assigned when the window was analysed and this was either from the interior or exterior depending on circumstances. Care was taken to ensure the same pane numbers were used for those windows where analysis was carried out on interior and exterior surfaces.

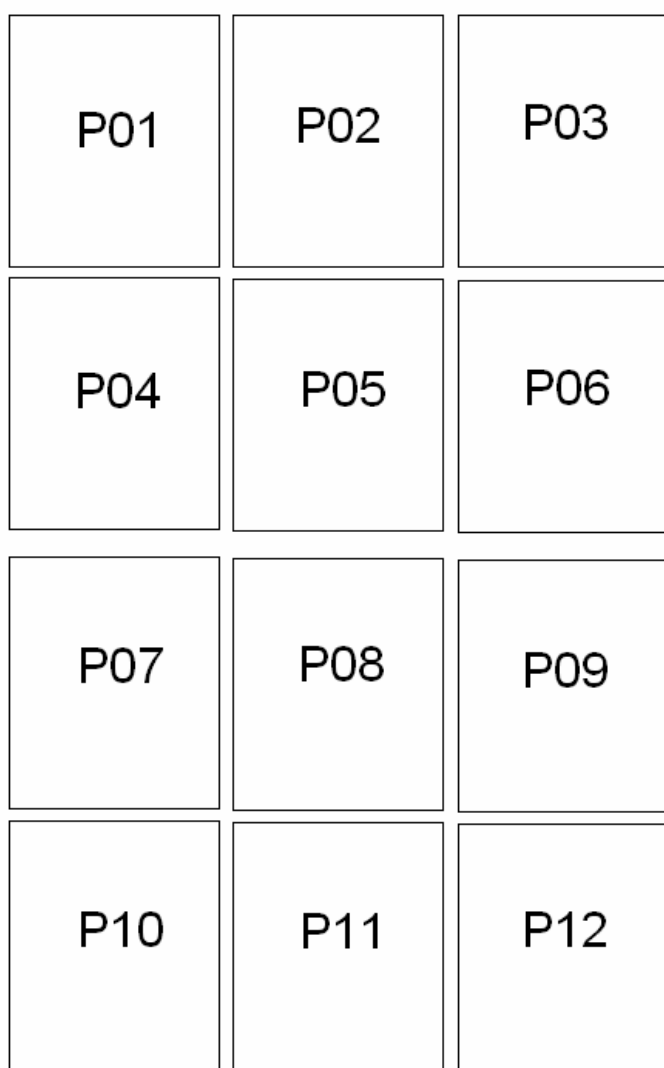


Figure 16. Hypothetical window showing the convention for numbering the panes

D12 (G19/21)

Twenty-seven panes of glass (two very small panes are not included) within a door and two flanking windows forming the main entrance to the shop (numbered from the outside, G19, see Figure 17). Twenty-three of the panes are synthetic soda (cylinder) 2 glass and share a virtually identical composition. This is the same composition of glass as used for D13 (see below). It is likely that all of these panes were installed at the same time and they may even represent the original glazing. This type of glass was most likely to have been manufactured between c1870 and c1930. The four replacement panes are 13, 16, 19 and 21 and each of these is a member of a separate sub-group of mechanised glass, suggesting the replacement of individual panes as this became necessary. Two out of the four replaced panes are in the door rather than the flanking windows probably because these panes would be subject to greater danger of breaking (eg slamming door).



Figure 17. D12

D13 (G23/24)

A door very similar to D12 with twenty-seven panes of glass (two very small panes are not included). This door and two flanking windows form the rear entrance to the shop (numbered from the outside, G24, see Figure 18). Twenty-three of the panes are synthetic soda (cylinder) 2 glass and share a virtually identical composition. This is the same composition of glass as used for D12 (see above). It is likely that all of these panes were installed at the same time and they may even represent the original glazing. This type of glass was most likely to have been manufactured between c1870 and c1930. The four replacement panes are 3, 4, 18 and 22 and each of these is a member of a separate sub-group of mechanised glass, suggesting the replacement of individual panes as this became necessary. Three out of the four replaced panes are in the door rather than the

flanking windows probably because these panes would be subject to a greater danger of breaking (eg slamming door).



Figure 18. D13

W01 (G14, Porter's Lodge)

Two panes of glass one of which is a synthetic soda (cylinder) 1 glass while the other is a mechanised glass. The first panes was probably manufactured between c1835 and c1870. This window was probably installed at the same time that alterations were made to this bastion for the Earl of Granville.

W02 (G15, Porter's Lodge)

Three panes of glass including one synthetic soda (cylinder) 1 glass and two different mechanised glasses. The synthetic soda (cylinder) 1 has a composition which is very close to that found in W01. This window was probably installed at the same time that alterations were made to this bastion for the Earl of Granville.

W03 (G04, Sackville Room)

A single pane with UV-absorbing film which prevented full analysis. The results are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The low levels of rubidium and strontium suggest that this is a synthetic soda glass but the data available are insufficient to distinguish between cylinder glass and mechanised glass.

W04 (G04, Sackville Room)

Four panes all with UV-absorbing film which prevented full analysis. The low levels of rubidium and strontium suggest that all of the panes in this window are synthetic soda glass. One pane has a high arsenic concentration which suggests that it is a synthetic soda (cylinder) 1 glass made between c1835 and c1870. If this pane represents the original glazing then it is likely that this window was installed during the period when the Earl of Granville was Lord Warden.

W07 (G03, Willingdon Room)

Four panes all with UV-absorbing film which prevented full analysis. The low levels of rubidium and strontium suggest that all of the panes in this window are synthetic soda glass. The apparent concentrations of all oxides appear to be near identical suggesting that all four panes were installed at the same time and that they are all original or all contemporary replacements.

W08 (G03, Willingdon Room)

A single pane with UV-absorbing film which prevented full analysis. The low levels of rubidium and strontium suggest that this is a synthetic soda glass but the data available are insufficient to distinguish between cylinder glass and mechanised glass.

W09 (G12, Gatehouse)

A single pane of mechanised glass which would place its manufacture after c1930.

W10 (G19/G28, Central Tower)

Nine panes with the six panes in the top two rows being synthetic soda (cylinder) glass while the three panes in the bottom row are mechanised glass. The synthetic soda (cylinder) glass in the top two rows is of varied origin. The middle row appears to be the earliest. All three panes are synthetic soda (cylinder) 1 glass but there are sufficient differences in composition to suggest that not all of this glass was made at the same time or place. This variety is most telling with pane 6 which has a distinct pink colour and 0.29wt% manganese oxide. As the iron oxide content of this glass is roughly equal to the manganese, it is possible that this glass was originally colourless. The manganese may have been added to the molten glass to reduce the effect that the iron had on the colour of the glass, but subsequent exposure to UV light has oxidised the manganese giving rise to the pink colour (ie solarisation, see Abd-Allah 2009; Long *et al* 1998). It is likely that all three panes in the middle row would have been manufactured and installed between

c1835 and c1870. The three panes in the top row are all synthetic soda (cylinder) glass and would have been manufactured between c1870 and c1930.

W12 (G16/G19, Boiler Room)

Twelve panes arranged in six rows of two. Two panes (2 and 12) are synthetic soda (cylinder) 1 glass, five are synthetic soda (cylinder) 2 glass and the remainder are mechanised glass. The earliest extant glass in this window was probably manufactured between c1835 and c1870.

W14 (G24/G26, Central Tower)

Twenty-five panes of glass making two separate windows, one above the other (Figure 19). The top window has nine panes arranged in three rows of three. The bottom window has sixteen panes arranged in four rows of four. All sixteen panes in the lower window are mechanised glass and all share the same composition. The glass in this window has been installed at some time after c1930. The upper window contains a single pane of synthetic soda (cylinder) 1 glass, four synthetic soda (cylinder) 2 glass panes and four mechanised glass panes. The earliest extant glass in this window was probably manufactured between c1835 and c1870.



Figure 19. W14

W15 (G25/G26, Central Tower)

Six panes of glass which make two separate windows, one above the other. The top window has four panes arranged in two rows of two. The bottom window has two panes: one above the other. The six panes include four synthetic soda (cylinder) 1 glass, one synthetic soda (cylinder) 2 glass and one mechanised glass. The earliest extant glass in both windows was probably manufactured between c1835 and c1870.

