

SCANNING ELECTRON MICROSCOPY-ENERGY DISPERSIVE SPECTROMETRY AND PROTON INDUCED X-RAY EMISSION ANALYSES OF MEDIEVAL GLASS FROM KOROINEN (FINLAND)*

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Thirteenth- to fourteenth-century ecclesiastical window glass, excavated from the administrative centre of Koroinen, Finland, represents the earliest window glass in the country and includes the only emerald green window glass known from Finland at this time. This was examined, together with some excavated vessel glass. X-ray analysis, using scanning electron microscopy-energy dispersive spectrometry and proton induced X-ray emission, reveals that while the vessels are made from potash-lime, soda-lime, mixed alkali and lead-silica glasses, the window glasses are lead-silica and wood ash-lead-silica glasses; they resemble similar glasses from central Europe and suggest that Koroinen shared the trading network of other European religious centres.

KEYWORDS: FINLAND, KOROINEN, MEDIEVAL, SCANNING ELECTRON MICROSCOPY-ENERGY DISPERSIVE SPECTROMETRY, PROTON INDUCED X-RAY EMISSION, GLASS, CHEMICAL COMPOSITION, PROVENANCE

INTRODUCTION

The religious and administrative centre of thirteenth-century Finland was the Cape of Koroinen that lies between the rivers of Aurajoki and Vähäjoki in the county of Varsinais-Suomi. Some 20 km to the north-west of Koroinen is Nousiainen, the very first religious centre of Finland. Two kilometres to the south-west of Koroinen, towards the lower course of the river Aurajoki, is the later religious centre, the Turku Dome church, the building of which began in the 1280s (Koivunen 1976). Koroinen and its region are central to the history of Finland, and the area from which the national and religious culture derived.

Between the years 1898 and 1902 the first large modern archaeological excavation in the history of Finland took place in Koroinen. The excavations were initiated by Dr Hjalmar Appelgren and they were continued in 1900 by Juhani Rinne. The area of excavation covered 3500 m² and the remains of two wooden churches, a bishop's house, a tower and an oven (for baking or heating) were found. The older church (Koroinen I) was of rectangular shape. The second church (Koroinen II) stood in the same place as the older church had, but was somewhat larger and on the east side it had a narrow stone chancel. The older church was built in approximately 1230 and was destroyed by fire in the middle of the thirteenth century. The successor church was built in 1270 and was destroyed by the Vitaali brothers, a band of pirates from the west (Koivunen 1976; Suvanto 1985, 41, 132–4; Hiekkänen 1994, 192–7, 238, 246, 261–3).

During the excavation in the Koroinen area more than 10 000 artefacts were found, including the 16 glass fragments that were analysed for the present paper. The general plan of the

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excavation and the findspots of analysed glass fragments are shown in Figure 1. Finds numbered from 1 to 4, 7 and 10 were excavated by Appelgren and we know the area where these artefacts were found, not exact findspots and depths, whereas Juhani Rinne documented precisely both position and depth of the excavated artefacts. The dark, or emerald, green window glass that was found in the course of the excavation has not been found anywhere else in Finland.

The window glass fragments excavated in Koroinen are the oldest window glasses found in Finland and they date from the era prior to the fifteenth century. Some vessel fragments may be earlier but they are at least late medieval (P. Koivunen, pers. comm.). The location of the production of the window glass is unknown. However, some conclusions can be drawn about the vessel glass, based on the forms (see 'Appendix: analysed samples'). Neither type of glass was manufactured in Finland at that time—the first glassworks in Finland was established in 1681. The aim of this investigation is to identify major, minor and trace elements of the vessel glass and window glass found at Koroinen and, thus, to obtain information about the origin of the glass.

EXPERIMENTAL

The major and minor elements have been analysed by scanning electron microscopy (SEM) with an energy-dispersive spectrometer (EDS) and trace elements by the proton induced X-ray emission (PIXE) method. Both methods are based on the detection of characteristic X-rays. The SEM-EDS method is convenient in measurement of elements with concentrations higher than 1 wt%. By the PIXE method, concentrations from 100% to the trace level may be detected. The PIXE method offers maximum sensitivity when the atomic number Z of the detected element is

