SEM-EDS AND PIXE ANALYSES OF MEDIEVAL GLASS FROM THE MUSEUM ABOA VETUS IN TURKU

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The scanning electron microscopy (SEM) with an energy-dispersive spectrometer (EDS) and the proton induced X-ray emission (PIXE) methods were used to determine the major, minor and trace elements in 54 fragments of medieval glass vessels from the museum Aboa vetus in Turku. The absolute concentrations of silicon, sodium, potassium, calcium, magnesium, aluminium, phosphorus, sulphur, chlorine, titanium, manganese, iron, copper, zinc, lead, arsenic, rubidium, strontium, zirconium and barium were measured. The possibilities of using analytical methods to reconstruct vessels and to obtain information on the origin of the glasses are discussed.

1. Introduction

Aboa vetus is a museum of archaeology and history in Turku. Over 30.000 objects have been discovered during excavations on the premises of the museum. The first finds are from the early 13th century. The excavations were particularly intensive in 1994. During these excavations at least 30 glass vessels and hundreds of glass fragments were found. This is a large glass find, not only on a Finnish scale, but on a European one as well which will change our view of the use of glass in Medieval times in Finland (Haggren 1996). In this study, 54 of the oldest layers excavated samples have been analysed. The aim of this study is to identify major, minor and trace elements of these glass fragments, aid archaeologists in reconstructing the vessels and to obtain information about the origin of these objects.

The major and minor elements have been analysed by scanning electron microscopy (SEM) with an energy-dispersive spectrometer (EDS) and trace elements by the PIXE method. Both methods are based on the detection of characteristic X-rays. The SEM-EDS method is well suited for the measuring of elements with concentrations higher than 1 wt%. By using the PIXE method concentrations from 100% to the trace level may be detected. The PIXE method offers its maximum sensitivity when atomic number Z of the detected element is in the region 18–40. SEM-EDS and PIXE methods complement each other in an earlier reference (Kuisma-Kursula and Räisänen, in print).

2. Experimental

2.1. Samples

The 54 samples analysed from the museum Aboa vetus consist of three types of glass fragments: 1) ornamented body sherds (samples 1–21), 2) mouth fragments (samples 22–38) and 3) base fragments (samples 39–54). Glass fragments were mainly colorless, of high quality, without serious corrosion or iridescence. Among the samples were sherds from Bohemian (?) beakers with applied drops drawn into ribs with applications of cobalt glass.

2.2. Standards

Absolute concentration values for the samples were obtained by using the Corning glass standards A and D along with the NIST (National Institute of Standards and Technology, USA) glass standard no. 620 in the SEM-EDS measurements. The Corning standard D and the NIST glass standards nos. 611 and 620 were used in the PIXE measurements. The description of the Corning standards may be found in the article by Brill (1971). The NIST glass standard 620 is soda-lime flat glass. The NIST glass standard no. 611 contains 61 trace elements in a soda-lime-silica glass matrix. The nominal trace element concentration is 500 ppm for each of the elements that have been added to the glass support matrix.

2.3. Sample preparation

For the SEM measurements small samples of less than 1 mm in length were cut with a diamond saw from the glass artifacts, mounted on epoxy resin and polished flat using 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 or reflection of the electron beam.

For the PIXE measurements a smooth area on each sample was cleaned with alcohol before analysis.

2.4. Analytical methods

In the SEM analyses, each sample was bombarded with 20 keV electrons in a Zeiss Digital Scanning Microscope 962 at the Electron Microscopy Unit of Institute of Biotechnology, University of Helsinki. Each sample was analysed at least twice and the measuring time was 50 seconds. A a result, the absolute concentrations of silicon, sodium, potassium, calcium, magnesium, aluminium, phosphorus, sulphur, chlorine, titanium, manganese and iron were determined. The precision of measurements was better than 2% for SiO_2 and CaO, 5% for K_2O and MgO and 10% for Na_2O and Al_2O_3.

In the PIXE analyses, 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 area was approximately 2.4 MeV. The emitted X-rays were detected with a 50 mm^2 x 6 mm intrinsic germanium detector. A 250 µm thick Kapton (Du Point, Geneva (Switzerland)) filter was used to eliminate low-energy characteristic X-rays originating from the major elements in the glass matrix. The spot size of the proton beam on the sample was about 1 mm (diameter), thus it was easy to find a flat, smooth and clean area on the sample. More details are given in reference (Anttila et al. 1985). All the standards and several samples were bombarded many times to evaluate precision of the measurements. The measuring time for each sample was approximately 3 min. The spectra were collected with Camberra S-100 measuring programme and analysed with the SAMPO peak fitting programme (Aarnio et al. 1988, 1990). As a result, the absolute concentrations of copper, zinc, lead, arsenic, rubidium, strontium, zirconium and barium were ascertained. The precision of the measurements was better than 5% for CuO, ZnO and PbO and better than 10% for the other compounds determined with PIXE.