W16 (G01, Gunners' Lodging)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but was analysed from the exterior only. The twelve panes include five synthetic soda (cylinder) 1 glass, four synthetic soda (cylinder) 2 glass and three mechanised glass. The earliest extant glass in this window was probably manufactured between c1835 and c1870.

W17 (G01, Gunners' Lodging)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but was analysed from the exterior only. The twelve panes include seven synthetic soda (cylinder) 1 glass, three synthetic soda (cylinder) 2 and two mechanised glass. The earliest extant glass in this window was probably manufactured between c1835 and c1870.

W18 (G08/G11)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but was analysed from the exterior only. The twelve panes are all mechanised glass and share the same chemical composition. The glass is not plane and so would have been produced using a drawn process rather than a float process. Therefore, the extant glass in this window was probably manufactured between c1930 and c1960.

W19 (G11/G27, Central Tower)

Nineteen panes of glass which make two separate windows, one above the other. The top window has nine panes arranged in three rows of three. The bottom window has four panes arranged in two rows of two. The four panes in the lower window are all synthetic soda (cylinder) 2 glass. Two panes from the upper window are synthetic soda (cylinder) 2 glass while the other seven are mechanised glass. The earliest extant glass in both windows was probably manufactured between c1870 and c1930.

W20 (G11/G28, Central Tower)

Sixteen panes in four rows of four (Figure 19). A single pane is a synthetic soda (cylinder) 1 glass but all of the others are synthetic soda (cylinder) 2. If the single pane of synthetic soda (cylinder) 1 glass represents the original glazing then this can be placed in the period c1835 to c1870.



Figure 19. W20

W21 (G02/G11, Gunners' Lodging)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but was analysed from the exterior only. The twelve panes include six synthetic soda (cylinder) 1 glass, three synthetic soda (cylinder) 2 and three mechanised glass. The earliest extant glass in this window was probably manufactured between c1835 and c1870.

W22 (G02/G11, Gunners' Lodging)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but was analysed from the exterior only. The twelve panes include five synthetic soda (cylinder) 1 glass, four synthetic soda (cylinder) 2 and two mechanised glass. The earliest extant glass in this window was probably manufactured between c1835 and c1870.

W24 (G11/G28, Central Tower)

Eight panes arranged in two rows of four. The eight panes include a single synthetic soda (cylinder) 1 glass, four synthetic soda (cylinder) 2 and three mechanised glass. If the single pane of synthetic soda (cylinder) 1 glass represents the original glazing then this can be placed in the period c1835 to c1870.

W25 (F20)

Twelve panes forming two rows of a bay window. Six of the panes are synthetic soda (cylinder) 1 glass and share virtually the same composition. This composition almost certainly represents the original glazing and can be dated to between c1835 and c1870. Glass with the same composition can also be found in W26, W27 and W61–W63. The remaining six panes in W25 are mechanised glass; five share almost identical compositions and probably represent a single period of repair (post-c1930).

W26 (F21)

Six panes in two rows. Two of the panes are synthetic soda (cylinder) 1 glass and share virtually the same composition. This composition almost certainly represents the original glazing and can be dated to between c1835 and c1870. Glass with the same composition can also be found in W25, W27 and W61–W63. The remaining four panes in W26 are mechanised glass and form two compositional pairs; these probably represent two separate periods of repair (post-c1930).

W27 (F22)

Six panes in two rows. Three of the panes (the entire top row) are synthetic soda (cylinder) 1 glass and share virtually the same composition. This composition almost certainly represents the original glazing and can be dated to between c1835 and c1870. Glass with the same composition can also be found in W25, W26 and W61–W63. The remaining three panes in W27 are mechanised glass; two of which share identical compositions and probably represent a single period of repair (post-c1930).

W28 (F23)

A single pane of mechanised glass. This pane of glass has been installed post-c1930.

W29 (F23/F31)

Two panes of glass, both of which are mechanised (ie post-c1930) but they do not share the same composition. The window surrounds and fittings are identical with those in W25–W27 and it is likely that all of the extant glass in W29 comprises later replacement.

W35 (F31, Loggia)

Sixteen panes arranged in eight rows. All of the glass is mechanised and shares the same composition. In addition, this glass composition is shared by W36. This glass was manufactured after c1930.

W36 (F31, Loggia)

Sixteen panes arranged in eight rows. All of the glass is mechanised and shares the same composition. In addition this glass composition is shared by W35. This glass was manufactured after c1930.

W37 (F13, Dining Room)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but was analysed from both the inside and outside. The twelve panes include eleven potash glass and one mechanised glass. The potash glass includes examples from all three sub-types. The type 1 examples have the highest manganese content and the strongest pink/purple colour. The type 3 examples have no manganese and are colourless. The potash glasses are discussed in more detail elsewhere in this report (see above 18–19 and below 42–43) but are tentatively dated to the early 19th century. The potash glass is likely to be the earliest surviving glass in this window. The synthetic soda (cylinder) and mechanised glass are likely to be later replacements.

W38 (F13, Dining Room)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but was analysed from both the inside and outside. The twelve panes include five potash glass, three synthetic soda (cylinder) glass and four mechanised glass. The potash glass includes examples of types 2 and 3, but only one is not colourless. Pane 9 is the only pink pane and contains c0.3wt% MnO; the remaining potash glasses are colourless (and contain no manganese). The potash glasses are discussed in more detail elsewhere in this report but are tentatively dated to the early 19th century. The potash glass is likely to be the earliest surviving glass in this window. The synthetic soda (cylinder) and mechanised glass are likely to be later replacements.

W39 (F13, Dining Room)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but was analysed from both the inside and outside. The twelve panes include seven potash glass, two synthetic soda (cylinder) glass and three mechanised glass. The potash glass includes examples of types 1 and 2, some that are distinctly purple and have a relatively high manganese content (c0.9wt% MnO) while others with a slight pink tint have a lower manganese content (c0.4wt% MnO). None of the potash glass can be described as colourless. The potash glasses are discussed in more detail elsewhere in this report but are tentatively dated to the early 19th century. The potash glass is likely to be the earliest surviving glass in this window. The synthetic soda (cylinder) and mechanised glass are likely to be later replacements.

W40 (F14, Ante Room)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but was analysed from both the inside and outside. The twelve panes include five potash glass, one synthetic soda (cylinder) glass and six mechanised glass. The potash glass includes examples of types 1 and 2, as well as colourless, pink and purple panes (with the usual correlation between colour and manganese content). The potash glasses are discussed in more detail elsewhere in this report but are tentatively dated to the early 19th century. The potash glass is likely to be the earliest surviving glass in this window. The synthetic soda (cylinder) and mechanised glass are likely to be later replacements.

W41 (F14, Ante Room)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but was analysed from both the inside and outside. The twelve panes include six potash glass, three synthetic soda (cylinder) glass and three mechanised glass. The potash glass includes examples of types 1 and 2, as well as colourless, pink and purple panes (with the usual correlation between colour and manganese content). The potash glasses are discussed in more detail elsewhere in this report but are tentatively dated to the early 19th century. The potash glass is likely to be the earliest surviving glass in this window. The synthetic soda (cylinder) and mechanised glass are likely to be later replacements.

W42 (F15, Drawing Room)

Four panes in two rows. The glass had a UV-absorbing film applied to the interior surface but was analysed from both the inside and outside. The four panes include one synthetic soda (cylinder) 1, one synthetic soda (cylinder) 2 and two mechanised glasses. None of

the four panes of glass share the same composition and most, if not all, are likely to represent replacements. The earliest extant glass is represented by the synthetic soda (cylinder) 1 glass (pane 4); however, this cannot represent the original glazing. This suite of rooms was built in the 1730s but the earliest surviving glass is at least 100 years later.

W43 (F15, Drawing Room)

Four panes in two rows. The glass had a UV-absorbing film applied to the interior surface but was analysed from both the inside and outside. The four panes include one synthetic soda (cylinder) 1 and three mechanised glasses. The synthetic soda (cylinder) 1 glass shares the same composition as two panes in W44 and one in W45. The top two panes share the same composition but they are mechanised glass (ie post-c1930) and so represent simultaneous replacement. The earliest extant glass is represented by the synthetic soda (cylinder) 1 glass; however, this cannot represent the original glazing.