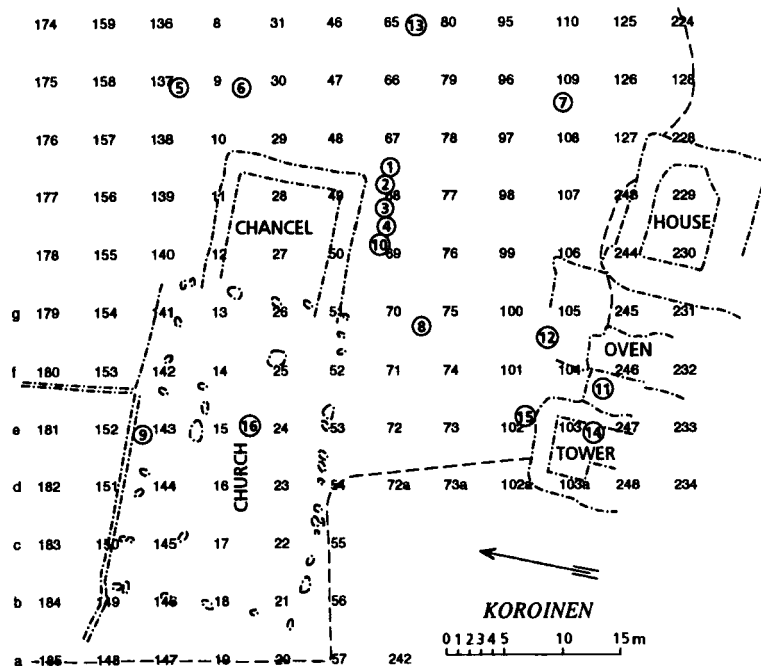


Figure 1 General plan of the excavations and findspots of the analysed glass fragments (circled numerals).

in the region 18–40. In the archaeological context, Hreglich and Verità (1986), for example, have analysed glass with the SEM-EDS method. The PIXE method has been widely used in the analysis of archaeological material, including glass (Gihwala *et al.* 1984; Peisach 1986; Kuisma-Kursula *et al.* 1991). Both methods have been used in a complementary fashion in analysing old European forest or potash glass (Kuisma-Kursula *et al.* 1997). In this study, for the first time old lead glass fragments were analysed using both SEM-EDS and PIXE methods.

STANDARDS

Absolute concentrations of Si and Na in SEM-EDS measurements were obtained by using the Corning glass standard D and concentrations of Pb in lead glass samples were obtained by using the Corning glass standard C (Brill 1972; Verità *et al.* 1994). The concentrations of Mg, Al, P, S, Cl, K, Ca and Cu in lead glass samples were calculated employing MAC (Micro-Analysis Consultants Ltd, St. Ives, UK) standard 3056. In the PIXE measurements the absolute concentrations of Ti, Mn and Fe in all samples were determined using the Corning glass standard D. The absolute concentrations of Cu, Zn, Pb, Rb, Sr, Zr and Ba in the lead-free samples were calculated employing the Corning glass standard D. Concentrations of arsenic in all samples were obtained with the NIST (National Institute of Standards and Technology, USA) glass standard number 620. The absolute concentrations of Zn, Rb, Sr and Zr in lead glass were obtained using the Corning glass standard C and concentrations of Ba were determined using the NIST glass standard number 611. The NIST glass standard 620 is soda-lime flat glass. The NIST glass standard 611 contains 61 trace elements, at nominal concentrations of 500 ppm by weight in a soda-lime-silica glass matrix.

SAMPLE PREPARATION

The glass samples were washed for three minutes with distilled water in an ultrasonic cleaner. For the SEM measurements small samples of the glass artefacts measuring less than 1 mm in length were cut with a diamond saw, mounted in epoxy resin and polished flat using a series of grades of diamond paste down to 1 μm grade. Since glass is a poor conductor, a carbon coating was evaporated on the polished surface to prevent localized charging and any resulting distortion and reflection of the electron beam. The samples were prepared at the Department of Electron Microscopy at Helsinki University.

For the PIXE measurements a smooth area of 1 cm^2 of each sample was cleaned with pumice.

ANALYTICAL METHODS

In the SEM analysis each sample was bombarded with 15 kV electrons from a Jeol JSM 6400 scanning electron microscope at the Institute of Electron Optics of Oulu University. The characteristic X-rays were detected with an Oxford Instruments Link eXL energy dispersive spectrometer. The programme ZAF4 was used in the spectrum analysis. The electron beam current was 1.2 nA. Each sample was analysed at least twice and the measuring time was 50 seconds. Si, Na, K, Ca, Mg, Al, P, S and Cl were detected in all samples, Pb in samples 8–16 and Cu in samples 8 (b)–16.