3. Results and discussion

3.1. SEM and PIXE results

The results of the quantitative analysis of the fragments of glass expressed as weight % of oxides are given in Table 1. The values for the average concentrations of different elements expressed as weight % of oxides and detection limits (in ppm by weight) are presented in Table 2. The data given in Table 1 indicates that all analysed samples (54) are potash-lime-silica type glass whose K_2O/MgO -ratio 4.1 (given in Table 2) points to a mixed fern and beech ash as alkali source (Tennent, N.V. et al. 1984). The concentration levels of MnO are quite high and it can be assumed that MnO was added as a decoloring agent. The blue drop and strip decorations of some fragments indicate a Bohemian origin (Haggren 1996; Vondruska 1989), but composition analyses of this type glass have not been reported in literature. For example, samples 32 and 33 belong together. The results of analysis are only one part in the resolution of the reconstruction problems. The analysis, in conjunction with other knowledge about glass use, for example, combustion tracks on glass surfaces, is a succesful method in the reconstruction of vessels.

4. Conclusions

It may be concluded that the SEM and PIXE methods can complement each other in analysis of major, minor and trace elements in glass. As a result of the present study the absolute concentrations of 20 elements have been determined.

The analysis of glass vessel fragments from the museum Aboa vetus indicates that all of the analysed 54 samples are potash-lime-silica glass. The blue drop decorations of some body sherds indicate a Bohemian origin. Though the fragments clearly belong to different objects, their composition is of a homogeneous nature, therefore they most probably have only one source.

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Table 1. Results of SEM and PIXE analyses of glass vessel fragments. Values are expressed as weight % oxides.