W44 (F15, Drawing Room)

Four panes in two rows. The glass had a UV-absorbing film applied to the interior surface but was analysed from both the inside and outside. The four panes include two synthetic soda (cylinder) 1 and two mechanised glasses. The two synthetic soda (cylinder) 1 panes share the same composition as each other (as well as one pane in W43 and one pane in W45). The earliest extant glass is represented by the two synthetic soda (cylinder) 1 glasses (panes 2 and 4); however, this cannot represent the original glazing.

W45 (F15, Drawing Room)

Four panes in two rows. The glass had a UV-absorbing film applied to the interior surface but was analysed from both the inside and outside. The four panes include one synthetic soda (cylinder) 1 and two mechanised glasses. The two synthetic soda (cylinder) 1 panes share the same composition as each other (and with a pane in W43 and two in W44). The earliest extant glass is represented by the synthetic soda (cylinder) 1 glass; however, this cannot represent the original glazing.

W46 (F15, Drawing Room)

Four panes in two rows. The glass had a UV-absorbing film applied to the interior surface but it could only be analysed from the inside. The results are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The low levels of rubidium and strontium suggest that all four panes are synthetic soda glasses. One of the four panes contains concentrations of a range of elements which are strikingly similar to the synthetic soda (cylinder) 1 glass present in W43–W45. The earliest extant

glass is represented by the synthetic soda (cylinder) 1 glass; however, this cannot represent the original glazing.

W47 (F35)

Four panes in two rows. Three of the panes had a UV-absorbing film applied to the interior surface but could only be analysed from the inside. The results for these three panes are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The remaining pane had UV-absorbing film applied but this was peeling away from the glass and it was possible to analyse the glass without the UV-absorbing film. The pane analysed without the UV-absorbing film is a mechanised glass (post-c1930). The low levels of rubidium and strontium suggest that the remaining three panes are synthetic soda glasses.

W48 (F16, Queen Victoria's Room)

A door with 12 panes arranged in four rows of three and flanked on either side by two windows each comprising four panes. The panes all had a UV-absorbing film applied to the interior surface but were analysed from the exterior surface. The panes were numbered from the exterior. Three of the panes (the top three panes from the window on the left side) are potash glass, six are synthetic soda (cylinder) 2 glass and eleven are mechanised glass. The potash glasses are all potash 3 and colourless. The synthetic soda (cylinder) 2 panes are virtually identical in composition and could have been made at the same time and place. The mechanised glass (post-c1930) all represents later replacement and nine of these share the same composition indicating that much of the glass was replaced in a single episode. It is likely that the potash glass represents glazing which predates the association between this room and Queen Victoria. The synthetic soda (cylinder) 2 glass (c1870 to c1930) and the mechanised glass represent at least two different phases of later repairs.

W49 (F16, Queen Victoria's Room)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but could only be analysed from that side. The results for these three panes are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The low levels of rubidium and strontium suggest that this is a synthetic soda glass but the data available are insufficient to distinguish between cylinder glass and mechanised glass.

W50 (F36, Prince Consort's Room)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but could only be analysed from that side. The results for these three panes are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The low levels of rubidium and strontium suggest that all of the glass is a synthetic soda glass. In addition, the concentrations of manganese and arsenic suggest that at least four of the panes are synthetic soda (cylinder) 1 glass. This glass is the earliest extant glass in this window and probably represents glazing between c1835 and c1870.

W51 (F37)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but could only be analysed from that side. The results for these three panes are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The low levels of rubidium and strontium suggest that all of the glass is a synthetic soda glass. In addition, the concentration of arsenic suggest that at least two of the panes are synthetic soda (cylinder) 1 glass. This glass is the earliest extant glass in this window and probably represents glazing between c1835 and c1870. The six lowest panes all appear to share the same composition and probably represent simultaneous repair.

W53 (F08, Wellington Museum)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but could only be analysed from that side. The results for these three panes are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The low levels of rubidium and strontium suggest that all of the glass is a synthetic soda glass. In addition, the concentrations of manganese and arsenic suggest that at least three of the panes are synthetic soda (cylinder) 1 glass. This glass is the earliest extant glass in this window and probably represents glazing between c1835 and c1870.

W54 (F08, Wellington Museum)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but could only be analysed from that side. The results for these three panes are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The low levels of rubidium and strontium suggest that all of the glass is a synthetic soda glass. In addition, the concentration of manganese suggest that

at least four of the panes are synthetic soda (cylinder) 1 glass. This glass is the earliest extant glass in this window and probably represents glazing between c1835 and c1870.

W55 (F06, Duke of Wellington's Room)

Four panes arranged in two rows of two. All of the glass is mechanised glass and shares virtually the same composition. It is likely that all of the glass in this window was replaced in a single episode post-c1930.

W56 (F06, Duke of Wellington's Room)

Four panes in two rows. The glass had a UV-absorbing film applied to the interior surface but it could only be analysed from the inside. The results are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The low levels of rubidium and strontium suggest that all four panes are synthetic soda glasses. Three of the panes have very high levels of titanium compared to the analyses of glass without UV-absorbing film; however, the UV-absorbing properties of titanium have led to its use in some UV-absorbing films.

W57 (F04)

Six panes arranged in two rows of three. The glass had a UV-absorbing film applied to the interior surface but it could only be analysed from the inside. The results are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The low levels of rubidium and strontium suggest that all four panes are synthetic soda glasses.

W58 (F05, Lucas Collection)

Two panes both with UV-absorbing film applied to the interior surface but which could only be analysed from that side. The results are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The low levels of rubidium and strontium suggest that all four panes are synthetic soda glasses.

W59 (F05, Lucas Collection)

Three panes arranged in a single row. Each pane is a different type of glass: one synthetic soda (cylinder) 1, one synthetic soda (cylinder) 2 and one mechanised glass. The synthetic soda (cylinder) 1 is the earliest extant glass in this window and probably represents glazing between c1835 and c1870.

W60 (F28)

Two panes both of which are mechanised glass and probably represent replacement post-c1930.

W61 (F17, Kitchen)

Six panes arranged in two rows. Three panes are synthetic soda (cylinder) 1 and three are mechanised glass. Two of the synthetic soda (cylinder) 1 glass panes share virtually the same composition as the synthetic soda (cylinder) 1 glass found in W25–W27, W62 and W63.

W62 (F18, Dining Room)

Ten panes forming two rows for a bay window. Seven of the panes are synthetic soda (cylinder) 1 glass, one is synthetic soda (cylinder) 2 glass and three are mechanised glass. Five of the synthetic soda (cylinder) 1 glass panes share virtually the same composition with each other and with glass in W25–W27, W61 and W63. This composition almost certainly represents the original glazing and can be dated to between c1835 and c1870. The remaining panes probably represent several different episodes of later replacement.

W63 (F19, Drawing Room)

Eight panes arranged in two rows. Six of the panes are synthetic soda (cylinder) 1 glass, one is synthetic soda (cylinder) 2 glass and one is mechanised glass. Four of the synthetic soda (cylinder) 1 panes share the same composition with each other and with glass in W25–W27, W61 and W62. This composition almost certainly represents the original glazing and can be dated to between c1835 and c1870. The remaining panes probably represent several different episodes of later replacement.

W65 (F30A)

Four panes in a single row, two of which are synthetic soda (cylinder) 2 glass while the other two are mechanised glass. The earliest extant glass in this window is the synthetic soda (cylinder) 2 glass which would have been manufactured between c1870 and c1930.

W66 (F10)

A single pane of mechanised glass which is likely to be a later (post-c1930) replacement.

W68 (F11)

Twelve panes arranged in four rows of three. The twelve panes include nine synthetic soda (cylinder) 1 glass and three mechanised glass. Eight of the synthetic soda (cylinder) 1 panes share the same composition with each other and with some of the glass from W69. This glass probably represents the original glazing (or a major re-glazing episode). The remaining panes represent later replacements. The synthetic soda (cylinder) 1 glass would have been manufactured in the period c1835 to c1870.