The accuracy and precision of the SEM measurements was checked by analysing the Corning

glass standards C and D and the NIST glass standard 620 five times. The results are given in Table 1. In general, the agreement between the certified values and the present results was reasonable. The precisions for the compounds determined were taken as relative standard deviations and were better than 2% for SiO₂ and CaO and 2–5% for the major and minor compounds.

In the PIXE analysis the samples and standards were bombarded with a 2 nA external proton beam from the 2.5 MV Van de Graaff accelerator of Helsinki University. The energy of the protons on the target was approximately 2.4 MeV. The emitted X-rays were detected with a 50 mm² × 6 mm intrinsic germanium detector. A 150 µm thick aluminium filter was used to eliminate low-energy characteristic X-rays originating from the major elements in the glass matrix. A 250 µm thick Kapton (Du Pont, Geneva, Switzerland) filter was used for measuring concentrations of Ti, Mn and Fe. The Corning glass standards C and D were bombarded five times to evaluate the precision and accuracy of the measurements. Results are given in Table 2. The measuring time for lead free samples was about 3 min and for lead glass samples about 8 min. The spectra were collected with the Canberra S-100 measuring program and analysed with the SAMPO peak fitting program (Aarnio *et al.* 1988 and 1990). As a result, the absolute concentrations of Ti, Mn, Fe, Zn, As, Rb, Sr, Zr and Ba in all samples and concentrations of Pb in samples 1–7 and that of Cu in samples 1–8 (a) were obtained. The precision was better than 3%

Table 1 SEM and PIXE results and certified values of the NIST glass standard 620 and the Corning glass standards C and D for major, minor and trace elements (values expressed as wt% oxide and standard deviations in parentheses)

Component	Method	NIST 620		Corning C		Corning D	
		Present work	Certified	Present work	Certified	Present work	Certified
SiO ₂	SEM	71.2 (0.9)	72.08	37.6 (0.4)	34.8	55.6 (0.8)	55.2
Na ₂ O	SEM	15.0 (0.7)	14.39	1.46 (0.11)	1.13	1.60 (0.02)	1.32
K ₂ O	SEM	0.36 (0.08)	0.41	2.57 (0.08)	2.79	10.6 (0.1)	11.5
CaO	SEM	6.90 (0.13)	7.11	5.06 (0.07)	4.99	14.7 (0.2)	15.0
MgO	SEM	3.63 (0.10)	3.69	2.55 (0.13)	2.76	3.80 (0.11)	4.09
Al ₂ O ₃	SEM	1.81 (0.12)	1.80	0.79 (0.09)	1.02	4.97 (0.08)	5.43
P ₂ O ₅	SEM				0.10	4.07 (0.19)	4.00
SO ₃	SEM				0.15	0.28 (0.01)	0.28
Cl	SEM				0.11	0.15 (0.03)	0.35
TiO ₂	PIXE			0.80 (0.05)	0.85	0.36 (0.02)	0.40
MnO	PIXE					0.51 (0.01)	0.47
Fe ₂ O ₃	PIXE			0.250 (0.004)	0.32	0.51 (0.01)	0.50
CuO	SEM			1.42 (0.19)	1.18		
	PIXE			1.14 (0.03)	1.18	0.38 (0.01)	0.40
ZnO	PIXE			0.040 (0.005)	0.04	0.112 (0.003)	0.10
PbO	SEM			37.2 (0.4)	36.8		
	PIXE					0.223 (0.006)	0.25
Rb ₂ O	PIXE			0.0230 (0.008)	0.01	0.0040 (0.0006)	0.005
SrO	PIXE			0.30 (0.02)	0.25	0.050 (0.001)	0.05
ZrO ₂	PIXE			0.006 (0.002)	0.005	0.016 (0.002)	0.01
BaO	SEM			11.8 (0.1)	12.1		
	PIXE					0.34 (0.002)	0.33

Table 2 Results of SEM and PIXE analyses of the fragments of vessel and window glass (values expressed as wt% oxide)