	Sample	SiO_2	CaO	K_2O	Na_2O	Al_2O_3	MgO	P_2O_5	SO_3	Cl	TiO_2	MnO	FeO	BaO	CuO*	ZnO*	PbO*	As_2O_3*	Rb_2O*	SrO*	ZrO_2*
1	304:a	62.8	17.4	11.8	0.6	0.8	3.1	0.7	0.2	<	0.2	1.6	0.4	0.5	80	180	<	90	410	610	200
2	325	62.7	18.0	11.2	0.5	0.7	3.2	1.0	0.2	0.1	0.2	1.0	0.2	0.1	120	160	220	<	220	310	250
3	437:c	61.4	17.8	12.9	0.7	1.2	3.3	1.2	0.3	<	0.1	1.3	0.1	0.4	180	270	200	90	320	630	240
4	739	61.1	19.3	12.4	0.6	0.7	3.1	1.1	0.2	0.1	0.2	0.8	0.4	0.3	100	130	130	<	190	210	60
5	916:g	61.0	17.4	14.1	0.7	0.5	2.9	1.1	0.2	<	0.2	1.4	0.2	0.5	80	160	40	90	470	560	190
6	916:h	61.0	17.6	14.2	0.6	0.7	3.0	1.3	0.2	<	0.1	1.2	0.2	0.4	100	150	50	50	430	530	190
7	1023:a	61.2	17.6	14.2	0.6	0.6	3.0	1.1	0.2	<	0.2	1.7	0.2	0.4	70	140	<	<	420	550	220
8	1180:f	62.9	18.7	11.3	0.7	1.1	3.5	1.7	0.2	0.1	0.2	1.2	0.2	0.4	50	830	40	20	140	280	130
9	1214:h	61.9	18.0	11.8	0.5	0.8	3.1	1.2	0.2	<	<	1.0	0.2	0.4	100	170	80	20	310	450	280
10	1214:m	58.9	18.0	14.7	0.7	0.5	3.2	1.2	0.2	<	<	1.0	0.2	0.4	110	200	60	<	100	180	100
11	1230:m	62.5	18.1	12.0	0.6	0.8	3.1	0.9	0.2	<	0.2	1.3	0.3	0.2	70	150	<	<	310	460	180
12	1230:o	62.1	18.3	12.0	0.5	0.9	3.3	1.0	0.2	<	0.2	1.4	0.2	0.3	70	130	<	40	240	330	230
13	1230:q	63.9	16.9	11.6	0.6	0.6	3.0	1.1	0.2	<	0.3	1.4	0.2	0.3	60	150	30	<	230	460	220
14	1240:a	61.1	17.9	12.8	0.7	1.0	3.4	0.9	0.2	<	0.2	1.4	0.5	0.3	190	200	<	20	280	520	230
15	1688	62.9	17.5	13.0	0.6	0.6	2.8	0.9	0.3	0.1	0.4	1.5	0.3	0.2	60	150	20	<	420	500	190
16	1913:k	61.6	17.4	12.2	0.6	0.9	3.2	1.2	0.2	<	0.2	1.2	0.2	0.3	85	150	50	<	340	470	120
17	1913:m	59.6	16.9	14.1	0.6	1.5	3.2	1.0	0.2	<	0.1	1.4	0.2	0.3	70	140	50	<	290	360	110
18	2244	61.9	16.9	12.6	0.6	0.8	2.8	1.1	0.2	0.1	0.1	1.4	0.2	0.4	40	110	20	60	310	420	185
19	2268:k	62.7	16.2	11.9	0.6	0.9	2.7	0.8	0.3	<	0.3	0.9	0.2	0.4	40	70	60	<	180	270	290
20	2268:s	62.9	16.3	12.2	0.8	1.1	2.8	1.1	0.3	<	0.3	1.0	0.4	0.3	40	70	50	<	190	240	240
21	2443:a	63.4	18.2	9.1	0.6	0.8	3.2	1.4	0.3	<	0.2	1.2	0.2	0.3	90	150	20	30	220	480	170
22	359	63.1	16.8	13.2	0.6	0.6	3.0	1.1	0.2	<	0.2	1.3	0.2	0.3	70	210	50	40	330	600	350
23	383	61.2	18.7	12.6	0.6	0.9	3.4	1.0	0.2	0.1	0.2	1.1	0.3	0.3	70	140	50	40	230	440	350
24	534	63.8	17.1	12.3	0.5	0.8	3.0	1.0	0.2	<	<	1.5	0.2	0.7	60	170	20	50	260	520	210
25	1056:a	61.4	17.7	13.7	0.5	1.0	3.2	1.3	0.2	0.1	0.2	1.6	0.4	0.4	70	160	20	70	280	520	110
26	1180:a	64.2	17.5	11.7	0.7	0.6	3.1	0.8	0.2	<	0.4	1.6	0.3	0.3	160	190	40	60	300	520	250
27	1180:b	62.6	18.3	11.9	0.6	0.7	3.2	1.0	0.2	<	0.2	1.6	0.3	0.4	100	190	60	50	280	550	230
28	1180:c	63.5	17.4	11.8	0.6	0.5	3.0	1.0	0.2	0.1	<	1.4	0.4	0.3	80	180	20	50	280	570	210
29	1214:a	63.5	18.3	12.5	0.6	0.7	3.1	1.0	0.1	0.1	0.1	1.4	0.3	0.4	70	170	30	100	270	560	250
30	1214:d	61.0	19.1	15.1	0.7	0.4	3.1	1.1	0.1	<	<	1.3	0.2	0.4	100	200	80	<	60	180	110
31	1214:e	58.7	18.6	14.6	0.5	0.4	3.0	0.8	0.1	0.1	0.1	1.5	0.2	0.4	130	230	20	40	240	400	110
32	1230:r	63.9	17.6	12.1	0.8	0.7	3.3	0.9	0.2	<	0.2	1.3	0.1	0.2	70	170	40	<	340	680	200
33	1230:s	63.8	17.7	11.9	0.8	0.6	3.1	0.9	0.1	<	<	1.5	0.3	0.6	70	150	20	70	300	580	220
34	1275:a	61.6	17.0	13.6	0.5	0.7	3.1	1.3	0.2	<	<	1.1	0.1	0.5	70	180	20	70	340	590	130
35	1890:b	60.9	16.9	14.7	0.7	1.5	3.1	1.0	0.2	<	0.4	1.6	0.2	0.2	80	200	30	40	320	550	100

Table 1. Cont.