W69 (F09)

Twelve panes arranged in four rows of three. Only the top six panes were available for analysis (the bottom six panes were obscured by translucent Perspex). The six analysed panes include four synthetic soda (cylinder) 1 glass and three mechanised glass. The four synthetic soda (cylinder) 1 panes share the same composition with each other and with some of the glass in W68. This glass probably represents the original glazing (or a major re-glazing episode). The remaining panes represent later replacements. The synthetic soda (cylinder) 1 glass would have been manufactured in the period c1835 to c1870.

W70 (F03)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but could only be analysed from that side. The results are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The low levels of rubidium and strontium suggest that all of the glass is a synthetic soda glass (post-c1835).

W71 (F03)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but could only be analysed from that side. The results are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The low levels of rubidium and strontium suggest that all of the glass is a synthetic soda glass (post-c1835).

W72 (F07, Pitt Museum)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but could only be analysed from that side. The results are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The levels of rubidium and strontium suggest that at least some of the glass is a potash glass.

W73 (F07, Pitt Museum)

Twelve panes arranged in four rows of three. The glass had a UV-absorbing film applied to the interior surface but could only be analysed from that side. The results are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. The levels of rubidium and strontium suggest that at least some of the glass is a potash glass.

W76 (F26)

A single pane of mechanised glass which is likely to be a later (post-c1930) replacement (composition matches W78).

W77 (F30)

Three panes (all in a single row) of mechanised glass which are likely to be later (post-c1930) replacements.

W78 (F25)

A single pane of mechanised glass which is likely to be a later (post-c1930) replacement (composition matches W76).

W80 (F32)

Twelve panes arranged in four rows of three. The twelve panes include six potash glass, two synthetic soda (cylinder) 1 glass and four mechanised glass. The potash glasses are all of type 1 composition and are pink in colour. The potash glass is likely to be the earliest surviving glass in this window. The remaining panes are later replacements.

W81 (F12)

Twelve panes arranged in four rows of three. Ten of the panes had a UV-absorbing film applied to the interior surface but could only be analysed from that side; the UV-absorbing film on two panes was peeling allowing analysis of the glass without the film. The two panes analysed without the film were both mechanised glasses and are later replacements. The results for the remaining ten panes are only meaningful for Mn–Pb and these elements do not allow a categorical identification of the glass type. One pane with UV-absorbing film has manganese, arsenic and rubidium concentrations which match potash 2 glass. The remaining panes have low levels of rubidium and strontium which suggests that they are synthetic soda glass (post-c1835).

W82 (F12A)

Twelve panes arranged in four rows of three. Only the top six panes were analysed (the bottom six panes had been replaced with rolled glass post c1895). The six analysed panes include three synthetic soda (cylinder) 1 glass, two synthetic soda (cylinder) 2 glass and one mechanised glass. The three synthetic soda (cylinder) 1 panes share the same composition with each other and probably represent the original glazing (or a major re-glazing episode). The remaining panes represent later replacements. The synthetic soda (cylinder) 1 glass would have been manufactured in the period c1835 to c1870.

W83 (S09)

Two panes of mechanised glass which are likely to be later (post-c1930) replacements.

W84 (S01)

Two panes of mechanised glass which are likely to be later (post-c1930) replacements.

W85 (S02)

A single pane of mechanised glass which is likely to be a later (post-c1930) replacement.

W86 (S06)

Three panes of mechanised glass which would have been manufactured after c1930 (all glass in W86–W90 shares the same chemical composition).

W87 (S07)

Four panes of mechanised glass which would have been manufactured after c1930 (all glass in W86–W90 shares the same chemical composition).

W88 (S08)

Four panes of mechanised glass which would have been manufactured after c1930 (all glass in W86–W90 shares the same chemical composition).

W89 (S03)

Two panes of mechanised glass which would have been manufactured after c1930 (all glass in W86–W90 shares the same chemical composition).

W90 (S04)

Two panes of mechanised glass which would have been manufactured after c1930 (all glass in W86–W90 shares the same chemical composition).

W92 (T01)

A single pane of mechanised glass which would have been manufactured after c1930.

W93 (T02)

Two panes of mechanised glass which would have been manufactured after c1930. One of these has the same chemical composition as the glass in W86–W90.

W94 (Tower Room)

A single pane of mechanised glass which would have been manufactured after c1930.

W95 (Tower Room)

A single pane of synthetic soda (cylinder) 1 glass which would have been manufactured between c1835 and c1870.

WI00 (GI2/GI3)

Twenty-four panes arranged in four rows. The twenty-four panes include four kelp glass, seven synthetic soda (cylinder) 1 glass, eight synthetic soda (cylinder) 2 glass four mechanised glass and one unclassified pane. The kelp glass would have been manufactured between c1700 and c1835 and represents some of the earliest surviving glass at Walmer Castle. The remaining glass has a variety of chemical compositions suggesting several episodes of replacement.

W101 (G24/G32)

Twelve panes arranged in four rows of three. The twelve panes include six synthetic soda (cylinder) 1 glass, four synthetic soda (cylinder) 2 glass and two mechanised glass. The earliest extant glass in this window is represented by the synthetic soda (cylinder) 1 glass which would probably have been manufactured between c1835 and c1870.

DISCUSSION

The chemical analysis of most of the window glass at Walmer Castle was undertaken to test the effectiveness of pXRF for non-destructive *in situ* chemical analysis of historic window glass. The development of suitable experimental conditions ensured that over 700 analyses of window glass could be completed over a three-day period. The pXRF analyses identified four major types of glass: kelp, potash, synthetic soda and mechanised.

The earliest type of glass (but represented by only four panes) is likely to be the kelp glass. This kelp glass is unlikely to have been installed prior to c1700. Given the military function of the Castle prior to the early 17th century it is quite possible that there was little or no window glass present until it became the residence of the Warden of the Cinque Ports (1708). This kelp glass may represent some of the glass installed at this time. The fact that only four panes of this glass (all in W100 in the gatehouse) have survived indicates the extent and intensity of later alterations and replacement of window glass by later Lords Warden.

The identification of potash glasses among the windows at Walmer Castle was unexpected. During the first stage of the Historic Window Glass Project quantitative compositional data on almost 800 samples of window glass ranging in date from the 13th century to the 20th century was obtained and reviewed (Dungworth forthcoming). None of these samples has the same chemical composition as the Walmer Castle potash glasses. Medieval forest glasses do contain high levels of potassium (sometimes as much as 16wt% K_2O) but these are still lower than many of the Walmer Castle potash glasses (5–20wt% K_2O). In addition, medieval forest glasses contain a wide range of elements (in particular magnesium, phosphorus) due to the nature of the plant ash used and often contain relatively high levels of iron (0.5–0.8wt% Fe_2O_3) largely due to the nature of the sands employed. The Walmer Castle potash glasses; however, contain no magnesium, no phosphorus and low concentrations of iron (<0.2wt% Fe_2O_3) that (in England) are usually only seen in glasses made after the introduction of synthetic soda.

The closest parallels for the Walmer Castle potash glass are to be found in Germany and Bohemia. A high-purity glass (in particular with low levels of iron) using potassium and calcium as the only additions to silica was developed in Bohemia in the 1670s (Douglas and Frank 1972, 18). This glass is described by Kunckel in his late 17th-century translation

of Neri's *Art of Glass* (Kunckel 1992) and its use for the manufacture of fine tablewares is well known. This glass (often referred to as 'chalk' glass) was used in much the same way as lead crystal was used in England. Smrcek's (2005) review of literature relating to the composition of window glass from 1830 to 1990, reveals that early and mid 19th-century window glasses made in Bohemia and Germany included some with 18wt% K_2O , 9wt% CaO and 73wt% SiO_2 . This is essentially the same as the composition of Bohemian crystal (Muspratt 1860, 192) and conforms very closely to the potash window glass identified at Walmer Castle. There is unfortunately very little evidence to indicate whether the manufacture of window glass using Bohemian crystal was carried out prior to the 19th century. Writing in 1703 Neve describes two types of German glass: 'white' and 'green' (Neve 1969, 146). It is possible that the former was made using a Bohemian crystal type glass.