Sample	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	P ₂ O ₅	SO	Cl	TiO ₂	MnO	Fe ₂ O ₃	CuO	ZnO	PbO	As ₂ O ₃	BaO	SrO	Rb ₂ O	ZrO ₂
1 A75	72.4	13.8	1.3	6.7	0.3	2.4	0.1	0.7	0.1	0.09	0.07	0.72	0.007	0.005	0.003	<0.001	<0.03	0.05	0.005	0.004
2 A76	73.1	13.9	1.4	6.6	0.5	2.4	0.1	0.6	0.1	0.05	0.29	0.76	0.004	0.008	0.006	0.04	<0.03	0.07	0.006	0.003
3 A110	53.9	1.5	10.1	21.7	3.7	2.1	2.9	0.2	0.2	0.09	0.46	0.95	0.007	0.070	0.026	<0.001	0.10	0.05	0.022	0.011
4 A111	59.3	5.0	4.8	19.7	4.5	1.4	3.4	0.2	0.9	0.05	0.52	1.00	0.006	0.064	0.003	0.35	0.08	0.06	0.044	0.006
5 1809	57.9	0.5	12.4	16.9	3.2	0.6	0.9	0.3	0.1	0.11	0.21	0.54	0.008	0.026	0.001	<0.001	0.45	0.07	0.070	0.033
6 1925	57.9	4.9	4.7	19.0	4.3	1.4	3.5	0.2	0.8	0.07	0.40	0.58	0.004	0.044	0.001	<0.001	0.10	0.01	0.010	0.070
7 64	45.5	1.4	14.0	21.9	4.9	2.0	4.3	0.2	0.1	0.07	1.2	0.70	0.002	0.035	0.001	0.01	0.30	0.05	0.047	0.010
8 2140(a)*	24.4	0.3	0.3	0.1	0.1	0.8	0.1	0.3	0.3	0.10	0.01	0.12	0.046	0.008	69.7	0.06	0.08	0.04	0.012	0.003
2140(b)*	25.0	0.4	0.3	0.2	0.1	1.0	0.1	0.2	0.5	0.06	0.01	0.40	1.2	0.020	69.5	<0.009	0.31	0.24	0.006	0.003
9 1689	34.4	1.0	3.2	4.4	0.8	1.1	0.6	0.2	0.7	0.23	0.10	0.36	1.2	0.070	52.6	0.12	0.12	0.02	0.011	0.003
10 A112	41.0	1.2	10.4	16.0	2.8	2.2	0.9	0.1	0.3	0.06	0.62	0.94	2.1	0.040	19.9	0.06	0.22	0.06	>0.003	>0.0015
11 2385	34.3	0.8	3.4	4.6	0.8	1.2	0.6	0.3	0.5	0.20	0.08	0.27	1.4	0.020	48.2	0.07	0.08	0.18	<0.003	0.003
12 2294	34.2	0.8	3.2	4.3	0.9	1.2	0.6	0.1	0.5	0.06	0.10	0.28	1.8	0.060	52.2	0.11	0.24	0.16	0.004	0.003
13 2194	40.0	1.2	10.4	16.0	2.8	2.0	1.1	0.4	0.2	0.12	0.56	0.85	2.1	0.060	18.8	0.07	0.24	0.08	0.005	0.002
14 2349	37.7	1.0	8.2	13.8	2.6	1.6	0.9	0.2	0.3	0.24	0.42	0.63	2.0	0.070	28.4	0.07	0.26	0.06	0.007	0.002
15 2399	38.3	1.2	8.2	11.6	2.3	1.3	0.6	0.2	0.4	0.03	0.52	0.48	2.1	0.060	31.1	0.08	0.15	0.12	0.006	0.002
16 1884	33.4	0.8	3.4	4.1	0.8	1.2	0.6	0.1	0.6	0.21	0.09	0.28	2.2	0.070	51.1	0.10	0.12	0.16	0.003	0.004

* Sample 8 consists of two parts: (a) a yellowish one and (b) a green one.

for MnO, Fe₂O₃, CuO, ZnO and PbO and better than 10% for TiO₂, SrO and BaO. The accuracy was better than 5% for Fe₂O₃, CuO, SrO and BaO.

In lead-rich material the intense Pb L X-ray peaks obscure the analysis of arsenic and strontium. A pure lead sample was measured to get the relative intensities of lead peaks. Thus, by subtracting the overlapping lead peaks it was possible to evaluate the intensities of arsenic and strontium peaks. The intense lead peaks also add to the general background throughout the X-ray spectrum and, therefore, the detection limits in lead-rich material are higher than in material with a low lead content.