	Sample	SiO_2	CaO	K_2O	Na_2O	Al_2O_3	MgO	P_2O_5	SO_3	Cl	TiO_2	MnO	FeO	BaO	CuO^*	ZnO^*	PbO^*	$As_2O_3^*$	Rb_2O^*	SrO^*	ZrO_2^*
36	1890:c	61.1	18.0	13.6	0.8	1.8	3.0	1.0	0.1	0.1	<	1.6	0.6	0.6	70	170	100	80	270	470	120
37	1913:a	62.2	18.1	12.6	0.5	0.5	3.2	0.8	0.2	0.1	0.1	2.1	0.3	0.4	70	180	80	230	360	800	240
38	2270	61.4	19.4	12.0	0.5	0.8	3.5	1.5	0.2	<	<	1.4	0.5	0.4	170	190	70	80	280	770	200
39	169:a	59.6	19.6	12.3	0.7	1.4	3.1	1.1	0.1	<	<	0.8	0.5	0.4	80	140	60	40	190	460	130
40	279	62.4	18.3	12.4	0.4	0.8	2.8	1.2	0.2	0.1	<	0.8	0.5	0.4	90	170	50	40	260	450	160
41	281	63.5	17.9	12.0	0.7	0.6	3.2	1.2	0.2	0.1	<	1.8	0.1	1.0	60	140	40	80	320	590	190
42	304:c	57.3	18.0	13.9	0.8	0.9	3.4	1.8	0.2	0.1	0.1	1.2	0.2	0.4	80	260	20	80	230	490	130
43	316:b	58.5	18.2	14.0	0.7	1.0	3.4	2.3	0.3	0.2	0.1	1.2	0.2	0.1	70	180	40	70	230	660	260
44	354	61.0	19.5	11.9	0.7	1.0	3.6	1.4	0.1	<	<	1.4	0.6	0.6	80	150	<	80	360	620	170
45	489	64.6	15.6	11.6	0.5	0.8	2.8	1.3	0.2	<	0.2	1.5	<	0.2	90	210	20	40	310	530	100
46	698:f	58.4	18.3	13.5	0.9	1.0	3.6	1.9	0.1	<	0.1	1.5	0.6	0.1	120	150	60	<	210	240	80
47	766:a	58.5	19.2	13.9	0.6	0.8	3.3	1.2	0.1	<	<	1.5	0.3	0.7	170	200	70	120	300	500	120
48	1414	57.6	19.2	13.8	0.7	0.7	3.2	1.4	0.1	0.1	0.2	1.7	0.4	0.5	90	210	<	120	270	720	130
49	1430:c	64.0	18.4	10.2	0.6	0.6	3.5	1.2	0.3	<	<	1.8	0.2	0.5	40	120	20	<	70	180	170
50	1485	60.3	17.0	13.7	0.6	0.5	3.1	1.1	0.2	<	0.2	1.1	0.3	0.1	100	180	20	30	310	490	170
51	1634	60.7	17.5	14.2	0.6	0.5	3.0	1.0	0.2	<	0.1	1.3	0.4	0.4	80	160	50	110	310	560	220
52	1977	62.7	16.0	14.2	0.7	0.4	2.7	0.7	0.3	0.1	0.1	1.0	<	0.6	160	230	80	100	460	690	270
53	2008:a	60.1	17.4	14.5	0.6	0.6	3.4	1.4	0.2	<	0.2	0.9	0.1	0.2	70	160	50	60	310	490	180
54	2281	64.6	16.4	14.4	0.6	0.4	3.1	1.1	0.2	<	<	1.0	0.3	0.2	80	120	50	50	170	280	110

* as ppm by weight, < below detection limit

Table 2. Average concentrations of compounds (weight %) determined by SEM and PIXE measurements and detection limits as ppm by weight.

Variable	Mean	Standard deviation	Min.	Max.	Detection limit
SiO_2	61.69	1.82	57.30	64.60	1500
CaO	17.81	0.91	15.60	19.60	1300
K_2O	12.82	1.24	9.10	15.10	1200
Na_2O	0.63	0.10	0.40	0.90	1100
Al_2O_3	0.79	0.29	0.40	1.80	1000
MgO	3.14	0.22	2.70	3.60	1100
P_2O_5	1.14	0.29	0.70	2.30	1800
SO_3	0.20	0.06	0.10	0.30	1100
Cl	0.10	0	0	0.10	1000
TiO_2	0.16	0.08	0.10	0.40	800
MnO	1.33	0.28	0.80	2.10	800
FeO	0.28	0.14	0.10	0.60	800
BaO	0.376	0.167	0	1.00	300
CuO	0.0030	0.0046	0	0.0100	15
ZnO	0.0131	0.0104	0	0.0800	20
Rb_2O	0.0279	0.0087	0.0060	0.0470	17
SrO	0.0483	0.0150	0.0180	0.0800	30
ZrO_2	0.0185	0.0066	0.0060	0.0350	34
PbO	0.0053	0.0041	0	0.0220	20
As_2O_3	0.0067	0.0038	0	0.0230	20
K_2O/MgO	4.11	0.50	2.84	5.26	
CaO/K_2O	1.40	0.17	1.13	2.00	