The potash window glass at Walmer Castle comes in several different sub-types (Figure 13; Table 8) with their colour (purple, pink and colourless) being the most significant characteristic. It is likely that all of the glass was obtained at the same time and from the same (broad) source (probably Bohemia or Germany), although the different types may have been produced at separate glasshouses. The transport of window glass over such long distances (500–1000km) would have added considerably to the cost of such glass.

The potash window glass at Walmer Castle is found only in the rooms created by the Duke of Dorset; the Dining Room (F13), the Ante Room (F14), the Kitchen (F32) and the Queen Victoria Bedroom (F16). Not all of the rooms created by the Duke of Dorset have windows with potash glass; in particular there is no potash glass in the Drawing Room (F15).

The creation of these rooms provides a *terminus post quem* of 1708 for the manufacture and installation of this glass. Lord Curzon's comments on the purple windows suggests that they were installed well before the late 19th century and may have been installed when the Earl of Liverpool was Warden (1806–1828). Current analysis of window glass from Kenwood House (the Music Room added by the Earl of Mansfield 1793–96) has identified the use of similar (although colourless) potash glass (Wilkes forthcoming). While further research is required into the manufacture and use of potash window glass, it is possible that it was used during the 18th and early 19th centuries and only in contexts where economy was not a consideration. German/Bohemian potash glass may have been desired due to its low iron content which would have ensured that it was colourless, especially compared to kelp glass. It is likely that this advantage was largely removed when English window glass manufacturers made the switch from kelp to synthetic soda during the 1830s.

The vast majority of the surviving window glass at Walmer Castle was made using a synthetic soda and would have been manufactured after c1835. The synthetic soda glass has been divided into two groups based on the magnesium content: those samples with little or no magnesium were made as cylinders (and most of these would have been

mouth-blown) while those with magnesium would have been mechanically produced as drawn sheets or float glass. The blown cylinder glass would have been made before c1930 while the mechanised glass can all be dated to after c1930.

A single type of synthetic soda (cylinder) glass with a distinctive arsenic content has been identified in W25–27 and W61–63 (Figure 20). These rooms were created in the 1870s by the Earl of Granville and this glass probably represents the glass originally installed in the 1870s. All of the remaining panes of glass in these rooms have compositions which are consistent with their being later replacements. The remaining synthetic soda glass (cylinder) displays considerable compositional variation suggesting the extensive but perhaps piecemeal replacement of much of the Walmer Castle window glass.

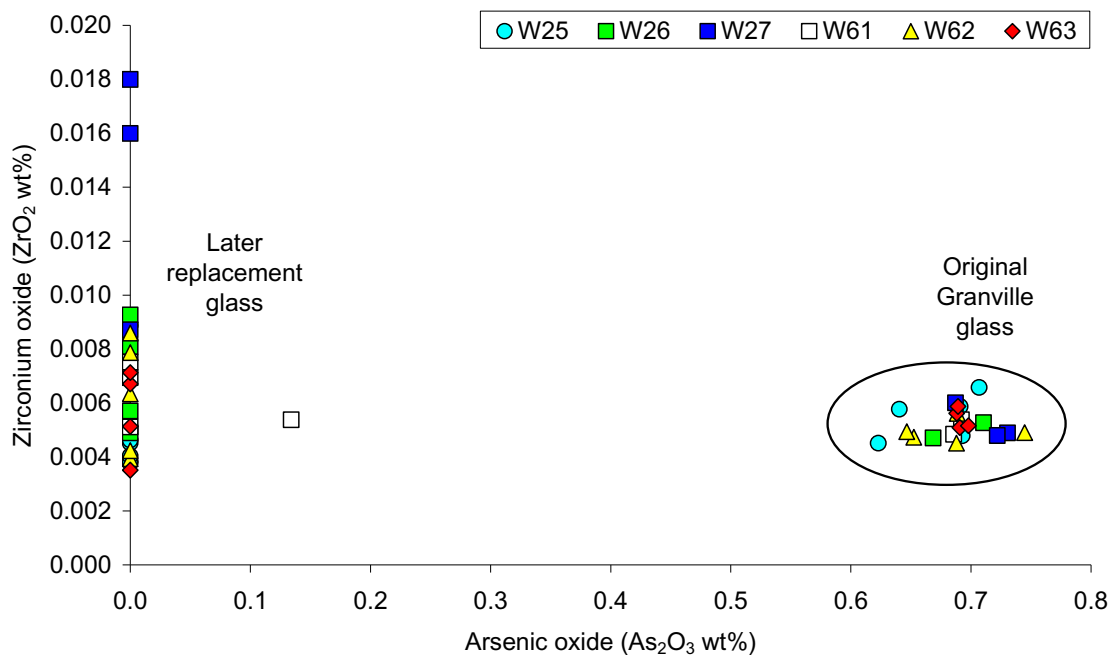


Figure 20. Arsenic oxide and zirconium oxide content of glass from six windows in the rooms added by the Earl of Granville in the 1870s

The mechanised window glass has been divided into eight sub-groups based on chemical composition. Sub-types 2 and 5 have relatively high Mg:Ca ratios and are likely to be float glass produced after c1960; the remaining sub-types are likely to be drawn glass manufactured between c1930 and c1960. Mech 1a is found in 26 different windows but this includes all of the panes in W18. Mech 1b is found in only two windows (W35 and W36) but all of the panes in both of these windows belong to this sub-type. Mech 2 is found in only three windows but two of these windows have only a single pane which belongs to this sub-type. W48 (Queen Victoria's bedroom) includes nine out of twenty panes of Mech 2 glass. Mech 3 is found in 29 different windows but usually only one or two panes per window. Five out of the eleven panes in W25 belong to this sub-type. Mech 4a is found in 31 different windows but usually only one to three panes per

window. Mech 4b is represented by all of the glass in W86–88 and is not found in any other windows. Mech 4c is found in seven different windows but usually only one or two panes per window. All seven panes in the top part of W19 belong to this sub-type. Mech 5 is represented by all sixteen panes in the bottom part of W14 and this sub-type is not found in any other window.

CONCLUSION

Recent research has established that the chemical composition of historic window glass can indicate the period in which it was manufactured (Dungworth forthcoming). This report has attempted to apply this method to *in situ* historic window glass using a portable X-ray fluorescence spectrometer. The analysis of a range of reference material has been used to demonstrate the limits of detection and accuracy.

The non-destructive *in situ* chemical analysis of window glass from Walmer Castle was carried out using a portable x-ray fluorescence spectrometer over a period of three days. During this time it was possible to obtain data on the chemical composition of 661 panes of glass. The repeated analysis of two window panes has demonstrated that errors due to analytical precision are generally lower than accuracy. The analysis of glass with UV-absorbing films has demonstrated that such materials will significantly affect the apparent concentration of most light elements ($Z < 19$). Such analyses are partial and will only occasionally be sufficiently distinctive to allow the type of glass to be identified. Despite these limitations the results have allowed the identification of the types of glass surviving in most windows.

The Walmer window glass falls into four major glass types. The first (represented by only four panes) was made using seaweed (kelp) ash as the flux. This glass type was used widely from the beginning of the 18th century into the 1830s when it was replaced by sodium compounds made using the Leblanc process. Most of the surviving window glass at Walmer Castle was made using such synthetic soda. This synthetic soda can be divided into a number of sub-types: the first contains little or no magnesium and was produced before the introduction of mechanised forming techniques. The high proportion of glass manufactured after c1835 reflects the history and use of Walmer Castle — it has been a home to a succession of rich and powerful individuals and many of them have carried out repairs and alterations.

The last glass type is a potash glass of a composition which has until now not been reported in England. This potash glass is mostly pink or purple in colour due to the presence of manganese in the glass. Most of this glass appears to have been originally manufactured with this colour (ie the Duke of Dorset's rooms, W37–41). Some historic glass (including some panes from Walmer Castle, eg W10) has a pink colour which was not deliberately produced during manufacture. Manganese has been used in small quantities to counteract the colouring effect of iron in glass but has subsequently

developed a pink tint due to exposure to ultraviolet light (solarisation). While the pink or purple potash glass has $\text{MnO}:\text{Fe}_2\text{O}_3$ ratios of 3–10, the slightly pink soda-lime glasses which have undergone solarisation have ratios close to one. The potash glass appears to have been an import from Germany or Bohemia. It is most likely to have been installed in the late 18th or early 19th century. The acquisition of such exotic window glass may reflect the desire by a Lord Warden to be seen to be extravagant. The fact that some potash glass is pink or purple and some is colourless suggests that the tint was probably intended to satisfy an aesthetic requirement rather than protect the delicate eyesight of the wife of a Lord Warden.