The detection limits (in ppm by weight) for the compounds as obtained by the SEM and PIXE measurements in a relatively lead-free glass matrix and in a lead-rich glass were calculated assuming that the minimum detectable peak is three times the square root of the background at full width at half maximum intensity of the peak. The results are given in Table 3. The PIXE detection limits are comparable with the values reported previously (Fleming and Swann 1986 and 1987; Swann *et al.* 1989). According to Reed (1993), the theoretical detection limits in SEM measurements are about 0.08 wt%.

RESULTS AND DISCUSSION

The results of the quantitative analysis of the glass vessel and window fragments expressed as weight per cent oxides are given in Table 2. These data show that two of the samples (samples 1 and 2) are soda-lime-silica glass, two are mixed alkali glass, three are potash-lime-silica glass and sample 8 is lead-silica glass, both of whose parts—the yellowish one and the green one—are essentially alkali-free (alkali content is less than 2 wt%). All the window glass samples are lead-silica glass or potash-lead-silica glass.

The chemical compositions of the two soda-lime glass fragments (samples 1 and 2) are very similar. Even though the colours of these samples are different (sample 1 is light blue and sample 2 light blue-green), the only differences in the chemical compositions of these samples are in the amounts of MnO. It has been suggested that MnO contents above 1 wt% could be a clue to the deliberate addition of manganese as a decolouring element (Henderson 1985), in which case the MnO is accidental here. The final tint of a glass fragment is determined in a complicated way by

Table 3 Detection limits (in ppm by weight) in (a) a glass matrix with a low Pb-content and in (b) a Pb-rich glass (i.e., when the PbO content is c. 20 wt%)

Component	Method	(a)	(b)	Component	Method	(a)	(b)
Na ₂ O	SEM	1100	1100	TiO ₂	PIXE	45	180
MgO	SEM	1100	1100	MnO	PIXE	40	60
Al ₂ O ₃	SEM	1000	1000	Fe ₂ O ₃	PIXE	30	35
P ₂ O ₅	SEM	1800	1800	CuO	PIXE	10	20
SO	SEM	1000	1000	ZnO	PIXE	10	20
Cl	SEM	1000	1000	PbO	PIXE	5	
K ₂ O	SEM	1200	1200	As ₂ O ₃	PIXE	10	90
CaO	SEM	1300	1300	Rb ₂ O	PIXE	10	30
				SrO	PIXE	15	100
				ZrO ₂	PIXE	10	15
				BaO	PIXE	300	500

many parameters. The reasons for the different colours of samples 1 and 2 are probably not only the different amounts of MnO but also the oxidation states of Mn as well as the melting conditions, that is, time, temperature and furnace atmosphere (Newton 1978; Sellner *et al.* 1979). In samples 1 and 2 the MgO and P₂O₅ levels are lower and Al₂O₃ and SO₃ levels higher than in the other samples from the site. The BaO concentrations of these samples are fairly low.

Sample 3 was burnt (G. Haggren, pers. comm.) and its surface is deeply corroded. In the SEM image of this sample we could see two distinct areas and we can assume that the area with lower Na₂O and CaO contents and higher SiO₂, Al₂O₃ and P₂O₅ is the corroded sample surface. The interior of the sample itself is green potash-lime-silica glass. The content of CaO is high.

Samples 4 and 6 are mixed-alkali glasses with high levels of CaO and samples 5 and 7 are potash-lime-silica glasses. Both parts of sample 8 are alkali-free lead glass. The green glass contains 1.2 wt% CuO which is a high copper content compared with the copper concentrations found in the other samples. According to the literature (Weyl 1951), copper, like other colouring elements, produces more intense colours in lead glass than in lead-free glass due to strong light absorption. The tints of sample 8 are like those of a German beaker from Braunschweig (Baumgartner and Krueger 1988, fig. 126) and the concentrations of all analysed compounds are approximately the same (Wedepohl *et al.* 1995; sample Bra3, Table 1). Lead isotope analysis might help to give a better idea about where and when this vessel was manufactured.

All the window glass samples contain lead oxide with concentrations varying in the range 19–53 wt%. These glass fragments are probably not all made from the same glass melt because they look very different and their major compounds concentrations differ so much. On the basis of concentrations of silica, potash, lime and lead oxide we could classify these samples into the following two groups (wt%):

I: (34.1 ± 0.4) SiO₂ 3.3 ± 0.1 K₂O 4.4 ± 0.2 CaO 51.0 ± 1.7 PbO (samples 9, 11, 12, 16);

II: 39.2 ± 1.9 SiO₂ 9.3 ± 1.1 K₂O 14.4 ± 1.8 CaO 24.6 ± 5.3 PbO (samples 10, 13, 14, 15).