Overall the use of pXRF for the chemical analysis of historic windows can be gauged to have been a considerable success. Some of the pXRF data is not of the same standard that can be achieved through the use of laboratory-based techniques. The pXRF was unable to detect sodium in any samples and the detection limits for many light elements were considerably higher than those associated with laboratory-based techniques. Surface weathering and UV-absorbing films both reduced data quality in some cases. These limitations are negligible when balanced against the fact that none of the window glass was damaged during the analysis. The ability to characterise (and so date) the window *in situ* overrides the reduced data quality. In addition, the pXRF allowed the collection of data at a much faster rate compared to the laboratory-based techniques. During the three days spent analysing glass at Walmer Castle a data set was created of almost the same size as that built up over a two-year period using laboratory-based techniques.

The use of pXRF for the characterisation and dating of historic window glass should become a routine conservation tool. The technique is a fast and effective way to discover the approximate age of historic windows; even a large and complex building can be surveyed over a period of days. The identification of the age of individual panes of historic window glass should be a starting point for their improved management and conservation. If glass can be identified as original then appropriate steps can be taken to protect it from accidental damage. Alternatively, the identification of later replacements may help to inform repair and replacement where necessary. For example, the use of pXRF might identify that a window has one pane of 18th-century glass but that all of the others are 20th-century replacements. The decision might then be taken to replace the 20th-century panes with a glass that more closely resembles the original. The analysis of the original glass can be provided to potential suppliers to assist with the formulation of the new replacement glass (in particular the concentration of iron, manganese and other elements which provide a tint to the glass).

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APPENDIX I: PLANS OF WALMER CASTLE

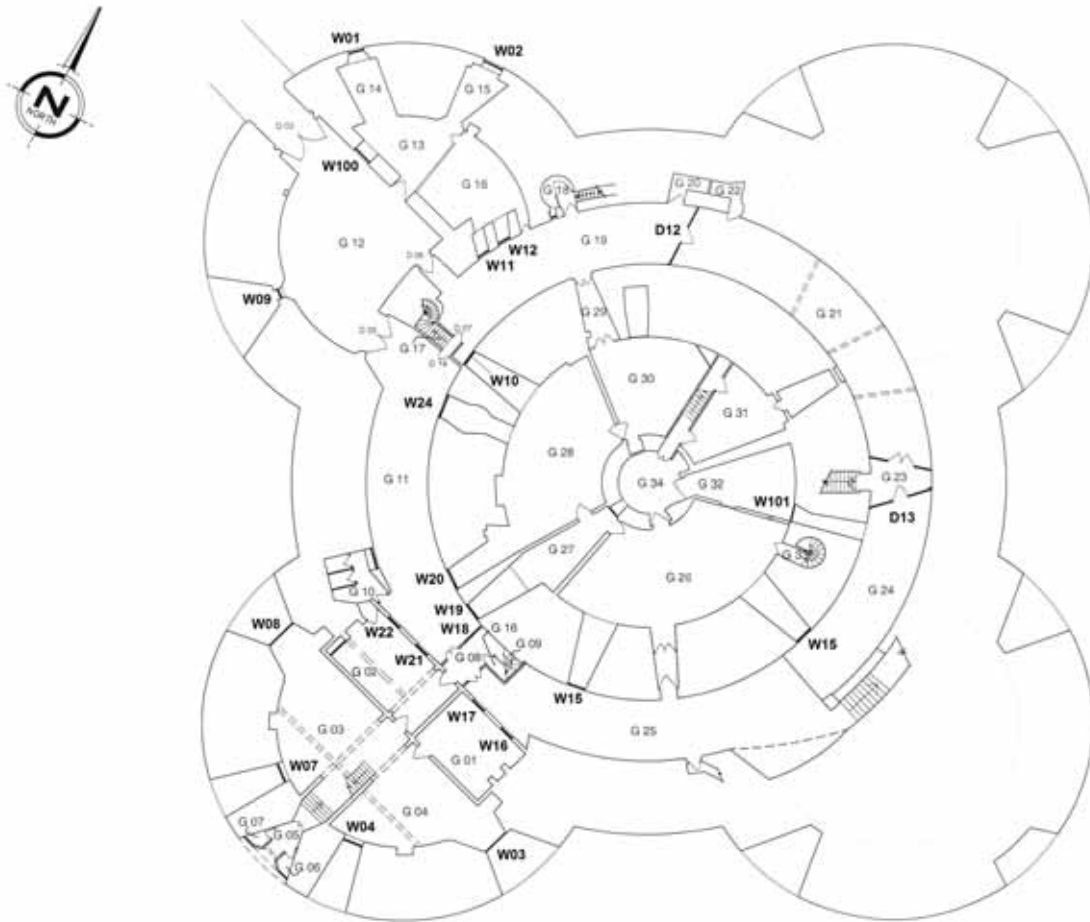


Figure 21. Ground floor plan of Walmer Castle (© Broadway Malyan)

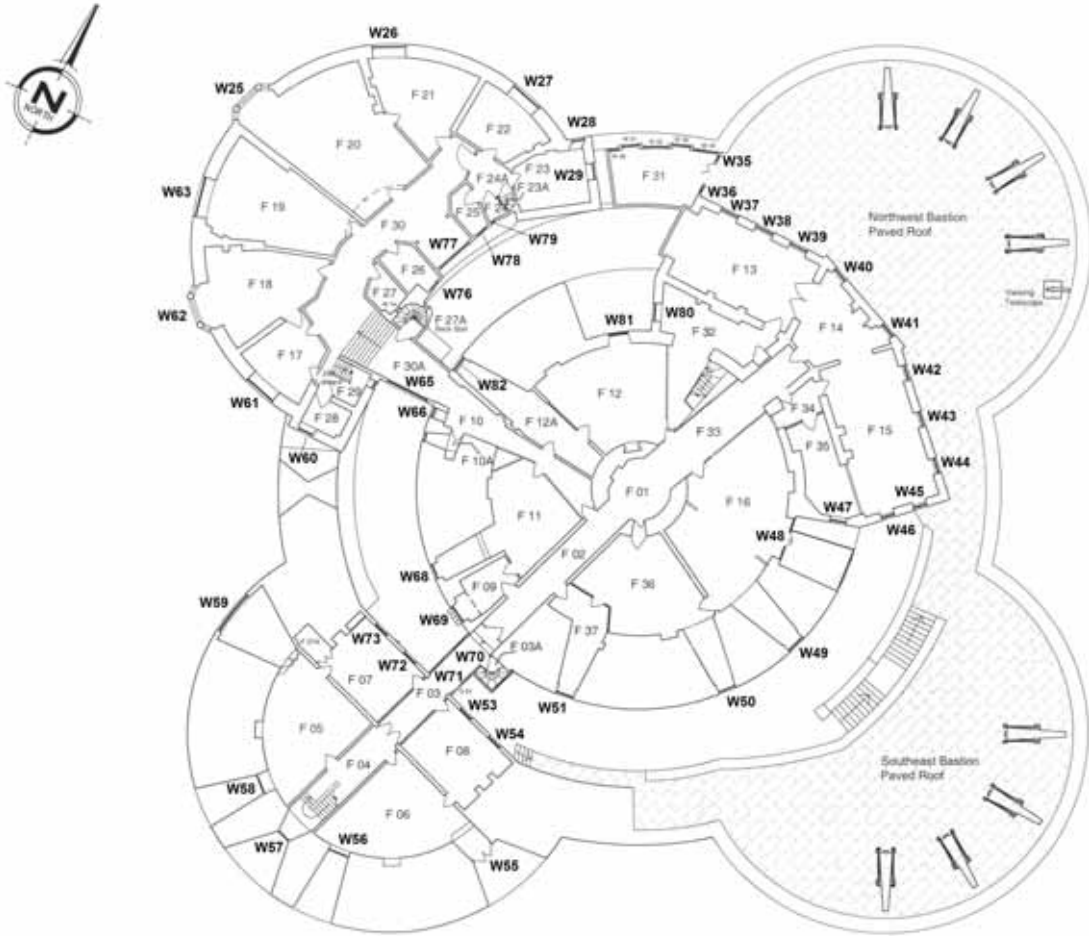


Figure 22. First floor plan of Walmer Castle (© Broadway Malyan)

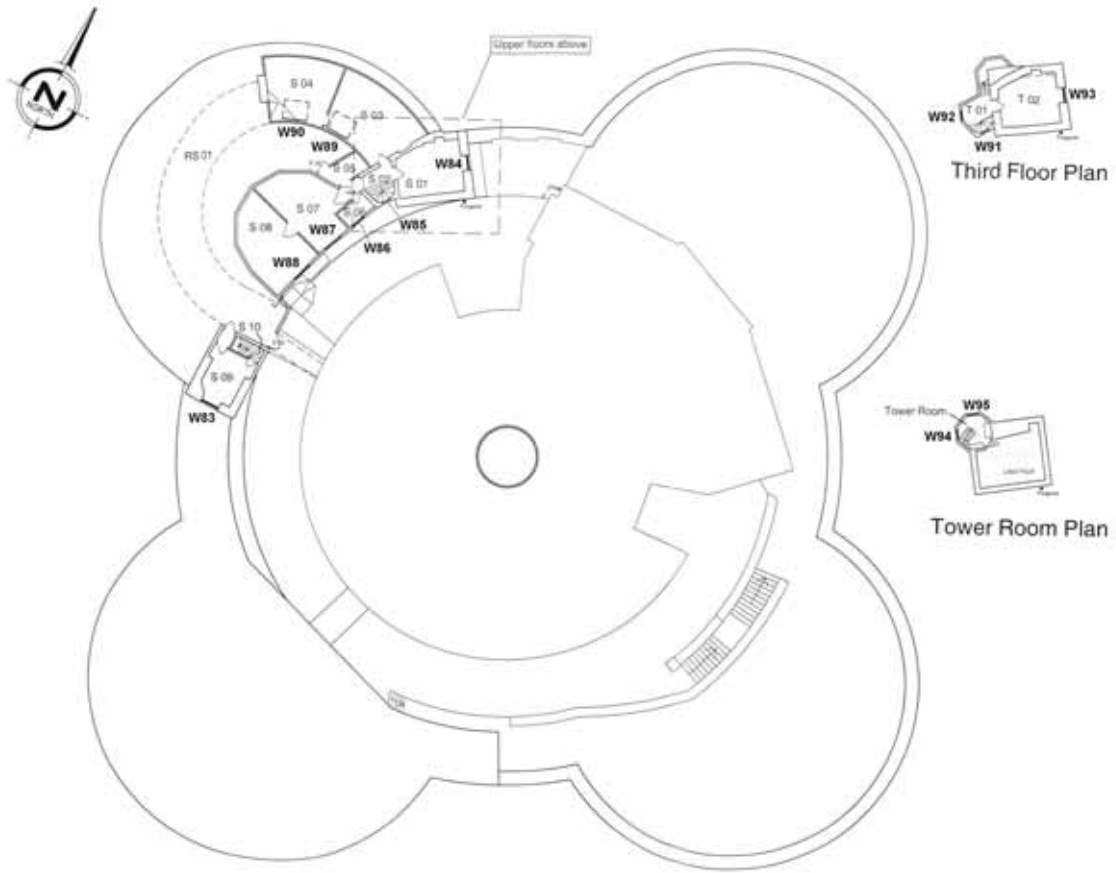


Figure 23. Second and upper floors plan of Walmer Castle (© Broadway Malyan)

APPENDIX 2. CATALOGUE OF ROOMS AND WINDOWS

Window	Room	Film	Name	Panes	Comments
W01	G14	No	Porter's Lodge	2	
W02	G15	No	Porter's Lodge	3	
W03	G04	Yes	Sackville Room	1	
W04	G04	Yes	Sackville Room	4	
W05	G06	NA	Toilet	NA	Not analysed
W06	G07	NA	Toilet	NA	Not analysed
W07	G03	Yes	Willingdon Room	4	
W08	G03	Yes	Willingdon Room	1	
W09	G12	No	Gatehouse	1	
W10	G19/G28	No	Central Tower	9	
W11	G16/G19	NA	Boiler Room	NA	Not analysed
W12	G16/G19	No	Boiler Room	12	
W13	G18/G19	NA		NA	Not analysed
W14	G24/G26	No	Central Tower	25	1–9 and 10–25 two separate windows
W15	G25/G26	No	Central Tower	6	1–4 and 5–6 two separate windows
W16	G01	No	Gunners' Lodging	12	
W17	G01	No	Gunners' Lodging	12	
W18	G08/G11	No	Corridor	12	
W19	G11/G27	No	Central Tower	13	
W20	G11/G28	No	Central Tower	16	
W21	G02/G11	No	Gunners' Lodging	12	
W22	G02/G11	No	Gunners' Lodging	12	
W23	G10/G11	NA	Toilet	4	Not analysed
W24	G11/G28	No	Central Tower	8	
W25	F20	No		12	
W26	F21	No		6	
W27	F22	No		6	
W28	F23	No		1	
W29	F23/F31	No		2	
W30	F31	NA	Loggia	NA	Not analysed
W31	F31	NA	Loggia	NA	Not analysed
W32	F31	NA	Loggia	NA	Not analysed
W33	F31	NA	Loggia	NA	Not analysed
W34	F31	NA	Loggia	NA	Not analysed
W35	F31	No	Loggia	16	
W36	F31	No	Loggia	16	
W37	F13	Yes	Dining Room	12	
W38	F13	Yes	Dining Room	12	
W39	F13	Yes	Dining Room	12	
W40	F14	Yes	Ante Room	12	
W41	F14	Yes	Ante Room	12	
W42	F15	Yes	Drawing Room	4	
W43	F15	Yes	Drawing Room	4	
W44	F15	Yes	Drawing Room	4	
W45	F15	Yes	Drawing Room	4	
W46	F15	Yes	Drawing Room	4	
W47	F35	Yes	Storeroom	4	
W48	F16	Yes	Queen Victoria's Room	20	
W49	F16	Yes	Queen Victoria's Room	12	

Window	Room	Film	Name	Panes	Comments
W50	F36	Yes	Prince Consort's Room	12	
W51	F37	Yes	Storeroom	12	
W52	F03A	NA	Stairs	NA	Not analysed
W53	F08	Yes	Wellington Museum	12	
W54	F08	Yes	Wellington Museum	12	
W55	F06	No	Duke of Wellington's Room	4	
W56	F06	Yes	Duke of Wellington's Room	4	
W57	F04	Yes	Stairs	6	
W58	F05	Yes	Lucas Collection	2	
W59	F05	No	Lucas Collection	3	
W60	F28	No	Toilet	2	
W61	F17	No	Kitchen	6	
W62	F18	No	Dining Room	10	
W63	F19	No	Drawing Room	8	
W64	F29	NA		NA	Not analysed
W65	F30A	No	Corridor	4	
W66	F10	No	Corridor	1	
W67	F10A	NA	Cupboard	NA	Not analysed
W68	F11	No	Bedroom	12	
W69	F09	No	Bathroom	6	
W70	F03	Yes	Corridor	12	
W71	F03	Yes	Corridor	12	
W72	F07	Yes	Pitt Museum	12	
W73	F07	Yes	Pitt Museum	12	
W74	F27/F27A	NA		NA	Not analysed
W75	F27A	NA	Stairs	NA	Not analysed
W76	F26	No		1	
W77	F30	No	Corridor	3	
W78	F25	No		1	
W79	F24	NA		NA	Not analysed
W80	F32	No	Kitchen	16	
W81	F12	Yes	Central Tower	12	
W82	F12A	No	Central Tower	6	
W83	S09	No		2	
W84	S01	No		2	
W85	S02	No		1	
W86	S06	No		3	
W87	S07	No		4	
W88	S08	No		4	
W89	S03	No		2	
W90	S04	No		2	
W91	T01	NA		NA	
W92	T01	No		1	
W93	T02	No		2	
W94	Tower Rm	No		1	
W95	Tower Rm	No		1	
W100	G12/G13	No		24	
W101	G24/G32	No		12	
D12	G19/G21	No		27	
D13	G23/G24	No		26	