The average composition of the Finnish samples 9, 11, 12 and 16 is fairly similar to north-western European lead glass and the average composition of the Finnish samples 10, 13, 14 and 15 is similar to north-western European wood ash lead glass (Wedepohl *et al.* 1995). CuO was detected in all these samples with concentrations varying in the range 1.2–2.2 wt%. It is this CuO that lends these fragments their dark green colour. ZnO level is the same in all samples. If Cu colourant was added as Cu-Zn alloy, this brass can be estimated to contain 97 wt% Cu and 3 wt% Zn on average.

Fragments of window and vessel glass with a high lead content from the eleventh to the thirteenth century have been found in Kiev (Besborodov 1957, esp. samples 111 and 112) and on various sites in north-western Europe (Wedepohl *et al.* 1995). Comparing the chemical composition of the window glass fragments found in Koroinen (samples 10 and 13) with those found in Kiev, we may conclude that the concentrations of lead and potassium are very similar. However, the concentrations of CaO and MgO are different. In the Kiev artefacts the CaO content varied in the range of 0.4–2.90 wt% and for the Koroinen samples it varies from 4.1 to 16.0 wt%. Thus, the average composition of the Finnish sample is similar to north-western European lead glass or to wood ash lead glass (Wedepohl *et al.* 1995).

CONCLUSION

The analysis of eight fragments of glass vessels from Koroinen churches indicates that three of the samples are a potash-lime-silica type glass, two are a mixed alkali glass, two are a soda-lime-

silica type glass and one is a lead glass. The soda-lime-silica compositions of fragments 1 and 2 suggest vessels imported from south of the Alps, but the decoration of these samples and also sample 5 indicates a German origin, as do the tints and forms of the lead glass vessel.

The analysed fragments of dark green window glass from Koroinen contain 19–53 wt% PbO. Although the appearance and concentrations of the major compounds vary, the average concentrations are similar to medieval lead glass or wood ash lead glass from north-western Europe and differ from the Russian type of lead glass. According to Wedepohl *et al.* (1995), there are several mid- to late medieval lead mines in central Europe which produced lead found in medieval glass. Lead isotope analysis could give more information about the origin of the lead glass fragments excavated at Koroinen.

The information from the analyses, in conjunction with what is known about glass use and production during the relevant historical period, suggests that the glass vessel fragments probably had multiple origins. The situation with the window glass samples is no clearer and it is possible that the eight pieces have at least two sources. The range of glass compositions parallels that found in central European sites and the absence of evidence for glassmaking in Finland at this time suggests that the finished vessels and sheet glass may have been imported from the same sources that produced the central European glasses of the same type. This indicates that Koroinen in Finland was part of the same trading network of glass as other religious centres elsewhere in western or central Europe.

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APPENDIX: ANALYSED SAMPLES

Further details of the analysed samples are given below (H. Matiskainen, pers. comm.). All samples are from the collection of the Finnish National Museum and the museum identification number is given in parentheses.

1. Bottom of beaker, thirteenth century, imported from south of the Alps, light blue (86020:75).
2. Wall of prunted beaker (Nuppenbecher), thirteenth or fourteenth century, imported from south of the Alps, light blue-green (86020:76).
3. Rim of bottle, green, deeply corroded, fourteenth century (86020:110).
4. Rim of bottle, light green forest type glass (86020:111).
5. Wall of prunted beaker (Nuppenbecher), thin colourless glass; this thinness is typical of glass made in the thirteenth or fourteenth century (52100:1809).
6. Rim of beaker, light green (52100:1925).
7. Wall of bottle, the thickness and appearance suggests a seventeenth- or eighteenth-century date (69053:64).
8. Bottom of beaker, yellow with green rim; the tints resemble those of vessels 126 and 136 in Baumgartner and Krueger (1988) (52100:2140).
9. Window glass, dark green, thickness 3.0 mm (52100:1689).
10. Window glass, dark green, thickness 2.1 mm (86020:112).
11. Window glass, dark green, thickness 2.6 mm (52100:2385).
12. Window glass, dark green, thickness 3.4 mm (52100:2294).
13. Window glass, dark green, thickness 1.9 mm (52100:2194).
14. Window glass, dark green, thickness 2.8 mm (52100:2349).
15. Window glass, dark green, thickness 2.4 mm (52100:2399).
16. Window glass, dark green, thickness 2.2 mm (52100:1884).