ID	Pane	Film	Type	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	As ₂ O ₃	Rb ₂ O	SrO	ZrO ₂	
W92	P01	No	mech	2	2.6	0.7	66.2	<1.0	0.3	0.2	7.0	0.06	<0.02	0.13	<0.02	<0.001	0.030	0.009
W93	P01	No	mech	4a	2.6	0.8	65.0	<1.0	<0.2	0.6	9.4	0.05	<0.02	0.16	<0.02	0.002	0.004	0.008
W93	P02	No	mech	1a	3.2	<0.5	63.8	<1.0	<0.2	<0.1	9.7	0.05	<0.02	0.08	<0.02	<0.001	0.007	0.009
W94	P01	No	mech	1a	2.8	1.0	66.7	<1.0	0.4	0.1	6.9	0.07	<0.02	0.04	<0.02	<0.001	0.005	0.016
W95	P01	No	SSC	1	<1.5	<0.5	67.7	<1.0	0.7	0.2	16.6	0.05	<0.02	0.23	<0.02	<0.001	0.009	0.004
W100	P01	No	SSC	1	<1.5	<0.5	69.9	<1.0	0.4	<0.1	14.4	0.04	0.64	0.19	0.13	<0.001	0.020	0.007
W100	P02	No	SSC	1	<1.5	0.6	67.4	<1.0	0.8	<0.1	18.2	0.08	<0.02	0.16	<0.02	<0.001	0.011	0.008
W100	P03	No	SSC	2	<1.5	1.6	70.4	<1.0	0.3	0.6	13.8	0.06	<0.02	0.20	<0.02	<0.001	0.009	0.006
W100	P04	No	mech	4c	2.7	0.9	67.8	<1.0	<0.2	0.5	8.3	0.03	<0.02	0.09	<0.02	<0.001	0.006	0.020
W100	P05	No	kelp		5.2	2.6	67.5	<1.0	<0.2	4.8	12.1	0.14	0.05	0.82	<0.02	<0.001	0.412	0.006
W100	P06	No	SSC	2	<1.5	1.2	67.2	<1.0	0.2	0.6	13.4	0.05	<0.02	0.14	<0.02	<0.001	0.009	0.006
W100	P07	No	kelp		4.8	2.4	67.0	1.1	<0.2	4.1	11.0	0.11	0.06	0.67	<0.02	<0.001	0.474	<0.002
W100	P08	No	SSC	1	<1.5	<0.5	69.2	<1.0	0.4	0.2	10.2	0.05	<0.02	0.21	0.03	<0.001	0.006	0.003
W100	P09	No	kelp		3.8	2.8	66.3	1.2	<0.2	3.3	14.2	0.10	0.05	0.65	<0.02	<0.001	0.373	<0.002
W100	P10	No	kelp		4.4	2.6	66.5	<1.0	<0.2	4.2	10.7	0.12	0.05	0.76	<0.02	<0.001	0.411	<0.002
W100	P11	No	SSC	2	<1.5	1.2	68.0	<1.0	0.2	0.6	14.0	0.05	<0.02	0.14	<0.02	<0.001	0.010	0.006
W100	P12	No	SSC	2	<1.5	1.1	68.3	<1.0	0.6	0.5	14.5	0.05	<0.02	0.15	0.61	<0.001	0.012	0.004
W100	P13	No	SSC	1	<1.5	<0.5	67.6	<1.0	0.7	<0.1	17.0	0.07	<0.02	0.17	<0.02	<0.001	0.010	0.008
W100	P14	No	SSC	1	<1.5	<0.5	69.8	<1.0	0.3	<0.1	14.3	0.05	0.43	0.17	0.13	<0.001	0.024	0.007
W100	P15	No	mech	?	2.8	0.6	67.9	<1.0	<0.2	7.7	8.9	0.09	<0.02	0.27	<0.02	0.005	0.099	0.005
W100	P16	No	mech	4	<1.5	1.0	66.1	<1.0	<0.2	0.6	8.8	0.05	<0.02	0.14	<0.02	<0.001	0.006	0.005
W100	P17	No	SSC	2	<1.5	1.1	66.8	<1.0	0.2	0.6	13.5	0.05	<0.02	0.15	<0.02	<0.001	0.009	0.005
W100	P18	No	SSC	2	<1.5	1.6	69.6	<1.0	0.4	0.5	15.6	0.06	<0.02	0.14	<0.02	<0.001	0.011	0.007
W100	P19	No	mech	3	2.6	1.0	64.8	<1.0	0.2	0.4	7.7	0.05	<0.02	0.10	<0.02	<0.001	0.018	0.015
W100	P20	No	SSC	1	<1.5	<0.5	69.1	<1.0	0.4	<0.1	14.1	0.04	0.11	0.21	0.15	<0.001	0.019	0.006
W100	P21	No	mech	1a	<1.5	0.5	67.3	<1.0	0.4	<0.1	8.5	0.08	<0.02	0.24	<0.02	<0.001	0.011	0.008
W100	P22	No	SSC	1	<1.5	<0.5	66.3	<1.0	0.6	0.1	15.6	0.04	<0.02	0.23	<0.02	<0.001	0.009	0.004
W100	P23	No	SSC	2	<1.5	1.6	70.4	<1.0	<0.2	0.6	13.0	0.07	<0.02	0.21	<0.02	<0.001	0.014	0.006
W100	P24	No	SSC	2	<1.5	1.1	69.6	<1.0	0.5	0.5	13.8	0.05	<0.02	0.16	0.31	<0.001	0.010	0.005
W101	P01	No	SSC	1	<1.5	<0.5	69.2	<1.0	0.5	0.2	15.8	0.03	<0.02	0.18	0.37	<0.001	0.020	<0.002
W101	P02	No	SSC	2	<1.5	1.5	68.5	<1.0	0.3	0.6	14.9	0.06	<0.02	0.16	<0.02	<0.001	0.009	0.005
W101	P03	No	mech	4a	2.5	0.9	67.8	<1.0	<0.2	0.5	9.3	0.04	<0.02	0.11	<0.02	<0.001	0.005	0.008
W101	P04	No	mech	4a	3.0	0.8	70.0	<1.0	<0.2	0.5	8.4	0.04	<0.02	0.11	<0.02	<0.001	0.006	0.008
W101	P05	No	SSC	2	<1.5	1.5	71.1	<1.0	0.3	0.6	13.4	0.06	<0.02	0.20	<0.02	<0.001	0.011	0.006
W101	P06	No	SSC	2	<1.5	1.4	71.5	<1.0	0.3	0.7	15.0	0.07	<0.02	0.19	<0.02	<0.001	0.011	0.006
W101	P07	No	SSC	1	<1.5	<0.5	70.3	<1.0	0.4	<0.1	15.0	0.05	0.10	0.21	0.13	<0.001	0.020	0.008
W101	P08	No	SSC	1	<1.5	<0.5	70.6	<1.0	0.8	0.1	17.4	0.05	<0.02	0.19	0.16	<0.001	0.024	0.003
W101	P09	No	SSC	1	<1.5	0.6	71.6	<1.0	0.4	0.2	15.8	0.06	<0.02	0.19	0.11	<0.001	0.029	0.006
W101	P10	No	SSC	1	<1.5	0.7	66.5	<1.0	0.6	<0.1	15.6	0.04	<0.02	0.24	0.19	<0.001	0.011	0.006
W101	P11	No	SSC	2	<1.5	1.2	70.1	<1.0	0.3	0.7	14.8	0.07	<0.02	0.20	<0.02	<0.001	0.011	0.008
W101	P12	No	SSC	1	<1.5	0.5	70.4	<1.0	0.7	<0.1	15.6	0.03	<0.02	0.15	0.09	<0.001	0.012	<0.002



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